NONCLASSICAL FREE RADICALS

KINETIC AND STEREOCHEMICAL STUDIES CONCERNING THE QUESTION OF NONCLASSICAL FREE RADICALS

By

EMERSON CECIL SANFORD, M.Sc.

A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

October, 1968

DOCTOR OF PHILOSOPHY (1968) McMASTER UNIVERSITY
(Chemistry) Hamilton, Ontario

TITLE: Kinetic and Stereochemical Studies Concerning the Question of Nonclassical Free Radicals

AUTHOR: Emerson Cecil Sanford, B.Sc. (Mount Allison University)
M.Sc. (Mount Allison University)

SUPERVISOR: Dr. J. Warkentin

NUMBER OF PAGES: xvii, 214

SCOPE AND CONTENTS:

The relative rates of tri-*n*-butyltin hydride reduction of several 7-halonorbornane derivatives have been obtained in search of evidence for the existence of non-classical free radicals. Reduction products were identified and the stereochemistry of reduction of 7-norbornenyl bromides was determined. Possible contributions to the relative rates by ground state effects were considered. The relative rates of reduction and reduction products provided evidence for the existence of non-classical free radicals.

The synthesis of several polychlorinated norbornane derivatives is described. A study of the relative rates of reduction and reduction products of some of these compounds was carried out. Further evidence in support of non-classical free radicals was obtained.

The polarographic reduction of alkyl halides is shown to proceed *via* free radical intermediates. Half-wave potentials of norbornyl and related bromides supplied further evidence of non-classical free radicals.

The relative rates of reduction of several acyclic homoallylic and related halides were determined. Evidence for non-classical free radicals was not found in these compounds.

Previous studies concerned with the question of non-classical free radicals, are described in the historical introduction.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. Warkentin for his guidance, constructive criticisms, warm friendship and many stimulating discussions throughout the experimental work and the writing of this thesis.

The author is grateful to Dr. O.E. Hileman for his assistance in setting up the polarographic apparatus and to many of his colleagues for recording the nuclear magnetic resonance spectra required.

Finally, the author wishes to express a note of appreciation to his wife, for the innumerable ways in which she has helped make the successful completion of this work possible.

Financial assistance from the Department of Chemistry, the Petroleum Research Fund and the Ontario Government is gratefully acknowledged.

TABLE OF CONTENTS

	Page
GENERAL INTRODUCTION.....	1
HISTORICAL INTRODUCTION	
General.....	4
I Rearrangement of Cyclopropyl-Allylcarbinyl Free Radicals	
(i) Simple Acyclic Systems.....	6
(ii) Semrigid Bicyclic Systems.....	18
II Rates of Formation of Cyclopropyl- Allyl-carbinyl Free Radicals	
(i) General Consideration.....	25
(ii) Simple Acyclic Systems.....	29
(iii) Semirigid Cyclic Systems.....	36
III The Mechanism of Reduction of Alkyl Halides	
(i) Trialkyltin Hydride Reduction.....	47
(ii) Polarographic Reduction.....	52
RESULTS AND DISCUSSION	
Introduction and Outline.....	60
I Transition State Change Polarization: The Mechanism of Polarographic Reduction of Alkyl Halides.....	62

TABLE OF CONTENTS (Continued.....)

Page

II Kinetic, Stereochemical and Product Studies on Monohalocycloalkanes

General..... 76

(i) Kinetics and Products..... 78

III Syntheses of Polychlorinated Norbornenes

General..... 106

(i) General Features of NMR Spectra.... 106

(ii) Derivatives of 1,2,3,4,7,7-Hexachloronorborn-2-ene..... 109

(iii) Derivatives of 1,2,3,4-*endo*-5,7,7-Heptachloronorborn-2-ene..... 115

(iv) Derivatives of 1,2,3,4,5,6,7,7-Octachloronorborn-2-ene..... 124

IV Kinetic and Product Studies on Polychlorinated Norbornenes..... 133

V Simple Acyclic Systems..... 160

EXPERIMENTAL

General

(i) Outline of Experimental Section... 169

(ii) Instrumental Analysis..... 170

I Synthesis of Compounds Required for Rate Studies

(i) Monobromocycloalkanes..... 171

TABLE OF CONTENTS (Continued.....)

Page

(ii) Monochlorocycloalkanes..... 172

(iii) Cycloalkanes..... 173

(iv) Acyclic Halides..... 174

(v) Derivatives of 1,2,3,4,7,7-Hexachloronorborn-2-ene..... 175

(vi) Derivatives of 1,2,3,4-*endo*-5,7,7-Heptachloronorborn-2-ene..... 179

(vii) Derivatives of 1,2,3,4-*endo*,*cis*-5,6,7,7-Octachloronorborn-2-ene... 181

II Relative Rates of Reduction and Reduction Products

(i) Relative Rates..... 185

(ii) Reduction Products from Monohalocycloalkanes..... 192

(iii) Reduction Products from 1,4-*anti*-7-Trichloronorborn-2-ene..... 194

(iv) Reduction Products from *syn*- and *anti*-1,2,4,7-Tetrachloronorborn-2-ene..... 195

(v) Reduction Products from *syn*- and *anti*-1,2,3,4,7-Pentachloronorborn-2-ene..... 196

TABLE OF CONTENTS (Continued.....)

Page

(vi) Reduction Products from *syn*- and *anti*-1,2,3,4,7-Pentachloronorborna-2,5-diene..... 197

III Polarographic Reduction..... 201

REFERENCES..... 209

LIST OF TABLES

Number	Title	Page
I	Decomposition of Azo Compounds.....	35
II	Relative Rates of Reduction of Cyclic Bromides by Tri-*n*-butyltin Hydride at 45°.....	40
III	Decarbonylation of Aldehydes.....	43
IV	Thermal Decomposition of Peresters.....	45
V	Polarographic Reduction of Substituted Benzyl Chlorides.....	58
VI	Relative Rates of Tin Hydride Reduction, Half-wave Potentials and Substituent Constants of Alkyl Bromides.....	66
VII	Relative Rates of Tin Hydride Reduction, Half-wave Potentials and Substituent Constants of Chloromethyl Halides.....	71
VIII	Half-wave Potentials, Polar Substituent Constants and Calculated Relative Rates of Tin Hydride Reduction of 2-Substituted Ethyl Bromides.....	73

LIST OF TABLES (Continued.....)

Number	Title	Page
IX	Relative Rates of Tin Hydride Reduction, Carbonyl Stretching Frequencies and Calculated Carbonyl Bond Angles for 7-Bromonorbornane Derivatives.....	79
X	Relative Rates of Tin Hydride Reduction, Carbonyl Stretching Frequencies and Calculated Carbonyl Bond Angles for 7-Chloronorbornane Derivatives.....	85
XI	Observed and Calculated Relative Rates of Tin Hydride Reduction of 7-Chloro-norbornane Derivatives.....	89
XII	Half-wave Potentials and Calculated Bond Angles of Cycloalkyl Bromides.....	101
XIII	Relative Rates of Reduction of Poly-chlorinated Norbornane Derivatives....	135
XIV	Effect of Bu_3SnH Concentration on the Product Ratio from Reduction of 1,4-*anti*-7-Trichloronorbornene.....	142
XV	Effect of Bu_3SnH Concentration on the Product Ratio from Reduction of 1,2,3,4-*anti*-7-Pentachloronorborn-2-ene.....	147

LIST OF TABLES (Continued.....)

Number	Title	Page
XVI	Effect of Bu_3SnH Concentration on the Product Ratios from Reduction of 1,2,3,4-*syn*-7-Pentachloronorborn-2-ene.....	148
XVII	Relative Rates of Tin Hydride Reduction of Acyclic Alkyl Chlorides.....	161
XVIII	Relative Rates of Tin Hydride Reduction of Norbornane- and Norbornene-1-carbinyl Chloride.....	163
XIX	Half-wave Potentials of Acyclic Alkyl Bromides.....	166
XX	Relative Rates of Reduction of Cycloalkyl Bromides with Tri-*n*-butyltin Hydride..	187
XXI	Relative Rates of Reduction of Cycloalkyl Chlorides with Tri-*n*-butyltin Hydride.	188
XXII	Relative Rates of Reduction of Chloronorbornane Derivatives with Tri-*n*-butylin Hydride.....	189
XXIII	Relative Rates of Reduction of Acyclic Alkyl Chlorides with Tri-*n*-butyltin Hydride.....	190

LIST OF TABLES (Continued.....)

Number	Title	Page
XXIV	Half-wave Potentials Obtained Using 0.100 M Et_4NBr in DMF.....	202
XXV	Half-wave Potentials Obtaining Using 0.100 M Et_4NCl in DMF.....	204

LIST OF FIGURES

Number	Title	Page
1	Plot of Half-wave Reduction Potentials *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Alkyl Bromides..	67
2	Plot of Half-wave Reduction Potentials (corrected for Steric Effects) *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Alkyl Bromides..	68
3	Plot of Half-wave Reduction Potentials (corrected for Steric Effects) *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Chloromethyl Halides.....	72
4	Plot of Polar Substituent Constants *vs* Calculated Relative Rates of Tri-*n*-butyltin Hydride Reduction for Substituted Ethyl Bromides.....	74
5	Plot of Relative Rates of Tri-*n*-butyltin Hydride Reduction *vs* C-7 Carbonyl Bond Angle for Cycloalkyl Bromides.....	82

LIST OF FIGURES (Continued.....)

Number	Title	Page
6	Plot of Relative Rates of Tri-*n*-butyltin Hydride Reduction *vs* Carbonyl Bond Angle for Cycloalkyl Chlorides.....	86
7	NMR Spectra at 100 Mc of (A) Norbornene, (B) *anti*-7-Deuterionorbornene from *anti*-Bromide and (C) *anti*-7-Deuterio-norbornene from *syn*-Bromide.....	93,94
8	Plot of Half-wave Reduction Potentials *vs* C-7 Carbonyl Bond Angle for Cyclo-alkyl Bromides.....	102
9	NMR Spectra of *anti*- and *syn*-1,2,3,4,7-Pentachloronorborn-2-ene.....	114
10	NMR Spectra of *anti*- and *syn*-1,2,3,4,7-Pentachloronorbornadiene, *anti*-1,4,7-Trichloronorbornene and 1,2,3,4-Tetra-chloronorbornadiene.....	122
11	NMR Spectra of 1,2,3,4-Tetrachloronorborn-ane, *anti*- and *syn*-1,2,3,4,7-Pentachloro-norbornane.....	129
12	NMR Spectrum of 1,2,4-Trichloronorborn-2-ene.....	132
13	NMR Spectra of *anti*- and *syn*-1,2,4,7-Tetrachloronorborn-2-ene.....	134

LIST OF FIGURES (Continued.....)

Number	Title	Page
14	NMR Spectra of 1,4-Dichloronorbornene and 1,4-Dichlorobicyclo[3.2.0]hept-6-ene.....	140
15	NMR Spectra of 1,4,6,7-Tetrachlorobicyclo[3.2.0]hept-6-ene and 1,2,3,4-Tetrachlorotricyclo[2.2.1.$0^{2,7}$]-heptane.....	145
16	NMR Spectra of 1,2,3,5-Tetrachloroquadricyclane, 1,2,3,4-Tetrachlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene and 1,3,4-Trichlorotricyclo[2.2.1.$0^{2,7}$]-hept-5-ene.....	154
17	Plot of Half-wave Reduction Potentials *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Alkyl and Cycloalkyl Bromides.....	167

LIST OF CHARTS

Number	Title	Page
I	Structures of Compounds I to XIII.....	77
II	Derivatives of 1,2,3,4,7,7-Hexachloro-norborn-2-ene.....	110
III	Reduction of 1,2,3,4,7,7-Hexachloronor-born-2-ene with Tri-*n*-butyltin Hydride	111
IV	Derivatives of 1,2,3,4,5,7,7-Heptachloro-norborn-2-ene.....	116
V	Catalytic Reduction of *syn*- and *anti*-1,2,3,4,7-Pentachloronorbornadiene....	118
VI	Derivatives of 1,2,3,4,5,6,7,7-Octachloro-norborn-2-ene.....125,126	
VII	Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,4,7-Trichloronorbornene.....	138
VIII	Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,2,3,4,7-Pentachloronorborn-2-ene.....	144
IX	Products from Tri-*n*-butyltin Hydride Reduction of 1,2,3,4,7,7-Hexachloro-norbornadiene.....	156

LIST OF CHARTS (Continued.....)

Number	Title	Page
X	Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,2,4,7-Tetrachloronorbornadiene.....	157
XI	Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,2,3,4,5-Pentachloronorbornadiene....	158
XII	Gas-liquid Partition Chromatographic Analysis of Products from Tri-*n*-butyltin Hydride Reduction of 1,2,3,4,7-Pentachloronorborn-2-ene.....	198

GENERAL INTRODUCTION

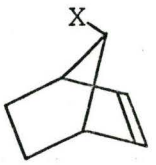
Homoallylic π-bond participation in solvolysis reactions, yielding non-classical carbonium ion intermediates, has been well established in certain cases (1). Molecular orbital calculations predict that non-classical free radicals resulting from homoallylic π-orbital overlap are energetically feasible and should exist as intermediates in certain free radical reactions (16,17). In the historical section of this thesis, earlier attempts to find evidence for non-classical free radicals are discussed. At the time the present work was undertaken, the prediction that non-classical free radicals should exist had not been substantiated by experiment. In this thesis, experimental evidence demonstrating the existence of non-classical free radicals is presented.

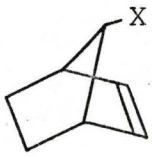
The tri-*n*-butyltin hydride reduction of alkyl halides was chosen as the method of generating free radicals. Relative rates of reduction were obtained by the competition method. In the Historical Introduction studies demonstrating the free radical nature of this reaction are discussed. In a later section, possible

contributions to the observed relative rates from charge polarization in the transition state are discussed.

Half-wave potentials obtained from polarographic reduction of alkyl halides are correlated with the relative rates of tin hydride reduction of these compounds. This serves to demonstrate the free radical nature of polarographic reduction of alkyl halides. Half-wave potentials were then used in conjunction with relative rates of tin hydride reduction in studies designed to demonstrate the existence of non-classical free radicals.

The system chosen for study was 7-norbornenyl and related bromides and chlorides. The rates of





X=Br,Cl

reduction of these compounds were found to be sensitive to bond angle differences at the reaction centre. The C-7 bond angle was estimated from carbonyl stretching frequencies of the corresponding 7-keto compounds. The relative rates were then corrected for differences in bond angle strain at the reaction centre. The reduction products from tri-*n*-butyltin hydride reduction were identified, and in two cases the stereoselectivity

of the product determining step was determined. The relative rates, stereochemistry and products are discussed in terms of non-classical free radical intermediates.

If non-classical free radicals are being observed in unsubstituted norbornenyl systems, electronegative substituents on one or more of the carbon atoms over which the radical is being delocalized should accelerate the rate. Several polychlorinated norbornyl derivatives were synthesized and their relative rates of reduction determined. Rearrangement products were obtained from reduction of these compounds. The sensitivity of product ratios to changes in tin hydride concentration was determined as a test for equilibrating free radical intermediates. The relative rates of reduction, reduction products, and product ratios provided further evidence in support of non-classical free radicals.

The relative rates of reduction of some simple acyclic homoallylic chlorides and bromides, and related compounds, were determined. For the homoallylic chlorides, the relative rates were as expected in terms of a polar contribution in the transition state for reduction. All data could be explained without invoking non-classical free radicals in these systems.

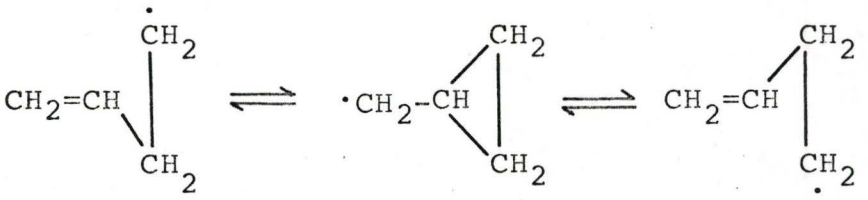
HISTORICAL INTRODUCTION

General

The question of whether or not bridged "non-classical" carbonium ions exist as intermediates in certain solvolysis reactions has stimulated a great deal of research and controversy over the past several years (1). von Schleyer (2) has described the properties associated with "non-classical" carbonium ions as 1. enhanced rates of formation, provided the precursor geometry is suitable; 2. high stereospecificity of kinetically controlled product formation; and 3. heightened propensity toward rearrangement. Carbonium ions with one or more of these unusual properties have often been assigned bridged structures implying increased stabilization by simultaneous and substantial charge delocalization over more than one carbon atom. He goes on to say that "for a symmetrical non-classical carbonium ion, in the absence of steric and conformational effects, enhanced rate of formation can only be associated with a bridged structure for the intermediate. The related and equivalent simple ions and their transition states must be less stable than those of bridged structure by definition".

The question of whether or not non-classical free radicals exist has important theoretical implications in organic chemistry. Non-classical intermediates have been proposed in a variety of free radical reactions. In no case, to date, has the existence of a "non-classical" free radical been unambiguously demonstrated. The problem has been attacked by studying the rate of formation of free radicals, the extent of rearrangement, the nature and stereochemistry of products, and the effect of concentration on product ratios.

Almost all studies of "non-classical" free radicals have been concerned with the interconversion of homoallylic and cyclopropylcarbinyl free radicals (equation [1]). Simple substituted and unsubstituted



[1]

homoallylic and cyclopropylcarbinyl systems have been studied, as well as systems in which the vinyl or cyclopropyl groups are part of a ring, which, in many cases, has a fixed geometry.

This thesis is concerned with the question of non-classical allylcarbinyl-cyclopropylcarbinyl free radicals in norbornenyl and related systems. In order

to develop the background for this study, previous studies on

1. rearrangements of homoallylic and cyclopropylcarbinyl free radicals,
2. the predicted stability of non-classical free radicals in these systems, and
3. the rates of formation of homoallylic and cyclopropylcarbinyl free radicals

are discussed.

In the present study, free radicals have been generated by

1. trialkyltin hydride reduction and
2. polarographic reduction of alkyl halides.

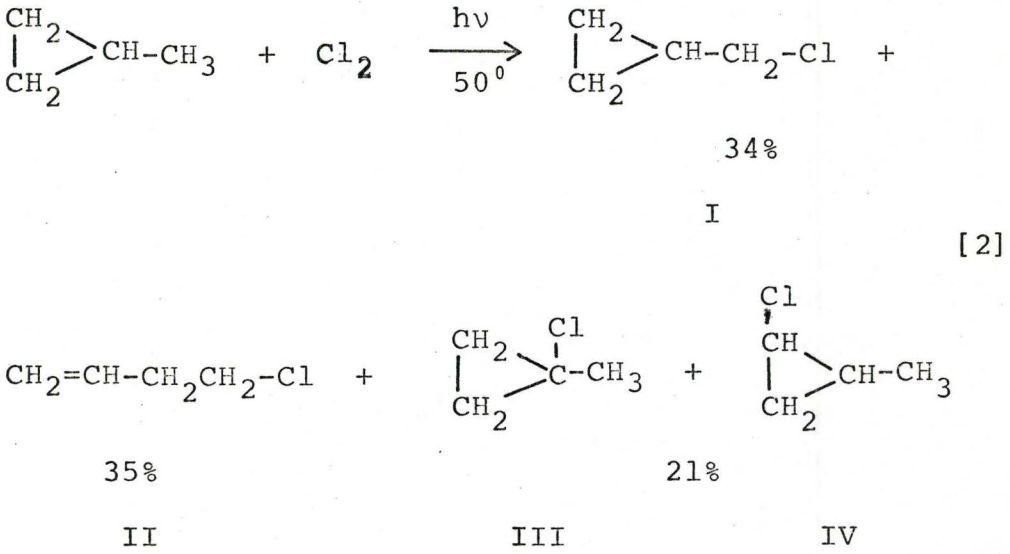
Evidence supporting the free radical nature of these reactions is presented.

I. Rearrangements of Cyclopropyl-Allylcarbinyl Free Radicals

(i) Simple Acyclic Systems

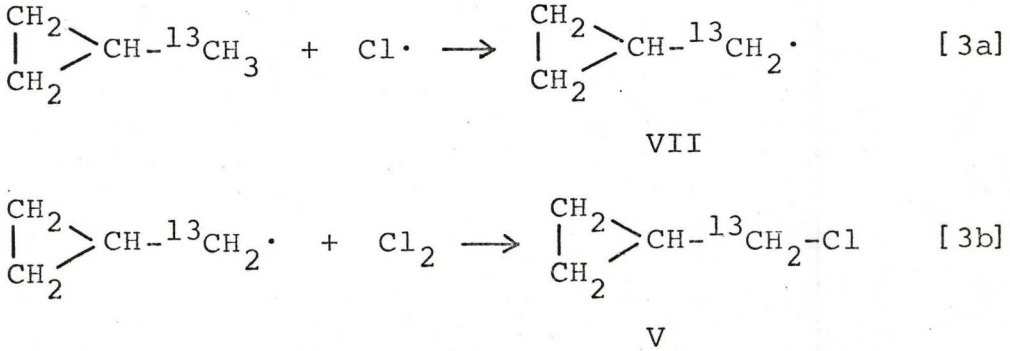
The rearrangement of cyclopropylcarbinyl free radicals is known to be facile. Roberts and Mazur (3) provided one of the first examples in their study of the vapor phase photochlorination of methylcyclopropane. The monochlorinated products were shown by infrared spectroscopy to be a mixture containing 34% of cyclopropylcarbinyl chloride (I), 35% of allylcarbinyl chloride

(II) and 21% of a mixture tentatively identified as 1- and 2-chloro-1-methylcyclopropane (III and IV) and 10% of intermediate fractions (equation [2]).



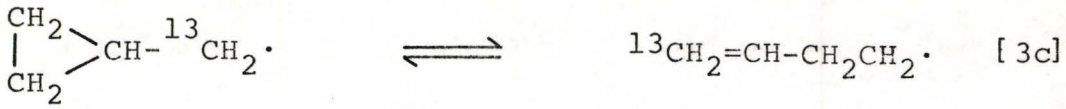
[2]

Further studies by Roberts *et al.* (4) showed that the photochlorination of methyl-^{13}C-cyclopropane proceeded without isotope position rearrangement to yield cyclopropylcarbinyl-α-^{13}C-chloride (V) and allyl-γ-^{13}C-carbinyl chloride (VI). Equation [3] illustrates how these products arise.



[3a]

[3b]



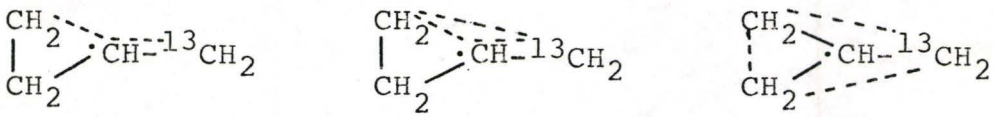
[3c]

VIII

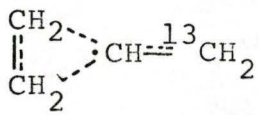
[3d]

VI

For simplicity, the reaction products have been written as arising from only classical intermediates VII and VIII. A number of types of delocalized radical intermediates can be written. These are given below (intermediates IX to XII). Of these, XI is a non-classical intermediate. Evidence for and against such intermediates will be presented in later discussion.



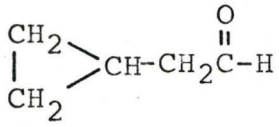
IX X XI



XII

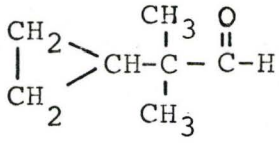
It is significant to note here that intermediate XI should result in significant ^{13}C scrambling in product VI obtained (equation [3]), and can be eliminated on this basis.

Schuster (5) has investigated the decarbonylation of cyclopropylacetaldehyde under a variety of experimental conditions. The only monomeric hydrocarbon product isolated in all cases was the rearranged allylcarbinyl product, 1-butene (XIII) (equation[4]). Similarly, the decarbonylation of dimethylcyclopropylacetaldehyde gave only the rearranged allylcarbinyl product, 2-methyl-2-pentene (XIV) (equation[5]).



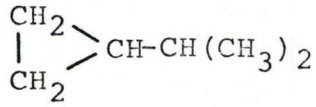
$$\longrightarrow \quad CH_2=CH-CH_2CH_3 \qquad [4]$$

XIII



$$\longrightarrow \quad (CH_3)_2C=CH-CH_2CH_3 \qquad [5]$$

XIV

$$+$$ 

XV

However, when the decarbonylation was carried out in the presence of benzyl mercaptan, the hydrocarbon product was found to consist of both XIV and isopropylcyclopropane (XV) in the ratio 41:9. In the presence of the active hydrogen donor, some of the dimethylcyclopropylcarbinyl radicals are being trapped before rearranging to the isomeric allylcarbinyl radical. This indicates that a single non-classical radical intermediate

cannot be involved.

The mechanism of aldehyde decarbonylations can be represented by the following simplified scheme (equation [6]).

$$ROOR \xrightarrow{\Delta} 2RO\cdot \qquad [6a]$$

$$RO\cdot + \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2CHO \longrightarrow ROH + \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2CO\cdot \qquad [6b]$$

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2\overset{O}{\overset{\|}{C}}\cdot \longrightarrow \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2\cdot + CO \qquad [6c]$$

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2\cdot \longrightarrow CH_2{=}CH\text{-}CH_2CH_2\cdot \qquad [6d]$$

$$CH_2{=}CH\text{-}CH_2CH_2\cdot + \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2CHO \longrightarrow CH_2{=}CHCH_2CH_3 + \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH\text{-}CH_2\overset{O}{\overset{\|}{C}}\cdot \qquad [6e]$$

Rosen (6) has investigated these decarbonylation reactions in greater detail, in order to obtain further information on the nature of the intermediates. These results will be discussed in connection with rate studies.

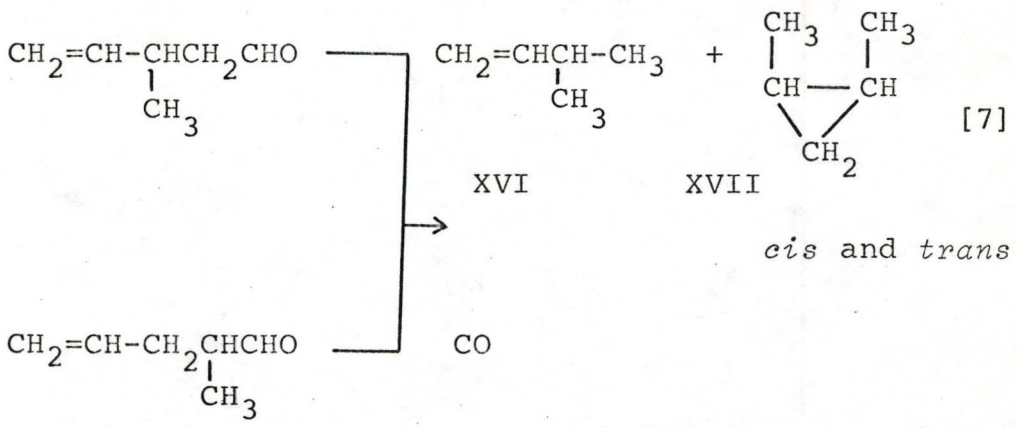
Clearly, cyclopropylcarbinyl radicals readily rearrange to give allylcarbinyl products. Perhaps the

most important question here is whether allylcarbinyl radicals can cyclize to give cyclopropylcarbinyl products, and if so, what is the nature of the intermediates involved in this cyclization? Cyclopropylcarbinyl products could arise from "classical" cyclopropylcarbinyl free radicals (intermediate VII) or from "non-classical" free radicals (intermediates IX to XII).

In 1953 Seubold (7) introduced a valuable technique for probing the number and type of intermediates in a free radical rearrangement. He found that the ratio of rearranged to unrearranged products obtained in the decarbonylation of β-phenylisovaleraldehyde depends upon the initial aldehyde concentration. This demonstrates that at least two intermediates are involved in the rearrangement sequence. The ratio of products obtained from a single "non-classical" intermediate should be independent of aldehyde concentration.

In order to determine if allylcarbinyl free radicals do cyclize to give cyclopropylcarbinyl free radicals, Montgomery and co-workers (8,9) investigated the free radical chain decarbonylation of 3-methyl-4-pentenal and 2-methyl-4-pentenal. Under comparable conditions, the principal hydrocarbon product from each was 1-pentene (XVIII). 3-Methyl-1-butene (XVI) was obtained in low yield, as well as trace quantities of

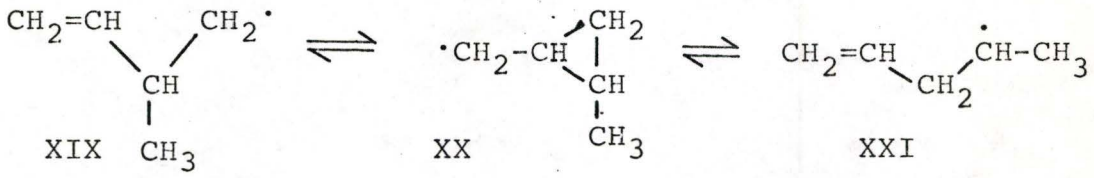
trans- and *cis*-1,2-dimethylcyclopropane (XVII) (equation [7]).

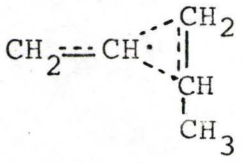


$CH_2=CHCH_2CH_2CH_3$

XVIII

The detection of trace quantities of XVII implies that cyclopropylcarbinyl-type radicals are rearrangement intermediates. The products can be explained in terms of three equilibrating classical radicals (intermediates XIX to XXI) or a single non-classical intermediate, XXII.



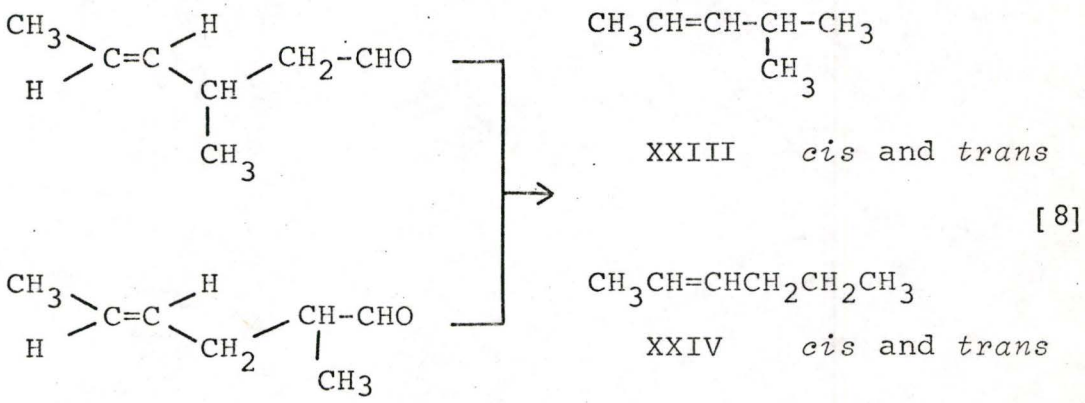


XXII

Further studies revealed that the amount of rearrangement products obtained from both aldehydes was dependent on the initial aldehyde concentration. This implies that at least two radical intermediates are involved in product formation, rather than a single "non-classical" intermediate.

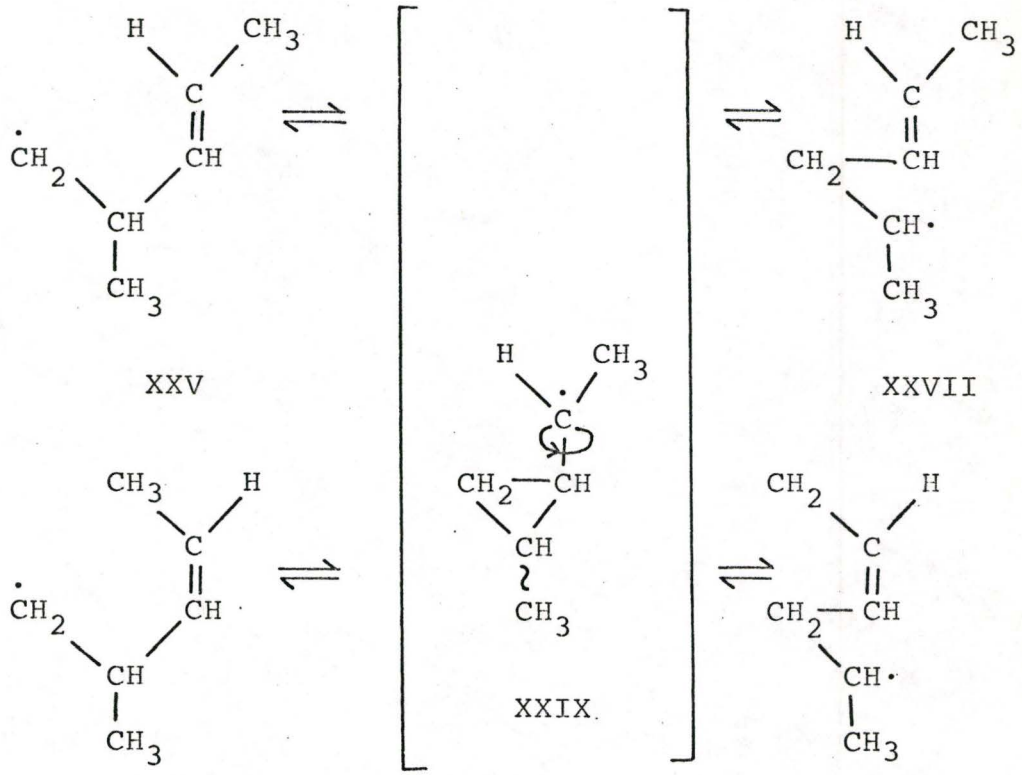
In order to obtain further information on the intermediacy of cyclopropylcarbinyl-type radicals in homoallylic free radical rearrangements, the decarbonylation of 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal was investigated (9). These experiments were also designed to provide some insight into the nature of the bonding in these intermediates.

The exclusive hydrocarbon products from both aldehydes were *trans*- and *cis*-2-hexene (XXIV), 4-methyl-*trans*-2-pentene and 4-methyl-*cis*-2-pentene (XXIII) (equation [8]). Again, the distribution of olefinic products was found to be a function of aldehyde concentration.



[8]

The proposed rearrangement scheme is outlined below.



XXV XXVII

XXVI XXIX XXVIII

This scheme proposes that homoallylic intermediates XXV to XXVIII are interconverted *via* cyclopropylcarbinyl radical XXIX. The cyclopropylcarbinyl free radical XXIX can be a transition state in the rearrangement sequence or an intermediate. The authors consider that transition state lifetimes are short compared to internal rotation lifetimes. If the cyclopropylcarbinyl species is merely a transition state for carbon skeletal rearrangement, the geometrical identity about the double bond should

be retained in the rearranged products. However, this is not observed experimentally. The facts can be accounted for by postulating that cyclopropylcarbinyl radicals are intermediates in the rearrangement. Rotation can then occur about the single bond in XXIX that replaces the double bonds in XXV and XXVI. One further consequence of this argument is that, since rotation does occur, the bonding in intermediate XXIX must be essentially classical in nature.

Roberts *et al.* (10) have observed that γ,γ-diphenylallylcarbinyl and cyclopropyldiphenylcarbinyl radicals (XXX and XXXI) rapidly and reversibly interconvert with respect to hydrogen abstraction by either from triethyltin hydride. The radicals were generated by thermolysis of either *t*-butyl-(γ,γ-diphenylallyl) peracetate XXXIII or *t*-butylcyclopropyldiphenyl peracetate XXXIV (equation [9]).

$$(C_6H_5)_2C{=}CH{-}CH_2CH_2\overset{\overset{O}{\|}}{C}{-}O{-}O{-}t\text{-}Bu \longrightarrow \qquad [9a]$$

XXXIII

$$(C_6H_5)_2C{=}CH\,CH_2CH_2\cdot + CO_2 + \cdot O{-}t\text{-}Bu$$

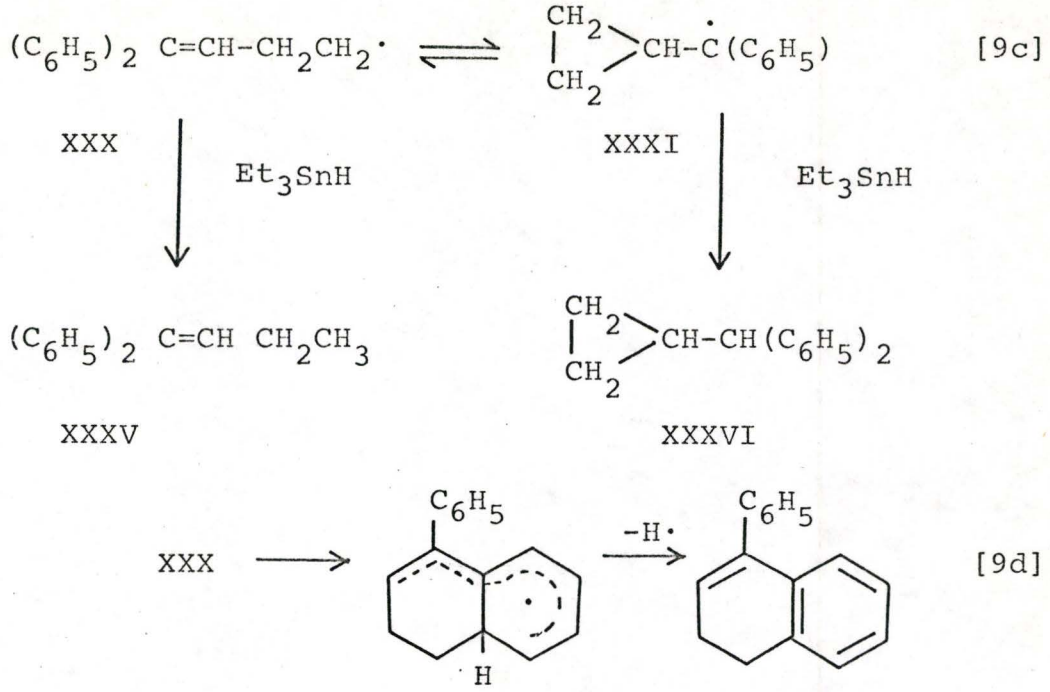
XXX

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH{-}C(C_6H_5)_2\overset{\overset{O}{\|}}{C}{-}O{-}O{-}t\text{-}Bu \longrightarrow \qquad [9b]$$

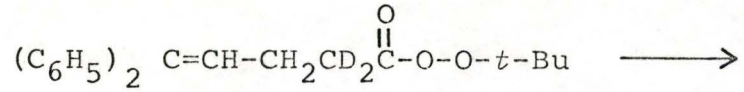
XXXIV

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>\!CH{-}\dot{C}(C_6H_5)_2 + CO_2 + \cdot O{-}t\text{-}Bu$$

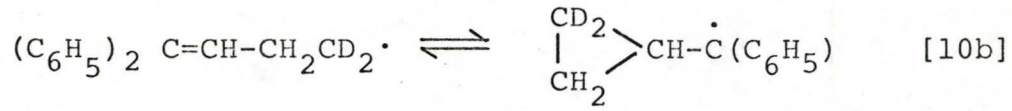
XXXI



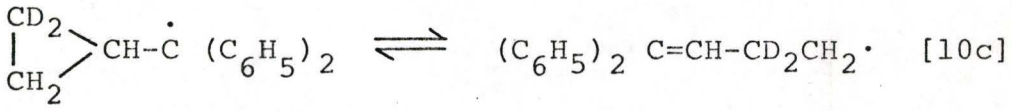
For the decomposition of XXXIII in triethyltin hydride-*n*-octane mixtures, the ratio of XXXV to XXXVI was independent of the tin hydride concentration. This indicates that the rearrangement of XXX to XXXI is fast with respect to hydrogen abstraction by XXX from the hydride, or that there is a single "non-classical" radical of intermediate structure which gives rise to both hydrocarbons. To determine the degree of equivalence attained by the methylene groups in XXX before conversion to product, the authors prepared perester XXXIII with 1.4 g atoms of deuterium in the α-position. Decomposition of the deuterated perester in the presence of 1.4M triethyltin hydride (equation [10]), followed by nmr analysis of the 1,1-diphenyl-1-butene (XXXV) formed, showed equilibration of the methylene groups to have occurred even in the presence of the active hydrogen donor.



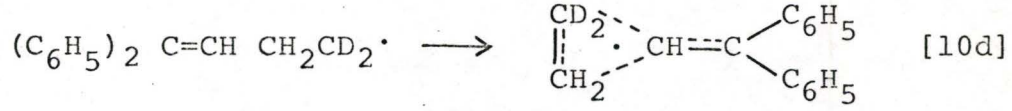
[10a]



[10b]



[10c]



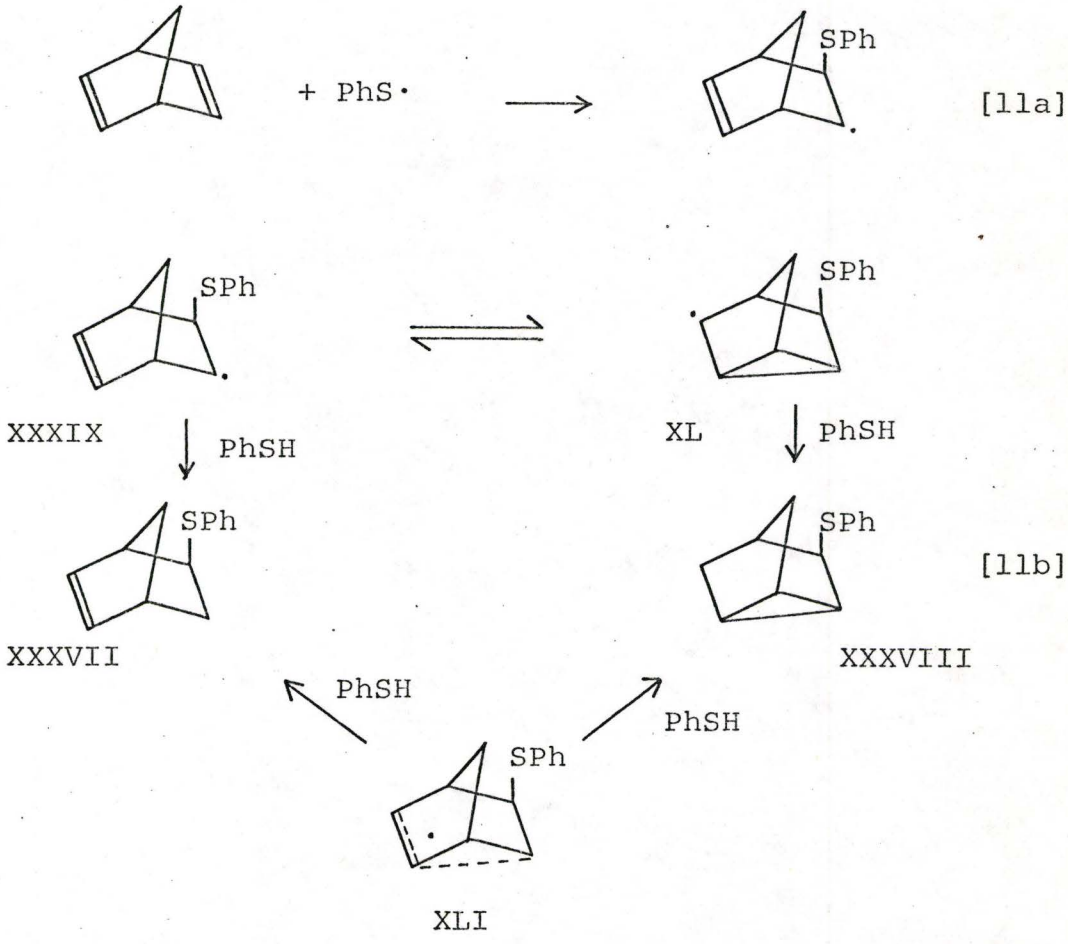
[10d]

The results can be explained in terms of two classical radicals undergoing rapid interconversion (equations [10b,c], or one symmetrical non-classical radical (equation [10d]). The authors conclude that "at present there is no reason to postulate the existence of a 'non-classical' radical species to account for the experimental results...".

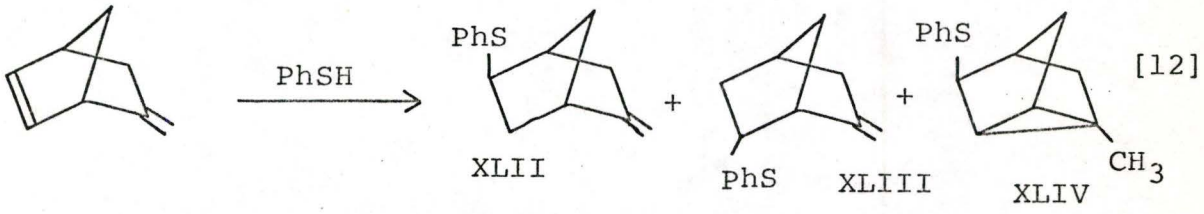
However, the fact that the product ratio (XXXV to XXXVI) was independent of hydride concentration, and that there was complete equilibration of the methylenes in the deuterated products strongly indicates, in this authors' view, that a "non-classical" intermediate (equation [10d]) may indeed exist in this system.

(ii) Semirigid Bicyclic Systems

The addition of mercaptans to 2,5-norbornadiene proceeds *via* a chain mechanism to give allylcarbinyl free radical intermediates (11). These can rearrange to cyclopropylcarbinyl intermediates, and products derived from both are possible. Again, a single non-classical intermediate could explain the formation of rearranged and unrearranged products.



Cristol *et al.* (11) have investigated the addition of thiols to 2,5-norbornadiene in order to determine whether the 1:1 addition products, XXXVII and XXXVIII, were derived from two isomeric free radicals (XXXIX and XL) or from a non-classical homoallylic radical XLI (equation [11]). Using Seubold's test for equilibrating classical intermediates, the ratio of nortricyclene XXXVIII to olefin XXXVII was found to increase markedly with a decrease in concentration of mercaptan. Therefore, a common non-classical free radical such as XLI cannot be involved. The experimental results indicate that classical radicals XXXIX and XL are the most likely precursors of products XXXVII and XXXVIII. In similar experiments, Cristol *et al.* (12) have studied the addition of thiophenol to 5-methylenenorbornene (equation [12]).

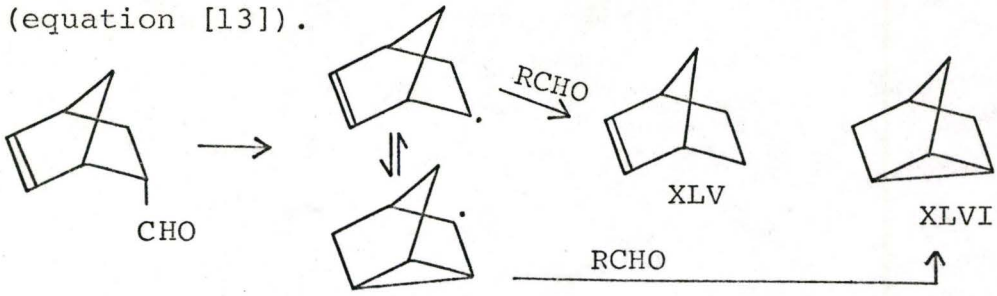


[12]

Two of the products, XLII and XLIII were formed by 1,2-addition and the third, XLIV, by homoconjugative addition. Dilution experiments again demonstrated that classical intermediates were involved.

Wilt and Levin (13) have studied the norbornenyl-nortricyclyl radical equilibrium by decarbonylating

bicyclo [2.2.1] hept-2-ene-*endo*-5-carboxaldehyde (equation [13]).



[13]

The ratio of norbornene (XLV) to nortricyclene (XLVI) was found to be approximately 45:55 and did not change appreciably over a five-fold change in aldehyde concentration.

If two classical radicals are undergoing equilibration much faster than chain transfer to products, the product ratio will not vary with concentration, the same as if one non-classical radical engenders both products. Chain transfer constants of aldehydes are lower than those of thiols used in Cristol's work, so either rapidly equilibrating classical radicals or a non-classical radical intermediate could be involved in the decarbonylation.

It is difficult to assess the significance of the results of Wilt and Levin, since only a 9% yield of hydrocarbon product was obtained. The corresponding CO yield was 28%. Analysis indicated that the main residue was a polymer with retained carbonyl. Even though there is an inherent uncertainty in this study, the invariance of the hydrocarbon product ratio with concentration

appears to support the conclusion that the equilibration or non-classical situation may be involved.

Further information on the norbornenyl-nortricyclyl radical equilibrium was obtained by Kuivila and co-workers (14). They used the tri-*n*-butyltin hydride reduction of norbornenyl and nortricyclyl halides in order to generate the free radical intermediates from both precursors. The mechanism of this reduction is given in equation [14].

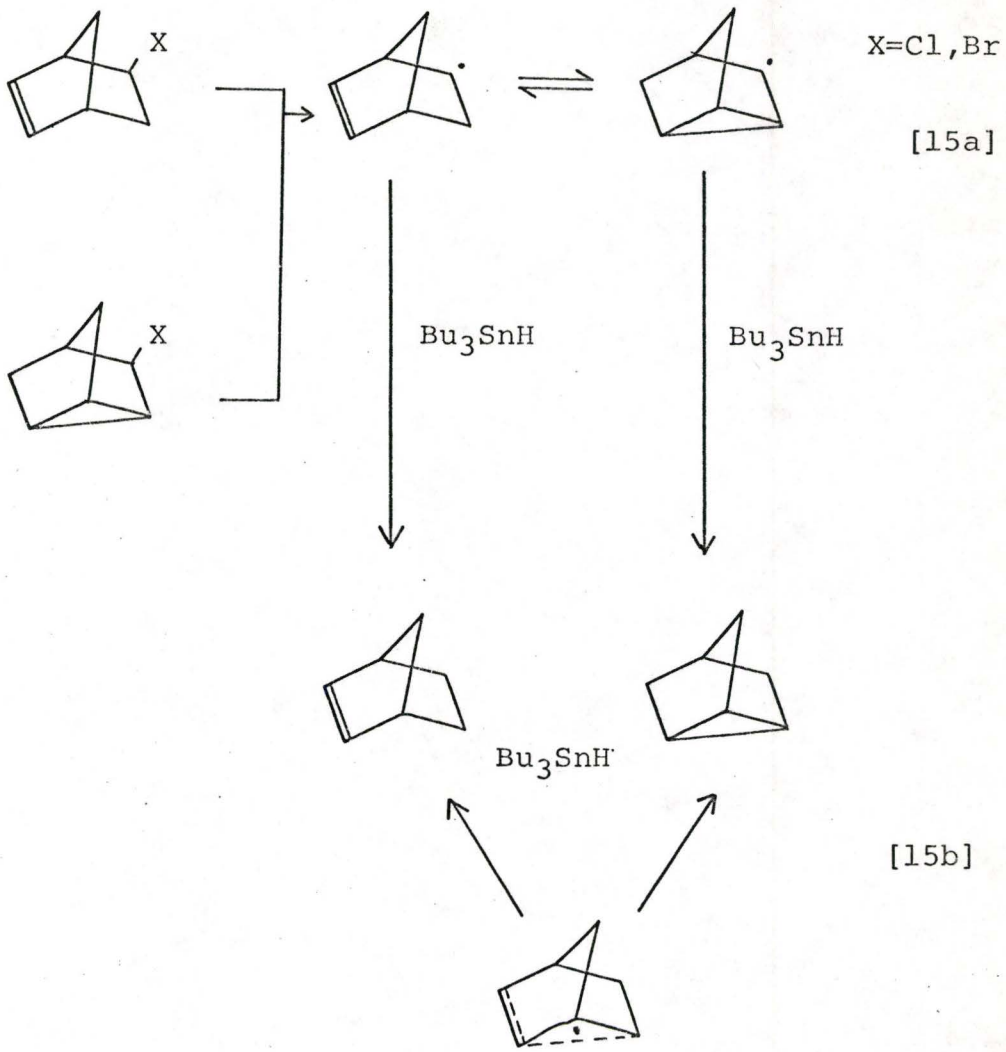
$$R_3Sn\text{-}H \xrightarrow{In\cdot} R_3Sn\cdot + InH \qquad [14a]$$

$$R_3Sn\cdot + R'CH_2\text{-}Br \longrightarrow R_3Sn\text{-}Br + R'CH_2\cdot \qquad [14b]$$

$$R'CH_2\cdot + R_3Sn\text{-}H \longrightarrow R'CH_3 + R_3Sn\cdot \qquad [14c]$$

A 6:4 ratio of norbornene to nortricyclene was obtained, either in neat hydride or in solution, regardless of whether the starting halide was the norbornenyl or nortricyclyl derivative (equation [15]). These results indicate that, if there are two intermediates, the rate of interconversion must exceed that of hydrogen transfer from the organotin hydride to either radical. A single non-classical radical intermediate (equation [15b] also explains the result.

When the reduction of nortricyclyl bromide was carried out, using varing concentrations of triphenyltin hydride (which is a better hydrogen donor to free radicals), the ratio of norbornene to nortricyclene decreased slightly



X=Cl,Br

[15a]

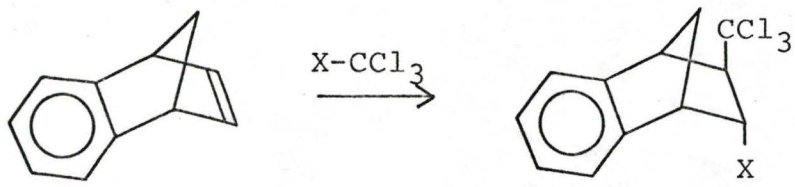
[15b]

as the concentration of hydrogen donor increased.

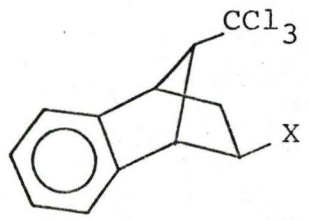
The authors conclude that this result, together with those of Cristol, confirms the existence of both norbornenyl and nortricyclyl radicals as intermediates, either of which can be trapped under appropriate conditions.

The method of calculating the norbornene to nortricyclene ratio in the trapping experiment does not appear to be completely unambiguous. Triphenyltin radicals added to norbornene, so the amount of nortricyclene was determined from a gas chromatogram, and the amount of norbornene was taken to be the difference between that value and the initial amount of hydride used. Since the variation in the product ratios with concentration is small, part of this may be due to the indirect method of calculating product ratios in these experiments.

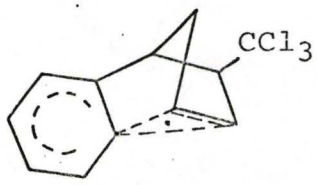
Barstow (15) has observed the exclusive formation of *trans* products from the free radical addition of carbon tetrachloride or bromotrichloromethane to benzonorbornadiene (equation [16]).



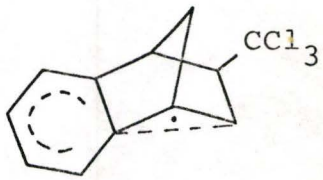
[16]



XLVII

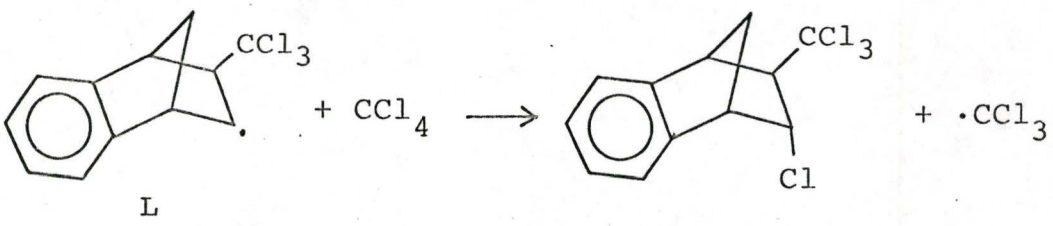


XLVIII



XLIX

The absence of any rearrangement product (XLVII) rules out the possibility of the symmetrical homobenzylic radical XLVIII as being either an intermediate, or a transition state between two rapidly equilibrating classical radicals. The data neither support nor rule out the unsymmetrical homobenzylic radical intermediate XLIX. The products can be explained on the basis of a classical radical intermediate L, with the stereochemistry



L

of the products being determined by the steric interactions between the intermediate radical L and the addend (CCl_4).

In conclusion, the results in this section show that allylcarbinyl and cyclopropylcarbinyl radicals undergo rapid and reversible interconversion. In most cases, equilibrating classical radical intermediates best explain the observed products. However, in two cases, non-classical radical intermediates can not be ruled out.

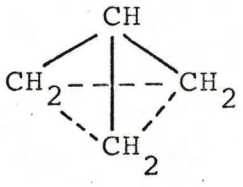
II. Rates of Formation of Cyclopropylcarbinyl-Allylcarbinyl Free Radicals

(i) General Considerations

We have seen thus far that, although cyclopropylcarbinyl-allylcarbinyl free radicals rapidly interconvert, non-classical radicals are generally unimportant in the product determining step. However, it is still possible that the rate-determining step leads to a non-classical structure which can either continue the chain leading to product, or rearrange to the classical radical. Indeed, theoretical arguments predict that allylcarbinyl radicals should be stabilized by some form of homoconjugative delocalization. A brief summary of some molecular orbital calculations, discussed in detail by Howden (16,17), follows.

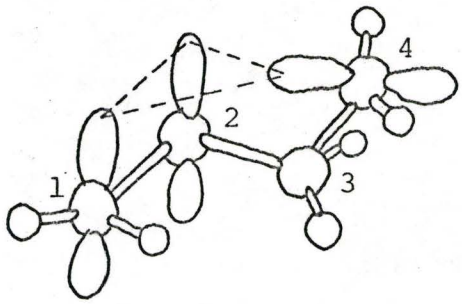
The systems studied were assumed to consist of three p-orbitals which overlapped in a manner determined by the geometry of the intermediate. Overlap was increased by decreasing the distance between carbon atoms bearing the p-orbitals, accomplished by compressing alternate bond angles. The total energy minimum was found by balancing electronic delocalization energy against strain energy due to bond-angle bending.

For the tricyclobutonium cation, radical, and anion (LI), calculations showed that for no configuration does the strain energy permit a negative total energy.



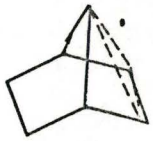
LI

Similar calculations on homoallylic intermediates (LII) showed that stabilization can be expected in all three cases. Pure 2,4-overlap gives homoallylic



LII

intermediates, whereas 1,4- as well as 2,4-overlap gives bicyclobutonium intermediates. These calcuations predict that the cation will gain more from increased 1,4-overlap than the radical, except for a system where the arrangement of the orbitals is already determined by the molecular geometry. For cases like the 7-norbornenyl free radicals (LIII), some stabilization due to 1,4-overlap can be expected.



LIII

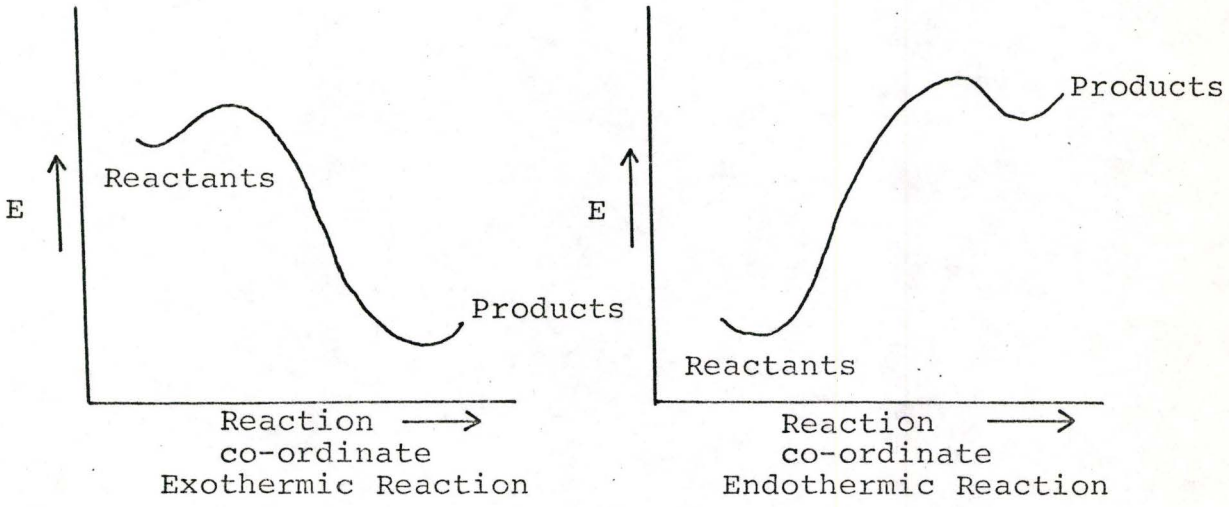
However, in no instance is the net stabilization energy for the bicyclobutonium radical or anion calculated to be greater than the most stable homoallyl case. The results therefore predict that pure 2,4- or "homoallylic" overlap leads to the most stable radicals and anions. The author concludes by stating that "although the stabilities calculated for the 'homoallyl' radical intermediate are much lower than for the bicyclobutonium cation, non-classical structures for the former are not ruled out".

Kinetic studies should yield more information on the nature of the product of the rate determining step than product studies. Before discussing some rate accelerations that have been observed, a few precautions should be noted.

Free radicals are neutral species. However, charge polarization in the transition state of a radical-forming reaction can occur (18). A small degree of carbonium ion character in the transition state of a free radical reaction could lead to a fortituous rate enhancement. Similarly, relief of strain (e.g.

opening of a three-membered ring) in going to the transition state must be considered. In this regard, model compounds used to assess rate enhancements should have similar steric requirements.

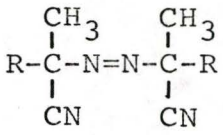
On the other hand, the absence of any rate enhancement in systems where it might be expected could be due to the position of the transition state in the rate-determining step. Hammond's postulate (19) predicts that for an exothermic reaction, the transition state can occur very early along the reaction co-ordinate and may resemble reactants. As one goes to less exothermic reactions, the transition state will occur farther along the reaction co-ordinate, and, for an endothermic reaction, will resemble products. For an



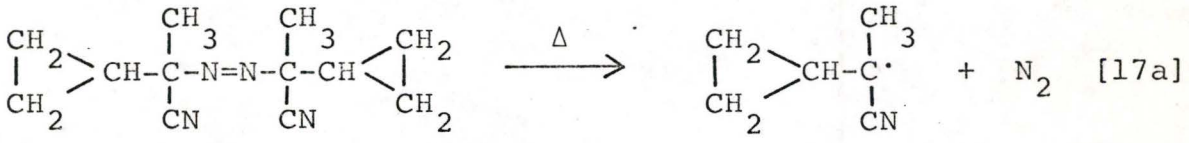
exothermic reaction, there would be little radical character on carbon in the transition state, and little rate acceleration can be expected. There are an infinite number of possibilities between the two extremes. The position of the transition state along the reaction co-ordinate in a given reaction is very difficult to assess.

(ii) Simple Acyclic Systems

Several cases have been reported in which radical-forming reactions were accelerated by the introduction of a cyclopropyl substituent directly on the incipient radical centre. Overberger and co-workers (20-22) have studied the decomposition of a series of azo-*bis*-nitriles derived from the corresponding methyl alkyl ketones.

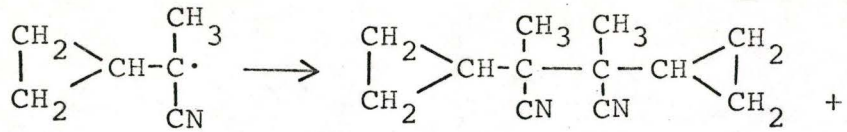


The rate of decomposition was twenty times faster when R=cyclopropyl than when R=methyl (equation [17]).



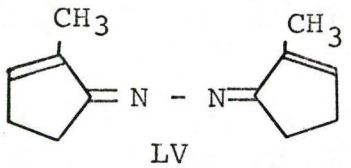
[17a]

LVI



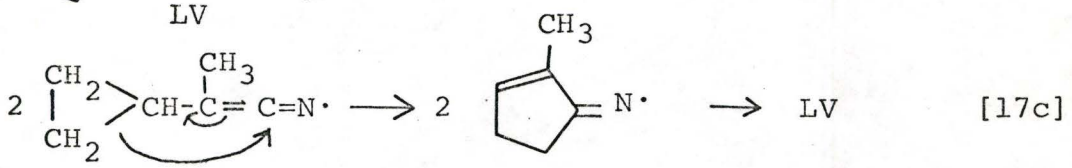
LIV

[17b]



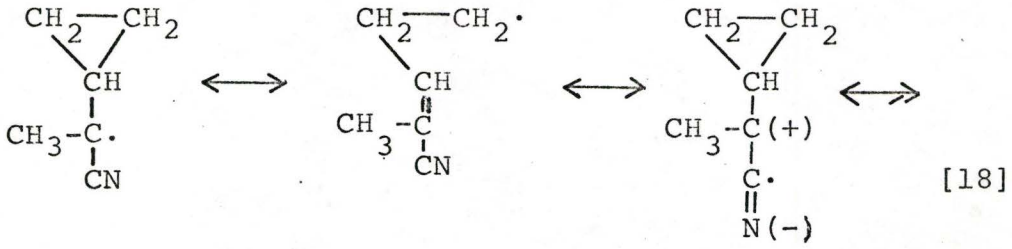
LV

+ polymer

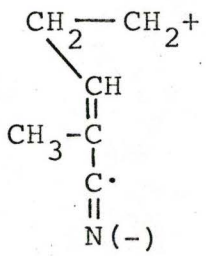


[17c]

Since the only product with cyclopropyl rings intact (LIV) was formed in only 19% yield in solution decomposition of LVI, the possibility remains that all or most of the observed acceleration could be due to a concerted clevage of C-N and C-C bonds. Also, charge polarization, as illustrated in equation [18], cannot be ruled out as a possible contributor to the

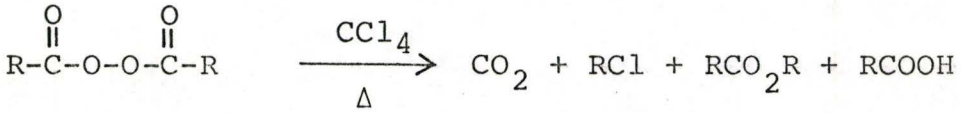


[18]



rate acceleration.

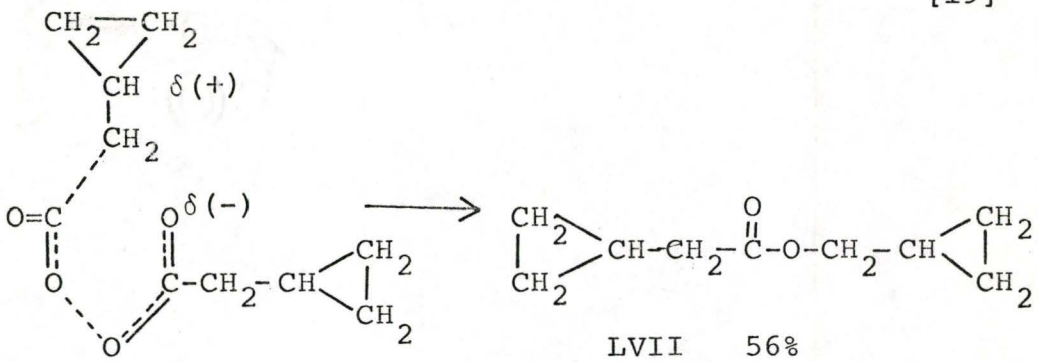
Hart and Cipriani (23) have examined the rate of decomposition of cyclopropylacetyl peroxide (equation [19]). It was found to decompose approximately fifty-five times faster than cyclohexylacetyl peroxide.



$$R\text{-}C(=O)\text{-}O\text{-}O\text{-}C(=O)\text{-}R \xrightarrow[\Delta]{CCl_4} CO_2 + RCl + RCO_2R + RCOOH$$

R = cyclopropyl
= cyclohexyl

[19]

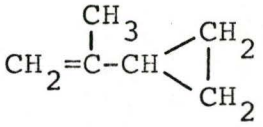


LVII 56%

The major product from the decomposition of cyclopropylacetyl peroxide was the ester LVII. Little, if any, alkylchloride could be detected, and 32-40% of the alkyl moiety could not be accounted for. In view of the product distribution, one cannot say with certainty if the observed rate enhancement is due to a stabilized cyclopropylcarbinyl radical or to a fast polar decomposition.

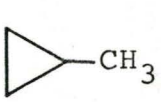
Rate accelerations in the formation of cyclo-

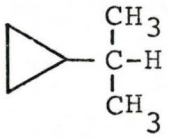
propylcarbinyl free radicals have been observed in the addition of thiyl radicals and trichloromethyl radicals to 2-cyclopropylpropene (24). Again, the

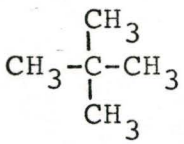


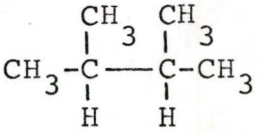
radical stabilizing effect of the cyclopropyl group could not be assessed due to possible ionic contributions in the transition state.

Rosen (6) has determined the relative reactivities of selected hydrocarbon hydrogen atoms by studying chain transfer constants of these hydrocarbons relative to polymerizing styrene. He found that the reactivity of the methyl hydrogens in methylcyclopropane was 6.10 relative to neopentane, yet the reactivity of isopropylcyclopropane was negligible compared to 2,3-dimethylbutane.

 6.10

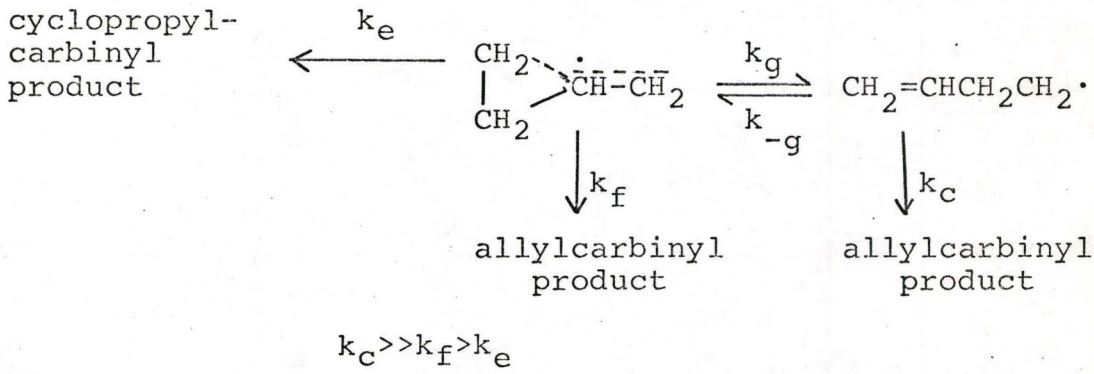
 negligible

 1.00

 1.00

The first result appears to reflect a true stabilization of the free radical intermediate by the

cyclopropyl group. The author feels that the rate enhancement observed in methylcyclopropane "demands the initial formation of a delocalized radical intermediate". In view of the fact that allylcarbinyl products are usually formed from cyclopropylcarbinyl substrates he proposes that the initially formed homoallyl radical isomerizes to the less stable classical allylcarbinyl free radical, which is capable of reacting with substrate to yield allylcarbinyl products with a greater specific rate constant than that for the similar reaction with the homoallyl radical.



$$k_c >> k_f > k_e$$

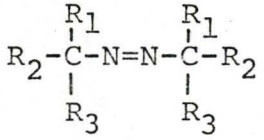
In another study, Neckers and Schaap (25) have generated α-hydroxylcyclopropylcarbinyl radicals *via* free radical hydrogen abstraction from the corresponding alcohols. They have concluded that rate accelerations associated with the formation of cyclopropylcarbinyl radicals are "manifestations of ring strain only".

The most definitive study on rate enhancements associated with cyclopropyl substituents is that of Martin and co-workers (26). They have obtained rates of thermal decomposition, and activation parameters, for a series of symmetrical azomethanes. Their results are given in Table I.

The authors consider it highly unlikely that transition state polarization is any greater than ground state polarization in these symmetrical trialkylsubstituted azo compounds. A consideration of the activation parameters in Table I shows an approximately additive change in the free energy of activation as each pair of cyclopropyl substituents is added. This provides an argument against reasoning that acceleration is provided for by relief of ring strain (25). Since the acceleration of decomposition rate seen on substituting cyclopropyl for methyl in azomethanes presumably does not depend on developing carbonium ion character at the central carbon atom in the transition state, it must reflect a stabilizing interaction between the cyclopropyl substituent and a developing radical centre. The authors do not speculate as to the nature of this stabilization. However, the large rate enhancement indicates some form of delocalization in the transition state. Their results are consistent with those of

TABLE I

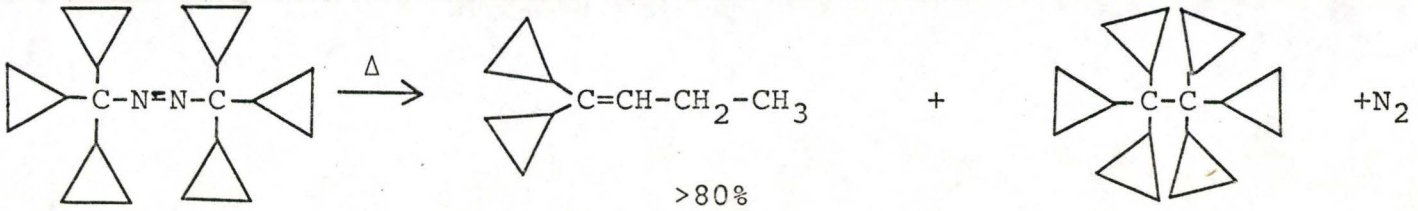
Decomposition of Azo Compounds



in Toluene at 80.2°

R_1	R_2	R_3	relative rates	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
CH_3	CH_3	CH_3	1.0	42.2±0.3	16.2±0.6	35.6
cyclo-C_3H_5	CH_3	CH_3	26.8	37.8±0.3	12.4±0.6	32.7
cyclo-C_3H_5	*cyclo*-C_3H_5	CH_3	362	35.6±0.2	12.1±0.6	30.6
cyclo-C_3H_5	*cyclo*-C_3H_5	*cyclo*-C_3H_5	2540	34.3±0.3	12.8±0.8	29.1
cyclo-C_3H_5	*cyclo*-C_3H_5	*i*-C_3H_7	286	38.0±0.7	17.6±0.6	30.8

Products in 1,4-cyclohexadiene



>80%

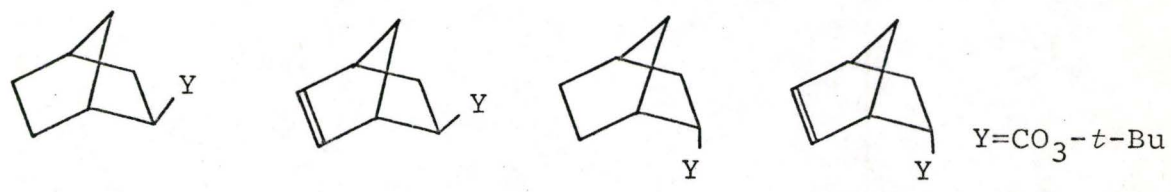
2%

Rosen (6) who proposed the initial formation of a delocalized homoallyl radical in the transition state.

The large rate enhancements observed in this study must mean that there is considerable radical character on the central carbon atom in the transition state for thermal decomposition of alkylazomethanes. Recent studies on the thermal decomposition of azocumenes (27,28) and of 1,1'2,2' tetraphenylazoethane (29) support Martin's (26) conclusion that polarization in the transition state is unimportant in these reactions. These two features make the decomposition of symmetrical trialkylazomethanes an excellent reaction through which to study participation in free radical reactions.

(iii) Semirigid Cyclic Systems

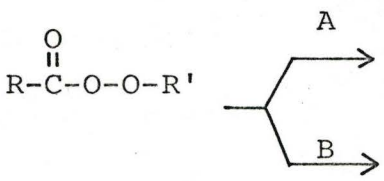
Martin and De Jongh (30) have determined the rates of homolysis of *exo* and *endo* bonds in norbornane and norbornene *t*-butylpercarboxylates. Solvolysis



studies on analogous compounds have shown that participation is possible only when the departing group is

exo (1). Hence, if non-classical radicals are formed, homolytic clevage of an *exo* C-Y bond should be accelerated over that for an *endo* C-Y bond.

Activation parameters for the decomposition of the four peresters showed that all decomposed by a concerted loss of CO_2. Furthermore, the activation parameters for each pair of isomeric *endo*- and *exo*-peresters were the same within experimental error. From this, one must conclude that participation, leading to non-classical intermediates, is absent in the transition state for perester decomposition in these systems. Peresters are known to decompose by a concerted pathway only when the alkyl radical R· (equation [20]) is of a stable type (path B) (31,32).

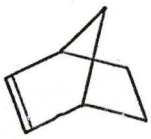


[20]

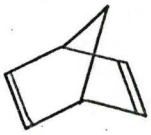
There must be considerable radical character on carbon in the transition state for concerted decompositions. It seems unlikely, then, that the position of the transition state along the reaction co-ordinate is responsible for the absence of participation.

Studies on the relative rate of addition of trichloromethyl radicals to norbornene (LVIII), 2,5-norbornadiene (LIX), 2-methylenenorbornane (LX), and

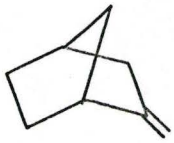
5-methylene-2-norbornene (LXI) show that homoconjugation does not lower the energy of the radical addition step and thus enhance the rate in these systems (33,34).



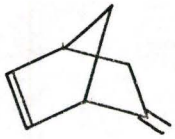
LVIII



LIX

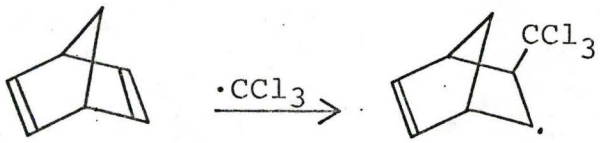


LX



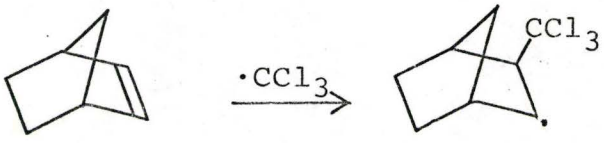
LXI

Trecker and Henry (33) have found that the rate of addition of trichloromethyl radical to 2,5-norbornadiene (equation [21]) is, within experimental error, exactly twice that of addition to norbornene (equation [22]). The effect of the second double bond appears to be strictly additive, providing evidence against anchimeric assistance involving intermediates such as LXII (equation [21]).



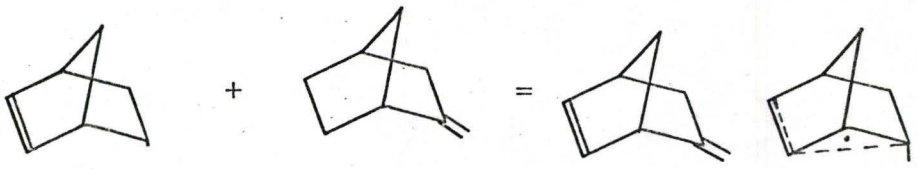
[21]

LXII



[22]

Similarly, Huyser and Echegarary (34) found no rate enhancement in the addition of trichloromethyl radical to 5-methylene-2-norbornene. Rather, the diene reacted as the sum of its isolated double bonds, providing further evidence against the existence of a



LXIII

non-classical radical, such as LXIII, in free radical addition reactions.

Kuivila and co-workers (14) have examined the relative rates of tri-*n*-butyltin hydride reduction of several bi- and tricyclic bromides in order to determine whether these systems showed any rate enhancement indicative of double bond participation. Their results are given in Table II.

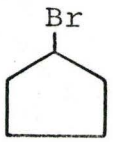
exo-Norbornenyl bromide is about 3.5 as fast as the *endo*-isomer and about 1.7 times as fast as the saturated analog, *exo*-norbornyl bromide. Similarly, the allylcarbinyl bromide, cyclopent-3-enyl bromide is about 1.7 times as fast as cyclopentyl bromide.

The difference in rate between the *exo*- and

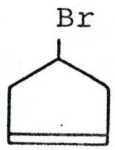
TABLE II

Relative Rates of Reduction of Cyclic Bromides by Tri-*n*-Butyltin Hydride at 45°

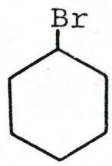
Entry	RX	Relative Rate
1	Cyclopentyl	1.0
2	Cyclopent-3-enyl	1.73
3	Cyclohexyl	0.62
4	*exo*-Bicyclo[2.2.1]hept-2-yl	0.81
5	*exo*-Bicyclo[2.2.1]hept-2-en-5-yl	1.40
6	*endo*-Bicyclo[2.2.1]hept-2-en-5-yl	0.37
7	Tricyclo [2.2.1.$0^{2,6}$]hept-3-yl	0.31



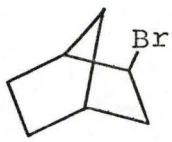
1



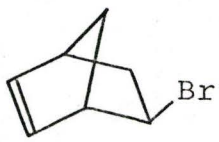
2



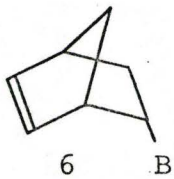
3



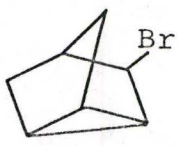
4



5



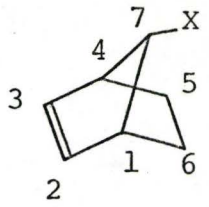
6



7

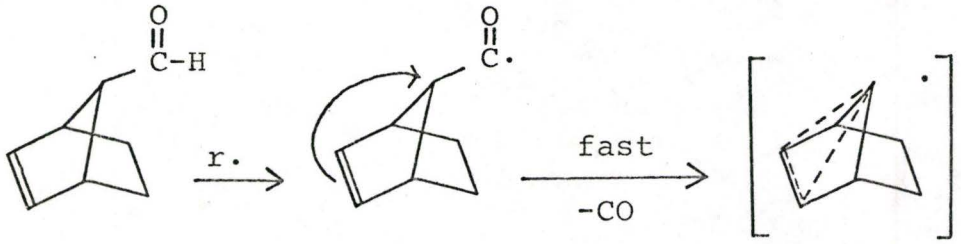
endo-isomers may be partially due to steric hindrance to approach of the tin radical in the *endo*-isomer (entries 5,6). The rate enhancement observed in entries 1 and 2, and 4 and 5 cannot be due to a steric effect, and may reflect π-bond assistance in the transition state. Another possibility for the rate enhancement is inductive electron withdrawal by the sp^2 carbons of the double bond. Earlier work on trialkyltin hydride reductions (35) has shown qualitatively that electron withdrawing substituents enhance the rate of these hydride reductions. However, in no case investigated could a polar effect be separated from a resonance or conjugative effect. Very little is known about the stabilizing effect of substituents on free radical reactions. Until such time that the effect of inductive electron withdrawal on trialkyltin hydride reductions is unambiguously demonstrated, and some estimate of it's magnitude is determined, the interpretation of the rates obtained by Kuivila and co-workers must remain in doubt. In view of the results obtained by other workers (13) on analogous systems, π-bond participation would not be expected.

The largest rate enhancements observed in solvolysis reactions of homoallylic substrates have been in 7-norbornenyl compounds (1). This can be largely



attributed to the proximity of the π-orbital of the C_2 double bond to the developing orbitals of the carbonium ion at C_7. The geometry of this system then provides the best conditions for homoallylic π-participation. Two studies have been concerned with possible rate enhancements during formation of 7-norbornenyl free radicals.

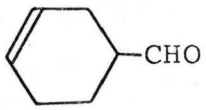
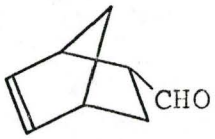
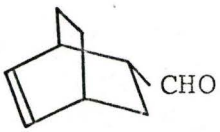
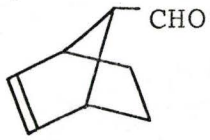
Wilt and Levin (13) have studied the decarbonylation of the cyclic aldehydes shown in Table III. As evidenced by the reaction time and CO yield, the first three aldehydes did not decarbonylate well. However, the fourth evolved 80% of the calculated amount of CO in considerably less time than the first three. Wilt and Levin suggested that the decarbonylation of *anti*-7-norbornene carboxyaldehyde is anchimerically assisted by the π-electrons, as outlined in equation [23].



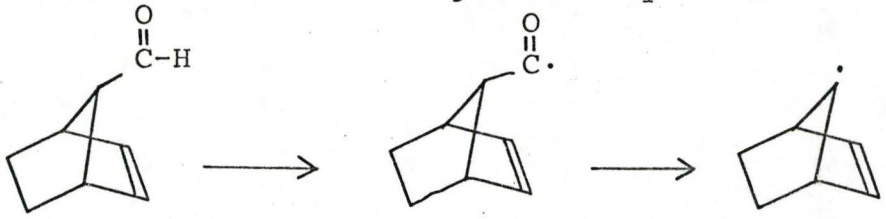
[23]

TABLE III

Decarbonylation of Aldehydes

Entry	Aldehyde	Time (hr.)	% Yield CO
1		4.5	25
2		3.0	13.6
3		4.75	19.8
4		2.0	80.0

Considerable strength would have been added to these conclusions if the *syn*-isomer, where π-bond assistance would not be expected, (equation [24]) were found to evolve CO at a significantly slower rate.



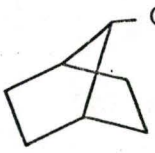
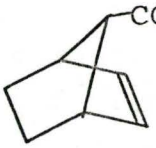
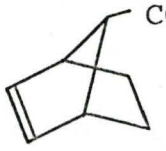
[24]

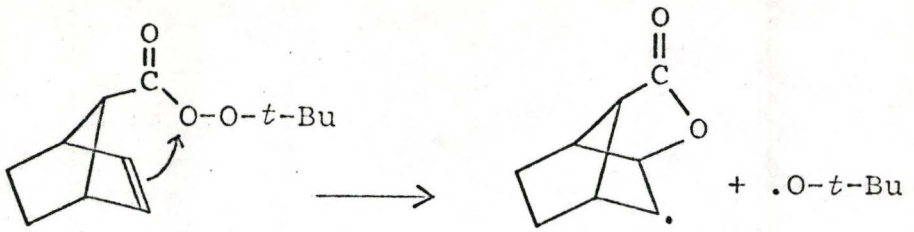
This study was not done.

With the aim of obtaining more information on the possible existence of the 7-norbornene non-classical free radical, Zador (36) studied the thermal decomposition of the peresters listed in Table IV. These peresters did not decompose by a concerted pathway but rather by rate-controlling perester O-O bond clevage. Thus, little radical character can be expected at C-7 in the transition state. The *syn*-perester (entry 2) did not evolve CO_2. The 7-norbornenyl free radical was not generated in this case. Instead, a lactone was formed. The rate enhancement observed for the *syn*-perester can be due to π-bond participation in the transition state for lactone formation (equation [25]).

TABLE IV

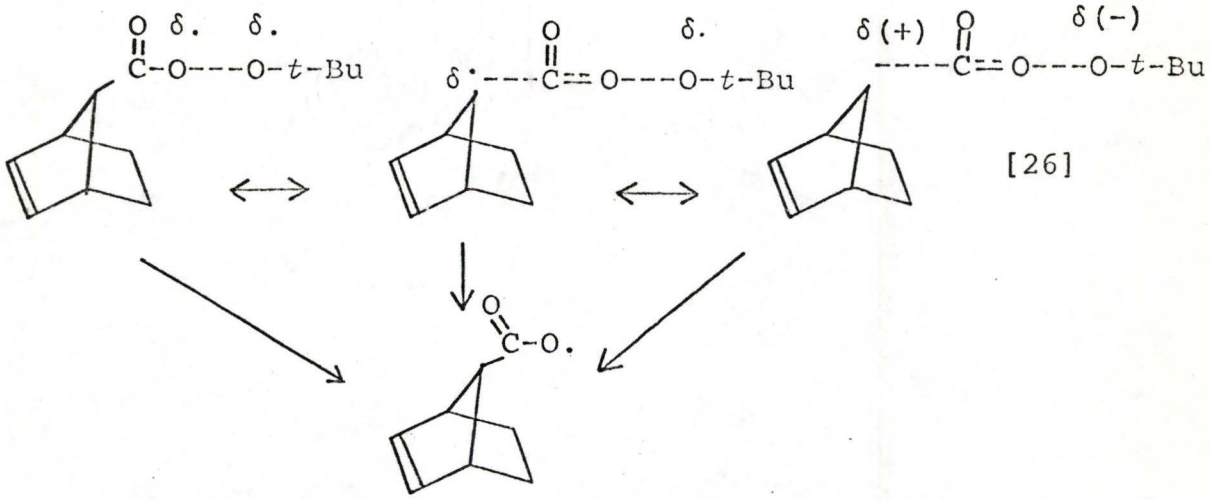
Thermal Decomposition of Peresters

Entry	Perester	CO_2 Yield %	Relative Rate
1		40	1.00
2		0	3.08
3		52	2.59



[25]

The small rate acceleration in *anti*-perester (entry 3) may be due to some radical character at C_7 in the transition state (equation [26]). If so, this is indicative of some stabilization of the radical by the double bond, as observed earlier by Wilt and Levin (13). However, ionic contributions (equation [26]) cannot be ruled out.*



[26]

---

* Results obtained in this laboratory since the writing of this thesis have shown that peresters I and II (Table IV) give quantitative CO_2 yields. These data were obtained by the more sensitive isotopic dilution technique. The high CO_2 yields indicate that the perester decomposition may be concerted, and the rate enhancement in the *anti*-perester may be due to π-bond participation.

In this section, the rates of formation of allylcarbinyl and cyclopropylcarbinyl free radicals have been discussed. Unambiguous rate enhancements have been observed during the formation of cyclopropylcarbinyl free radicals. These rate enhancements are probably due to some form of delocalization in the transition state. No unambiguous rate enhancements have been observed in bicyclic systems. Results indicate that π-bond participation may be involved during formation of the 7-norbornenyl free radical from some substrates.

III. The Mechanism of Reduction of Alkyl Halides

(i) Trialkyltin Hydride Reduction

The main body of work contained in this thesis deals with free radicals generated *via* tri-*n*-butyltin hydride reduction of alkyl chlorides and bromides. This method was chosen for two main reasons. Firstly, 7-norbornyl halides are relatively easy to synthesize compared to other 7- substituted norbornyl compounds, e.g. aldehydes, acids, amines, etc. Secondly, this method did not appear to suffer from the experimental difficulties encountered in other systems, e.g. Zador's peresters, Wilt's aldehydes, Hart's peroxides, and Overberger's azonitriles. These difficulties were discussed in Parts I and II. A system similiar to Martin's trialkyl azomethanes would undoubtly have

been good. However, the precursor to the 7-norbornyl azo compounds, the 7-norbornyl amines, were unknown when this work was begun. They have since been synthesized in low yield (37).

The mechanism of reduction of alkylhalides has been elucidated by Menapace and Kuivila (35). The following mechanism has been proposed.

$$Sn\text{-}H + Q\cdot \longrightarrow Sn\cdot + Q\text{-}H$$

$$Sn\cdot + RX \longrightarrow Sn\text{-}X + R\cdot$$

$$R\cdot + Sn\text{-}H \longrightarrow Sn\cdot + RH$$

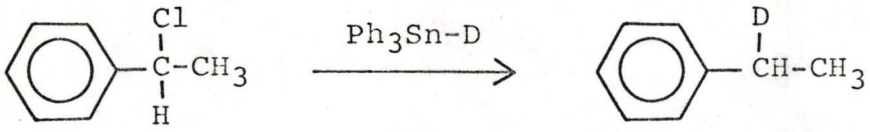
$$2Sn\cdot \longrightarrow Sn\text{-}Sn$$

$$2R\cdot \longrightarrow R\text{-}R \text{ or } R(+H) + R(-H)$$

Initiation is brought about by the abstraction of a hydrogen atom from the tin hydride by some free radical Q·. Small amounts of oxygen can initiate the reaction, although large amounts (20% or more) were found to inhibit the reaction. Azobisisobutyronitrile is an effective initiator. Thermal decomposition of the tin hydride can also lead to Sn·.

The authors give several examples as evidence of the free radical nature of the intermediates in the propagation step. Only a few will be mentioned here. Reduction of optically active α-phenylethyl chloride by triphenyltin deuteride produced racemic α-deuterio-

ethylbenzene under conditions where racemization prior



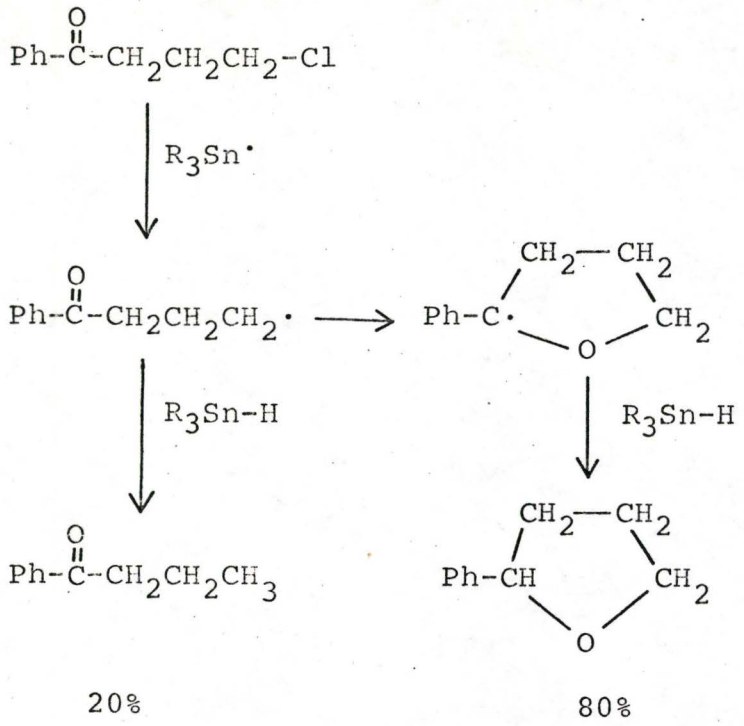
[27]

optically active racemic

to reduction did not occur (equation [27]). Since an S_N2 mechanism would lead to inversion, and a four-centre reaction would lead to retention, each of these was eliminated on the basis of this observation.

If the proposed mechanism is correct, then the chain reaction should be susceptible to inhibition. This was found to be so. Both azobisisobutyronitrile catalyzed reduction and thermal reduction were retarded by hydroquinone.

The reduction of γ-chlorobutyrophenone was examined in an attempt to trap the intermediate free radical. A driving force for ring closure is provided by the formation of a five-membered ring and by the formation of a free radical which is stabilized by both the benzene ring and the α-alkoxy group (equation [28]).



[28]

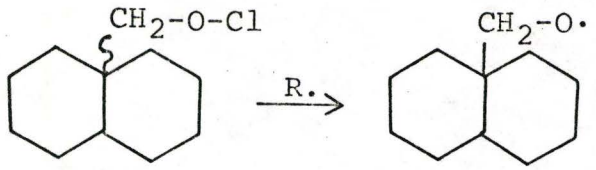
20% 80%

Two reduction products, butyrophenone and 2-phenyltetrahydrofuran were obtained in a 1:4 ratio.

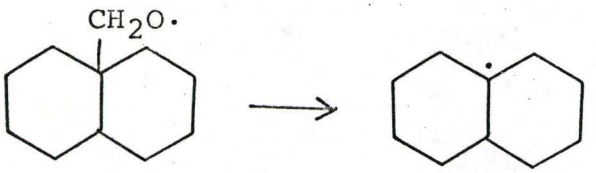
The relative reactivities of twenty-two halides were determined by allowing pairs to compete for an insufficient amount of tin hydride. The relative reactivities did not agree with either S_N2 or S_N1 reactivities, but were of the same order as those observed for abstraction of chlorine from alkyl chlorides by methyl radicals (38).

In another study, Green and Lowry (39) have generated 9-decalyl radicals by the free radical chain decomposition of *cis*- and *trans*-9-decalyl carbinyl hypochloride in fluorotrichloromethane. The major products

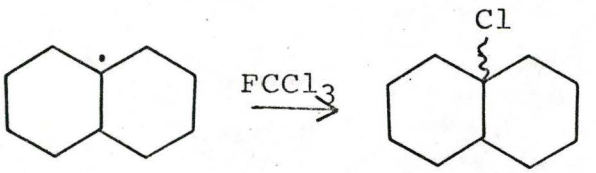
were *cis*- and *trans*-9-chlorodecalin.



[29a]



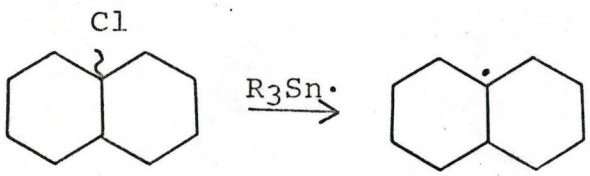
[29b]



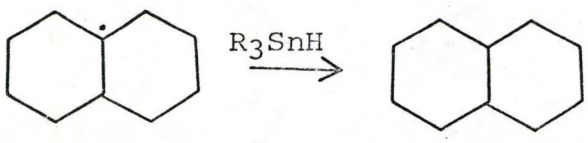
[29c]

cis and *trans*

The ratio of *cis*- and *trans*-9-chlorodecalin obtained from this known free radical chain reaction (equation [29]) was the same as the ratio of *cis*- and *trans*-decalin obtained from the trialkyltin hydride reduction of *cis*- and *trans*-9-chlorodecalin (equation [30]).



[30a]



[30b]

cis and *trans*

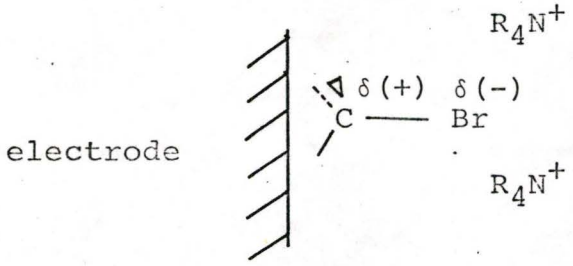
This provides further evidence for the free radical nature of trialkyltin hydride reductions.

In conclusion, studies on the initiation and propagation steps of trialkyltin hydride reductions conclusively show that free radical intermediates are involved.

(ii) Polarographic Reduction

In the reductive process for alkyl halides, the following basic mechanism for the electrode process has been generally accepted (40). As the R-Br compound diffuses toward the immediate vicinity of the negative electrode, the bromine end of the C-Br dipole should be orientated away from the electrode surface. The electrostatic field of the electrode acts to increase the polarization of the carbon-halogen bond as this C-Br portion of the molecule nears the electrode.

The reaction point just prior to the transition state is



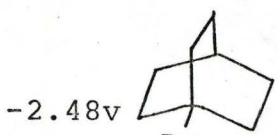
Depending on several factors, the actual potential determining step for an R-Br compound may involve direct ionization to form R(+) and Br(-) (S_N1-like) or may involve adding an electron to a σ-antibonding orbital to form $(\dot{R}\text{-}Br)^{(-)}$ i.e. an S_N2-like step (41).

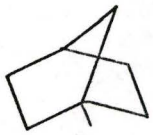
Lambert and Kobayashi (42) have shown that the half-wave potentials of ethyl- (-2.13), propyl- (-2.20), isobutyl- (-2.32) and neopentylbromides (-2.37 volts) are in qualitative accord with S_N2 substitution rates in this series. Similiarly, half-wave potentials for ethyl- (-2.13), isopropyl- (-2.26), and *t*-butylbromides (-2.19 volts) are in qualitative accord with substitution rates where a change in mechanism and rate is found between isopropyl- and *t*-butyl bromide (i.e. S_N2 to S_N1). A good qualitative correlation between S_N2 reactivity and half-wave potentials for cycloalkyl bromides was also observed.

Lambert and Kobayashi (42) feel that these results emphasize two aspects of the polarographic process: (1) The effect of the strong negative electric field surrounding the mercury drop prior to and during the reduction; and (2) the great bulk of the portion of the mercury drop which is responsible for actual electron transfer to the new orbital being formed in the potential determining step.

Both Sease and co-workers (43) and Lambert and co-workers (41) have investigated the polarographic reduction of bridgehead bromides as a test of the S_N2-like mechanism. Two different conclusions were reached regarding the orientation of the C-Br bond during reduction, and the nature of the intermediate species.

The observed reduction of 1-bromobicyclo [2.2.2] octane and 1-bromobicyclo [2.2.1] heptane could not take place by any mechanism which involves back-side attack on carbon (an S_N2-like process) due to the nature of these ring systems.





-2.86v (*vs* S.C.E.)

Sease *et al.* (43) propose that reduction at the mercury electrode takes place *via* displacement on bromine to give an alkyl free radical and a bromide ion. This process would require the transfer of electrons through the bromine atom from the cathode to the carbon atom, a direction opposite to that encountered in the S_N2 displacement reaction. They conclude that all reductions may occur *via* reductive attack on bromine, the more negative half-wave potentials for the bicyclo compounds being simply the result of steric strain in transition

states leading to non-planar free radicals.

Lambert *et al.* (41) felt that as the electrode potential is made more negative, a correspondingly greater polarization of the C-Br bond towards $C^{\delta(+)}\text{-}Br^{\delta(-)}$ occurs. If the electrode potential is made negative enough, ionization would be expected to occur, and to occur at potentials in an order determined by the relative ease of formation of the carbonium ions from the bridgehead compounds.

Further conclusions regarding the geometry of the transition state during polarographic reduction have resulted from another study by Lambert (44). He was able to obtain a quantitative correlation of the half-wave potentials of twenty-four alkyl bromides with the Taft polar (σ^*) and steric (E_s) constants. The following relationship was observed.

$$E_{\frac{1}{2}}(\text{in volts}) = 0.32_5\sigma^* + 0.12E_s - 2.16_5$$

The results show that electron-withdrawing groups aid polarographic reduction, thus supporting the frequently mentioned mechanism involving formation of the radical anion, $(\dot{R}\text{-}Br)^{(-)}$, in the potential determining step for these compounds. However, far milder steric effects were observed than those operative in normal S_N2 chemical displacements. On this basis, the simple

picture of "S_N2-like" attack in electrochemical reduction of alkyl bromides must be discarded. Similarily, Sease's (43) frontal attack on bromine should be independent of any conventional steric effects and is at variance with the experimental results. On the basis of the experimental results obtained, Lambert proposes a third possibility for the geometry of the transition state. This involves addition of an electron from the mercury electrode to the σ-antibonding orbital of the alkyl bromide, in a direction perpendicular to the axis of the C-Br bond, similar to the attack of nucleophiles perpendicular to the axis of the () bond.

At the present time, two features of the polarographic reduction of alkyl halides appear well established: (1) electron withdrawing groups aid the reduction, and (2) steric effects are important, and are quantitatively in agreement with attack of an electron perpendicular to the axis of the C-Br bond. Beyond that, there is considerable doubt as to the nature of the intermediates involved. There are three basic proposals: (1) A radical anion is formed $(\dot{R}\text{-}Br)^{(-)}$. This can add another electron to give $R(-) + Br^{(-)}$, or (2) can form $R\cdot + Br^{(-)}$. For free radical formation, the radical anion can be a transition state or an

intermediate. (3) Ionization can occur to give a carbonium ion, which can undergo reduction.

$$R\text{-}Br \longrightarrow R^{(+)} + Br^{(-)}$$

$$R^{(+)} + 1e \longrightarrow R\cdot \xrightarrow{1e} R^{(-)}$$

Streitwieser and Perrin (45) have examined the polarographic reduction of a series of related benzyl chlorides in order to determine if half-wave potentials would provide a simple measure of the relative stabilities of the related carbanions (Table V).

$$RX + 2e \longrightarrow R^{(-)} + X^{(-)}$$

A satisfactory Hammett σ-ρ plot was not obtained. The authors proposed that the transition state for polarographic reduction of these substituted benzyl halides has free-radical character. Considering the transition state in terms of the following resonance structures, the polar effect, as measured by σ, operates

$$ArCH_2\text{-}Cl + e \longrightarrow \underset{\text{LXIV}}{ArCH_2\cdot}\ Cl^{(-)} \longleftrightarrow \underset{\text{LXV}}{ArCH^{(-)}}\ \dot{Cl}$$

on LXV but radical stabilizing effects, which are not all measured by σ, operate on LXIV. In order to test this point, the methylthio group was chosen. The σ-value of *p*-CH_3-S is 0.00, but the radical stabilizing effect of sulfide is well known. The powerful effect of the

TABLE V

Polarographic Reduction of Substituted Benzyl Chlorides

Substituent	$\Delta E_{1/2}$
H	0.00
m-Br	0.155
m-Cl	0.148
p-Cl	0.124
m-F	0.091
p-F	0.026
m-MeO	0.021
p-MeO	-0.025
m-Me	-0.001
p-Me	0.01
p-MeS	0.153
p-F_3C	0.238

thioether substituent ($\Delta E_{1/2}$ = 0.153) shows clearly the radical nature of the transition state.

The possibility that all polarographic reductions of alkyl halides have considerable radical character in the transition state will be discussed in a later section of this thesis.

RESULTS AND DISCUSSION

Introduction and Outline

The bicyclo [2.2.1] heptane carbon skeleton has proved to be particularly useful in demonstrating many mechanistic aspects of organic chemistry (46). Perhaps the largest single body of work has been concerned with solvolysis reactions of various bicyclo [2.2.1] heptane derivatives (1). Due to the unique semi-rigid geometry of the system, large rate enhancements have been observed in solvolysis reactions of *anti*-7-substituted norbornenes (see Historical Introduction, Section II (iii)). The large rate accelerations have been attributed to participation of the π-orbitals of the double bond in the transition state, leading to "non-classical" intermediates. The phenomenon of participation in the transition state during ionization, by both π- and σ-orbitals, has been the subject of numerous publications over the past several years. This area of mechanistic organic chemistry is still under active investigation.

Molecular orbital calculations (see Historial Introduction, Section II (i)) predict that the π-orbitals of a homoallylic double bond should participate in the

transition state for radical formation. Participation would lower the energy of the bond breaking step, and enhance the rate. Non-classical free radical intermediates would be expected as a result. Attempts in this direction by other workers have been discussed in the Historical Introduction. No unambiguous examples of non-classical free radicals, in either the rate or product determining step of a free radical reaction, have been put forth.

Since the largest rate enhancements observed in carbonium ion reactions have been observed in studies on *anti*-7-substituted norbornenes, this same system would be expected to lead to the most fruitful results in a search for π-bond participation during free radical formation. For the present study, the tri-*n*-butyltin hydride reduction of 7-halonorbornane derivatives and the polarographic reduction of 7-bromonorbornane derivatives were chosen in an attempt to determine if non-classical free radicals exist as either transition states or as discrete intermediates during reduction.

In order to attribute an enhanced rate of reduction to π-bond participation, one must be sure that ground state differences in the compounds under investigation do not account for all of the observed rate differences. The next section of this thesis deals with

possible contributions to rate differences by charge polarization in the transition state for reduction. This is followed by a discussion of the rate and product data obtained for monohalonorbornane derivatives. In later sections, the synthesis of polychlorinated norbornane derivatives is discussed, followed by kinetic and product studies on these compounds. Some further studies on related acyclic halides completes the discussion.

I Transition State Charge Polarization: The Mechanism of Polarographic Reduction of Alkyl Halides

A radical has been defined as an atom or group of atoms with an unpaired electron (47). Although radicals are electrically neutral, it would be naïve to assume that every bond dissociation which leads to free radical intermediates proceeds without charge polarization in the transition state (equation [1]). In fact,

$$R\text{-}X \longrightarrow \underbrace{\left[R^{\delta\cdot} \cdots\cdots X^{\delta\cdot}\right]}_{\text{transition state}} \longrightarrow \underbrace{R\cdot + X\cdot}_{\text{intermediates}} \qquad [1]$$

for all except the dissociation of completely symmetrical bonds, such as those in hexaphenylethane (equation [2]), or symmetrical trialkylazomethanes, (equation [3]), the opposite is probably true (see Historical Introduction,

$$Ph_3C\text{-}CPh_3 \longrightarrow 2Ph_3C\cdot \qquad [2]$$

$$R_3C\text{-}N{=}N\text{-}CR_3 \longrightarrow 2R_3C\cdot + N_2 \qquad [3]$$

section II (i)). Two types of charge polarized transition states are possible (equation [4]). Either of these could lead to rate enhancements in free radical reactions.

$$R\text{-}X \longrightarrow \left[R^{\delta(+)}\text{----}X^{\delta(-)}\right] \leftrightarrow \left[R^{\delta(-)}\text{----}X^{\delta(+)}\right] \rightarrow R\cdot + X\cdot \qquad [4]$$

The proposed rate determining step for reduction of alkyl halides by tri-*n*-butyltin hydride (35) is shown in equation [5]. Menapace and Kuivila (35) have

$$Bu_3Sn\cdot + R\text{-}X \longrightarrow R\cdot + Bu_3SnX \qquad [5]$$

found that electron withdrawing substituents facilitate the reduction. They propose polar contributions in the transition state (equation [6]), due to the ability

$$\left[R^{\delta\cdot}\text{----}X\text{---}Sn^{\delta\cdot}Bu_3\right] \leftrightarrow \left[R^{\delta(-)}\text{---}X\text{---}Sn^{\delta(+)}Bu_3\right] \leftrightarrow \left[R\text{---}X^{\delta(-)}\text{---}Sn^{\delta(+)}Bu_3\right] \qquad [6]$$

of the tin atom to accommodate a positive charge, to explain the polar effect.

The main body of work which is reported in this thesis is concerned with rate studies on homoallylic halides. Before attributing any enhanced rates to

participation by the π-orbitals, it is necessary to be able to quantitatively evaluate any polar contribution by the electronegative vinyl group to the observed rate. A quantitative evaluation of the polar effect on tri-*n*-butyltin hydride reductions of alkyl halides was obtained through a study of the polarographic reduction of alkyl halides. The mechanism of reduction at the dropping mercury electrode will be discussed first.

In previous studies on polarographic reduction of alkyl halides (see Historical Introduction, Section III (ii)) half-wave potentials have been correlated with S_N2 displacement and S_N1 ionization rates (42). The electrode process has been likened to these two processes. The correlations were qualitative at best, and not too convincing.

Streitwieser and Perrin (45) have shown that the half-wave potentials obtained from a series of substituted benzyl chlorides reflect a free radical transition state. It appeared reasonable that half-wave potentials of other alkyl halides should be correlated with known free radical stabilities.

In order to test this point, nine alkyl bromides were chosen for which the relative rates of tri-*n*-butyltin hydride reduction were known (35). The corresponding half-wave potentials were taken from the literature

(42,44) or determined experimentally. The relative rates and half-wave potentials are given in Table VI.

A plot of $E_{1/2}$, the half-wave potential, *vs* k/k_o, the relative rate of tri-*n*-butyltin hydride reduction, is shown in Figure 1. A general trend is apparent, but the correlation is not very good.

Lambert (44) has shown, through a correlation of $E_{1/2}$ with σ^*, the Taft polar substituent constant, that reduction of alkyl halides at the dropping mercury electrode is subject to steric effects in the alkyl portion of the molecule. He has evaluated the steric factor as $0.12E_s$, where E_s is the steric substituent constant, determined from ester hydrolyses data (48). Using the Lambert steric factor of $0.12E_s$, the $E_{1/2}$ values in Table VI were corrected for steric effects, and replotted *vs* k/k_o (Figure 2).

In previous correlations (42), the half-wave potentials for primary and secondary alkyl bromides were found to be in qualitative agreement with S_N2 displacement rates. However, *t*-butyl bromide reduced at a considerably lower potential and did not fit into the general scheme. The potential determining step for this compound was likened to an SN_1 ionization and a change of mechanism from "S_N2-like" to "S_N1-like" was proposed.

TABLE VI

Relative Rates of Tin Hydride Reduction, Half-wave Potentials and Substituent Constants of Alkyl Bromides

Entry		k/k_o[a]	$E_{1/2}$[f]	E_s[d]	0.12 E_s	$E_{1/2}$-0.12E_s
1	Cyclohexyl bromide	1.46	-2.29[b]	-0.79	-0.09	-2.20
2	*n*-Octyl bromide	1.10	-2.29[b]	-0.53	-0.06	-2.23
3	*n*-Butyl bromide	1.00	-2.24[c]	-0.39	-0.05	-2.19
4	*sec*-Butyl bromide	2.99	-2.29[c]	-1.13	-0.14	-2.15
5	Cyclopentyl bromide	2.37	-2.19[b]	-0.51	-0.06	-2.13
6	*t*-Butyl bromide	7	-2.19[b]	-1.54	-0.18	-2.01
7	Allyl bromide	30.5	-1.34[c]	≈0.30[e]	-0.04	-1.30
8	Benzyl bromide	33.5	-1.23[c]	-0.38	-0.05	-1.18
9	*m*-Br-Benzyl bromide	36.2	-1.11[c]	-0.38[e]	-0.05	-1.06

(a) Reference 35

(b) References 42,44

(c) this work

(d) Reference 44

(e) Estimated

(f) volts *vs* saturated calomel electrode

Figure 1. Plot of Half-wave Reduction Potentials *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Alkyl Bromides

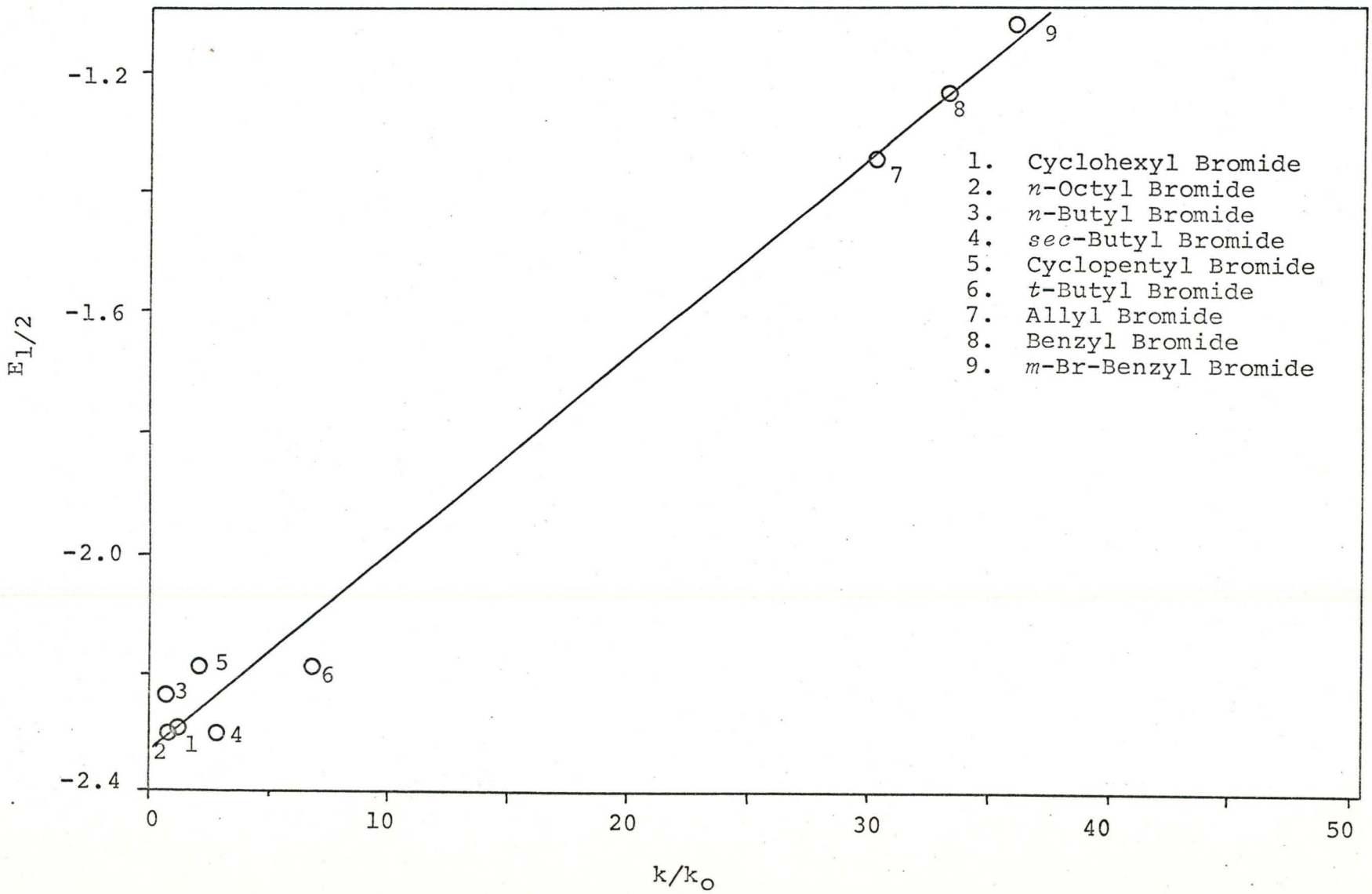
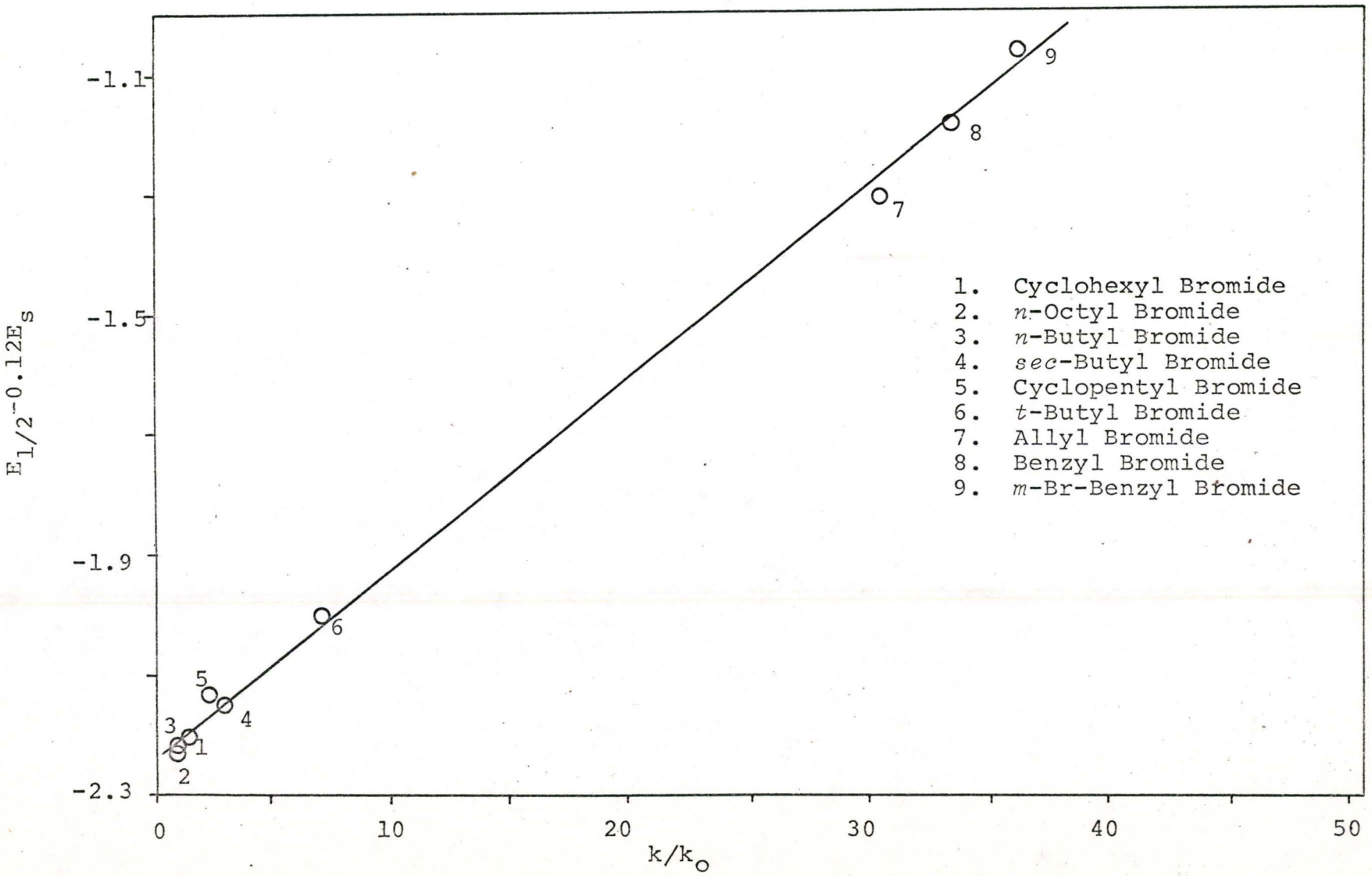


Figure 2. Plot of Half-wave Reduction Potentials (corrected for Steric Effects) *vs* Relative Rates of Tri-*n*-Butyltin Hydride Reduction for Alkyl Bromides



The excellent correlation (Figure 2) of half-wave potentials of primary, secondary, tertiary, allylic and benzylic bromides with a known free radical process eliminates "S_N2-like" and "S_N1-like" transition states for polarographic reduction. The linear correlation demands that there be considerable radical character in the transition state. Some charge polarization in the transition state is required to explain the acceleration by electron-withdrawing substituents (44).

A mechanism which adequately explains all of the available data on polarographic reduction of alkyl halides is given in equation [7]. The potential

$$R_3C\text{-}Br + e \longrightarrow \underset{\text{transition state}}{\left[R_3\dot{C} \cdots {}^{(-)}Br\right]} \longrightarrow R_3C\cdot + Br^{(-)} \qquad [7]$$

determining step involves addition of an electron to the σ-antibonding orbital of the carbon to bromine bond, in a direction perpendicular to the axis of the C-Br bond (44). The carbon radical and bromide ion arise from a transition state which has radical anion character. The amount of radical character on carbon in the potential determining step is dependent on the extent of carbon to halogen bond cleavage. Since the half-wave potentials are correlated with the relative rates of radical formation, the bromine atom with its negative charge

must be quite far away in the transition state, leaving mainly radical character on carbon.

In another study, the relative rates of reduction of chloromethyl bromides were correlated with half-wave potentials for the corresponding chloromethyl chlorides (Table VII, Figure 3). Again, a linear correlation was obtained, indicating radical character in the transition state for polarographic reduction of these alkyl chlorides.

We are now in a position to obtain a quantitative estimate of the effect of polar substituents on tri-*n*-butyltin hydride reductions. Lambert (44) has obtained half-wave potentials and steric substituent constants for a series of primary alkyl bromides for which the polar substituent constant is known. A series of nine substituted ethyl bromides (Table VIII) was chosen from Lambert's work. Their relative rates of tin hydride reduction were calculated, using Lambert's $E_{1/2} - 0.12E_s$ values and the graph in Figure 2. The relative rates obtained in this manner (Table VIII) were plotted against σ^* (Figure 4). The slope of this line is 9.5 k/k_o units per σ^* unit. If σ^* is known for a given substituent, the rate enhancement for tin hydride reduction, due to polar effects, can be estimated.

TABLE VII

Relative Rates of Tin Hydride Reduction, Half-wave Potentials and Substituent Constants of Chloromethyl Halides

Compound	k/k_o[a] X=Br	$E_{1/2}$[b] X=Cl	E_s[c]	$E_{1/2} - 0.12E_s$
$ClCH_2$-X	1.00	-1.95	-0.24	-1.92
Cl_2CH-X	4.34	-1.30	-1.54	-1.11
Cl_3C-X	8.77	-0.33	-2.06	-0.08

(a) Reference 35

(b) Volts *vs* A_g/A_g^+ electrode in 0.100M Et_4NCl in DMF

(c) Reference 48

Figure 3. Plot of Half-wave Reduction Potentials (corrected for Steric Effects) *vs* Relative Rates of Tri-*n*-Butyltin Hydride Reduction for Chloromethyl Halides

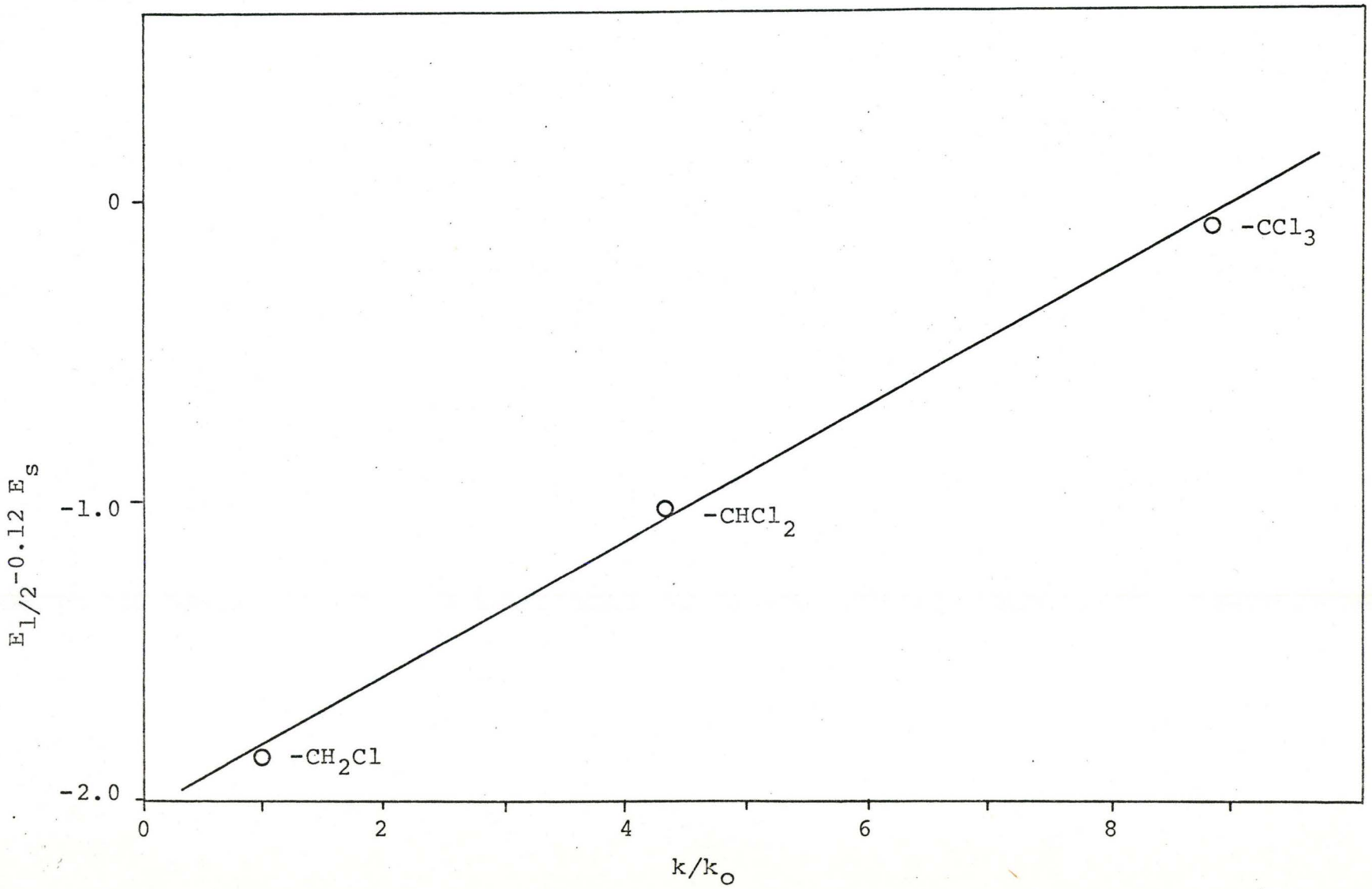


TABLE VIII

Half-wave Potentials, Polar Substituent Constants and Calculated Relative Rates of Tin Hydride Reduction of 2-Substituted Ethyl Bromides

Entry	Compound	σ^* [a]	$E_{1/2} - 0.12E_s$ [a]	k/k_o (calculated)
1	$PhCH_2CH_2CH_2$-Br	0.08	-2.12	3.8
2	Ph-CH_2CH_2-Br	0.215	-2.08	5.0
3	$EtO_2(CH_2)_2CH_2CH_2Br$	0.09	-2.13	3.5
4	Ph-O-$CH_2CH_2CH_2Br$	0.30	-2.06	5.7
5	F-$CH_2CH_2CH_2$-Br	0.39	-2.03	6.5
6	NC-$CH_2CH_2CH_2$-Br	0.47	-2.00	7.5
7	$EtO_2CH_2CH_2$-Br	0.72	-1.93	9.7
8	Ph-O-CH_2CH_2-Br	0.85	-1.91	10.3
9	NC-CH_2CH_2-Br	1.30	-1.76	15.2

(a) Reference 44

Figure 4. Plot of Polar Substituent Constants *vs* Calculated Relative Rates of Tri-*n*-Butyltin Hydride Reduction for Substituted Ethyl Bromides

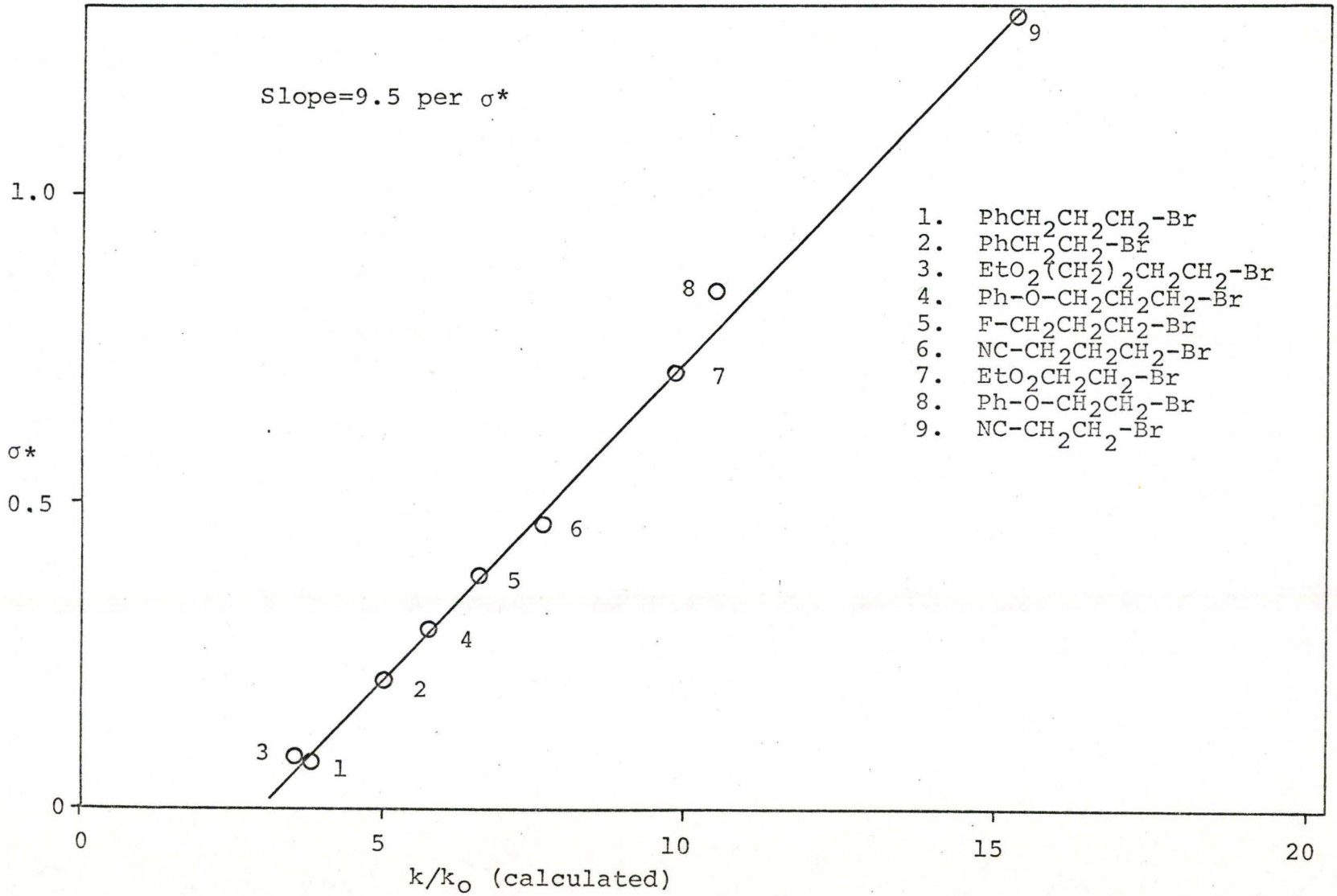
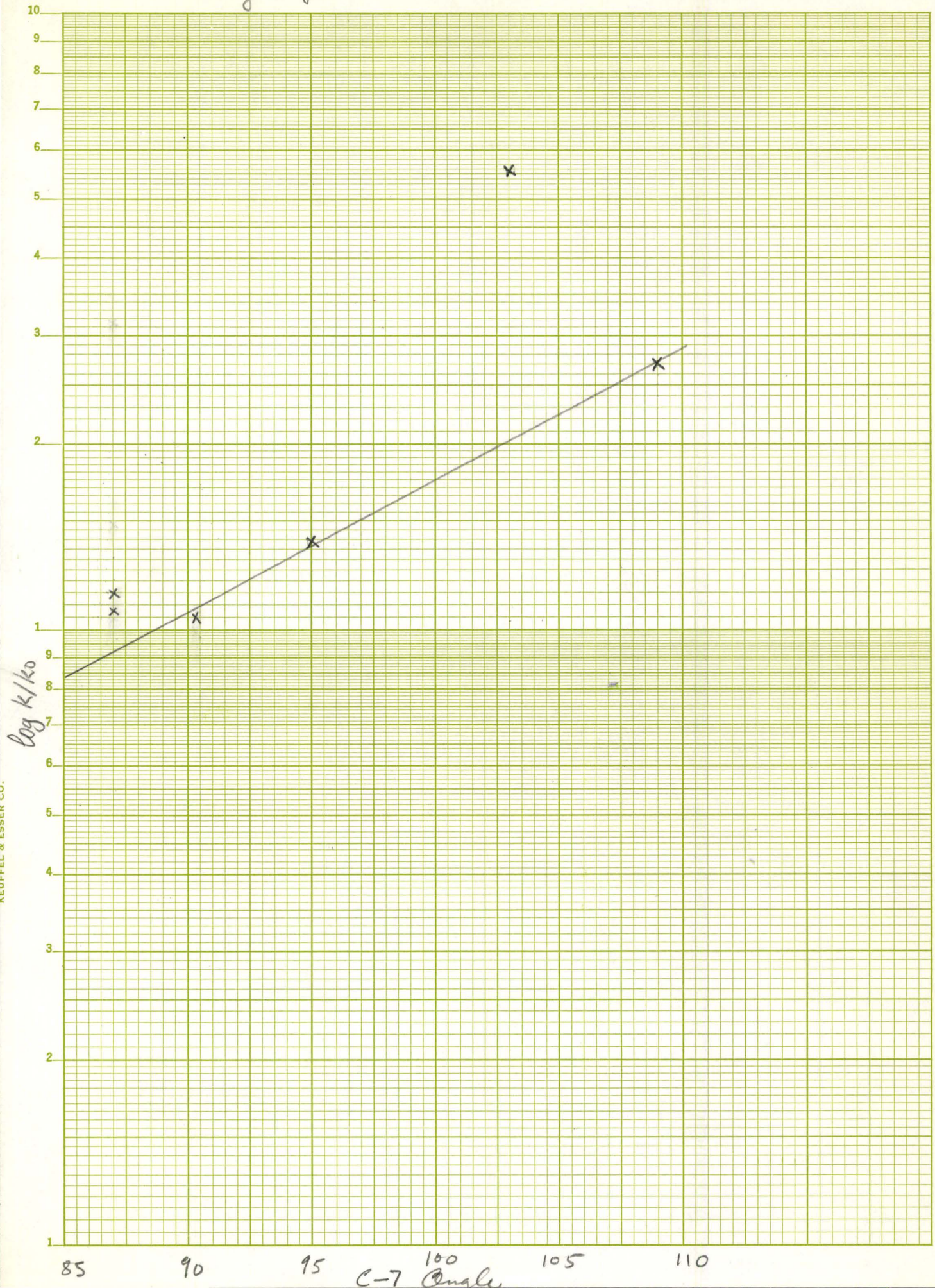
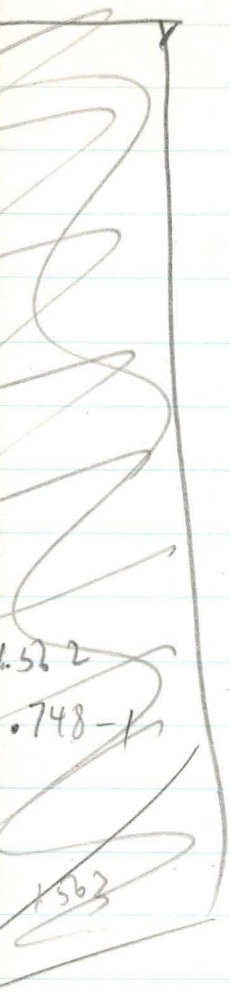


Figure 5

Fig 6 p 86





$\Delta(E_{1/2} - E_s)$

Ref 2.19

$\Delta E_{1/2}$	$\log(E_{1/2} - .12E_s)$
−.01	.342
−.04	.348
00	.341
+.04	.333
+.06	.329
+.18	.303
+.89	.114
+1.01	.072
+1.13	.026

$E_{1/2} \propto Re$

1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
R/Ro
log
$\frac{1}{T}$
$\frac{1}{T}$
$\frac{1}{T}$
$\frac{1}{T}$
$E_{1/2} = .13 E_g$

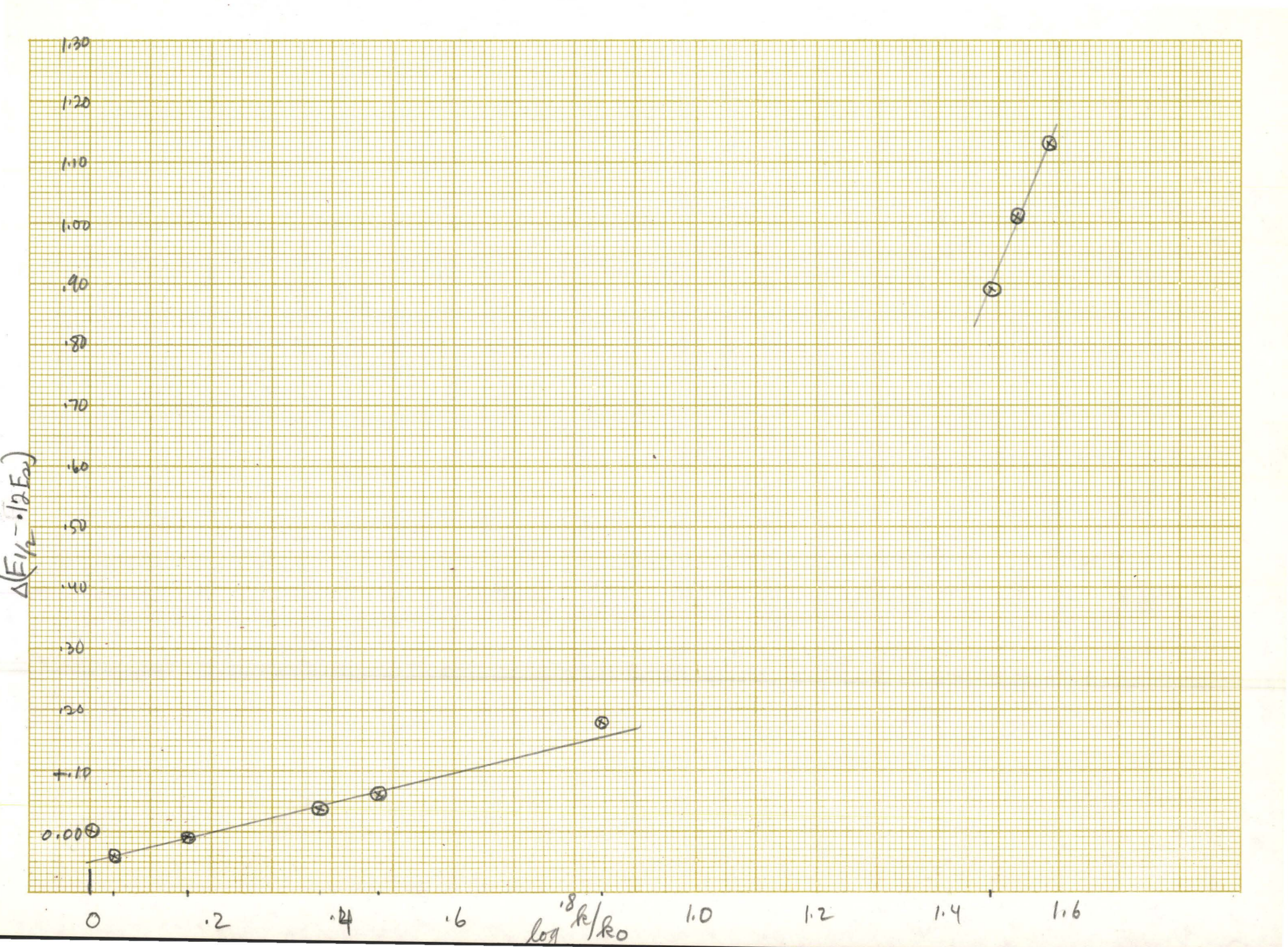

1.30
1.20
1.10
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00
$\Delta(E_{1/2} - .12E_{ox})$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
$\log k/k_0$

Fig 5 p


1.562
Br
1.50
Br
1.225
1.25
log k/k₀
Br
1.00
1.00
Br
.875
Actual
Br
.748
0.75
85
90
95
100
105
110

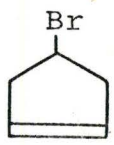
log |E1/2 − .12E2|
.35
.30
.25
.20
.15
.10
.05
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
log k/k0

The σ* value for an allyl carbinyl substituent has not been determined. It can be estimated as follows: σ* for CH_3-CH=CH-CH_2- is 0.13 (48). Using the fall-off factor of 2.6 per methylene group (48), σ* (calculated) for CH_3-CH=CH-CH_2CH_2- is 0.05. For the saturated analog, n-pentyl, σ* can be estimated from σ* for n-butyl, using the increment of 0.015 per methylene group for aliphatic substituents (48).

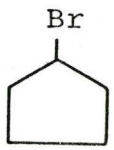
	σ*
CH_3-CH=CH-CH_2CH_2-	+ 0.05
$CH_3CH_2CH_2CH_2CH_2$-	-0.130

The difference in σ* between a homoallylic substituent and its saturated analog is thus estimated as 0.18. This corresponds to a rate enhancement of 1.7, due to the polar effect.

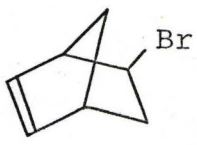
Two examples are available in the literature to test these calculations (14).



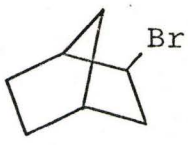
k/k_o 1.73



1.00



k/k_o 1.73



1.00

These relative rates were discussed previously in terms of π-bond participation in the transition state for free radical formation (Historical Introduction, Section II (iii)). A possible polar contribution was suggested. In view of the present work, these rates are entirely consistent with a rate enhancement due to

the electron withdrawing ability of the homoallylic double bond.

In this section, the free radical character of polarographic reductions of alkyl halides has been firmly established. A quantitative estimate of the effect of polar substituents on tri-*n*-butyltin hydride reductions has been calculated. These results will be used in later discussion.

II Kinetic, Sterochemical and Product Studies on Monohalocycloalkanes

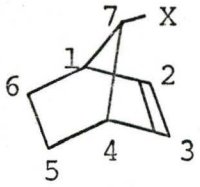
General

The synthesis of compounds required for this part of the study has been previously described in the literature. For convenience, the structures of all compounds to be discussed in this section are given in Chart I. Syntheses and identification are given in the Experimental (Section I (i,ii,iii)).

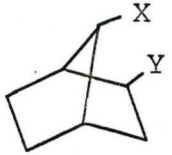
The mechanism of tri-*n*-butyltin hydride reduction has been discussed in the Historical Introduction (Section III (i)). The method for determining relative rates is given in the Experimental (Section II (i)).

CHART I

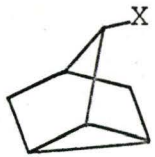
Structures of Compounds I to XIII



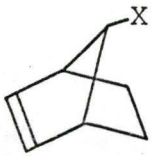
I (a) X=H
(b) X=Br
(c) X=Cl



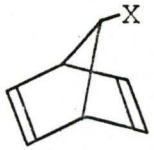
II (a) X=H Y=Br
(b) X=Y=Br
(c) X=Y=Cl
(d) X=Br Y=H
(e) X=Cl Y=H
(f) X=Y=H



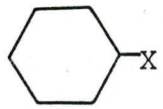
III (a) X=H
(b) X=Br
(c) X=Cl



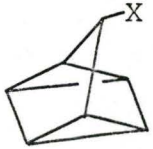
IV (a) X=Br
(b) X=Cl
(c) X=OH
(d) X=D



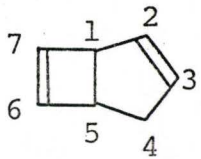
V (a) X=H
(b) X=Cl
(c) X=OH



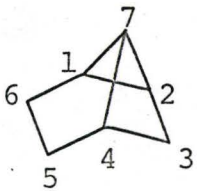
VI (a) X=H
(b) X=Br
(c) X=Cl



VII (a) X=H
(b) X=Cl

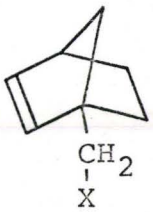


VIII

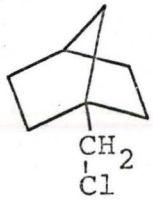


IX

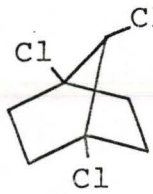
X



XI (a) X=OH
(b) X-Cl



XII



XIII

(i) Kinetics and Products

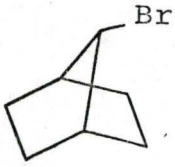
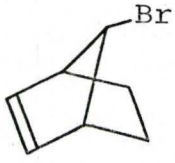
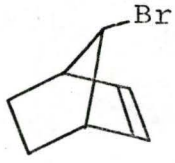
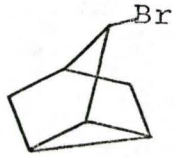
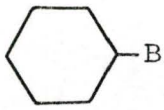
In the initial stage of this investigation, the relative rates of tin hydride reduction of *syn*- and *anti*-7-bromonorbornene (Ib and IVa) and related cycloalkyl bromides (IId, IIIb and VIb) were determined in a search for π-bond participation in the rate determining step. The relative rates are given in Table IX.

Earlier calculations predict that a homoallylic double bond should accelerate the rate of tin hydride reduction of an alkyl halide by approximately 1.7, due to a purely inductive effect. A rate enhancement larger than this would be necessary in order to invoke delocalization in the transition state. The homoallylic bromides Ib and IVa reacted more slowly than the saturated analog, 7-bromonorbornane (IId). The inductive effect of the double bond must clearly be relatively insignificant in these 7-bromonorbornane derivatives. Other effects must come into play, retarding the rate of reduction of Ib and IVa.

X-ray crystallographic studies indicate that the C_1-C_7-C_4 bridge angle in norbornane (IIf) is in the neighbourhood of 96 to 97° (50). This is considerably less than tetrahedral (109°). Bond angle differences

TABLE IX

Relative Rates of Tin Hydride Reduction, Carbonyl Stretching Frequencies and Calculated Carbonyl Bond Angles for 7-Bromonorbornane Derivatives

Entry	Compound	k/k_o (a) 100°	Carbonyl stretching frequency cm^{-1} (b)	Calculated C-7 bond angle, in degrees (c)
1	 (IId)	1.00	1773	90.3
2	 (IVa)	0.56	1780	87.1
3	 (Ib)	0.75	1780	87.1
4	 (IIIb)	1.68	1762	95
5	 (VIb)	3.65		109 (d)

(a) Relative rates of reduction with tri-*n*-butyltin hydride.
(b) Carbonyl stretching frequency of the corresponding 7-keto-compounds (49).
(c) Carbonyl bond angle calculated from the carbonyl stretching frequency (56).
(d) Normal sp^3 bond angle.

at C-7 in the substrates (Table IX) may be the main contributor to the rate differences observed. Free radical reactions are known to be sensitive to deviations in bond angle from the normal tetrahedral value. For example, cyclopropane C-H bonds show decreased reactivity towards radicals (51). Similarly free radical chlorination of norbornane (IIf) (52-54) and benzonorbornane (55) give mainly the *exo*-2-chloride. Little, if any, free radical chlorination takes place at C-7. The decreased reactivity of C-H bonds in cyclopropane and the 7-CH bonds in norbornanes has been attributed to a strengthening of the C-H bonds due to the decreased C-C-C bond angle (55).

7-Bromonorbornane (IId) undergoes reduction much more slowly than bromocyclohexane (VIb) (Table IX). The decreased C_1-C_7-C_4 bond angle in IId must strengthen the C-Br bond, thus accounting qualitatively for the rate retardation. If the rates in Table IX reflect mainly differences in the strength of the C-Br bond, the rates should be correlated with bond angle differences at the reaction centre.

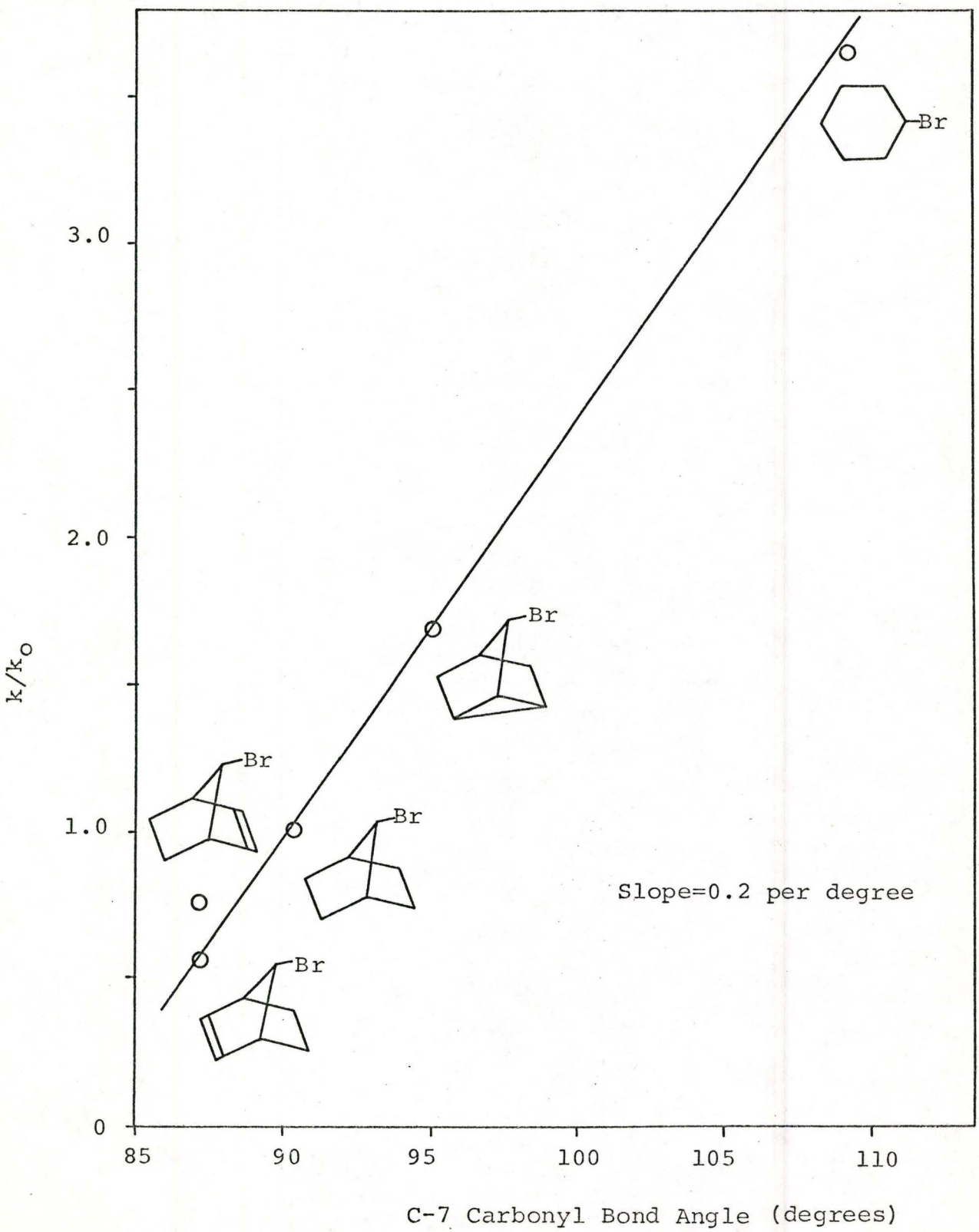
The C-7 bond angles in norbornane (IIf), norbornene (Ia) and nortricyclene (IIIa) are not known accurately. It has been shown, however, that carbonyl stretching

frequencies are sensitive to bond angle changes, and that a linear relationship exists between the two (56). The carbonyl stretching frequencies in Table IX were used to calculate the C_1-C_7-C_4 bond angles for the sp^2 hybridized analogs of the compounds listed.

In these semi-rigid molecules, geometric restraint prevents the C-7 bond angle from changing much on going from sp^3 to sp^2 hybridization. Consequently, chemical changes involving a change from sp^3 to sp^2 hybridization are strongly resisted (49). For this reason, the sp^2 bond angle at C-7 in the 7-keto compounds should not be too different from the sp^3 bond angle in the 7-halonorbornane derivatives. The calculated C-7 bond angles should be porportional to the C-7 bond angles in Ib, IId, IIIb and IVa. For the unstrained molecule, cyclohexyl bromide (VIb), the normal sp^3 bond angle of 109° was taken as the best estimate of the bond angle at the reaction centre for this compound. The relative rates for the five bromocycloalkanes in Table IX were then plotted *vs* the calculated bond angles. The result is shown in Figure 5. A similar correlation line, although of different slope, would result from the use of actual bond angles for all of the compounds.

The excellent linear relationship strongly indicates that the rates are due largely to bond angle

Figure 5. Plot of Relative Rates of Tri-*n*-Butyltin Hydride Reduction *vs* C-7 Carbonyl Bond Angle for Cycloalkyl Bromides



differences in the substrates. These bond angle differences probably affect the strength of the C-Br bond, giving rise to rate differences. Polar effects appear to be negligible, and π-bond participation in the transition state for free radical formation, if present, is not observable from the rate data. *syn*-7-Bromonorbornene (Ib) is above the correlation line. There must be another ground state or transition state effect which causes this deviation. A plausible explanation of this anomaly will be presented in later discussion.

Reduction of *syn*- and *anti*-7-bromonorbornene (Ib and IVa) and bromocyclohexane (VIb) with tri-*n*-butyltin hydride gave the corresponding hydrocarbon reduction products, norbornene (Ia), norbornane (IIf) and cyclohexane (VIa). These were identified by glpc using authentic samples as internal standards. Yields were 70-80%, as calculated from glpc analyses. No other volatile products were observed. Bromonortricyclane (IIIb) gave a mixture of norbornene (I a) and nortricyclane (IIIa) as previously determined by Warner, Strunk,and Kuivila (14).

Two possibilities regarding π-bond participation in the transition state for free radical formation arise:

1. the homoallylic double bond in norbornene derivatives

does not stabilize an incipient radical centre at C-7 to an appreciable extent, i.e., non-classical free radicals do not exist in this system, or 2. there is only a small degree of radical character at C-7 in the transition state for reduction of 7-bromonorbornenes and, for this reason, no participation is observed.

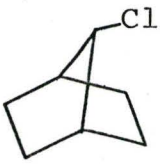
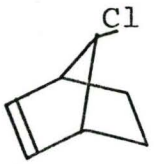
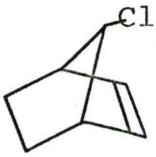
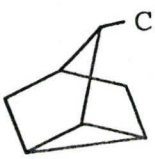
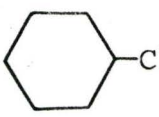
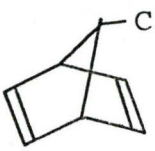
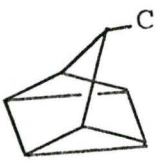
The second possibility can be tested by using a process of higher activation energy. The Hammond Postulate (19) predicts that, as a process becomes more endothermic, the transition state will be shifted further along the reaction coordinate, and become more product-like. In our case, if the process of halogen abstraction is one of higher activation energy, there should be more radical character at C-7 in the transition state, and any anchimeric assistance should be more easily detected.

To this end, the relative rates of *syn*- and *anti*-7-chloronorbornene and related compounds were determined. These are listed in Table X. A plot of the relative rates *vs* the calculated C-7 bond angle for the corresponding 7-keto compounds is shown in Figure 6.

The rates for 7-chloronorbornane (IIe), chloronortricyclane (IIIc) and chlorocyclohexane (VIc) are well correlated with bond angle differences at the incipient radical centre. The rates for *syn*- and *anti*-7-

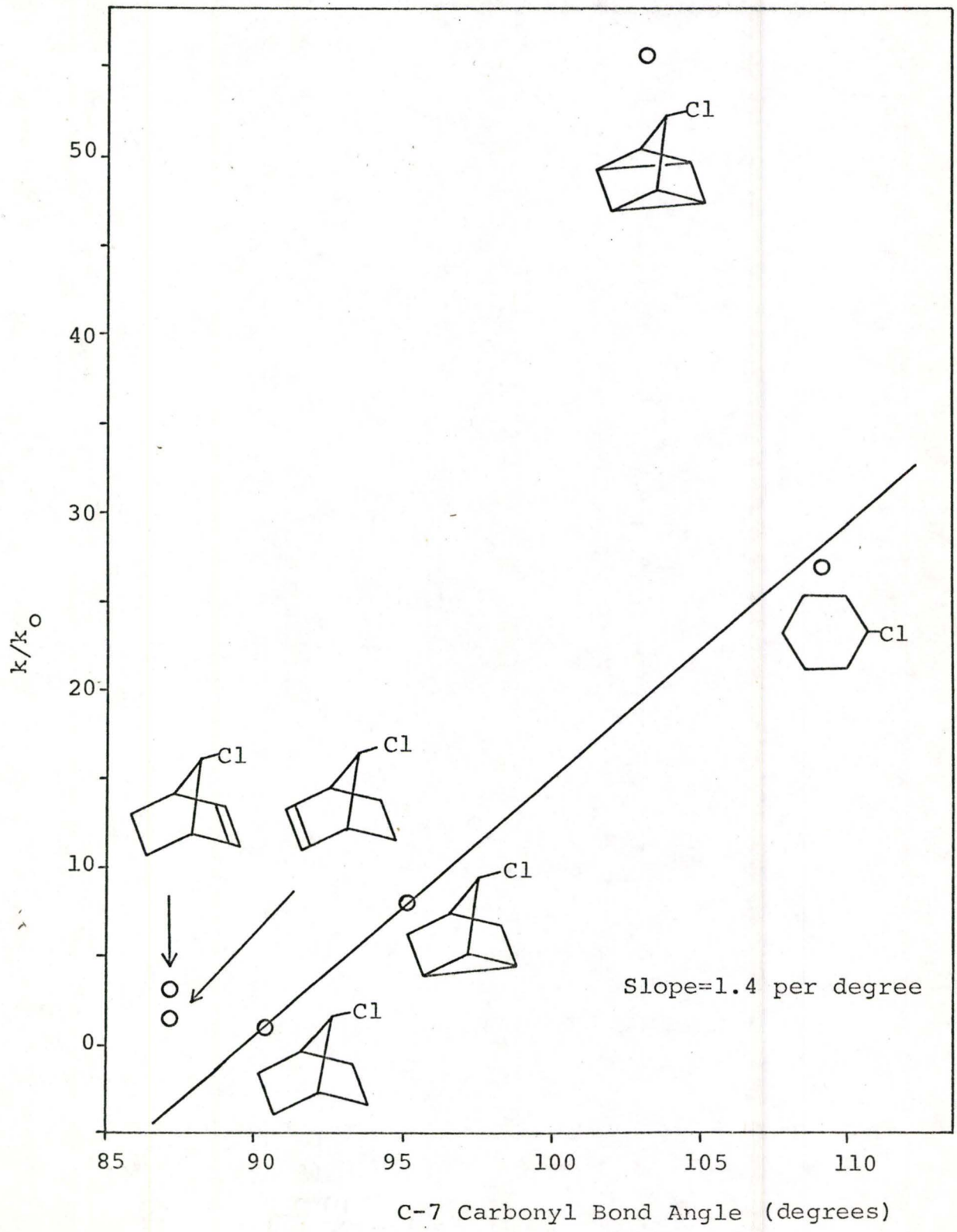
TABLE X

Relative Rates of Tin Hydride Reduction, Carbonyl Stretching Frequencies and Calculated Carbonyl Bond Angles for 7-Chloronorbornane Derivatives

Entry	Compound	k/k_o (a) 100°	Carbonyl stretching frequencies cm^{-1} (b)	Calculated C-7 bond angle, in degrees (c)
1	 (IIe)	1.00	1773	90.3
2	 (IVb)	1.49	1780	87.1
3	 (Ic)	3.09	1780	87.1
4	 (IIIc)	8.08	1762	95
5	 (VIc)	26.9	-	109
6	 (Vb)	-	-	-
7	 (VIIb)	55.7	1746	103

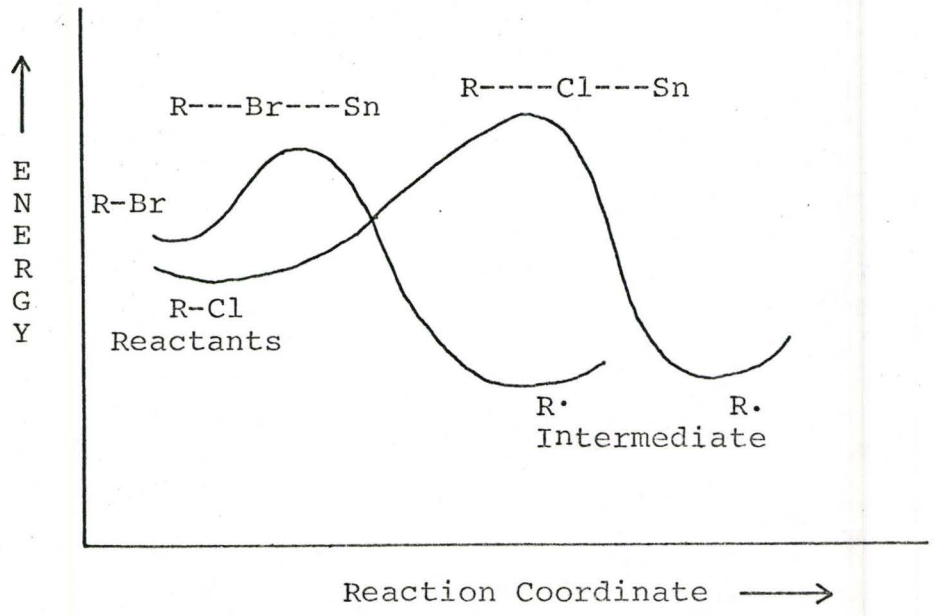
(a) Relative rates of reduction with tri-*n*-butyltin hydride.
(b) Carbonyl stretching frequency of the corresponding 7-keto compounds (49).
(c) Carbonyl bond angle calculated from the carbonyl stretching frequency (56).

Figure 6. Plot of Relative Rates of Tri-*n*-butyltin Hydride Reduction *vs* Carbonyl Bond Angle for Cycloalkyl Chlorides



chloronorbornene (Ic and IVb) are faster than that of the saturated analog IIe, and are above the correlation line. These rates will be considered first.

The slope of the line in Figure 6 is 1.4 k/k_o units per degree of bond angle as compared to 0.2 k/k_o units per degree in Figure 5. Reduction of the chloronorbornane derivatives is approximately seven times more sensitive to bond angle differences at the reaction centre than the corresponding bromo-compounds. This is consistent with the argument that bond breaking during reduction of alkyl chlorides (a process of higher activation energy) should have proceeded further along the reaction coordinate at the transition state, placing more radical character on carbon. A qualitative energy profile for the two reduction processes is shown below.



For *anti*-7-bromonorbornene (IVa), acceleration of the rate due to an inductive effect of the homoallylic double bond was found to be small or absent. Bond angle strain at the reaction centre was proposed to explain the observed rates.

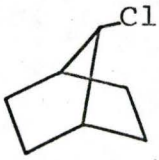
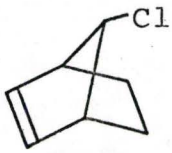
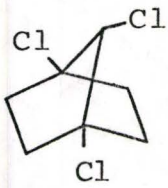
Tri-*n*-butyltin hydride reduction of the corresponding 7-chloro-compounds is approximately seven times as sensitive to bond angle strain at the reaction centre. That polar effects are likewise negligible for these compounds was proven to be so by studying the relative rate of reduction of 1,4,7-trichloronorbornane (XIII). The observed relative rate, as well as the relative rate expected in terms of polar contributions, for IVb and XIII is given in Table XI.

The bond angle at the reaction centre in IIe and XIII should be nearly identical. The negligible rate difference between IIe and XIII, due to the electronegative chlorine atoms in XIII, is taken as strong evidence that bond angle strain at C-7 in norbornane derivatives completely swamps any polar contribution involving the double bond. The rate acceleration observed for IVb cannot, therefore, be due to charge polarization in the transition state for tri-*n*-butyltin hydride reduction.

The rate of reduction of *anti*-7-chloronorbornene (IVb) is 1.49 times greater than that of 7-chloronorbornane

TABLE XI

Observed and Calculated Relative Rates of Tin Hydride Reduction of 7-Chloronorbornane Derivatives

Substrate	 IIe	 IVb	 XIII
$\Delta\sigma^*$ (calculated)	0	0.18[a]	2.1[b]
k/k_o due to the polar effect[c]	1.0	1.7	20
k/k_o observed	1.0	1.49	1.08

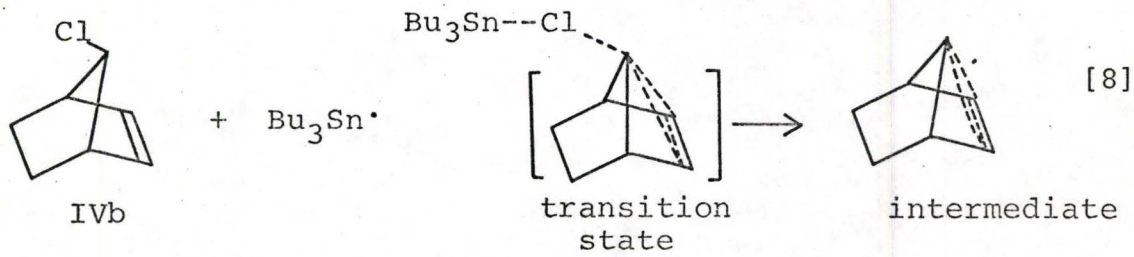
(a) Calculated in previous section.

(b) Taken as twice σ^* for $-CH_2-Cl$ (48).

(c) Using 9.5 k/k_o units per σ^* unit.

(IIe). Bond angle considerations, taken alone, show that IVb should be slower than IIe. A better estimate of the rate acceleration can be obtained from the graph in Figure 6. The distance that the point for IVb is above the correlation line, 4.5 k/k_o units, is taken as the actual rate acceleration.

In terms of the large rate differences observed in analogous carbonium ion reactions ($\simeq 10^7$) (1), a rate enhancement of 4.5 is very small. However, it is nonetheless significant. Having taken into account possible ground state effects, reduction of *anti*-7-chloronorbornene (IVb) is best visualized in terms of π-orbital delocalization in the transition state. A non-classical free radical intermediate (equation [8]) may be formed.

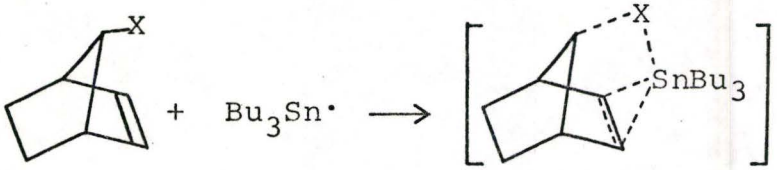


IVb — transition state — intermediate [8]

syn-7-Bromonorbornene (Ib) was 0.2 k/k_o units above the correlation line in Figure 5. This was thought to be due to some effect other than bond angle strain. The distance that the point for *syn*-7-chloronorbornene (Ic) is above the line in Figure 6 corresponds to a

6-fold rate enhancement. In terms of π-bond participation, little if any rate enhancement would be expected for the *syn*-isomer. The possibility exists that all of the rate difference observed for Ic is due to a magnification of the effect observed in Ib. An explanation for the "*syn*-effects" is offered in the next paragraph.

The *syn*-halogen atom in Ib and Ic is so situated that a five-membered transition state, involving the tin atom and the π-orbitals of the norbornene nucleus, may be favourable (equation [9]). This could account for the observed rate differences. A similar transition



transition state

[9]

state is not possible for the *anti*-isomers. Further evidence in favour of such a transition state (equation [9]) will be discussed later in connection with polarographic reductions.

Delocalization in the transition state, leading to a non-classical free radical intermediate, has been proposed to explain the enhanced rate of reduction of *anti*-7-chloronorbornene (IVb). If a non-classical free radical intermediate is formed, a high degree of stereo-selectivity should be observed in the product determining

step. The easiest way to determine the stereochemistry of the reduction product, norbornene (Ia), is to do the reduction with tri-*n*-butyltin deuteride. Since 7-bromo- and 7-chloronorbornenes give the same intermediate radical, either could be used.

The same 7-deuterionorbornene was obtained from reduction of *syn*- and *anti*-7-bromonorbornene (Ib and IVa) with tri-*n*-butyltin deuteride (57). This is evident from the 100Mc nmr spectra in Figure 7 (pages 93 and 94). The 7-deuterium atom was assigned the *anti*-stereochemistry on the basis of a stereospecific synthesis of *anti*-7-deuterionorbornene (IVd) by Marchand and Rose (58).

The stereoselective reduction of Ib and IVa can best be explained in terms of a non-classical radical intermediate (equation [10]). For a classical intermediate

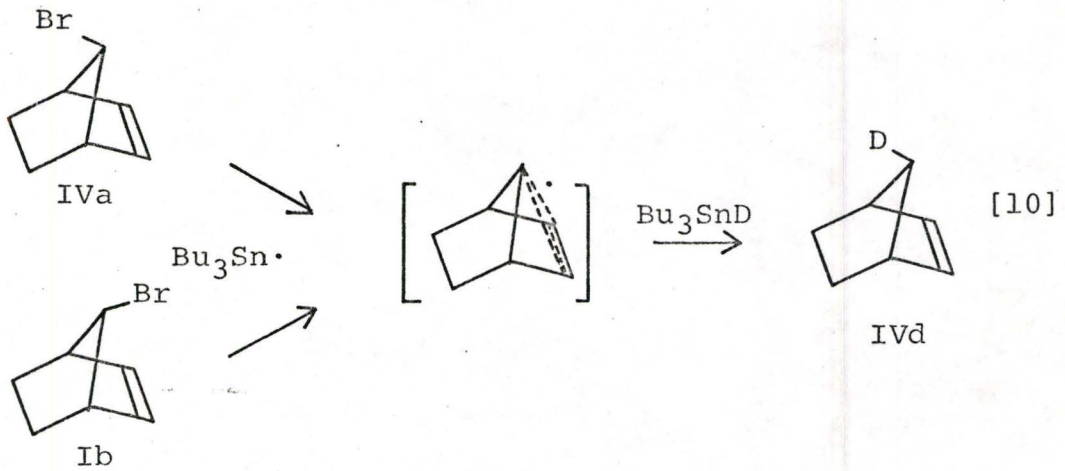


Figure 7. NMR Spectra at 100 Mc of (A) Norbornene, (B) *anti*-7-Deuterionorbornene from *anti*-Bromide and (C) *anti*-7-Deuterionorbornene from *syn*-Bromide

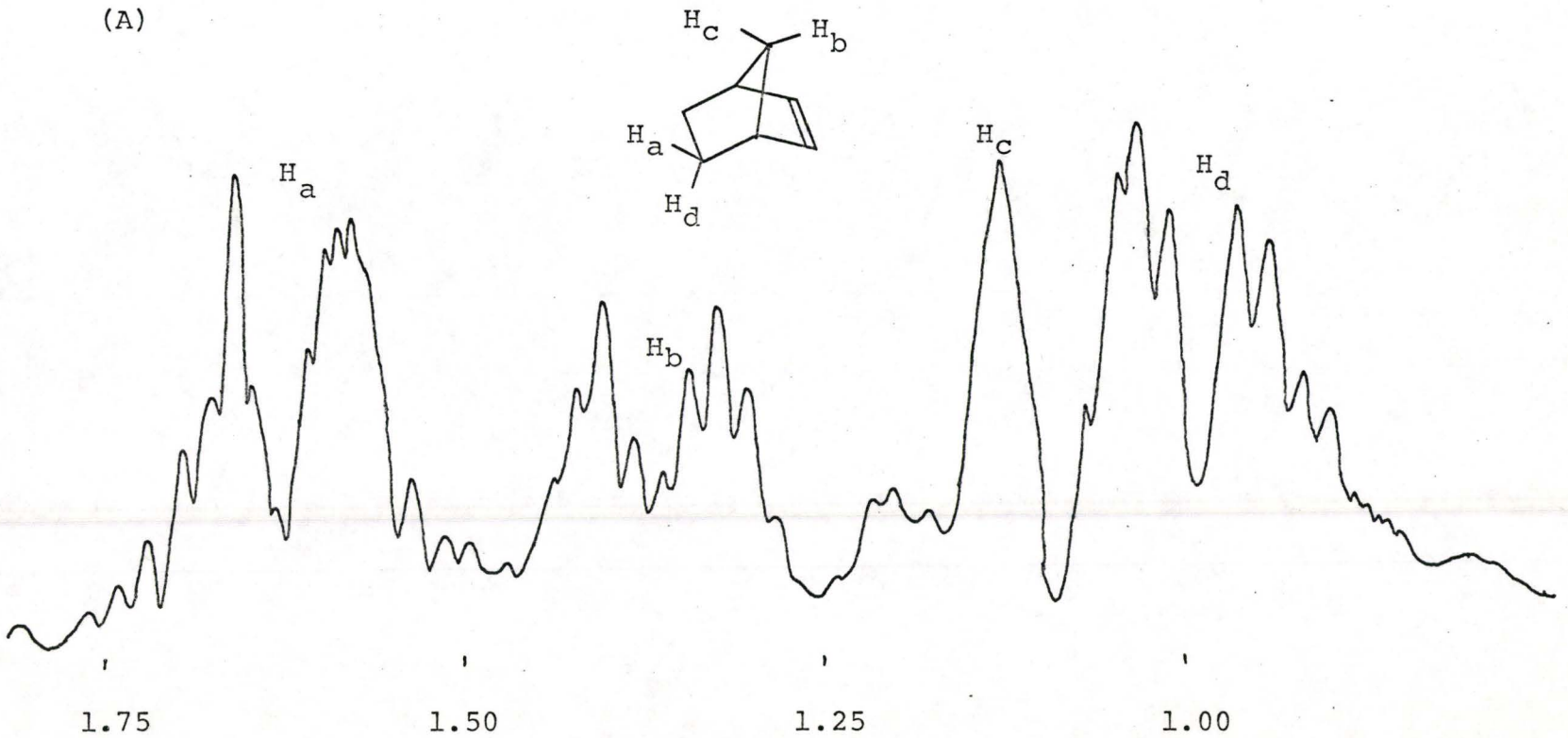
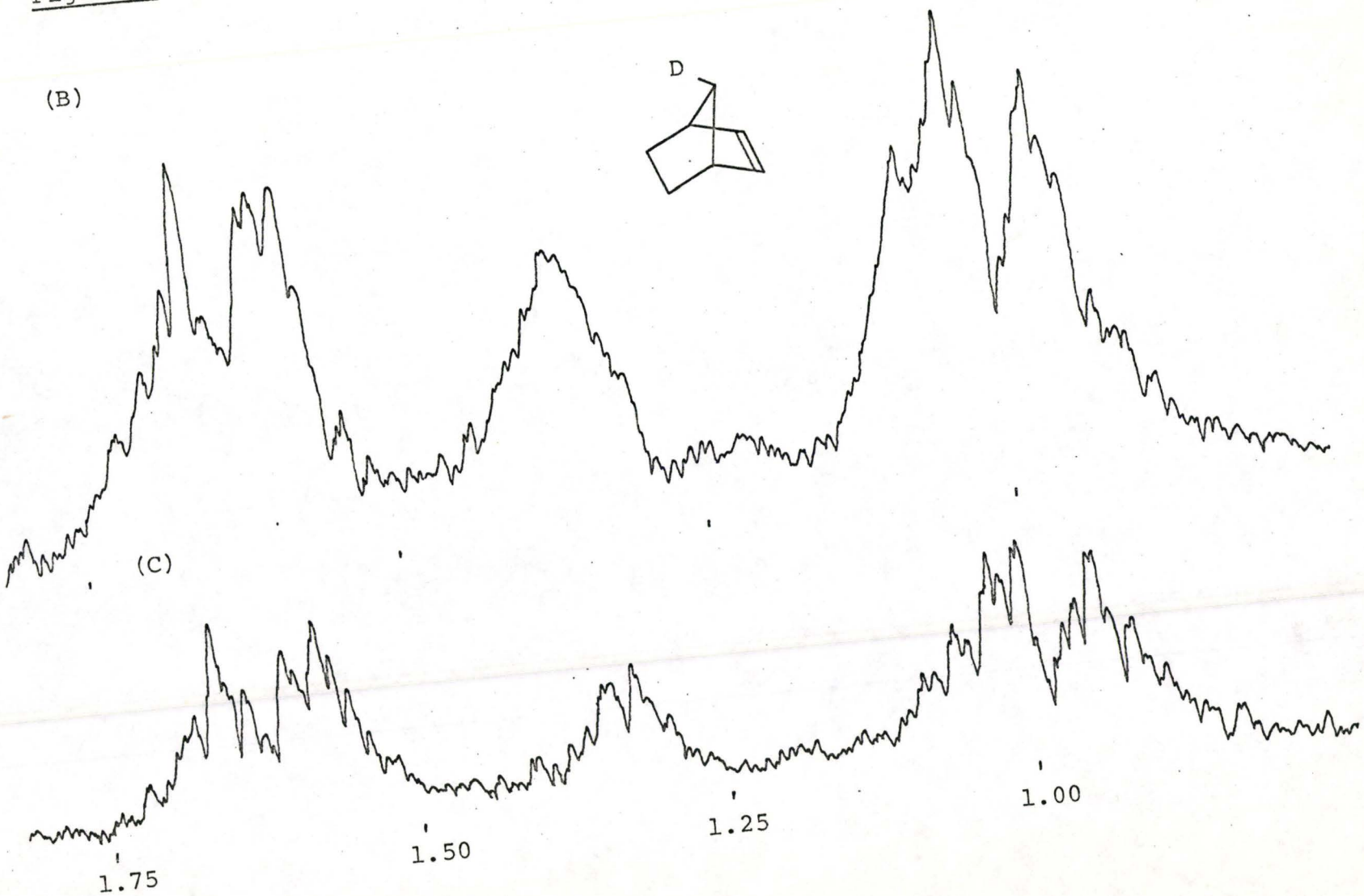
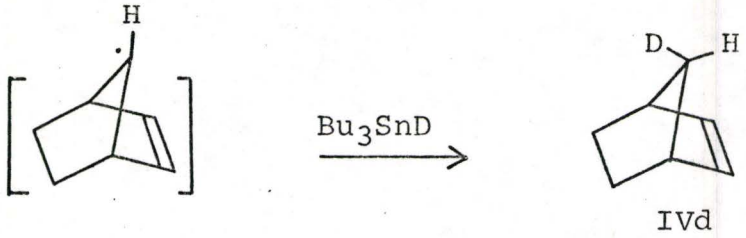


Figure 7. (Continued.....)

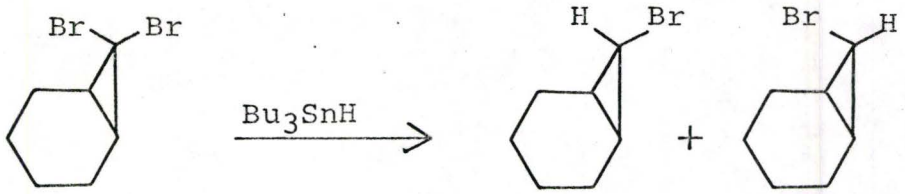


(equation [11]) to accommodate this result, a highly



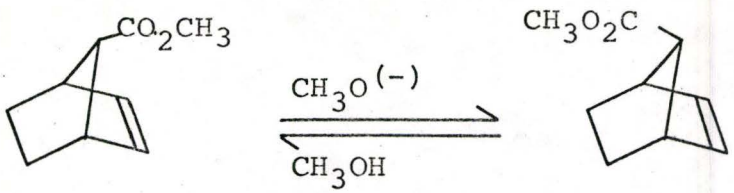
IVd [11]

stereospecific reaction of the unhindered classical C-7 radical is required. This stereoselectivity would not be expected in this system. Green and Lowry (39) have shown that reduction of *cis*- and *trans*-9-chloro-decalin afforded a common product composition, regardless of whether tri-*n*-butyltin hydride, di-*n*-butyltin dihydride or triphenyltin hydride was used; i.e. the products were not sensitive to the widely different steric situations in the three hydrides. Similarly, Seyferth *et al.* (59) found that steric factors in 7,7-dibromobicyclo [4.1.0] heptane (equation [12]) did not result in a stereospecific reduction with tri-*n*-butyltin hydride. In another study, Sauers (60) has equilibrated the methyl esters of *syn*-



[12]

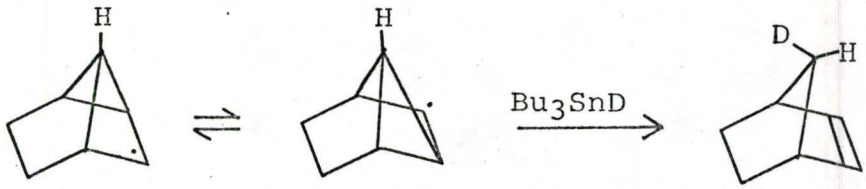
and *anti*-7-norbornene carboxylic acids (equation [13]). For these esters, the *syn*-isomer was found to be slightly more stable. The small equilibrium constant shows that there is little difference in the steric factors on each



[13]

side of the molecule. Thus steric factors in the norbornene molecule (equation [13]) and steric requirements of the tri-*n*-butyltin hydride (equation [12]) would not be expected to result in a stereoselective reduction of the classical 7-norbornenyl free radical (equation [11]).

For equilibrating classical radicals (equation [14]) to accommodate the result, reaction of a cyclopro-



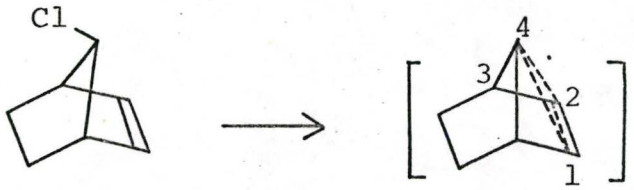
IVd

[14]

pylcarbinyl radical at a carbon which does not have radical character is required. There is no precedent for reaction of the type required in equation [14]. Furthermore, if equilibrating classical radicals were present as intermediates (equation [14]), they should be trapped, at least to a small extent. Analysis of the product mixture from reduction of Ib, using a 10-fold change in tri-*n*-butyltin hydride concentration (0.5 and 5 mol equivalents) (see Experimental, Section II (ii)) revealed that none of the tricyclic hydrocarbon, tricyclo [2.2.1.$0^{2,7}$] heptane (IX) was present. The analysis was carried out under conditions such that an authentic sample of IX was stable, and well separated from Ia.

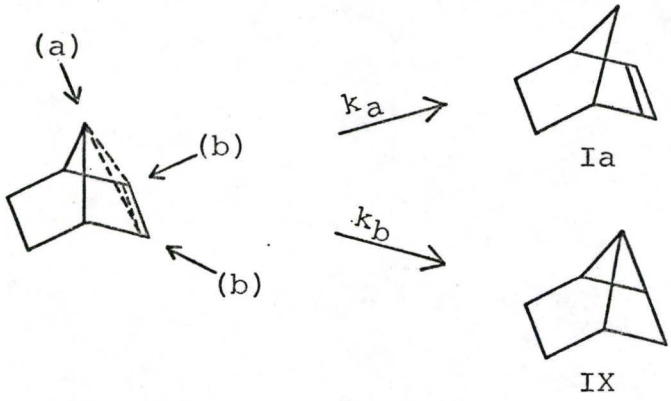
Amounts far less than one per cent could have been detected.

The kinetic and stereochemical results discussed thus far provide the first unambiguous example of a non-classical free radical. The observed delocalization has been written as involving both 1,4- and 2,4-overlap (equation [15]). Molecular orbital calculations



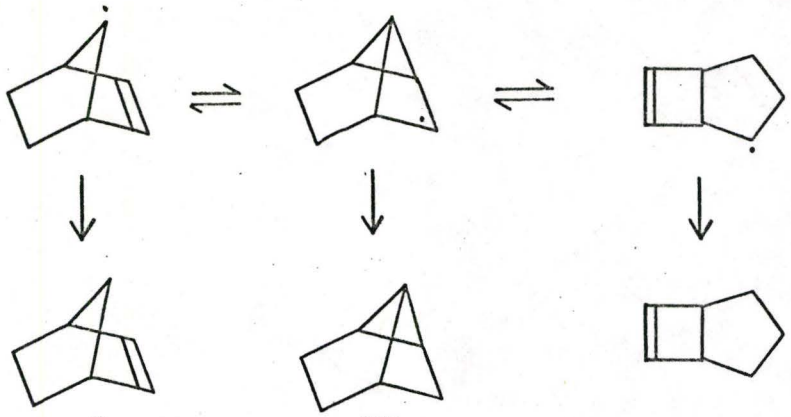
IVb [15]

predict that this should be favourable in rigid systems (16,17). The proposed intermediate (equation [15]) might be expected to give more than one product (equation [16]). The fact that norbornene (Ia) is the



[16]

only reduction product requires that $k_a >>> k_b$ for reduction of 7-halonorbornenes. Equation [17] shows the products expected from three possible classical radical intermediates.



Ia IX [17]

Rate data could not be obtained for 7-chloro-norborna-2,5-diene (Vb). Addition of tin radicals to the double bond appeared to be much faster than chlorine abstraction at C-7. No hydrocarbon reduction products were obtained.

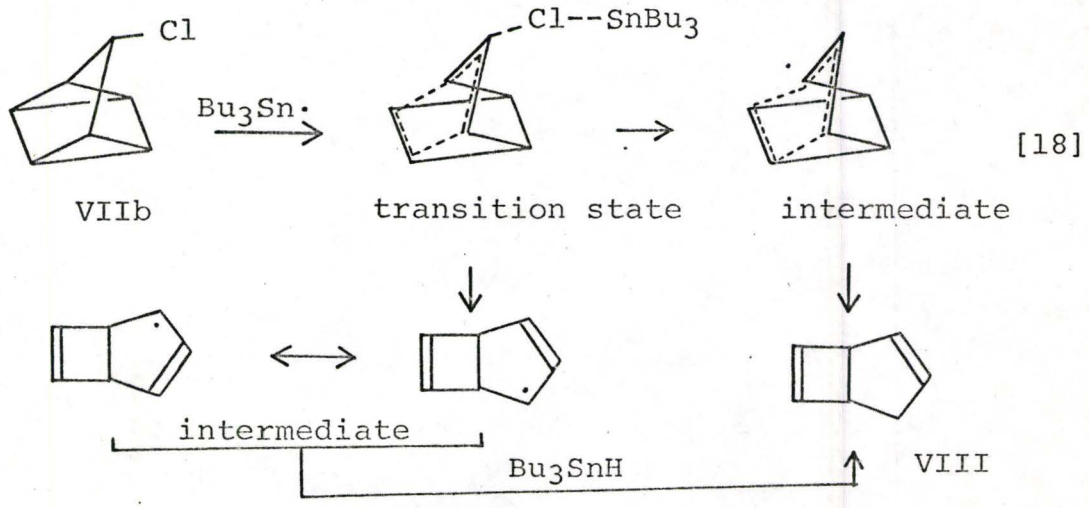
The observed rate for reduction of 7-chloro-quadricyclane (VIIb) is 55.7 times that of 7-chloronor-bornane (IIe) (Table X). Again, the actual acceleration is taken as the distance the point for VIIb is above the correlation line (Figure 6). This corresponds to a rate factor of 37, and is by far the largest rate enhancement observed for these 7-chloronorbornane derivatives.

Martin and co-workers (26) (see Historical Introduction, Section II (ii)) have observed large rate accelerations,

due to the presence of cyclopropyl groups, in the decomposition of symmetrical alkylazomethanes. The radical formed from reduction of VIIb is formally a dicyclopropylcarbinyl free radical. The large rate of formation, in both our case and that of Martin's (26), demands some form of delocalization in the transition state for radical formation.

The rearranged bicyclic diene, bicyclo [3.2.0] hepta-2,6-diene (VIII), was the only product obtained from reduction of 7-chloroquadricyclane (VIIb) with tri-*n*-butyltin hydride. The product (VIII) was identified by comparison of its glpc retention time and nmr spectrum with that of an authentic sample. No quadricyclane (VIIa) or norborna-2,5-diene (Va) was obtained.

A transition state involving delocalization over both cyclopropyl rings (equation [18]) leading to a non-classical intermediate can explain both the rate



[18]

and product data. It is also possible that the intermediate is the classical 7-bicyclo [3.2.0] hepta-2,6-dienyl radical, the rate of formation of which might be high because of relief of ring strain.

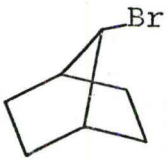
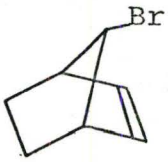
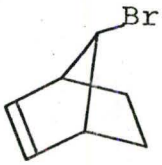
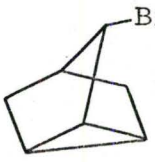
The mechanism of reduction of alkyl halides at the dropping mercury electrode has been discussed in Part I. Half-wave potentials of the four 7-bromo-norbornane derivatives listed in Table XII were determined in order to obtain more information on π-orbital participation in the transition state for free radical formation. The waves consisted of single steps, and no maxima, pre- or post-waves were present.

The half-wave potential of *syn*-7-bromonorbornene (Ib) is particularly informative. The fact that Ib reduces at a more negative potential than the saturated analog IId rules out any important rate acceleration effects due to a polar contribution. Again, the C-7 bond angle is the important factor. A plot of $\Delta E_{1/2}$ *vs* the calculated C_7-bond angle is shown in Figure 8. The half-wave potentials of Ib, IId and IIIb are well correlated with bond angle differences. Even though the steric substituent constant, E_s, is not known for these compounds, they would be expected to have similar steric requirements for polarographic reduction. The linearity of the plot bears this out.

The rates of reduction of Ib and Ic with tri-*n*

TABLE XII

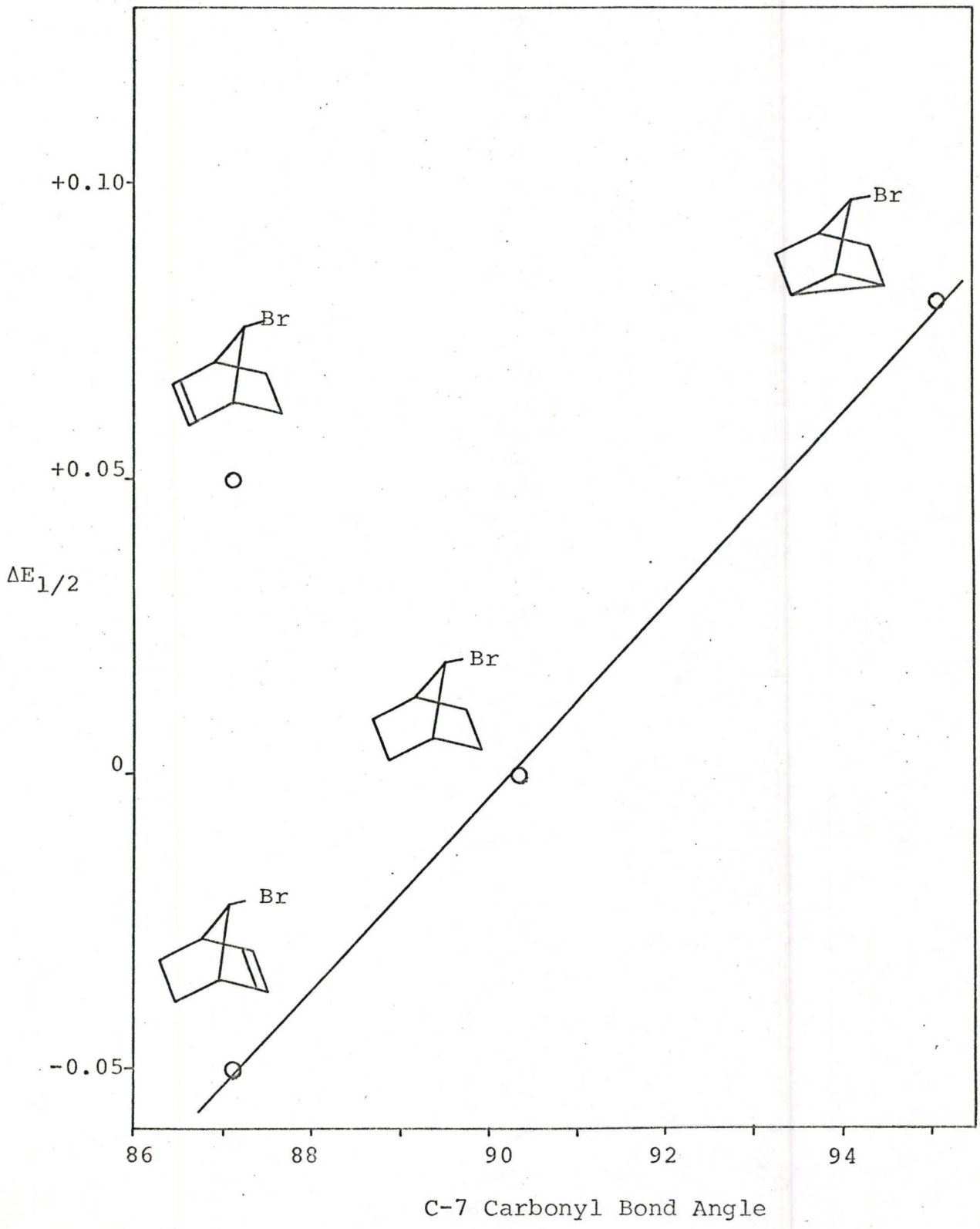
Half-wave Potentials and Calculated Bond Angles of Cycloalkyl Bromides

Compound	$E_{1/2}$[a]	$\Delta E_{1/2}$	Calculated C-7 bond angle, in degrees[b]
 IId	-2.05	0	90.3
 Ib	-2.10	-0.05	87.1
 IVa	-2.00	+0.05	87.1
 IIIb	-1.97	+0.08	95

(a) Volts *vs* A_g/A_g^+ electrode in 0.100M Et_4NBr in DMF

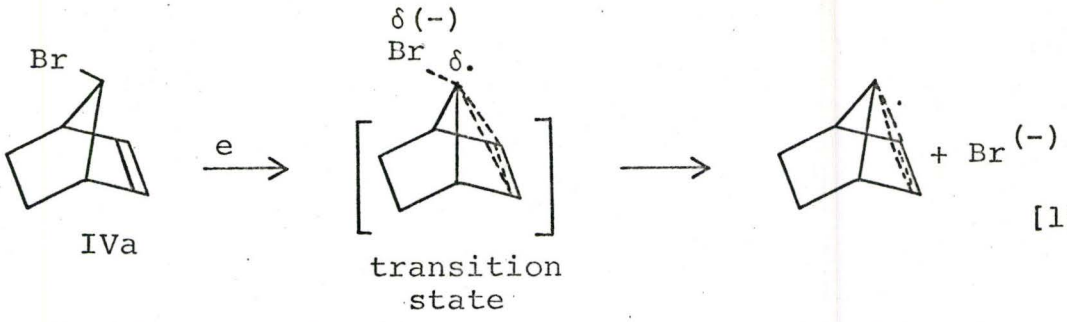
(b) Taken from Table IV.

Figure 8. Plot of Half-wave Reduction Potentials *vs* C-7 Carbonyl Bond Angle for Cycloalkyl Bromides



butyltin hydride were faster than expected. Some type of involvement of the tin atom with the π-electrons, through a cyclic transition state, was invoked to explain the anomalous rates. For polarographic reduction, ground state effects should be the same as for tin hydride reductions. However, the transition state for polarographic reduction would be expected to be quite different from that proposed in equation [9] for tin hydride reduction. The half-wave potential for *syn*-7-bromonorbornene (Ib) is in agreement with that expected in terms of bond angle strain (Figure VIII). The anomolous tin hydride reduction rate for Ib must involve a transition state effect which is not present in the *anti*-isomer IVa. The cyclic transition state proposed in equation [9] appears reasonable.

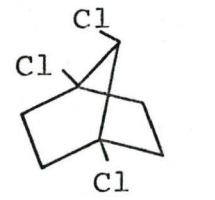
The half-wave potential for *anti*-7-bromonorbornene (IVa) is above the correlation line in Figure 8. This is consistent with non-classical free radical formation during polarographic reduction. If the explanation is correct, then there must be more radical character on carbon in the transition state for polarographic reduction (equation [19]) of this alkyl bromide than for the corresponding tin hydride reduction. It will be recalled that, in the latter reaction, both unsaturated bromides were slower than the saturated counterpart. The half-wave



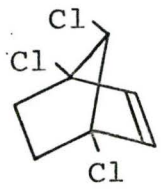
[19]

potential for *anti*-7-chloronorbornene (IVb) would be expected to show an even larger rate enhancement. Unfortunately, the very negative potentials required for reduction of alkyl chlorides have not yet been obtained. Solvent-electrolyte discharge occurs before reduction.

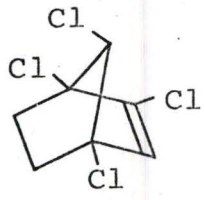
In order that a free radical be stabilized by overlap with a π-electron system, one electron must be placed in an anti-bonding orbital. An electronegative substituent on one or more of the carbon atoms over which the charge is delocalized should stabilize the radical further, and enhance the rate. The following compounds were synthesized to test this hypothesis.



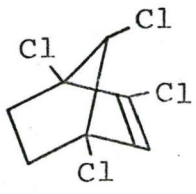
XIII



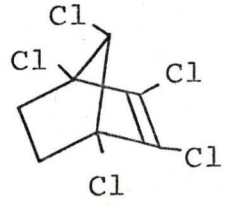
XIV



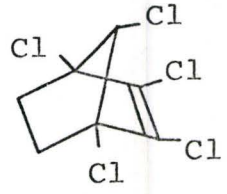
XV



XVI



XVII



XVIII

In the next section of this thesis, the synthesis of these and related compounds is described. A discussion of the relative rates of tin hydride reduction and reduction products follows. If the reader wishes to continue with the discussion of rates and mechanism, the section on syntheses can be postponed without loss of continuity.

In this section, it has been shown that the rate of tin hydride reduction of 7-bromonorbornane derivatives is porportional to bond angle changes at the reaction centre. No rate acceleration was observed. However, for tin hydride reduction of 7-chloronorbornane derivatives, a process of higher activation energy, enhanced rates of formation of 7-norbornenyl- and 7-quadricyclyl radicals were observed. These enhanced rates were attributed to delocalization in the transition state for radical formation. The 7-norbornenyl free radical underwent reduction stereospecifically to give the *anti*-product, regardless of whether the initial halide was *syn* or *anti*. This stereoselective reduction was taken as strong evidence for the existance of the non-classical 7-norbornenyl free radical. *anti*-7-Bromonorbornene was reduced at the dropping mercury electrode at a lower potential than the saturated analog. This was explained in terms of π-bond participation in the transition state

for polarographic reduction, analogous to that observed for tin hydride reduction of *anti*-7-chloronorbornene.

III Synthesis of Polychlorinated Norbornenes

General

Several polychlorinated norbornenes were required for this part of the study. The general synthetic method, based on previous studies by Wilcox and Zajacek (61) and Alden and Davies (62), involved the selective reduction or elimination of chlorine atoms from Diels-Alder adducts of hexachlorocyclopentadiene. Nuclear magnetic resonance was used to identify the new compounds prepared. In this section, synthetic schemes are outlined, some general features of the nmr spectra of these compounds are discussed, and the structures of compounds required for rate studies are rigorously established. Some general conclusions are drawn regarding the stereochemistry and mechanism of reduction of these compounds. For convenience, all compounds are grouped according to the Diels-Alder adduct from which they are derived.

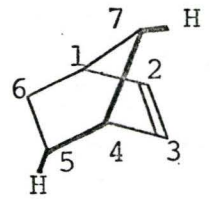
(i) General Features of NMR Spectra

The nmr spectra of compounds with the bicyclo [2.2.1] heptane skeleton exhibit some general features which allow, in many cases, unambiguous assignment of the position and stereochemistry of substituents.

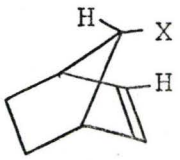
Several of these features which have been observed in chlorine substituted derivatives are useful in structure assignments and will be discussed here.

There are four regions of absorption: 1. vinyl proton; 6.8-5.9δ, 2. proton on the same carbon as a chlorine atom; 4.9-3.8δ, 3. bridgehead protons in norbornene or norbornadiene derivatives; 3.6-2.8δ and 4. ring methylenes; 2.7-1.5δ. This separation allows accurate integration of the protons in each region. The number of protons in each region defines the positions of the chlorine atoms.

There are five characteristics which define the stereochemistry of the chlorine atoms at C-7, C-2 and C-3. Perhaps the most informative is weak W-plan coupling between two protons separated by three carbon atoms. In C-7 substituted norbornenes, only a C-7 proton *syn* to the double bond can couple with the *endo*-5,6-hydrogens. This permits assignment of the stereochemistry

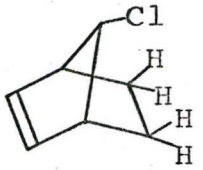


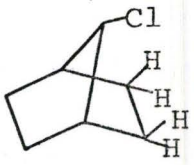
at C-7. Secondly, a C-7 hydrogen *anti* to a C-2 vinyl proton couples with the vinyl proton, with a much larger



coupling constant than that observed for W-plan coupling. This can also be used to assign stereochemistry at C-7.

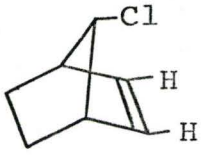
Thirdly, a C-7 chlorine atom lying over C-5 and C-6 hydrogens shields the *exo*-hydrogens. This spreads out the methylene region in a characteristic manner,

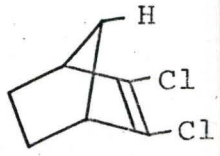




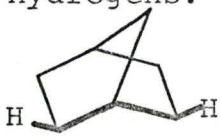
allowing one to determine the stereochemistry at C-7.

Fourthly, a chlorine atom at C-7 *syn* to the double bond shifts the vinyl protons upfield. Similarly, a dichlorovinyl group shifts a *syn* C-7 proton upfield.





Lastly, W-plan coupling can be used to determine the stereochemistry of chlorine atoms at C-2. Such coupling of the *exo*-2,3-hydrogens can only occur with *exo*-5,6-hydrogens. The presence or



absence of this coupling can be used to define *exo*, *endo* stereochemistry of substituents at C-2 and C-3.

Using these criteria, it is possible to assign unambiguously the structure and stereochemistry of polychlorinated norbornanes, norbornenes, and norborna-

dienes in a large number of cases.

(ii) Derivatives of 1,2,3,4,7,7-Hexachloronorborn-2-ene

The synthesis of compounds derived from 1,2,3,4,7,7-hexachloronorborn-2-ene (XIX) is outlined in Chart II. Reduction of XIX with 1 mole equivalent of tri-*n*-butyltin hydride gave 42% *anti*-1,2,3,4,7-pentachloronorborn-2-ene (XVII) and 58% *syn*-1,2,3,4,7-pentachloronorborn-2-ene (XVIII). If the intermediate radical XIXa (Chart III) were being stabilized by delocalization over the π-bond (XIXb), one would expect predominant *anti*-attack by the Bu_3SnH to give XVIII, the *syn*-isomer. The *syn*-isomer is favoured slightly, but the main mode of stabilization of the intermediate XIXa must involve the C-7 chlorine atom, rather than the disubstituted double bond. This is to be expected since the free radical intermediate can be stabilized by overlap with the p-orbitals on the chlorine atom bonded to the reaction centre. Attack can then take place from both sides to give the *syn*- and *anti*-isomers, as observed.

It is interesting to note that the reduction of XIX with zinc in acetic acid (61) (Chart II) gave approximately 62% XVIII, 2% XVII and 36% XX when analyzed by glpc before distillation. Reduction of alkyl halides with zinc in acetic acid is thought to take place *via*

CHART II

Derivatives of 1,2,3,4,7,7-Hexachloronorborn-2-ene

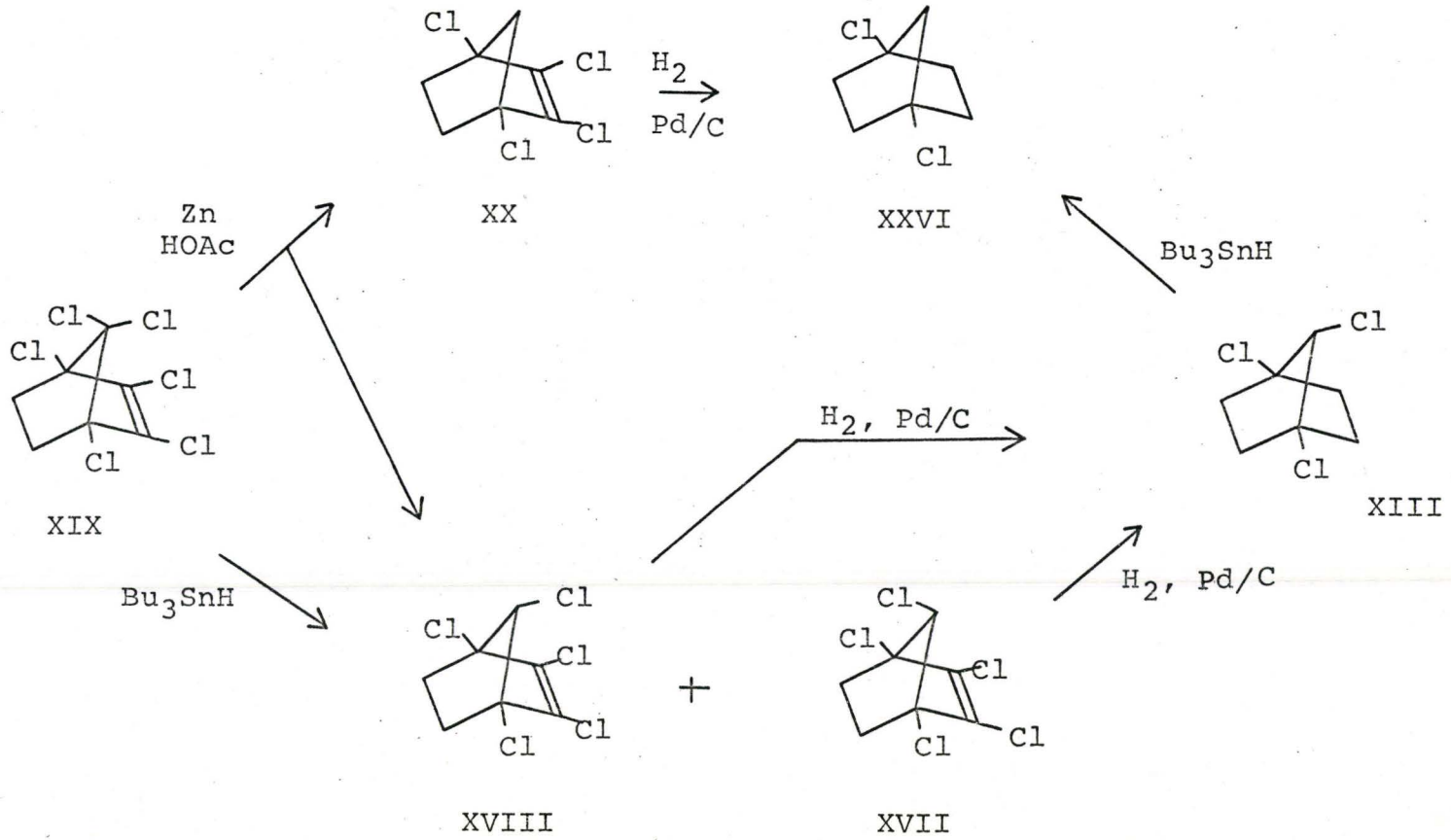
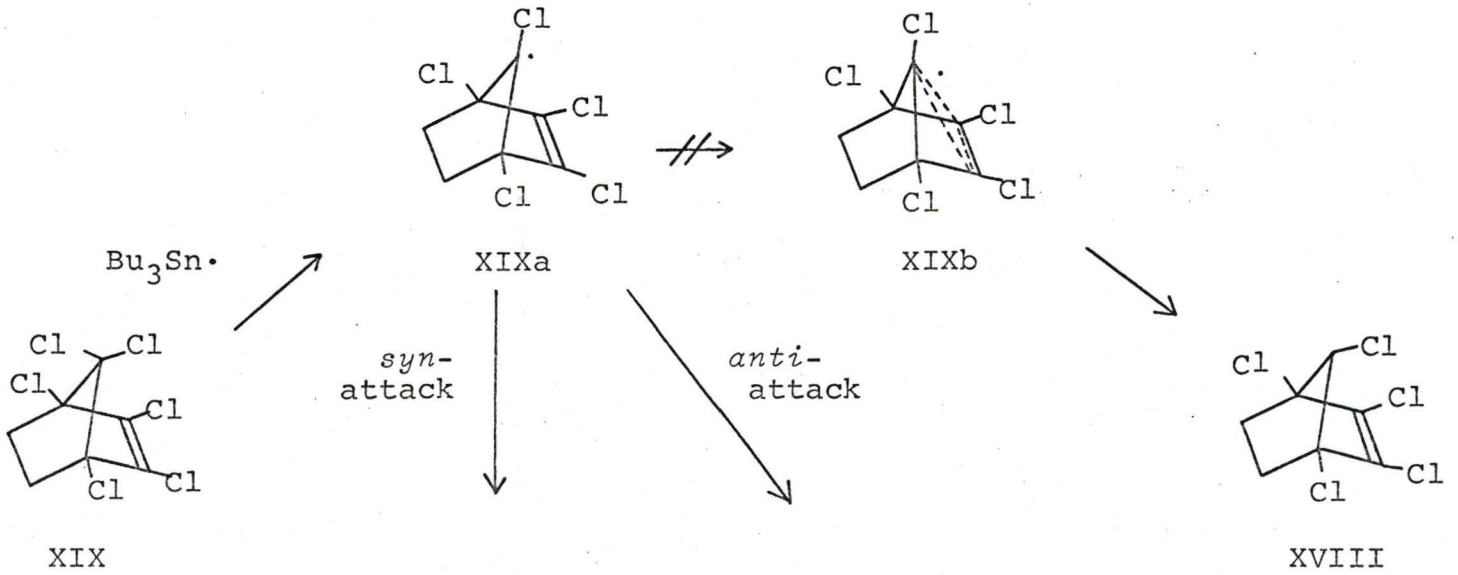


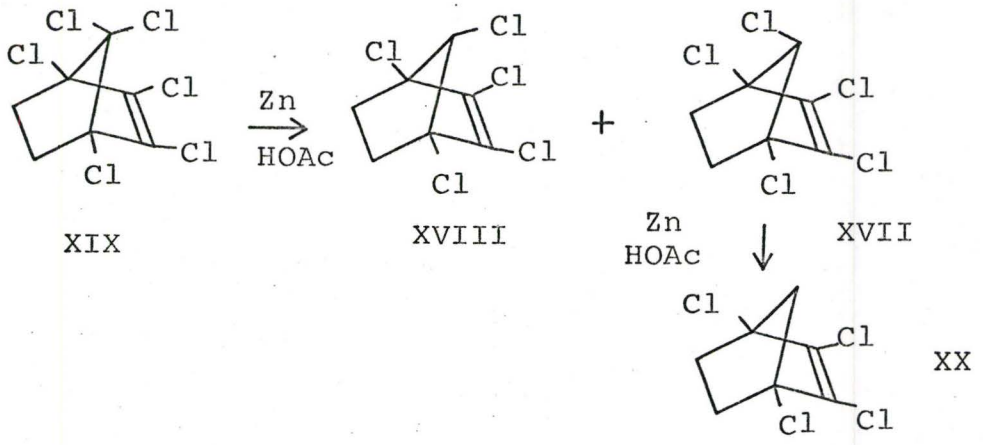
CHART III

Reduction of 1,2,3,4,7,7-Hexachloronorborn-2-ene

with Tri-*n*-butyltin Hydride

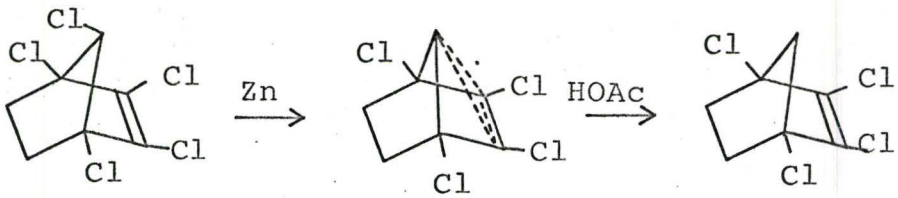


a radical or anion mechanism (63). The most likely reaction sequence for reduction of XIX is shown in equation [20]. Initial reduction of XIX must give



XIX XVIII XVII XX [20]

62% XVIII and 38% XVII. Further reduction of XVII gives XX. The selectivity observed in this dissolving metal reduction is only slightly higher than that observed in the free radical reduction (Chart II). This implies that reduction with zinc in acetic acid occurs by a free radical mechanism. Wilcox and Zajacek (61) found that the percentage of XX isolated was reproducable from one run to another. This supports the assumption that only the *anti*-isomer (XVII) reduces to give XX. The reason that the *anti*-isomer reacts in preference to the *syn*-isomer must be participation of the disubstituted double bond in the transition state for radical formation (equation [21]).

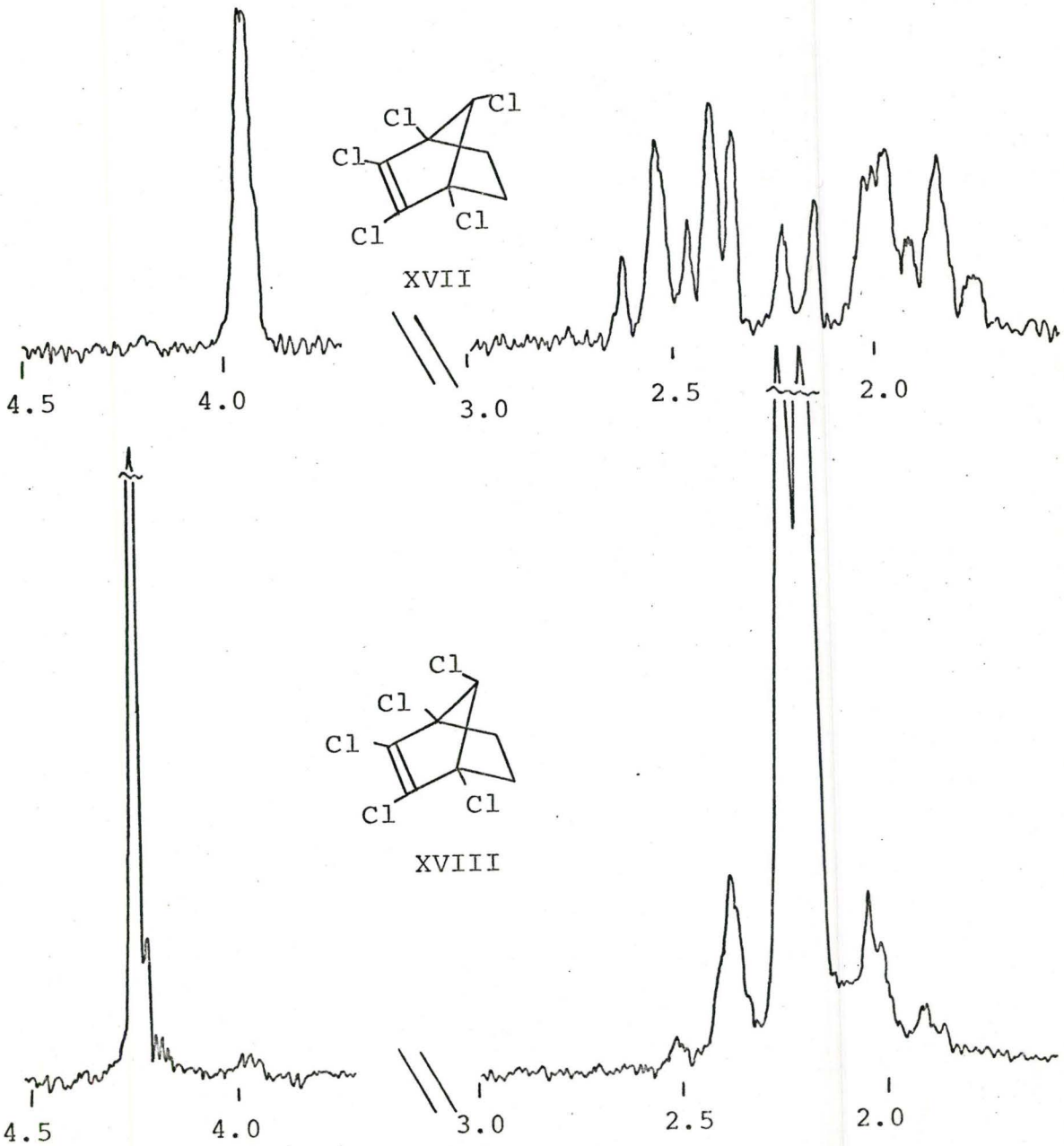


XVII XX [21]

A mixture of XVII and XVIII was quantitatively reduced over palladium on charcoal (Chart II) to the known 1,4,7-trichloronorbornane (XIII). This rigorously establishes the bicyclo[2.2.1]heptane skeleton in XVII and XVIII and fixes the position of three chlorine atoms. The nmr spectra of XVII and XVIII (Figure 9) show absorption in the region expected for a hydrogen atom on the same carbon as a chlorine atom (4.9-3.8δ) and absorption in the methylene region (2.7-1.5δ), in the ratio of 1:4. This is consistent with the 1,2,3,4,7-hexachloronorborn-2-ene structure. The *syn-anti* assignments can be established unambiguously by nmr (Figure 9).

The *anti*-isomer XVII exhibits a complex multiplet in the region 2.6-1.9δ, characteristic of ring methylene protons with a C-7 chlorine atom *syn*- to the ring methylenes. Also the absorption at 4.23δ is a multiplet with a coupling constant less than 1 Hz, characteristic of a C-7 proton *syn* to the double bond

Figure 9. NMR Spectra of *anti*- and *syn*-1,2,3,4,7-Pentachloronorborn-2-ene



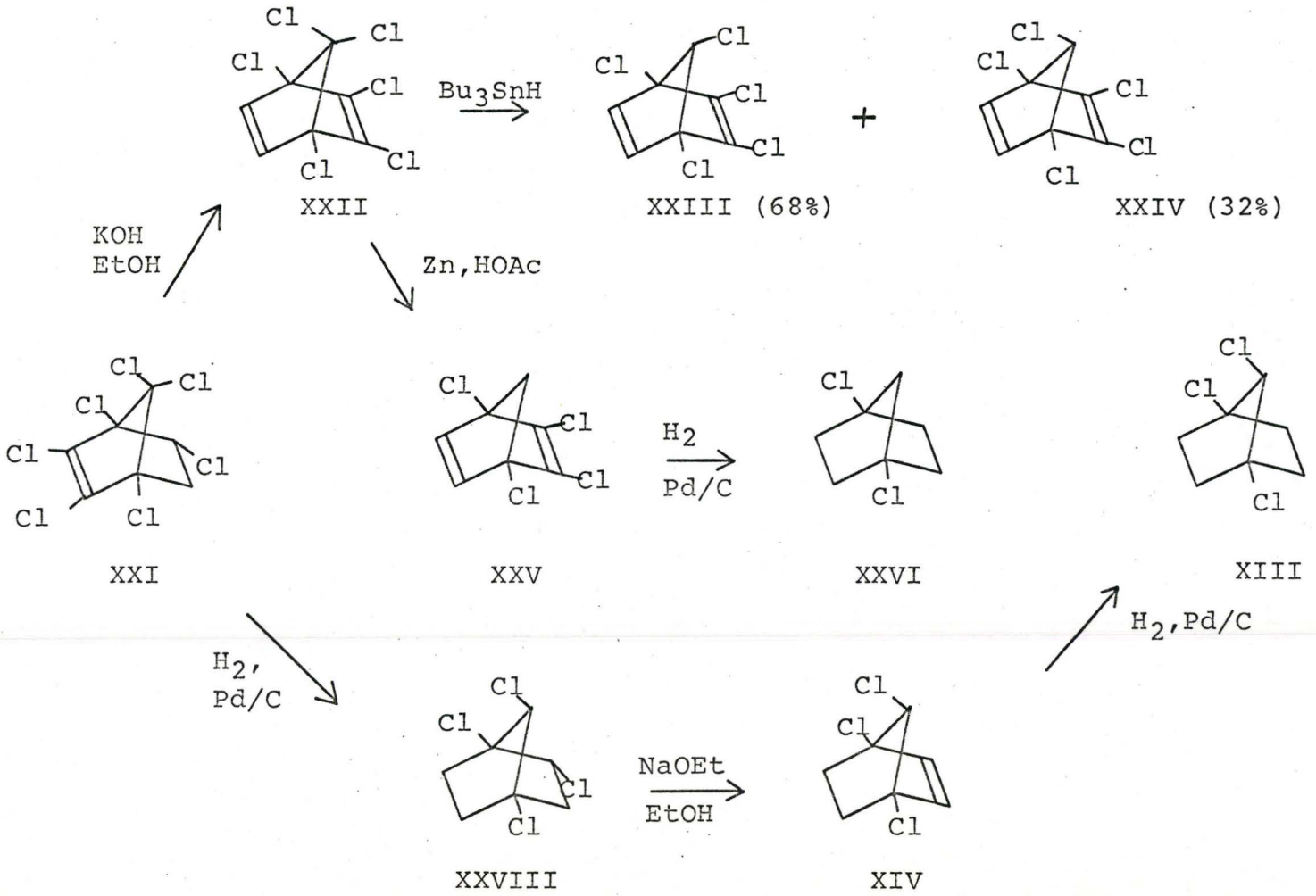
coupling with the *endo*-5,6-hydrogens (W-plan coupling). The *syn*-isomer XVIII shows a singlet at 3.95δ and a multiplet between 2.7-1.7δ. For the *syn*-isomer there can be no W-plan coupling at C-7. It is also worthy of note that the C-7 proton absorption of XVII is shifted upfield relative to the C-7 proton signal in XVIII. This is characteristic of a C-7 proton *syn*- to a dichlorovinyl group in norbornenes.

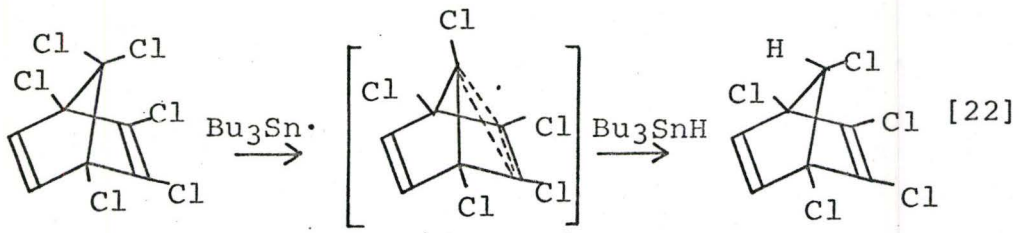
(iii) Derivatives of 1,2,3,4-*endo*-5,7,7-Heptachloronorborn-2-ene

The synthesis of compounds derived from 1,2,3,4-*endo*-5,7,7-heptachloronorborn-2-ene (XXI) is outlined in Chart IV. Reduction of 1,2,3,4,7,7-hexachloronorborna-2,5-diene (XXII) with one mole equivalent of tri-*n*-butyltin hydride gave *syn*-1,2,3,4,7-pentachloronorborna-2,5-diene (XXIII) (*syn* to the disubstituted double bond) 68% and *anti*-1,2,3,4,7-pentachloronorborna-2,5-diene (XXIV) 32% (relative per cent, calculated from glpc). This selectivity is slightly higher than that observed previously for Bu_3SnH or Zn/HOAc reduction of 1,2,3,4,7,7-hexachloronorborn-2-ene (XIX). Again the *syn*-isomer predominates, suggesting that the dichlorovinyl group may be participating in the product determining step (equation [22]).

CHART IV

Derivatives of 1,2,3,4,5,7,7-Heptachloronorborn-2-ene





[22]

XXII XXIIa XXIII

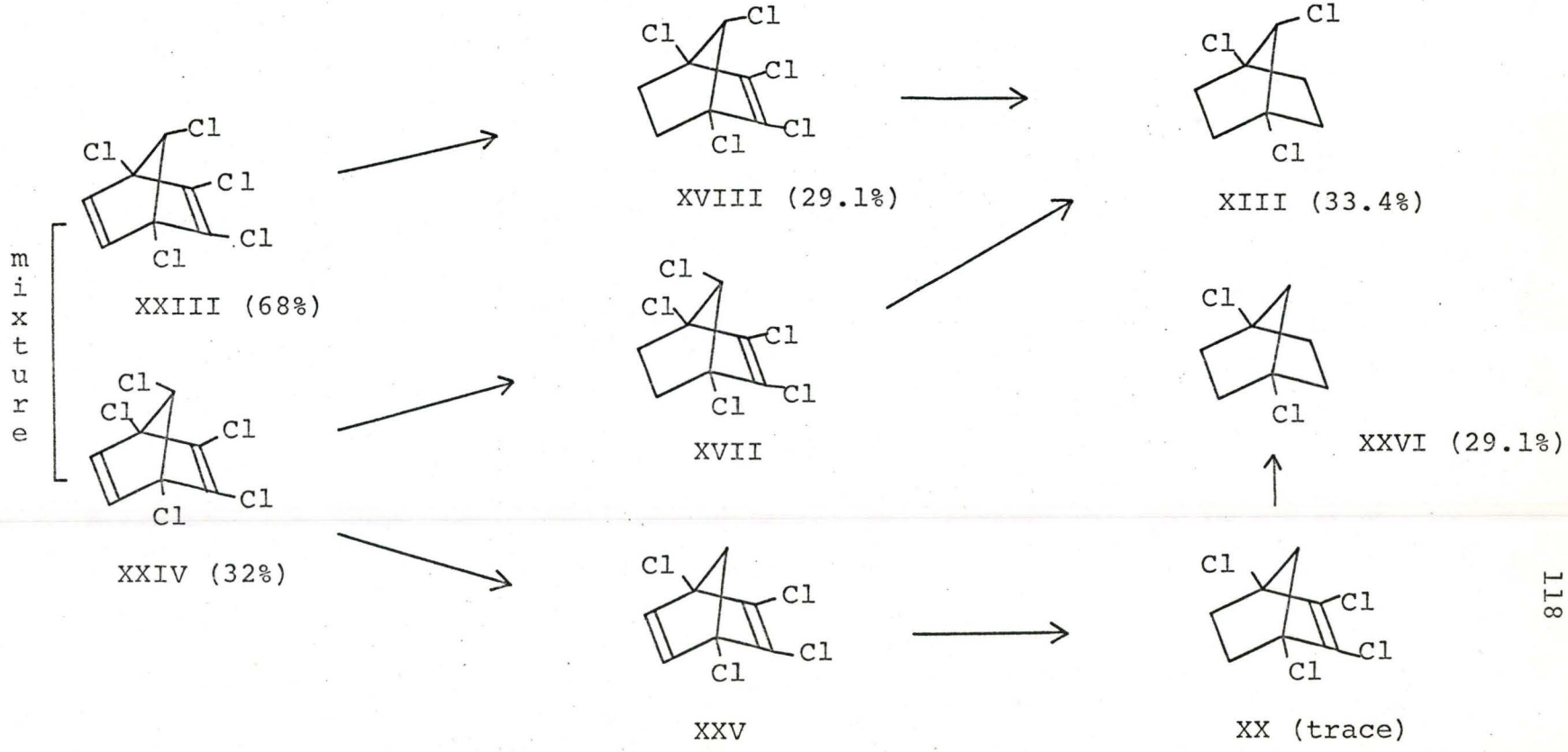
However, the radical probably derives most of its stabilization from the chlorine atom bonded directly to the reaction centre. If that were the only factor, a ratio near 1:1 of the *syn*- and *anti*-isomers, XXIII and XXIV, should result. Perhaps an intermediate such as XXIIa (equation [22]) is involved.

Reduction of XXII with zinc in acetic acid did not stop at the pentachloro derivatives XXIII or XXIV. 1,2,3,4-Tetrachloronorborna-2,5-diene (XXV) was the only reduction product. No estimate can be made from this result of the selectivity of the first step of the reduction. However, the presence of the two vinyl groups in XXII must enhance the ease of reduction at C-7 since no XXIII or XXIV was obtained.

Further information regarding the ease of reduction at C-7 in polychlorinated norborna-2,5-dienes was obtained from catalytic reduction of a mixture containing 68% XXIII and 32% XXIV. The products obtained from reduction in ether over palladium on charcoal catalyst, and a possible reaction sequence, is outlined in Chart V. The products were identified by glpc, using authentic

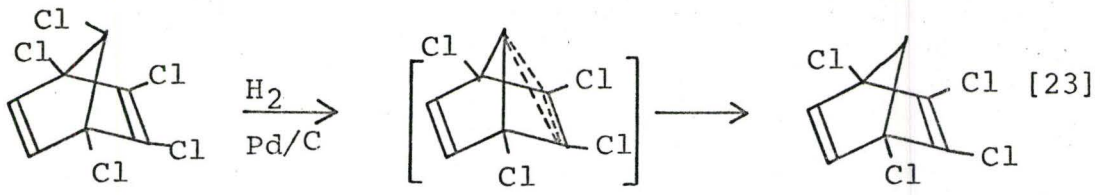
CHART V

Catalytic Reduction of *syn*- and *anti*-1,2,3,4,7-Pentachloro-norbornadiene



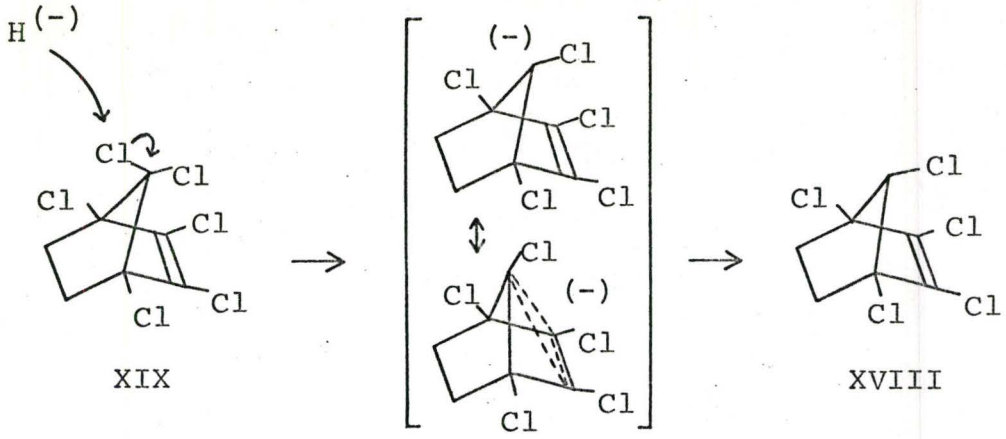
samples as internal standards.

The unsubstituted double bond in XXIII, being unhindered by the C-7 chlorine atom, is probably reduced first to give XVIII, which further reduces to XIII. Reduction at C-7 does not appear to take place. The other isomer, XXIV, which has the C-7 chlorine atom *anti* to the disubstituted vinyl group, reduces at C-7 almost exclusively to give XXV which is readily reduced to XXVI. Although the unsubstituted vinyl group is hindered sterically by the C-7 chlorine atom, this should not prevent reduction of the double bond (e.g. XVIII reduces to XIII). The dichlorovinyl group in XXIV must therefore participate in the reduction of the *anti*-C-7 chlorine atom (equation [23]), making this more favourable than reduction of the unsaturated centre.



XXIV XXIVa XXV [23]

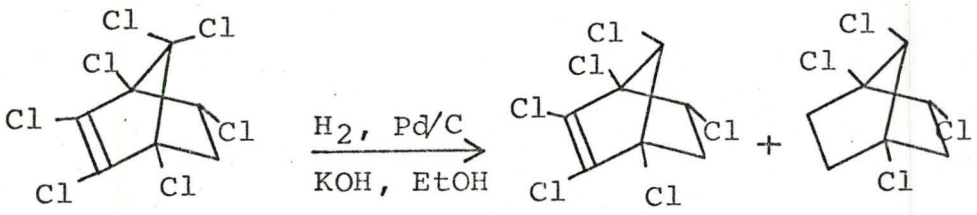
In a recent publication, Alden and Davies (62) have interpreted some results of hydrogenolysis of polychlorinated norbornenes in terms of a displacement of chlorine by $H^{(-)}$, to give an anion intermediate (equation [24]). They propose that this intermediate



XIX XVIII [24]

may be stabilized by delocalization of the negative charge over the π-electron system. The hydrogenolysis (equation [24]) was done in KOH-ethanol over Raney nickel catalyst and the only product isolated was XVIII (94% yield). The stereoselectivity observed in this reduction is much higher than that observed for the analogous free radical reduction (Chart III). The intervention of a delocalized anion intermediate during reduction in this catalyst-solvent system (equation [24]) appears to be the most reasonable explanation of the product observed. The chlorine substituted double bond system is relatively electron deficient, and this can account for its ability to stabilize carbanions.

In a similar experiment, Alden and Davies (62) observed the reduction of 1,2,3,4-*endo*-5,7,7-heptachloro-norborn-2-ene (XXI) to 1,2,3,4-*endo*-5-*syn*-7-hexachloro-norborn-2-ene (XXVII) and 1-*endo*-2,4-*anti*-7-tetrachloro-norborn-2-ene (XXVIII) (equation [25]). This reduction



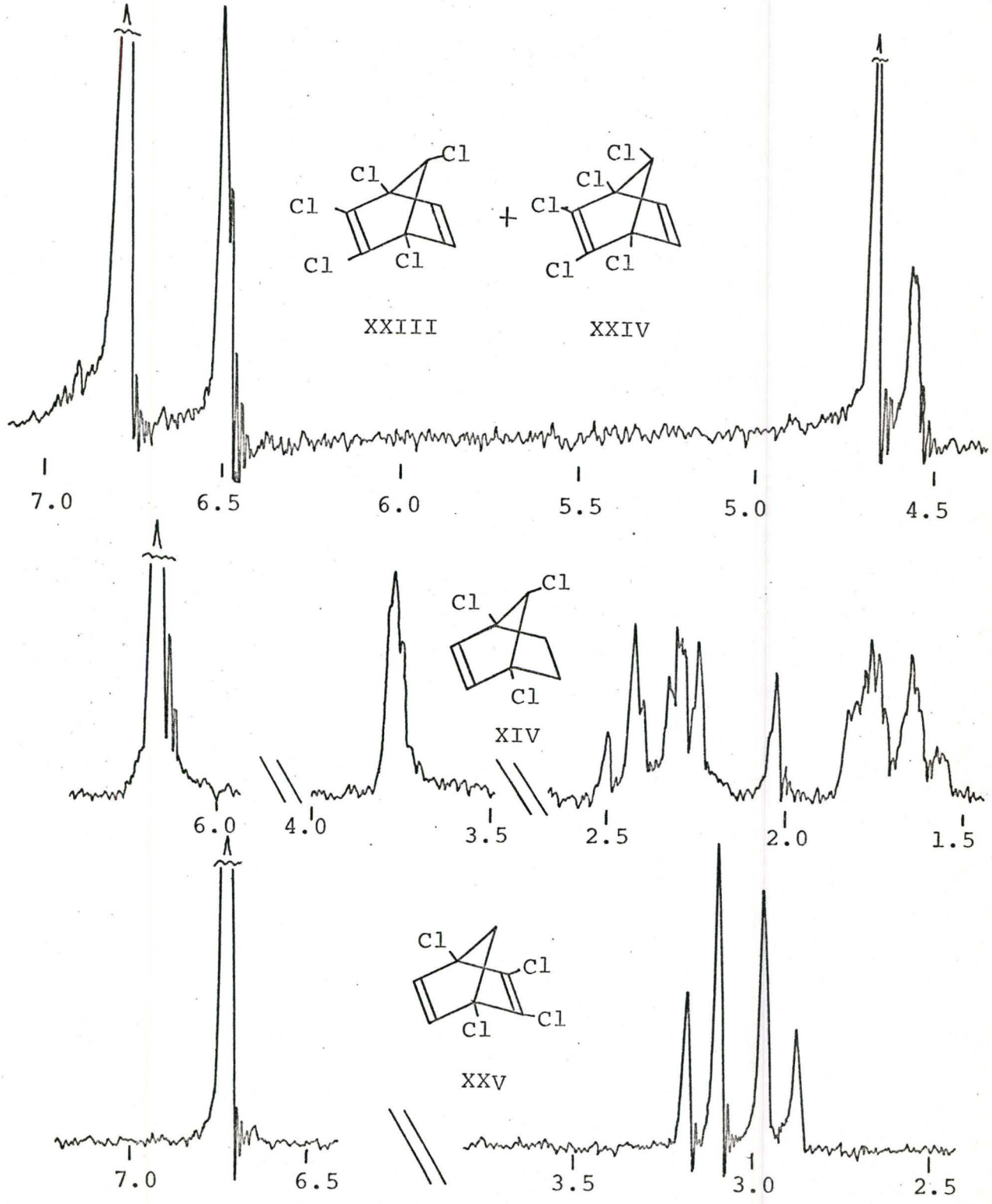
XXI XXVII XXVIII [25]

was carried out in ethanol solvent containing KOH and palladium on charcoal catalyst. Again reduction takes place exclusively from the *anti* side to give the *syn*-isomers, providing further evidence for a delocalized anion intermediate.

In view of the above results, the intermediate XXIVa in the reduction of XXIV (equation [23]) is probably a delocalized anion intermediate.

syn- and *anti*-1,2,3,4,7-Pentachloronorborna-2,5-diene (XXIII and XXIV) were isolated as a mixture and identified from an nmr spectrum of the mixture (see Figure 10). The nmr spectrum of the *anti*-isomer (XXIV) consisted of a doublet at 6.50, 6.48δ (vinyl protons) and a multiplet with very small coupling constant at 4.58δ, relative area 2:1. The C-7 proton in XXIV is *anti* to the vinyl protons, so the multiplicity is as expected. The nmr spectrum of the *syn*-isomer (XXIII) consisted of two sharp singlets at 6.77, 4.67δ, relative area 2:1. For this compound, the C-7 proton is *syn* to the vinyl protons, and no coupling would

Figure 10. NMR Spectra of *anti*- and *syn*-1,2,3,4,7-Pentachloronorbornadiene, *anti*-1,4,7-Trichloronorbornene and 1,2,3,4-Tetrachloronorbornadiene



be expected. In XXIV, the C-7 proton is *syn* to the dichlorovinyl group and is shielded relative to the C-7 proton in XXIII. Similarly, the C-7 chlorine atom in XXIV is *syn* to the vinyl protons, and shields them, relative to the vinyl protons in XXIII. The nmr spectrum of XXIII is in agreement with the published spectrum (62).

The structure of 1,2,3,4-tetrachloronorborna-2,5-diene (XXV) was assigned from its nmr spectrum (Figure 10) and by reducing it to the known 1,4-dichloro-norbornane (XXVI) (Chart IV). The reduction product XXVI establishes the norbornane skeleton and fixes the position of the bridgehead chlorine atoms in XXV. The vinyl protons appeared as a singlet at 6.73δ in the nmr spectrum. The C-7 protons are made non-equivalent by the dichlorovinyl group. They absorbed as an AB quartet (3.18, 3.08, 2.96, 2.86δ). The C-7 proton *syn* to the dichlorovinyl group would be shielded relative to the other C-7 proton and absorb at higher field. The relative area of vinyl protons to methylene protons was 1:1.

1,4-*anti*-7-Trichloronorborn-2-ene (XIV) was obtained from the base catalyzed elimination of HCl from 1-*endo*-2,4,7-tetrachloronorbornane (XXVIII). Alden and Davies (62) reported that no elimination took

place with KOH in ethanol at reflux temperature. With the stronger base, sodium ethoxide in ethanol at reflux temperature, elimination slowly took place.

The position of the three chlorine atoms in XIV was unambiguously established by catalytic reduction of XIV to 1,4,7-trichloronorbornane (XIII). The nmr spectrum of XIV (Figure 10) consisted of a singlet at 6.24δ (vinyl protons), a multiplet at 3.83δ (coupling constant less than 1 Hz) (C-7 proton) and a multiplet between 2.6-1.6δ (methylene protons). The relative areas were 2:1:4 in agreement with the proposed structure. W-plan coupling between the C-7 proton and the *endo*-5,6-protons observed here can only occur in the *anti*-isomer. Also, the methylene protons on C-5 and C-6 are spread out, characteristic of a C-7 chlorine atom *syn* to the methylenes shielding the *exo*-protons. These last two features of the spectrum confirm the *anti* assignment of the C-7 chlorine atom in XIV.

(iv) Derivatives of 1,2,3,4,5,6,7,7-Octachloronorborn-2-ene

The synthesis of *anti*- and *syn*-1,2,4,7-tetrachloronorborn-2-ene (XV and XVI) is based on reduction and elimination reactions carried out on 1,2,3,4,5,6,7,7-octachloronorborn-2-ene (XXIX) (see Chart VI, pp. 125-126). The Diels-Alder adduct XXIX was obtained from the

CHART VI

Derivatives of 1,2,3,4,5,6,7,7-Octachloronorborn-2-ene

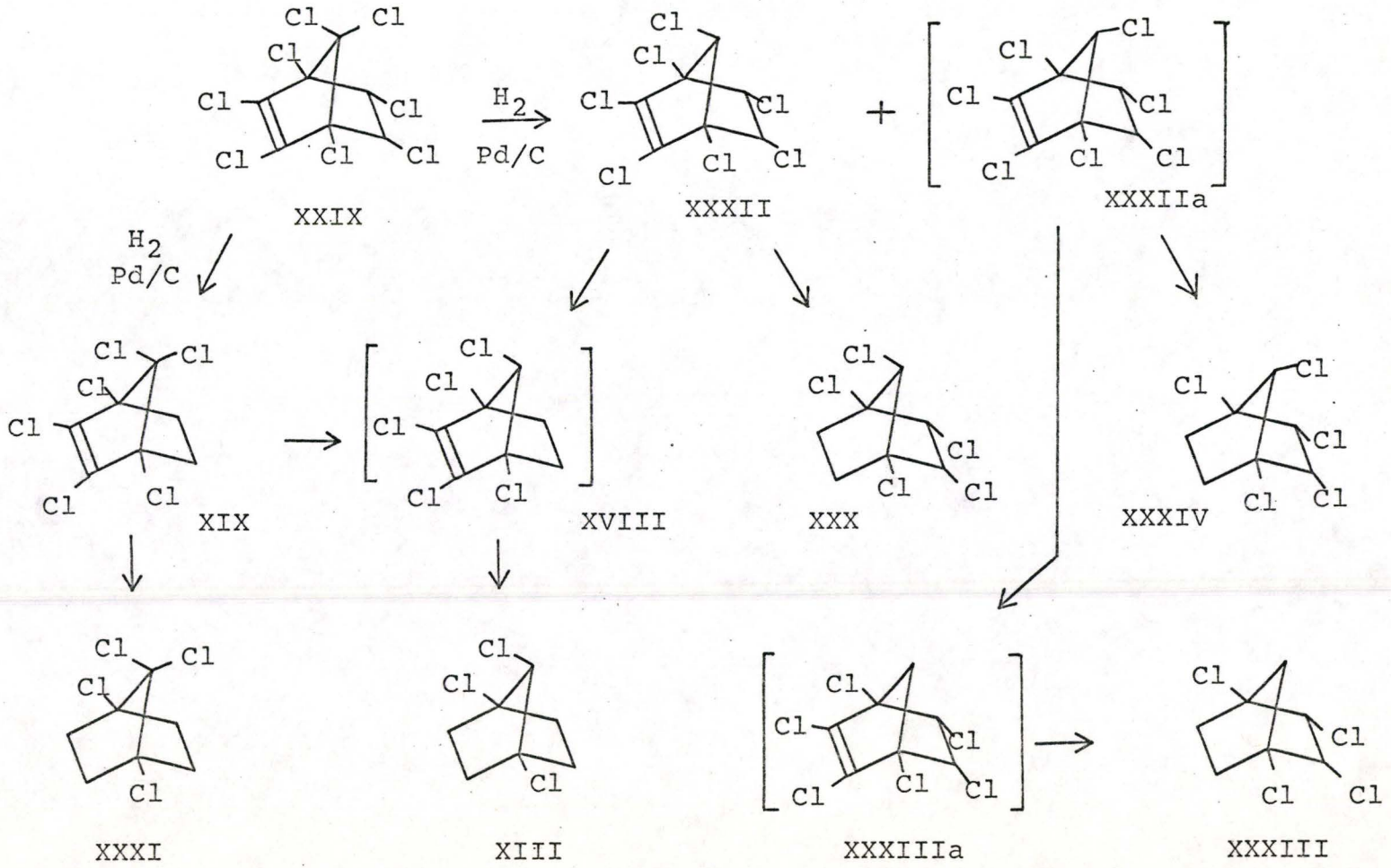
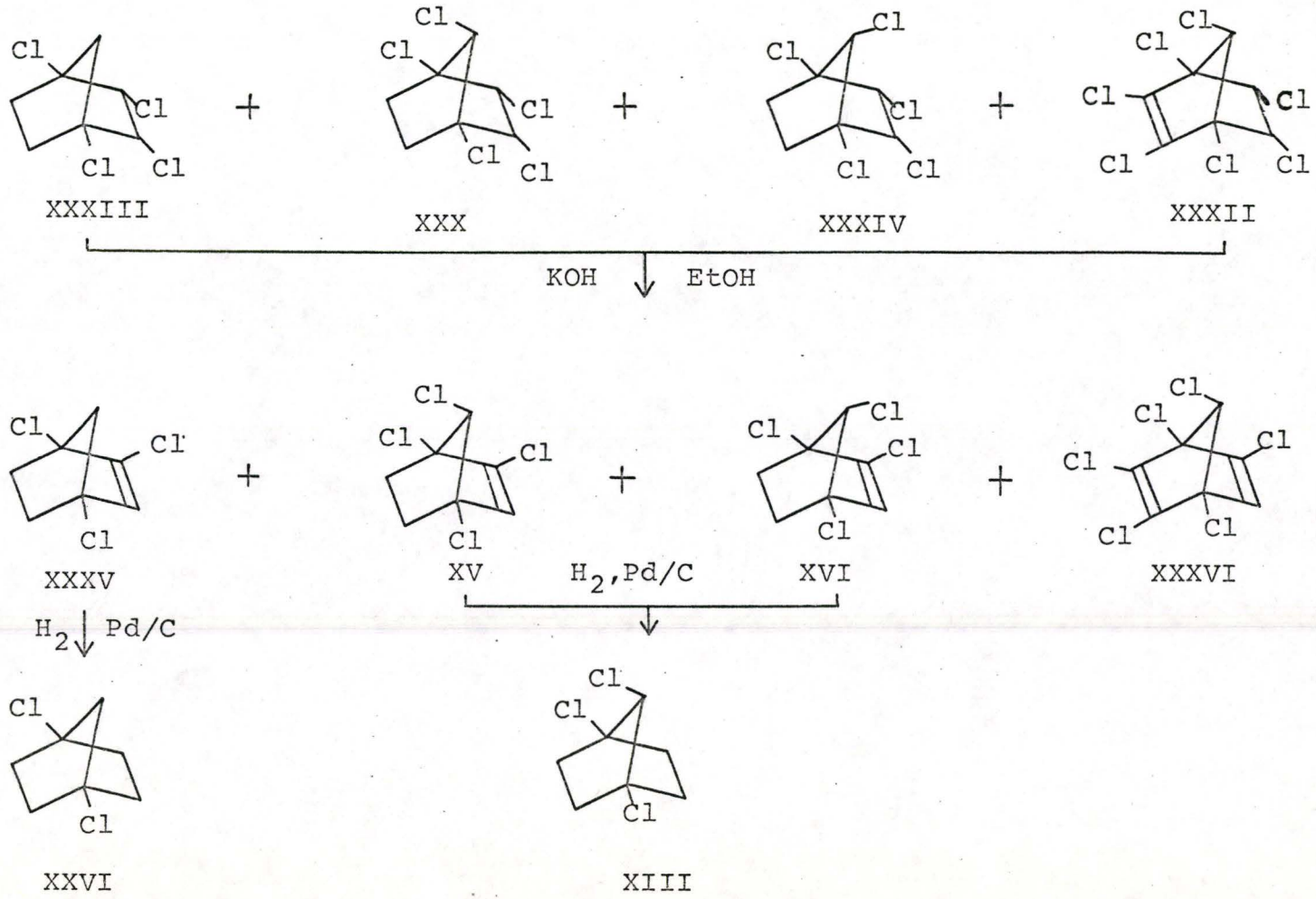
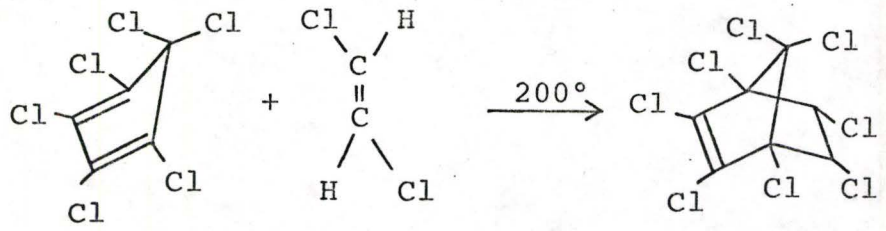


CHART VI (Continued....)



1,4-addition of hexachlorocyclopentadiene to *trans*-1,2-dichloroethylene at 200°C (equation [26]). The



[26]

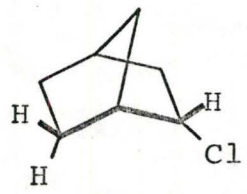
XXIX

nmr spectrum of XXIX consisted of a sharp singlet at 4.95δ, indicating that the two protons on C-5 and C-6 must be both *exo* or both *endo*. Diels-Alder additions of cyclopentadiene to dienophiles usually give the *endo*-adduct (64). The *endo*, *cis* assignment for XXIX (equation [26]) will be substantiated in later discussion on derivatives of XXIX.

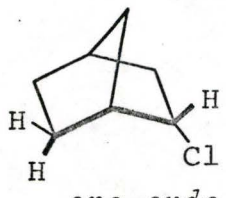
Catalytic reduction of XXIX in ethanol-triethyl amine was expected to give mainly 1-*endo*-*cis*-2,3,4-*anti*-7-pentachloronorbornane (XXX), based on previous studies reported here and those of Alden and Davies (62). When the reduction was carried out using 2 mole equivalents of triethyl amine over palladium on charcoal catalyst, six products were obtained (Chart VI). These were 1,4,7-trichloronorbornane (XIII) (5%), 1,4,7,7-tetrachloronorbornane (XXXI) (trace), 1,2,3,4-*endo*,*cis*-5,6-*syn*-7-heptachloronorborn-2-ene (XXXII) (53%), 1-*endo*,*cis*-2,3,4-tetrachloronorbornane (XXXIII) (6%) and *anti*- and *syn*-1-*endo*, *cis*-2,3,4,7-pentachloronorbornane (XXX and XXXIV) (36%).

Reduction with three mole equivalents of triethylamine gave 8.1% XIII, 10.8% XXXIII, and 69.5% of a mixture of XXX and XXXIV (mainly XXX). Reduction of pure XXXII under the same conditions gave 67% XXX and 33% XIII as the only reduction products. When XXIX was reduced over palladium on charcoal in KOH-ethanol solution, XXXII was the main product formed.

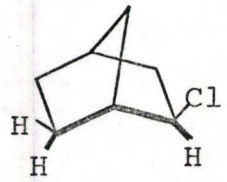
The four compounds derived from XXIX were identified from their nmr spectra. The nmr spectrum of XXXIII (see Figure 11) consisted of a multiplet at 4.49δ (W-plan coupling, less than 1 Hz) and a multiplet between 2.82 and 1.80δ. The relative areas were 1:3. The protons on C-2 and C-3 can only undergo W-plan coupling with the protons on C-5 and C-6 if they are *exo*. *Exo,endo* or *endo,endo* coupling will not be observed due to the unfavourable angle. The nmr spectrum of XXXIII confirms the *endo,cis* assignment for the C-5 and C-6



exo,exo



exo,endo



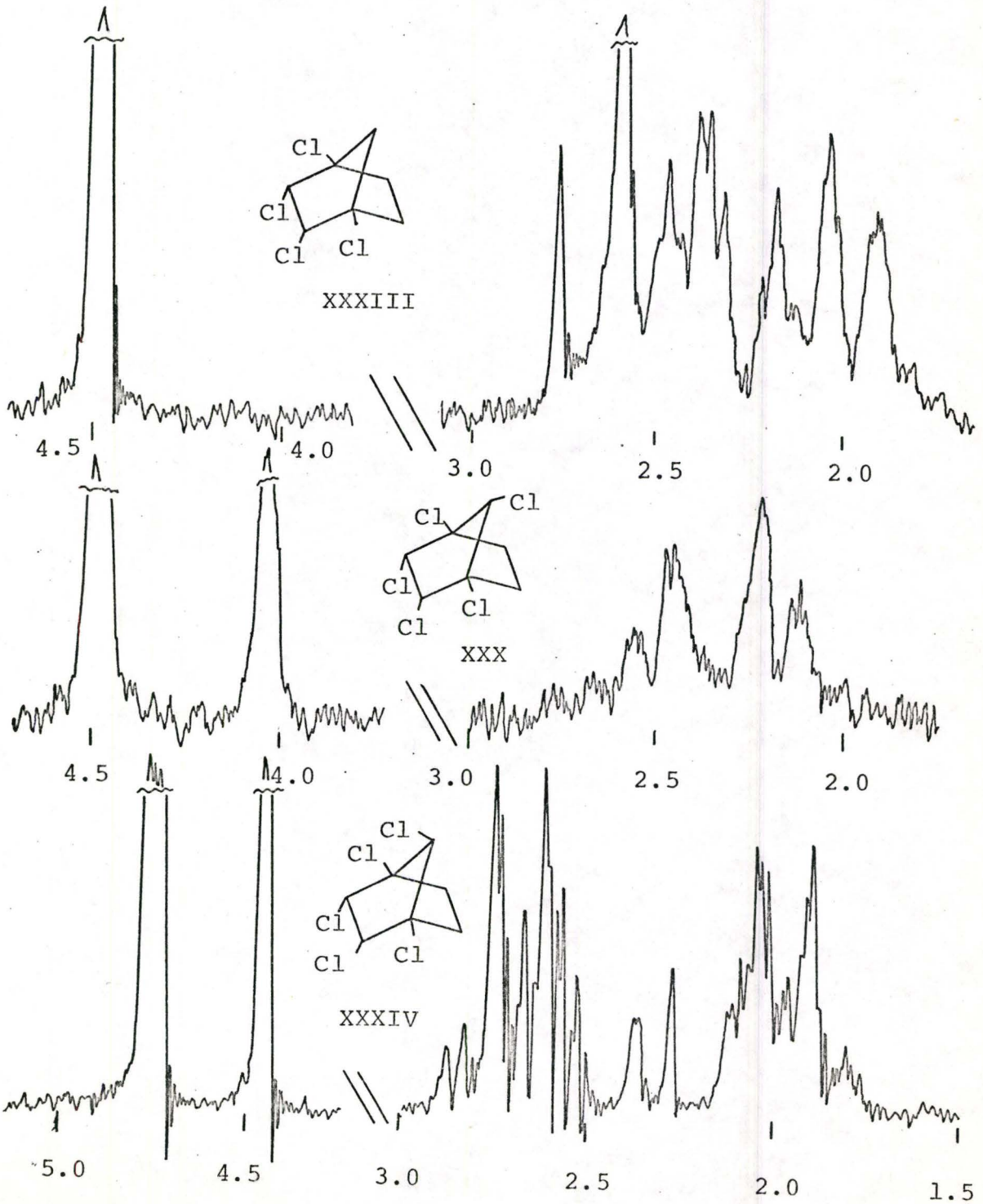
endo,endo

chlorine atoms in XXIX.*

---

* Alden and Davies (62) have synthesized 1-*exo*-2-*endo*-3,4-tetrachloronorbornane and report different chemical shift values for the *exo*- and *endo*-C-2 and C-3 hydrogens.

Figure 11: NMR Spectra of 1,2,3,4-Tetrachloro-norbornane, *anti*- and *syn*-1,2,3,4,7-Pentachloronorbornane



The nmr spectrum of XXX (Figure 11) consisted of a multiplet centered at 4.51δ, a multiplet centered at 4.05δ and a multiplet between 2.70 and 1.92δ, relative areas 2:1:4. The absorption of 4.51δ is due to W-plan coupling of the *exo*-2,3-hydrogens with the *exo*-5,6 hydrogens. Similarly, the C-7 hydrogen (4.05δ) *anti* to the C-5 and C-6 hydrogens is W-plan coupled to the *endo*-5,6 hydrogens. This confirms the assigned stereochemistry at C-7. The nmr spectrum of the *syn*-isomer XXXIV (Figure 11) consisted of a multiplet at 4.78δ (C-2 and C-3 protons, W-plan coupling) a singlet at 4.48δ (C-7 hydrogen, no W-plan coupling) and a multiplet between 2.92 and 1.74δ (ring methylenes), relative area 2:1:4.

The nmr spectrum of XXXII consisted of two singlets at 4.68 and 4.36δ, relative area 2:1. Since XXXII reduces to XXX, the C-7 chlorine atom in XXXII must be *syn* to the double bond.

The proposed reduction scheme is outlined in Chart VI. Again, catalytic reduction at C-7 proceeds with a high degree of stereoselectivity to give predominantly the *syn*-isomer XXXII. Although none of the *anti*-isomer (XXXIIa) was detected, XXXIV must arise from hydrogenation and hydrogenolysis of XXXIIa. Likewise, XXXIII most likely arises from reduction of the *anti*-C-7

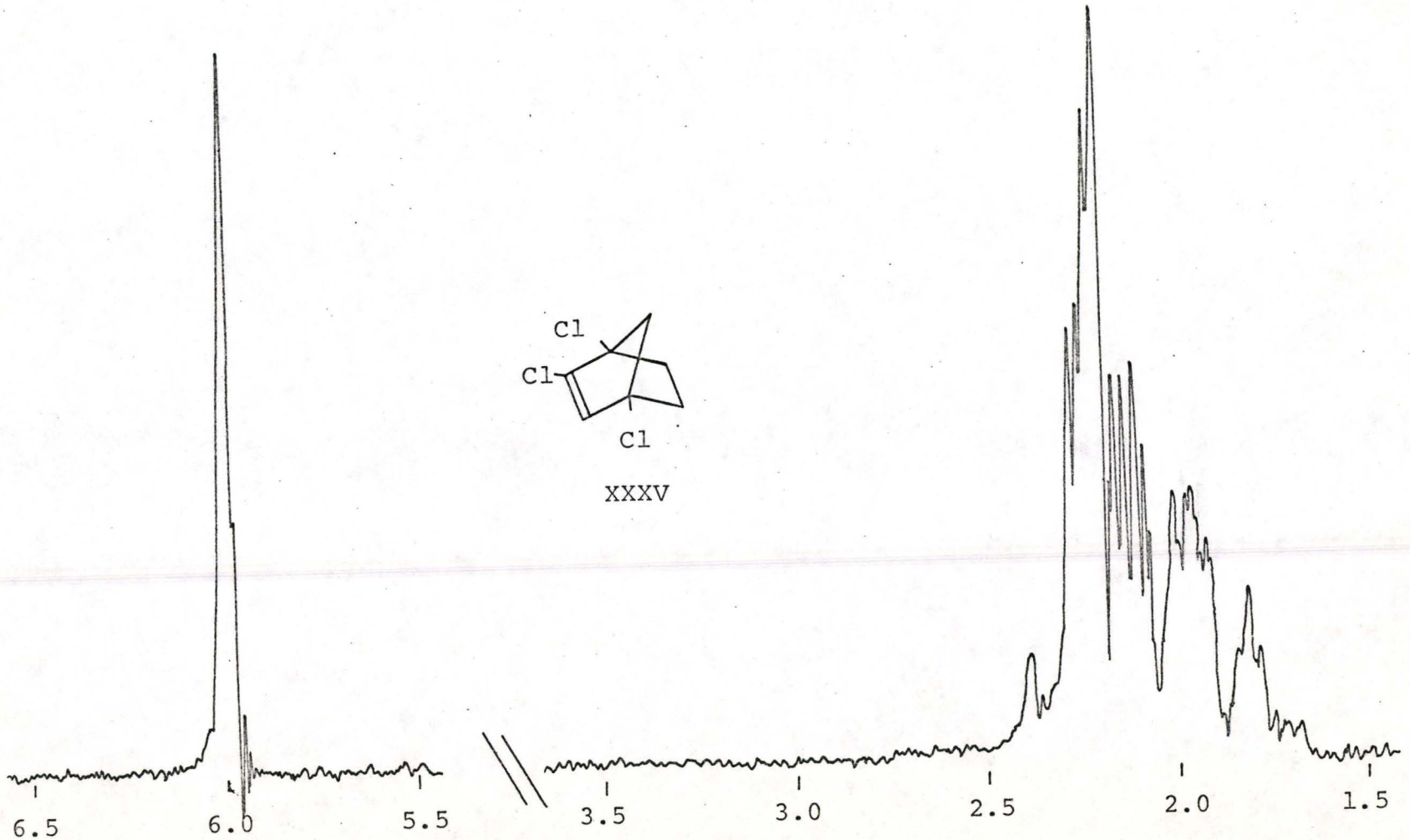
chlorine atom in XXXIIa to give XXXIIIa, which is further reduced to XXXIII. Both XXXIII and XXXIV were present in small quantities in the reduction mixture.

A mixture of the four reduction products, XXX, XXXII, XXXIII, and XXXIV (see Chart VI, pp.125-126), readily eliminated the elements of HCl when heated under reflux with KOH in ethanol. The main product was 1,2,4-*anti*-7-tetrachloronorbornene (XV). The *syn*-isomer XVI as well as 1,2,4-trichloronorborn-2-ene (XXXV) and 1,2,3,4,5-*syn*-7-hexachloronorborna-2,5-diene (XXXVI) were present in small amounts.

The nmr spectrum of XXXV (Figure 12) consisted of a multiplet at 6.06δ (coupling constant less than 1 Hz) and a multiplet between 2.5 and 1.8δ. The relative areas were 1:6, consistent with the proposed structure. A small amount of XXXV was readily reduced to 1,4-dichloronorbornane (XXVI), further confirming the structure.

The nmr spectrum of the diene XXXVI consisted of two singlets at 6.69 and 4.84δ in the ratio of 1:1. This is consistent with a vinyl proton and a proton on the same carbon as a chlorine atom, as demanded by the proposed structure. Since XXXVI must arise from XXXII, the C-7 chlorine atom must be *syn* to the disubstituted double bond. The absence of coupling between C-6 and C-7 confirms this.

Figure 12: NMR Spectrum of 1,2,4-Trichloronorborn-2-ene



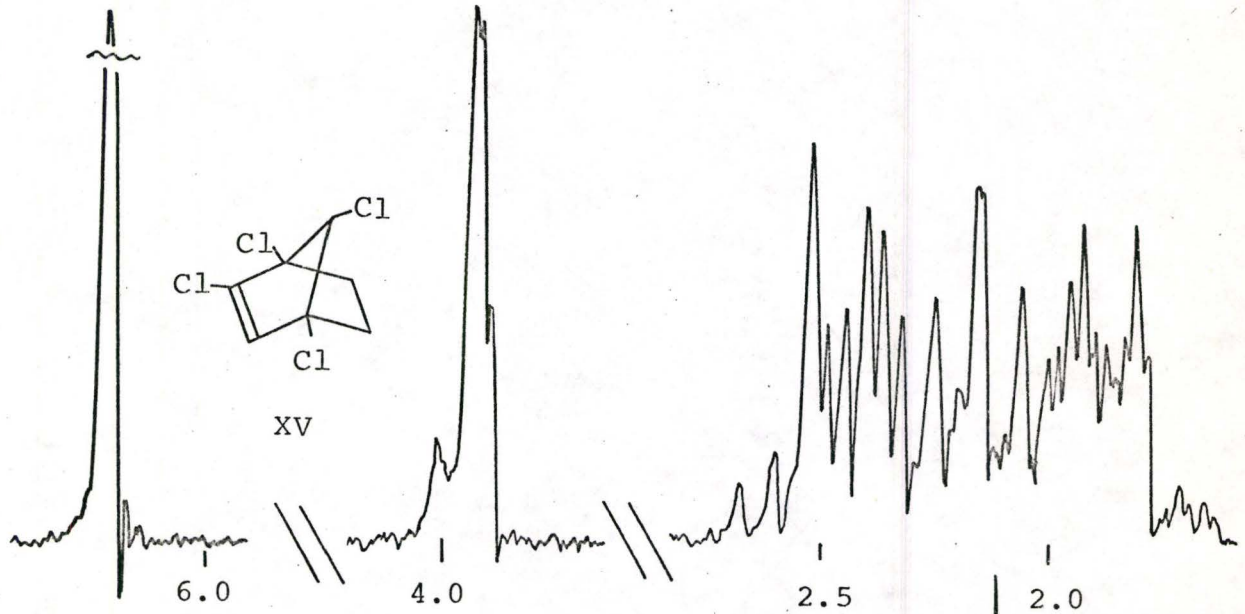
XXXV

The *anti*-isomer XV (Figure 13) exhibited a vinyl proton singlet at 6.21δ, a multiplet at 3.92δ due to W-plan splitting of the C-7 proton signal, and a multiplet between 2.75 and 1.58δ (ring methylenes), relative areas 1:1:4. The W-plan splitting of the C-7 hydrogen, the absence of splitting of the vinyl signal, and the broad methylene adsorption all confirm the *anti* assignment. In the *syn*-isomer, XVI (Figure 13), the C-7 hydrogen is *anti* to the vinyl hydrogen, and the expected coupling between these two hydrogens is observed in the nmr spectrum. The vinyl hydrogen absorbs as a doublet (5.92, 5.88δ) as does the C-7 hydrogen (4.11, 4.07δ). The methylene protons appear as a multiplet between 2.5 and 1.9δ, relative areas 1:1:4. The structures of XV and XVI were further confirmed by catalytic reduction. A quantitative yield of 1,4,7-trichloronorbornane (XIII) was obtained.

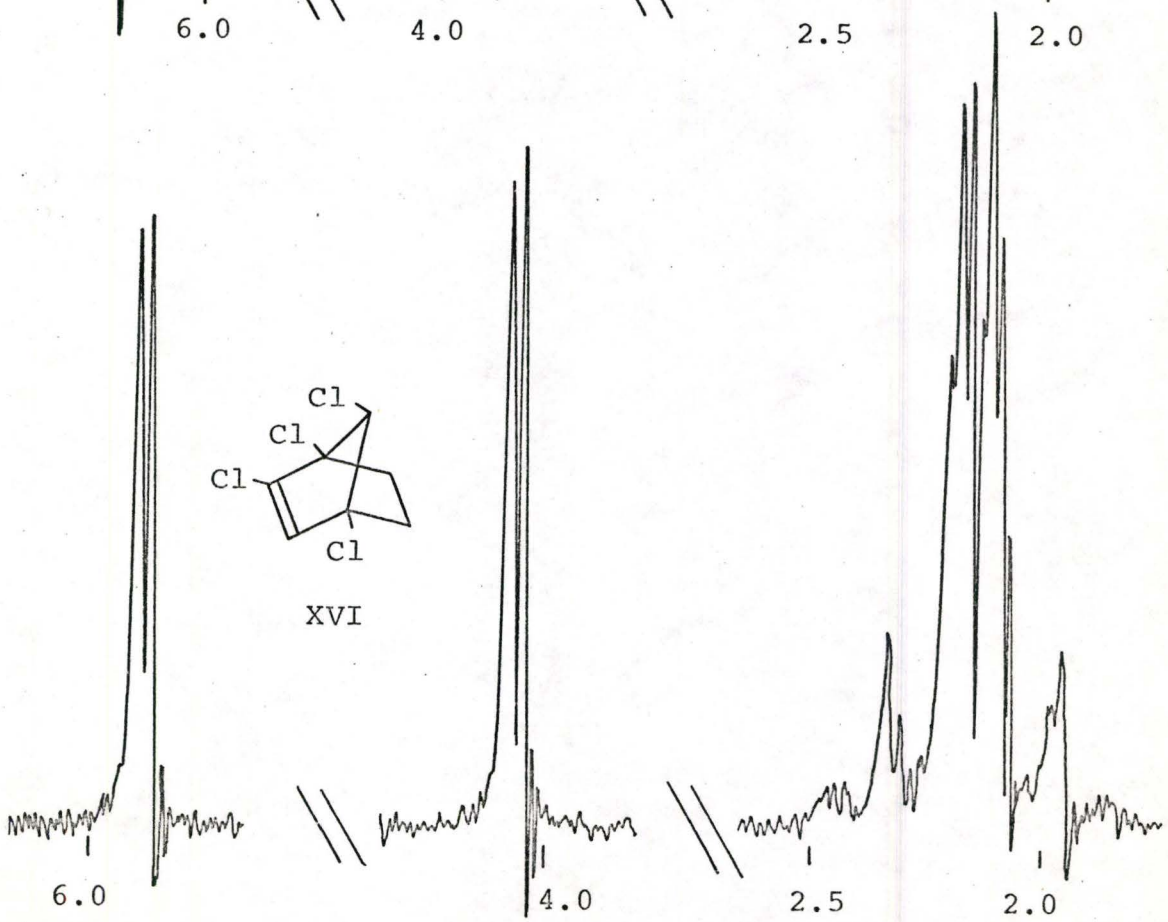
IV Kinetic and Product Studies on Polychlorinated Norbornenes

Relative rates of reduction of a series of polychlorinated norbornane derivatives with tri-*n*-butyltin hydride are given in Table XIII. The rates of reduction of IIe and XIII (Table XIII, entries 1 and 2) have been discussed previously in terms of a possible polar contribution by the bridgehead chlorine atoms. Any significant

Figure 13: NMR Spectra of *anti*- and *syn*-1,2,4,7-Tetrachloronorborn-2-ene



XV



XVI

TABLE XIII

Relative Rates of Reduction of Polychlorinated Norbornane Derivatives

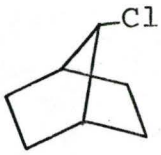
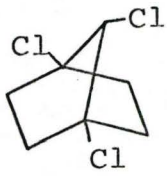
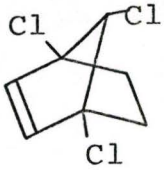
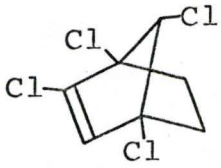
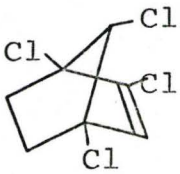
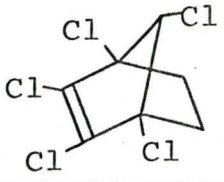
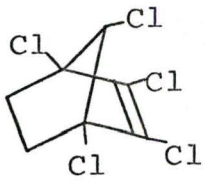
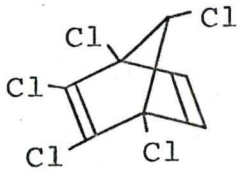
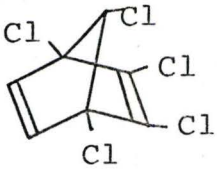
Entry	Compound	k/k_o
1	 IIe	1.00
2	 XIII	1.08
3	 XIV	16.8
4	 XV	-
5	 XVI	-

TABLE XIII (Continued.....)

Entry	Compound	k/k_o
6	 XVII	280
7	 XVIII	150
8	 XXIV	-
9	 XXIII	-

charge polarization in the transition state is ruled out by the negligible rate difference between IIe and XIII.

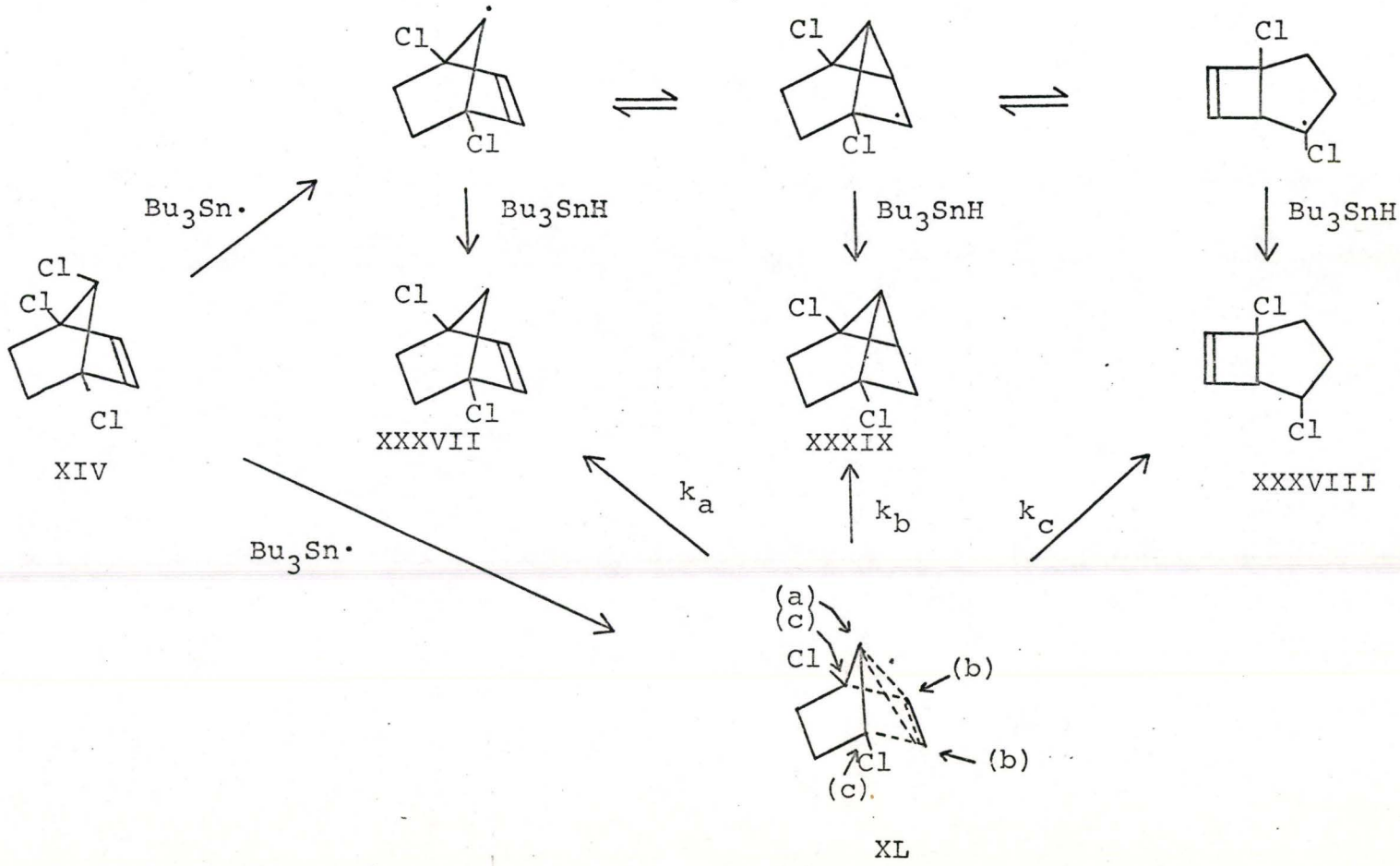
When a double bond is introduced into the molecule (Table XIII, entry 3), a substantial rate increase is observed. π-Orbital delocalization must be stabilizing the incipient radical in the transition state. At least one of the bridgehead chlorine atoms must be involved, making delocalization more favourable in 1,4-*anti*-7-trichloronorborn-2-ene (XIV) compared to *anti*-7-chloronorbornene (IVb). A much smaller rate enhancement (4.5) was observed in the latter case.

Before considering possible intermediates, it is instructive to examine the reduction products obtained from XIV. Analysis by glpc of the reaction mixture showed the presence of three products. These could arise from equilibration of an initially formed classical homoallyl radical with its isomeric cyclopropylcarbinyl counterpart. The three possible products are shown in Chart VII. A single "non-classical" radical intermediate, XL, which can give the same three products is also shown.

The two main reduction products were isolated by preparative glpc. They were identified as 1,4-dichloronorbornene (XXXVII) and 1,4-dichlorobicyclo[3.2.0]hept-

CHART VII

Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,4,7-Trichloronorbornene

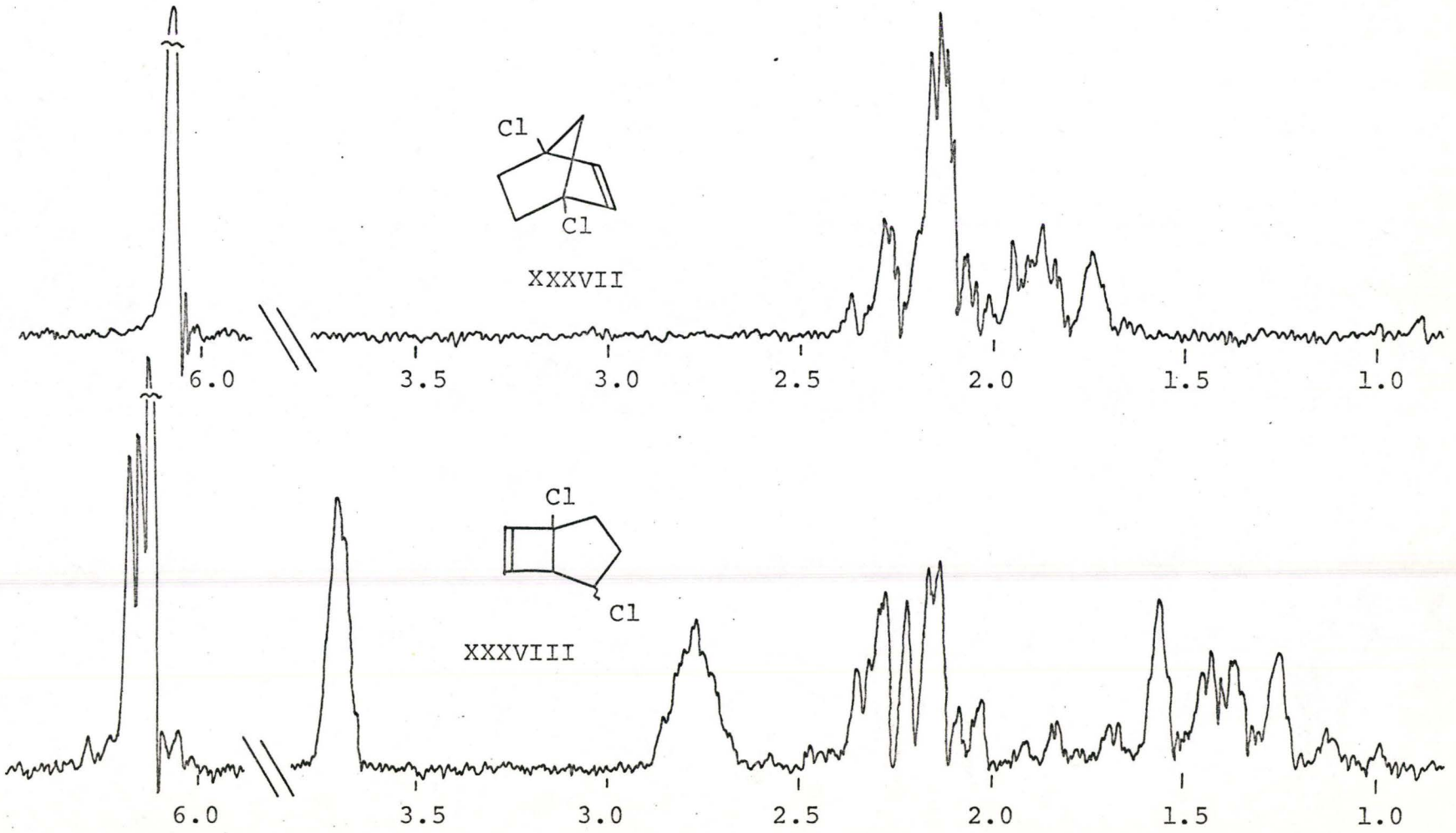


6-ene (XXXVIII) by their nmr spectra. Isolation and identification of the third component, assumed to be 1,4-dichlorotricyclo[2.2.1.$0^{2,7}$]heptane (XXXIX), was not accomplished due to the small amount formed.

The nmr spectrum of XXXVII, shown in Figure 14, exhibited a vinyl singlet at 6.06δ (1H) and a methylene multiplet between 2.42 and 1.70δ (3H). This is consistent with the published spectrum of XXXVII (62). The signal due to the vinyl protons in XXXVIII (Figure 14) appeared to consist of a doublet (6.18, 6.15δ) and a singlet (6.12δ) in the nmr spectrum. Weak splitting was observed in the absorption (3.72δ) assigned to the hydrogen on the same carbon as the chlorine atom. The bridgehead hydrogen absorbed as a multiplet at 2.76δ while the methylenes appeared as a multiplet between 2.38 and 0.92δ. A lack of suitable model compounds prevents any assignment of the *syn-anti* stereochemistry at C-4. Relative areas were 2:1:1:4, consistent with the proposed structure.

If the reduction products from XIV are derived from three equilibrating classical radicals (Chart VII), the initially formed radical should be trapped at high tin hydride concentrations. At lower tin hydride concentrations, the intermediate radicals would have more time to equilibrate, and a different ratio of products

Figure 14: NMR Spectra of 1,4-Dichloronorbornene and 1,4-Dichlorobicyclo[3.2.0]hept-6-ene



would be obtained. Table XIV shows the product ratios observed for reduction of XIV with varying concentrations of tri-*n*-butyltin hydride.

The variation in the ratio of the two main products over a five-fold change in tin hydride concentration is less than ±4%. Also, the variations are random rather than exhibiting a trend in one direction. The latter would be expected if equilibrating classical radicals were being trapped.

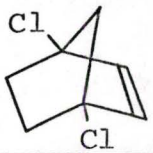
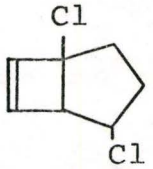
The single non-classical radical XL shown in Chart VII best explains the kinetic and product data for reduction of XIV. In this instance, $k_a > k_c >> k_b$ is required.

Table XIII does not contain kinetic data for reduction of *anti*- and *syn*-1,2,4,7-tetrachlornoborn-2-ene (XV and XVI, entries 4 and 5). The vinyl chlorine atom in XV underwent reduction with tri-*n*-butyltin hydride much faster than the C-7 chlorine atom so that 1,4-*anti*-7-trichloronorborn-2-ene (XIV) was the main reduction product. Similarly, reduction of XVI did not give products arising from reduction at C-7. In this case, the structure of the main product was not determined (see Experimental, Section II (iv)).

Large rate accelerations were observed for reduction of *anti*- and *syn*-1,2,3,4,7-pentachloronorborn-2-ene (XVII and XVIII) (Table XIII, entries 6 and 7).

TABLE XIV

Effect of Bu_3SnH Concentration on the Product Ratio from Reduction of 1,4-*anti*-7-Trichloronorbornene

Concentration of Bu_3SnH (mol l^{-1})*	% 	% Minor Component	% 
	XXXVII	XXXIX	XXXVIII
1.5	33.6 ± 0.3	8.8 ± 0.3	57.6 ± 0.6
0.9	32.7 ± 0.4	15.7 ± 0.2	51.6 ± 0.5
0.3	38.9 ± 0.1	4.5 ± 0.1	56.6 ± 0
Average	35.1 ± 3.8%	9.7 ± 6.1%	55.3 ± 3.6%

* 0.3M solution of XIV in hexane.

As was the case for XIV, three main reduction products were obtained from XVII and XVIII. A small amount of XV, presumably from reduction of one of the vinyl chlorine atoms in XVII, was detected in the reaction mixture.

The three products which can result from allylcarbinyl radicals equilibrating with cyclopropylcarbinyl radicals are given in Chart VIII. Again, a single non-classical radical intermediate (XLI) which could give all three products is shown.

The reduction product XX was identified by comparison of its glpc retention time with that of an authentic sample. This product (XX) was only partially separated from XV on the glpc. A mixture of these two was obtained by preparative glpc. A comparison of the nmr spectrum of the mixture with nmr spectra of XV and XX confirmed the structures of the compounds in the mixture.

The other two reduction products, XLII and XLIII, were obtained pure by preparative glpc and their nmr spectra were recorded. Both of the proposed structures, XLII and XLIII, have one bridgehead hydrogen, one hydrogen on the same carbon as a chlorine atom and four ring methylene hydrogens. Their nmr spectra were found to be very similar (see Figure 15). The relative areas in both spectra were 1:1:4 and the general features

CHART VIII

Intermediates and Products from Tri-*n*-butyltin Hydride

Reduction of 1,2,3,4,7-Pentachloronorborn-2-ene

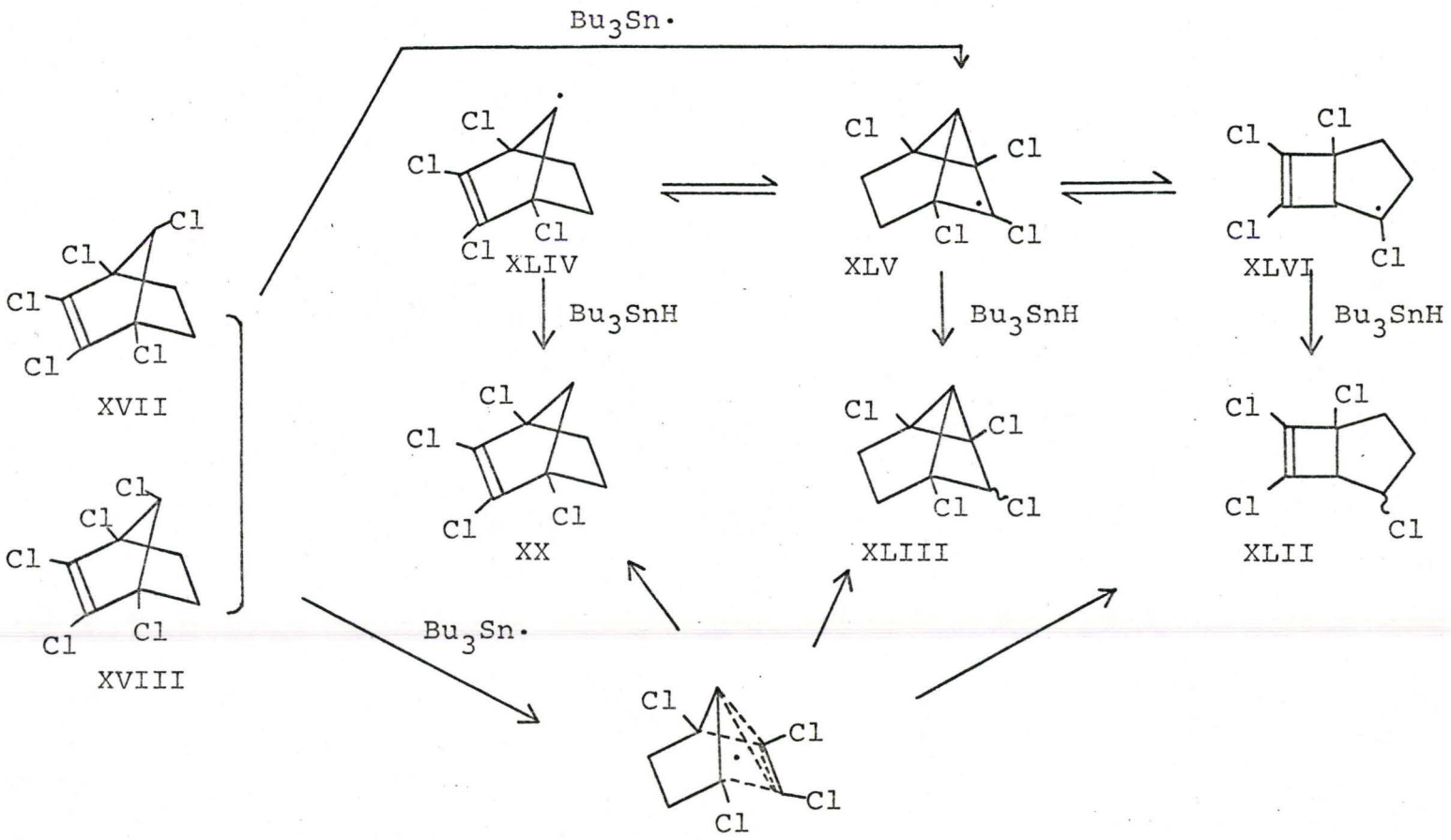
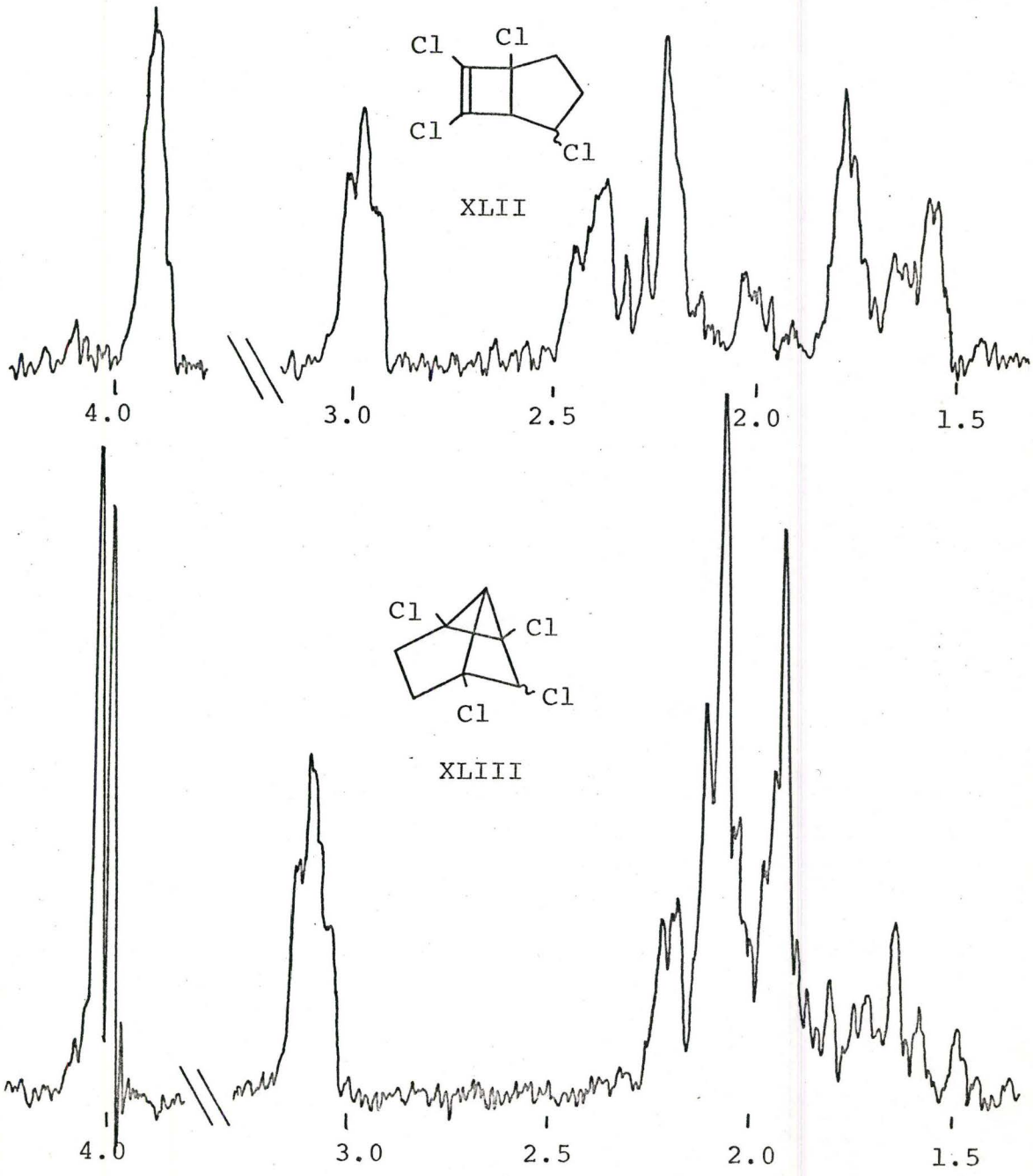


Figure 15: NMR Spectra of 1,4,6,7-Tetrachloro-bicyclo[3.2.0]hept-6-ene and 1,2,3,4-Tetrachlorotricyclo[2.2.1.$0^{2,7}$]-heptane



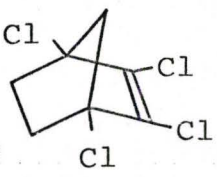
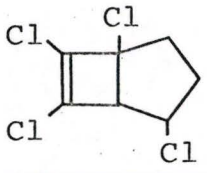
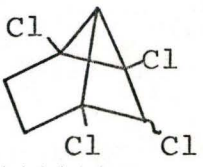
are entirely consistent with the proposed structures. The assignments in Figure 15 are based on comparison of the spectra with the spectrum of 1,4-dichlorobicyclo[3.2.0]hept-6-ene (XXXVIII) (Figure 14). The spectrum assigned to XLII is very similar to the spectrum of XXXVIII,a compound with the same carbon skeleton.

The sensitivity of the ratio of products from XVII and XVIII to changes in tin hydride concentration was determined (Tables XV and XVI). The product ratio (XX:XLII:XLIII) from both XVII and XVIII is very dependent on tri-*n*-butyltin hydride concentration. This is strong evidence against the single non-classical free radical XLI (Chart VIII) as the precursor of the products XX, XLII and XLIII. It is also noteworthy that widely different product ratios were observed from the *syn*- and *anti*-isomers. The same intermediates cannot be present in both reductions.

The relative rate of reduction of XVII is very large in terms of the other compounds investigated. This demands some form of delocalization in the transition state. Three possible modes of π-orbital participation in the transition state are shown in equation [27]. The vinyl chlorine atoms in XVII make the π-orbital system

TABLE XV

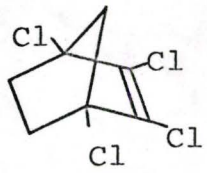
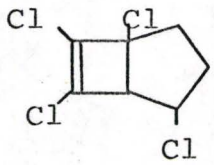
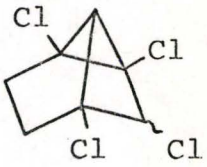
Effect of Bu_3SnH Concentration on the Product Ratio from Reduction of 1,2,3,4-*anti*-7-Pentachloronorborn-2-ene

Concentration of Bu_3SnH (mol l^{-1})*	%  XX	%  XLII	%  XLIII
0.9	-	trace	>99
0.3	9	77	14
0.18	32	58	10

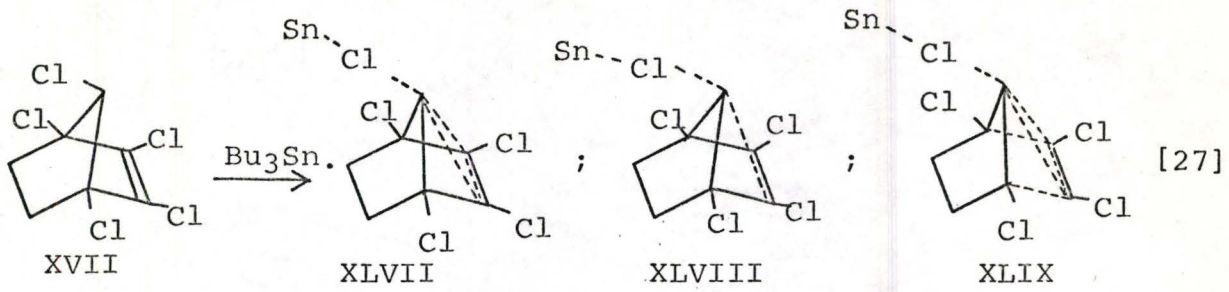
* 0.3M solution of XVII in hexane.

TABLE XVI

Effect of Bu_3SnH Concentration on the Product Ratio from Reduction of 1,2,3,4-*syn*-7-Pentachloronorborn-2-ene

Concentration of Bu_3SnH (mol l^{-1})*	%  XX	%  XLII	%  XLIII
0.9	-	-	100
0.3	trace	-	> 99
0.15	17	-	83

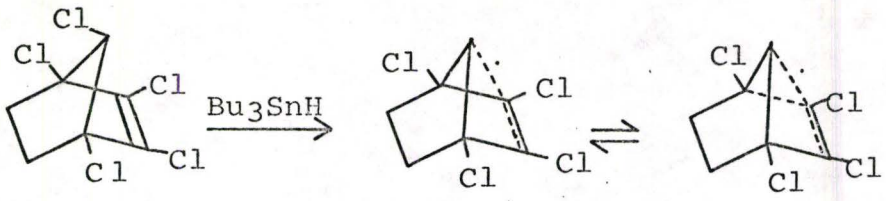
* 0.3M solution of XVIII in hexane.



[27]

relatively electron deficient. Transition state XLVII pictures both vinyl chlorine atoms acting equally to help delocalize the unpaired electron in the rate determining step. The unsymmetrical transition state XLVIII pictures one carbon bearing a chlorine atom as having considerable radical character, while the other has very little. The third possibility, XLIX, pictures both bridgehead chlorine atoms, as well as the two vinyl chlorines, participating in transition state delocalization. Without kinetic data on 1,2,4-*anti*-7-tetrachloronorborn-2-ene (XV), no choice can readily be made among the three possibilities.

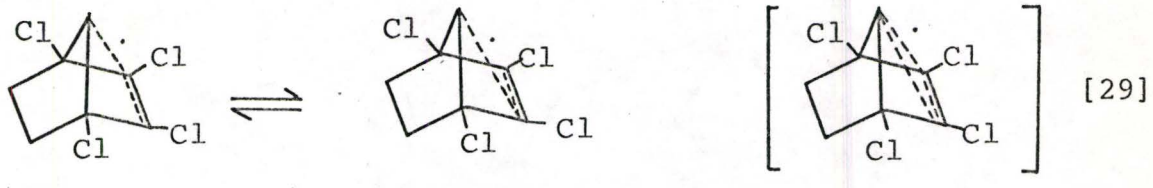
The substantial delocalization in the transition state required to explain the accelerated rate would be expected to result in delocalized radical intermediates. A scheme which accounts for the products in terms of such intermediates is shown in equation [28]. At high tin hydride concentrations, the tricyclic product XLIII is obtained almost exclusively (Table XV). The intermediate



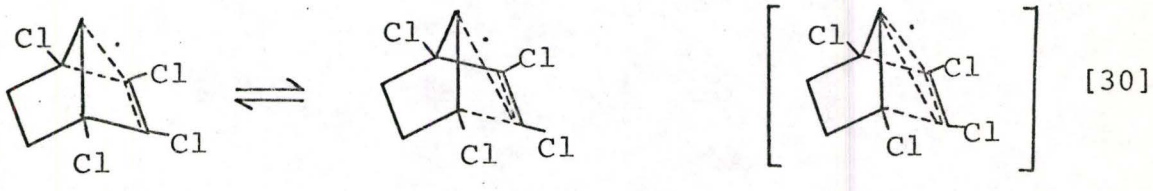
XVII L LI [28]

from which XLIII is derived must be trapped before equilibration can take place. Classical intermediate L (equation [28]) adequately fills this role. The electron density in L would be highest on the chlorine-bearing carbon and reaction might take place most readily at this carbon atom to give XLIII. At lower tin hydride concentrations, intermediate L (equation [28]) can equilibrate with LI to give the other two products, XX and XLII.

If the delocalized radicals L and LI are intermediates in the reaction, L and LI would be equilibrating with their mirror images (La, LIa, equations [29,30]). The symmetrical



L La LII [29]



LI LIa XLI [30]

delocalized intermediate LII (equation [29]) must then be a transition state for interconversion of L and La, i.e. a higher energy species. Similarly, XLI (equation [30]) must be a transition state for interconversion of LI and LIa. By definition, a non-classical intermediate must be lower in energy than its classical counterpart. If the highly delocalized species XLI is merely a transition state for interconversion of LI and LIa (equation [30]), then all intermediates in equations [29 and 30] must be regarded as classical intermediates.

The experimental evidence obtained for tin hydride reduction of 1,2,3,4-*anti*-7-pentachloronorborn-2-ene (XVII) can be summed up as follows. The large rate enhancement observed for free radical formation at C-7 in XVII demands substantial delocalization in the transition state. The dependence of product ratio on concentration of reducing agent, however, demands that there be more than one intermediate. Delocalization in the transition state should lead to delocalized intermediates, and for this reason, equilibrating delocalized free radical intermediates are proposed to explain the products formed.

1,2,3,4-*syn*-7-Pentachloronorborn-2-ene (XVIII) reduced 150 times faster than 1,4,7-trichloronorbornane (XIII), but only 0.54 times as fast as the *anti*-isomer XVII (Table XIII). The relative rates of reduction of

syn-7-bromonorborn-2-ene (Ib) and *syn*-7-chloronorborn-2-ene (Ic) were explained in terms of involvement of the tin atom with the π-electrons of the double bond in the transition state. No estimate can be made as to whether the rate enhancement observed for XVIII is entirely or partially due to tin atom involvement in the transition state. The very different product ratios observed for reduction of the isomers XVII and XVIII (Tables XV and XVI) are indicative of different intermediates. For reduction of XVIII, the tin species may still be associated with the intermediate radical, and in this way, influence the product ratio. As with the other *syn*-halides, reduction of XVIII appears to give ambiguous results, and nothing definite can be said about the kinetic and product data in terms of classical or non-classical radicals.

Attempted kinetic studies on *syn*- and *anti*-1,2,3,4,7-pentachloronorborna-2,5-diene (XXIII and XXIV) resulted in the same complications encountered with 7-chloronorborna-2,5-diene (Vb). Addition of the tin radical to the double bonds appeared to be faster than chlorine abstraction at C-7. However, some reduction did take place at C-7 and three reduction products were isolated from a mixture of XXIII and XXIV and identified by their nmr spectra (see Experimental, Section II (vi)). The nmr

spectra and assigned structures, are given in Figure 16.

1,2,3,5-Tetrachloroquadricyclane (LIII) had a longer glpc retention time than XXIII and XXIV on a SE-30 column. This is to be expected since quadricyclane (VIIa) has a considerably longer retention time than norborna-2,5-diene (Va), from which it is derived. The nmr spectrum of LIII consisted of four separate absorption regions (ratio 1:1:1:1) consistent with four non-equivalent hydrogen atoms in the molecule. The general features of the spectrum are in complete agreement with the proposed structure.

Very similar nmr absorption patterns were observed for the other two compounds isolated (Figure 16). The regions of absorption are as expected for vinyl protons (7.0-6.68δ), a proton on the same carbon as a chlorine atom (4.65-4.46δ) and bridgehead protons (3.68-3.50δ). The nmr spectrum of the compound with the shortest glpc retention time, assigned the structure 1,2,4-trichlorotricyclo[2.2.1.$0^{3,7}$]hept-5-ene (LIV), integrated in the ratio 2:1:2, consistent with the proposed structure.

The third compound isolated integrated in the ratio of two vinyl hydrogens, one bridgehead hydrogen, and one hydrogen on the same carbon as a chlorine atom. The structure 1,2,3,4-tetrachlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene (LV) was assigned on this basis.

Figure 16: NMR Spectra of 1,2,3,5-Tetrachloroquadricyclane, 1,2,3,4-Tetrachlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene and 1,3,4-Trichlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene

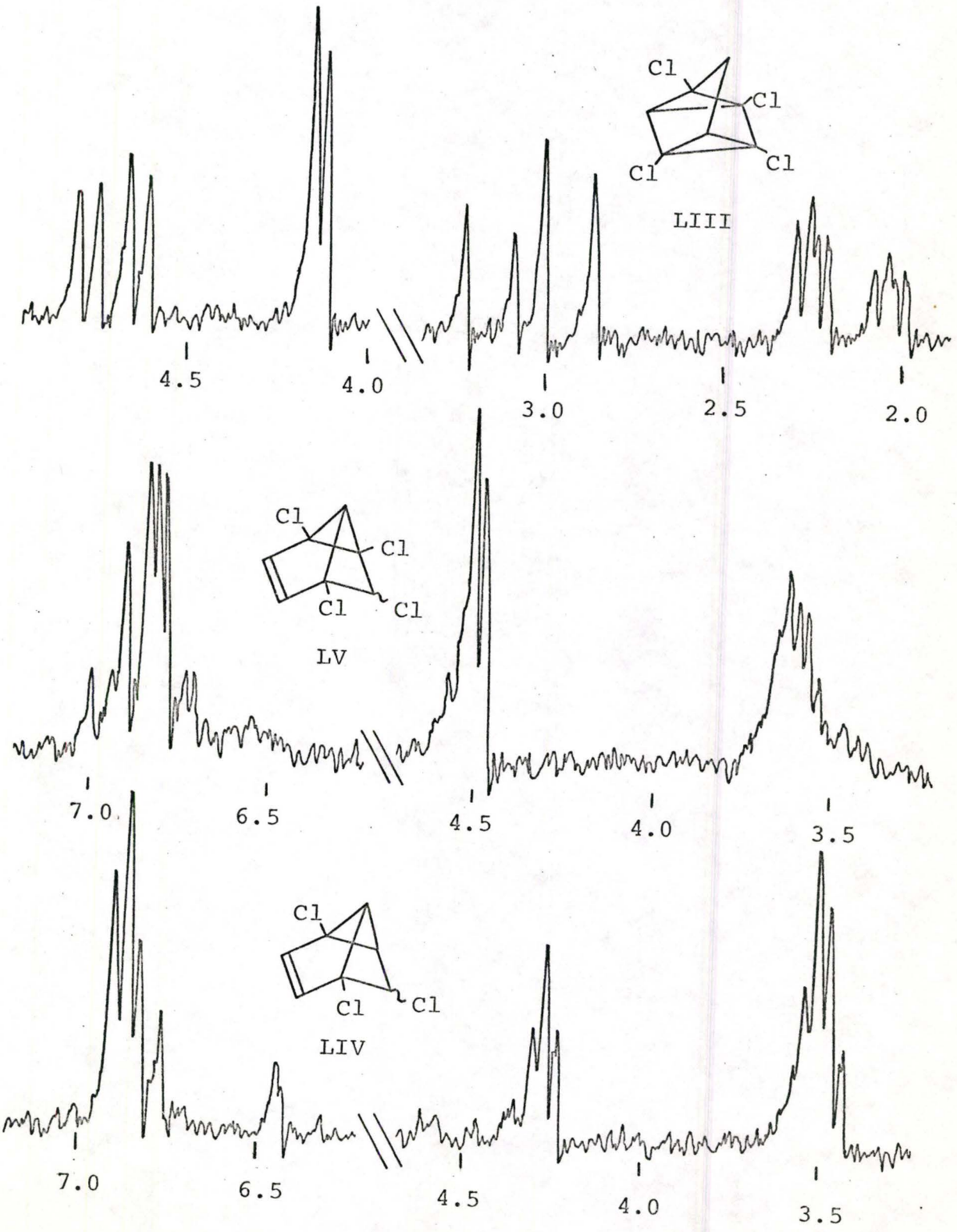


Chart IX shows how these three products could arise from reduction of 1,2,3,4,7,7-hexachloronorborna-2,5-diene (XXII) with two mole equivalents of tri-*n*-butyltin hydride. Reduction of XXII with one mole equivalent of tin hydride gives only XXIII and XXIV. It is likely that a vinyl chlorine atom in the *anti*-isomer XXIV reduces to give *anti*-1,2,4,7-tetrachloro-norborna-2,5-diene (LVI) since the C-7 chlorine atom does not sterically hinder this reaction.

Chart X shows three of the possible products that could result from equilibrating classical radicals derived from LVI. The nmr spectra of the two diene products would be quite different from the spectrum of the observed product LIV. A non-classical radical intermediate which could give the observed product is also shown.

Chart XI shows how four products could result from reduction of XXIII and XXIV. Both classical intermediates and a non-classical intermediate are shown. Although kinetic data could not be obtained for XXIII and XXIV, it is interesting to consider the observed products in terms of possible intermediates. The three products isolated (LIII, LIV and LV) all contain cyclopropyl rings. The reason that no diene products

CHART IX

Products from Tri-*n*-butyltin Hydride Reduction of

1,2,3,4,7,7-Hexachloronorbornadiene

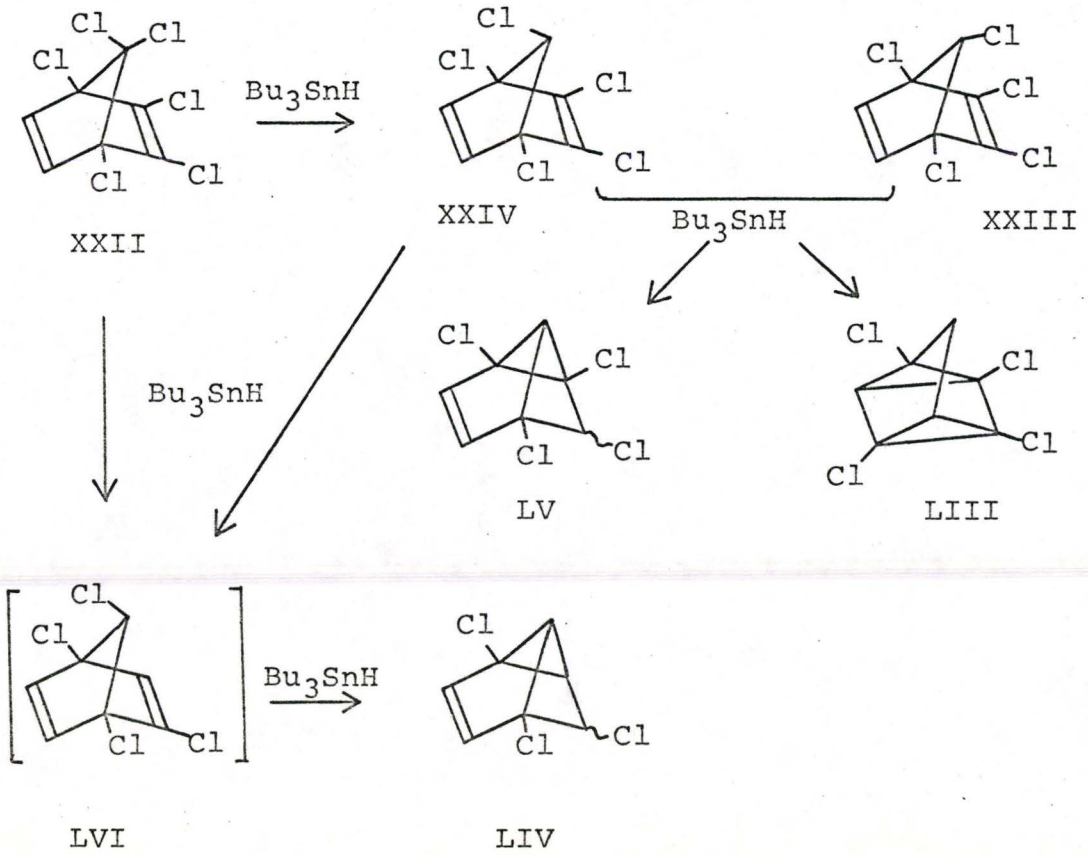


CHART X

Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,2,4,7-Tetrachloronorbornadiene

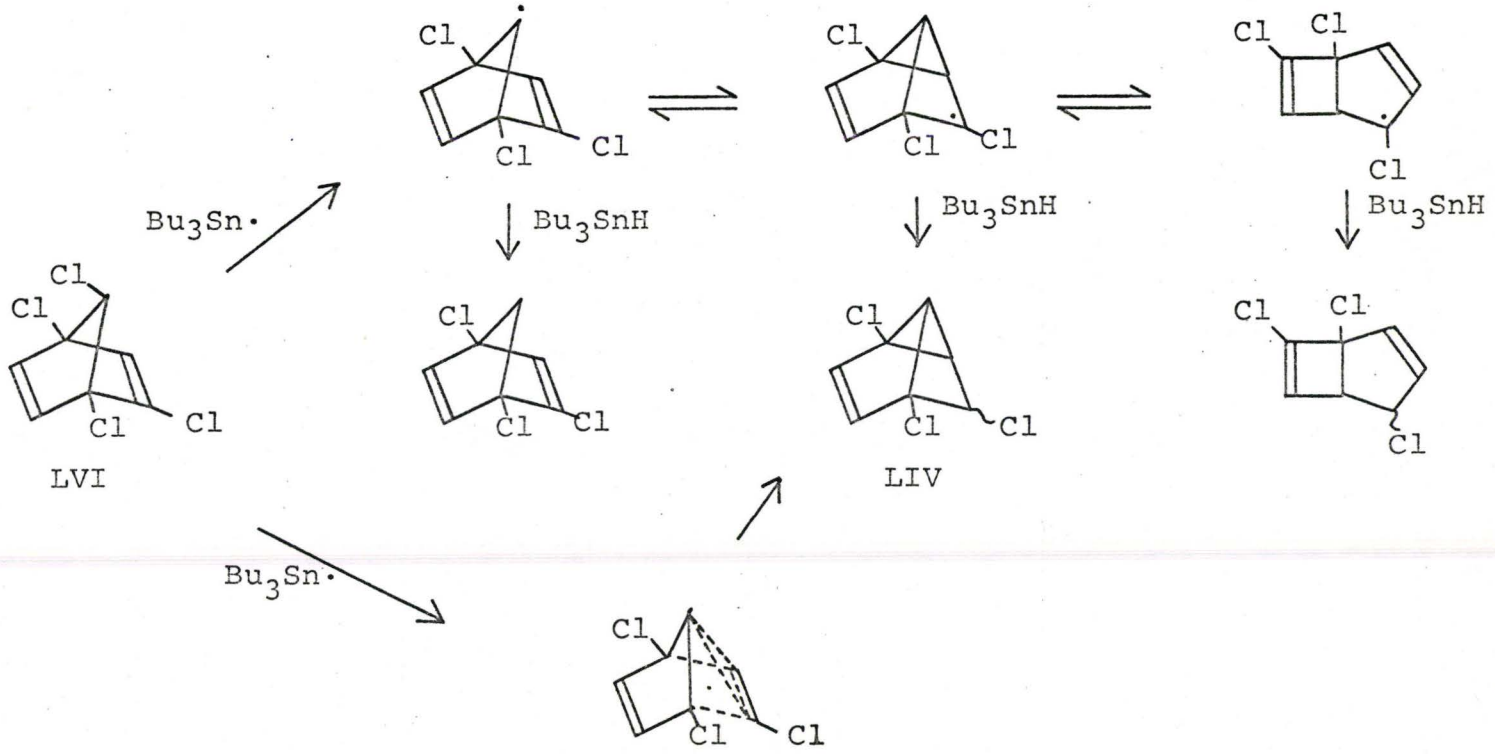
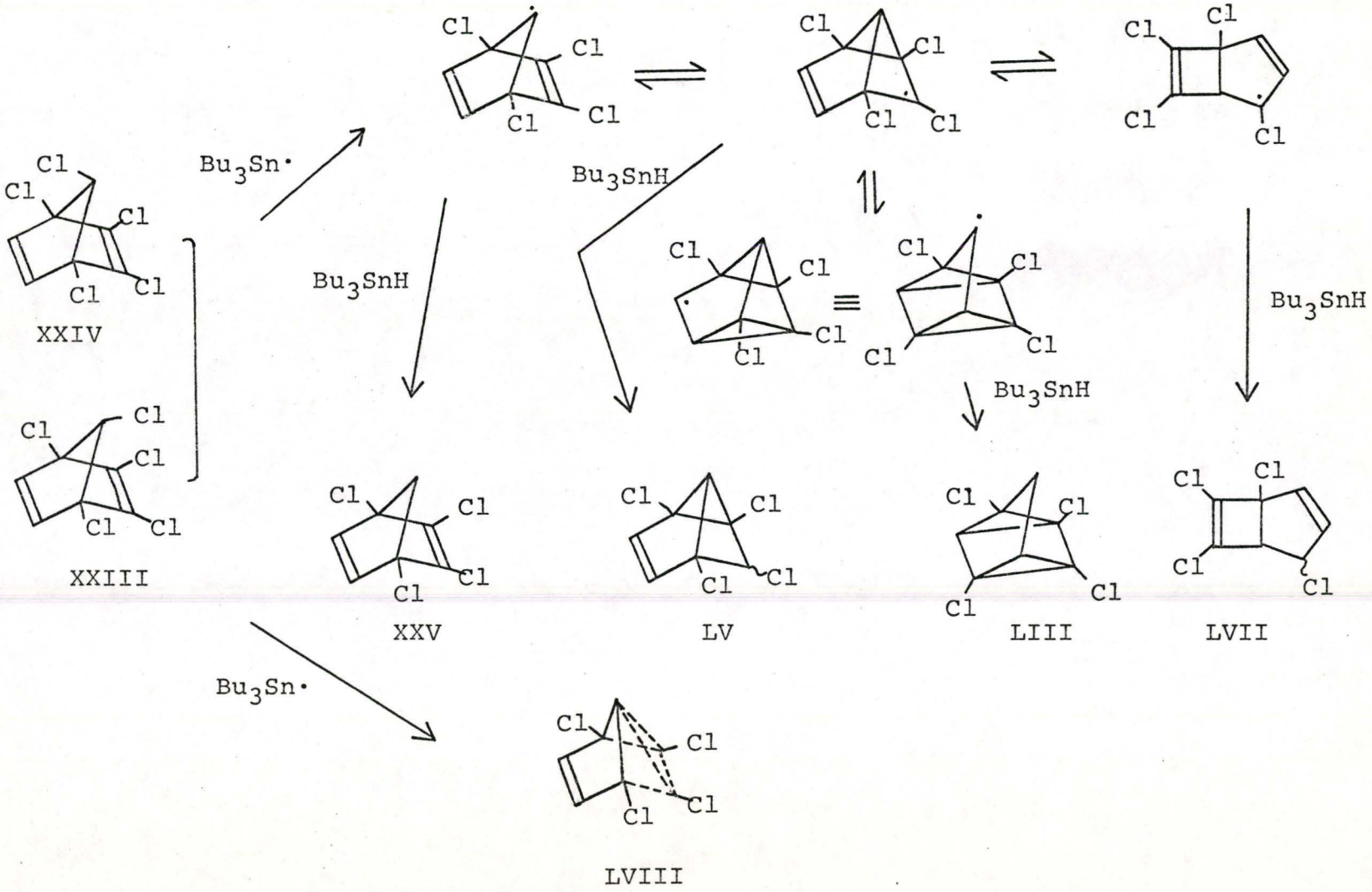


CHART XI

Intermediates and Products from Tri-*n*-butyltin Hydride Reduction of 1,2,3,4,5-Pentachloronorbornadiene

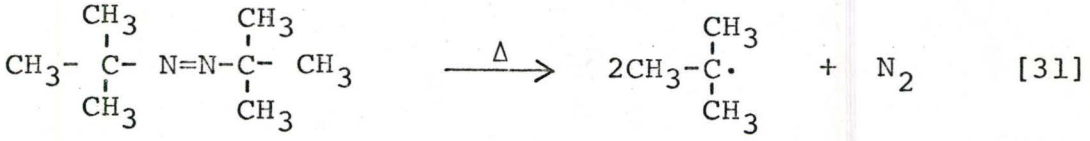


were obtained may be due to addition of the tin radical after the diene products were initially formed. However, if XXV and LVII were formed in appreciable amounts, it seems unlikely that they would disappear almost completely, since some XXIII and XXIV remained in the reaction mixture. Of the reduction products formed, LIII comprised 34% of the total amount of reduction products, LV made up 41% and 25% was LIV. Two unidentified minor components were present.

The classical radical intermediate from which LIII could arise (Chart XI) is not stabilized by a chlorine atom on the same carbon as the free radical. The chlorine containing cyclopropyl rings must, therefore, impart considerable stability to a free radical intermediate. This stabilization can be represented as delocalization of the free radical over the cyclopropyl rings through a non-classical intermediate (See LVIII, Chart XI). Although LV arises from reaction at a chlorine containing carbon atom, it is formed in only a slightly higher yield than LIII. The same non-classical intermediate LVIII could give rise to LV.

The proposal that LIII is derived from a non-classical intermediate is in complete agreement with earlier kinetic studies. A large rate enhancement was observed for reduction of 7-chloroquadricyclane (VIIb).

Delocalization over the two cyclopropyl rings was proposed to explain the enhanced rate. Similarly, Martin and co-workers (26) observed large rate enhancements during thermal decomposition when the methyl groups in hexamethylazomethane were replaced by cyclopropyl groups (equation [31]).



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{\Delta} 2CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot + N_2 \qquad [31]$$

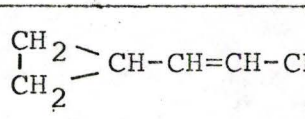
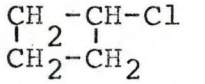
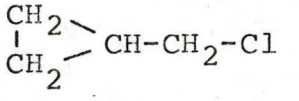
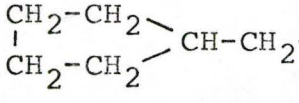
V Simple Acyclic Systems

The kinetic data discussed thus far have dealt with the rates of formation of cyclopropyl- and allylcarbinyl radicals in semi-rigid ring systems. For comparison, relative rates of reduction of several simple allylcarbinyl chlorides, as well as cyclopropylcarbinyl- and cyclobutyl chloride, were determined. The relative rates are given in Table XVII.

Allylcarbinyl chloride (entry 2) shows a small rate enhancement over the saturated alkyl chloride, 1-chloro-4-methylpentane (entry 1). With two methyl groups on the double bond (entry 3), the rate is decreased slightly. An increase in rate is observed with a cyclopropyl group on the double bond (entry 4). These

TABLE XVII

Relative Rates of Tin Hydride Reduction of Acyclic Alkyl Chlorides

Entry	Compound	k/k_o
1	$(CH_3)_2CHCH_2CH_2CH_2$-Cl	1.00
2	CH_2=$CHCH_2CH_2$-Cl	1.43
3	$(CH_3)_2$C=$CHCH_2CH_2$-Cl	1.28
4		1.77
5	$CH_3CH_2CH_2CH(CH_3)$-Cl	2.23
6	CH_2=$CHCH_2CH(CH_3)$-Cl	3.10
7	$CH_3CH_2CH_2C(CH_3)_2$-Cl	10.5
8	CH_2=$CHCH_2C(CH_3)_2$-Cl	9.8
9		0.31
10		2.79
11		0.97

variations in rate are as expected in terms of inductive acceleration by the vinyl group. The electron donating methyls retard the rate slightly whereas the electronegative cyclopropyl group accelerates the rate.

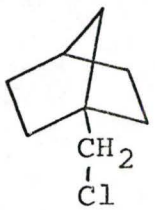
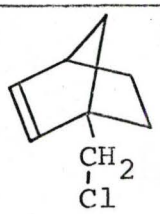
For tri-*n*-butyltin hydride reduction of alkyl bromides, the rate acceleration due to a homoallylic double bond was found to be 1.7. A similar rate enhancement was expected for reduction of alkyl chlorides. Norbornane-1-carbinyl chloride (XII) and norbornene-1-carbinyl chloride (XIb) were chosen to determine the effect of a homoallylic double bond on tin hydride reduction. The rigid geometry of XIb should effectively prevent any delocalization in the transition state for free radical formation. Solvolysis studies on analogous compounds (65) have been used to determine the inductive effect of a homoallylic double bond on carbonium ion formation. The homoallylic double bond was found to retard the rate in the latter case.

The relative rates of tin hydride reduction of XIb and XII are given in Table XVIII. The observed rate acceleration is larger than that for allylcarbinyl chloride (Table XVII, entry 2). The rigid geometry in XIb may be more favourable for transmission of polar effects.

The homoallylic double bond in the secondary alkyl chloride, 2-chloro-4-pentene (Table XVII, entry 6),

TABLE XVIII

Relative Rates of Tin Hydride Reduction of Norbornane- and Norbornene-1-carbinyl Chloride

Entry	Compound	k/k_o
1	 (XII)	1.0
2	 (XIb)	2.5

accelerates the rate by a factor of 1.39 over its saturated analog, 2-chloropentane (entry 5). Again, this is as expected in terms of inductive effects. On the other hand, the tertiary alkyl chlorides, 2-chloro-2-methylpentane and 2-chloro-2-methyl-4-pentene (entries 7 and 8), show approximately the same rates. Polar effects are unimportant for the tertiary alkyl chlorides.

Cyclobutyl chloride (entry 9) was much slower than the primary alkyl chlorides. The decreased bond angle in this strained ring system is assumed to be the rate determining factor here. Cyclopropylcarbinyl chloride (entry 10) showed a rate enhancement of 2.79 relative to 1-chloro-4-methylpentane (entry 1). This is the largest rate enhancement observed in this series, and may be due to some stabilization in the transition state for free radical formation. However, contributions to the rate enhancement from the inductive effect of the cyclopropyl group, and from relief of ring strain through opening of the cyclopropyl ring in the transition state, cannot be evaluated (σ^* for cyclopropyl has not been evaluated). When the size of the ring is increased from three to five carbon atoms (entries 10 and 11), no rate enhancement is observed.

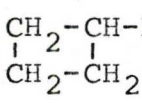
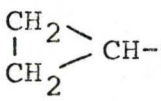
The relative rates in Table XII suggest that a homoallylic double bond in simple acyclic alkyl chlorides does not participate in free radical formation through delocalization in the transition state. Polar effects appear to be the governing factor for tri-*n*-butyltin hydride reduction. The cyclopropyl group in cyclopropylcarbinyl chloride may stabilize a radical to a small extent. Further information on the possible stabilizing effect of a cyclopropyl group was obtained from polarographic reduction.

The half-wave potentials for four alkylbromides are shown in Table XIX. It was shown earlier that half-wave potentials of alkyl bromides could be correlated with relative rates of tin hydride reduction of alkyl chlorides. The half-wave potentials in Table XIX were correlated with relative rates for tin hydride reduction of the corresponding chlorides (Table XII). The result is shown in Figure 17. A linear correlation is obtained for cyclobutyl-, isohexyl- and allylcarbinyl halides, but the point for cyclopropylcarbinyl is off the line.

Steric substituent constants for these compounds have not been evaluated, so that the half-wave potentials could not be corrected for steric effects. However, differences in steric effects are expected to be small. The half-wave potential for cyclopropylcarbinyl bromide

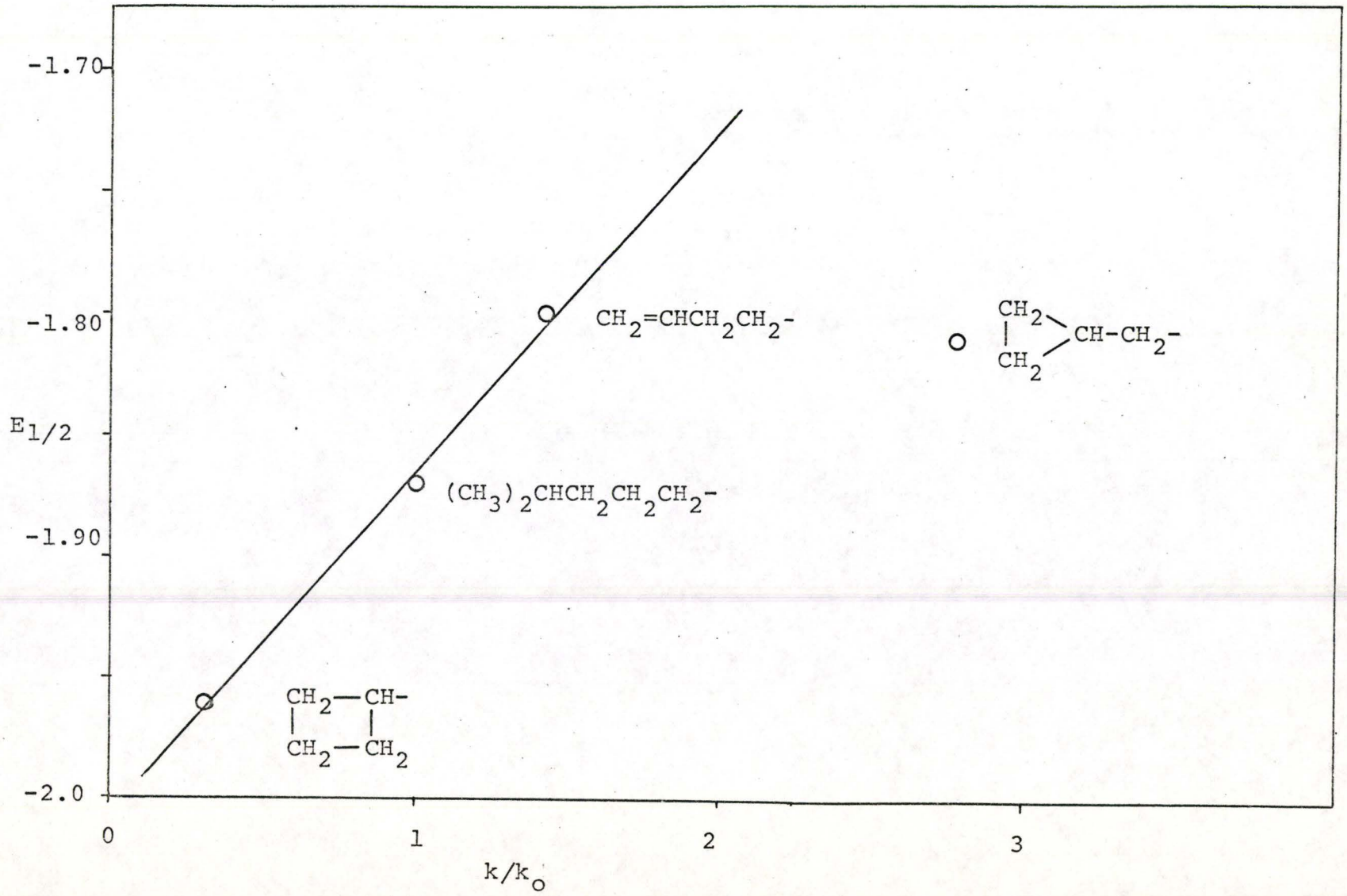
TABLE XIX

Half-wave Potentials of Acyclic Alkyl Bromides

Entry	Compound	$E_{1/2}$ (a)
1	$(CH_3)_2CHCH_2CH_2CH_2$-Br	-1.87
2	CH_2=$CHCH_2CH_2$-Br	-1.80
3		-1.96
4		-1.81

(a) Done in 0.100M Et_4NBr in DMF *vs* Ag/Ag^+ electrode.

Figure 17. Plot of Half-wave Reduction Potentials *vs* Relative Rates of Tri-*n*-butyltin Hydride Reduction for Alkyl and Cycloalkyl Bromides



is approximately the same as that for allylcarbinyl bromide, indicating that the polar effect of a cyclopropyl group is similar to that of a homoallylic double bond. Also, relief of ring strain from opening of the cyclopropyl ring in the transition state cannot be important, at least for polarographic reduction.

The rate of reduction of cyclopropylcarbinyl chloride is twice that of allylcarbinyl chloride. Since the half-wave potentials for allylcarbinyl bromide and cyclopropylcarbinyl bromide were the same, the rate acceleration of 2 observed for tri-*n*-butyltin hydride reduction of cyclopropylcarbinyl chloride may be due to participation of the cyclopropyl group in the transition state for reduction.

EXPERIMENTAL

General

(i) Outline of Experimental Section

The experimental section consists of three parts. In the first, the syntheses of the compounds required for rate studies is described. Most of the alkyl- and cycloalkyl halides required for this study have been previously described in the literature. For these compounds, references are cited but detailed experimental procedures are not repeated. All compounds synthesized were purified by distillation and/or preparative gas-liquid partition chromatography (glpc). A nuclear magnetic resonance (nmr) spectrum consistent with the proposed structure was obtained in every case. Due to space limitations, only data on the nmr spectra of new compounds, or those required as models for new compounds, are presented here.

The second part consists of a description of the method used to determine relative rates of reduction and reduction products. The kinetic data on duplicate runs and the average error are listed in tabular form.

In the third part, the apparatus and conditions

used for polarographic reduction are described. Half-wave potentials obtained, and the average error are tabulated.

(ii) Instrumental Analysis

Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer or a Varian HA-100 spectrometer. Gas-liquid partition chromatographic analyses were carried out on a Varian Aerograph Model 90-P3 instrument equipped with a thermal conductivity detector or on a Varian Aerograph Model 204-B instrument equipped with a flame ionization detector. All preparative scale analyses were done on the former model. Helium was used as carrier gas in all cases. Column packings were 20% SE-30 or 15% Carbowax-20M on 60-80 mesh Chromosorb-W. Column dimensions were 10'x1/8", 10'x1/4", 5'x1/4", 10'x3/8" or 15'x3/8". All columns were prepared by the author and preconditioned before use. A Varian Aerograph Model 476 electronic digital integrator with a Victor printout was used to obtain quantitative peak ratios from glpc analyses.

Infrared spectra were recorded on a Beckman Model IR-5 spectrometer. Indices of refraction were obtained with a Bausch and Lomb refractrometer equipped with a Haake circulating constant temperature bath. Melting points were determined on a Thomas capillary

melting point apparatus and were not corrected for stem exposure. Catalytic hydrogenations were carried out using a Parr low pressure shaker type apparatus. Half-wave potentials were measured with a Sargent Model XV polarograph equipped with a Haake constant temperature bath.

I. Synthesis of Compound Required for Rate Studies

(i) Monobromocycloalkanes

The structures of all compounds described in this section are given in Chart I, page 77. Treatment of norbornene (Ia) (Aldrich Chemical Co.) with bromine in carbon tetrachloride (66) gave a mixture of *exo*-2-bromonorbornane (IIa), bromonortricyclane (IIIb) and *exo*--2-*syn*-7-dibromonorbornane (IIb). The monobromides were readily deparated from the dibromide by simple fractionation under reduced pressure. Pure bromonortricyclane (IIIb) was separated from *exo*-2-bromonorbornane (IIa) by preparative glpc (10'x3/8" Carbowax). Treatment of the dibromide IIb with potassium *t*-butoxide in refluxing *t*-butyl alcohol (66) gave *syn*-7-bromonorbornene (Ib): bp 64° (11 mm); $\underline{n}^{20}$ $\underline{D}$ 1.5235 [lit. (66) bp 68-70 (13 mm), $\underline{n}^{20}$ $\underline{D}$ 1.5260]. Catalytic hydrogenation of *syn*-7-bromonorbornene (Ib) (66) gave 7-bromonorbornane (IId): $\underline{n}^{22}$ $\underline{D}$ 1.5178 [lit. (66) $\underline{n}^{20}$ $\underline{D}$ 1.5169].

anti-7-Bromonorbornene (IVa) was prepared as

follows. The reaction of norbornadiene (Va) (Aldrich Chemical Co.) with benzoyl peroxide (67), after hydrolysis, gave 7-norbornadieneol (Vc): bp 60° (20 mm); $\underline{n}^{22}$ $\underline{D}$ 1.5096 [lit. (67) bp 78-80° (56 mm), $\underline{n}^{26}$ $\underline{D}$ 1.5097]. Reduction of 7-norbornadieneol with lithium aluminum hydride (68) gave *anti*-7-norbornenol (IVc): mp 117-118° [lit. (68) mp 117-118°]. Treatment of IVc with phosphorous tribromide in pyridine gave *anti*-7-bromonorbornene (IVa): $\underline{n}^{22}$ $\underline{D}$ 1.5350. This could be readily distinguished from *syn*-7-bromonorbornene (Ib) by its nmr spectrum. The *anti* compound shows weak W-plan coupling between C-2 and C-7. This is absent in the *syn*-isomer.

Bromocyclohexane (VIb) was purchased from the Baker Chemical Company.

(ii) Monochlorocycloalkanes

The structures of all compounds described in this section are given in Chart I, page 77. Chlorination of norbornene (Ia) (69) gave a mixture of chloronortricyclene (IIIc) and *exo*-2-*syn*-7-dichloronorbornene (IIc). Pure chloronortricyclene (IIIc) was readily separated from the dichloride IIc by distillation: bp 48-50° (10 mm); $\underline{n}^{20}$ $\underline{D}$ 1.4937 [lit. (69) bp 64-65° (27 mm), $\underline{n}^{25}$ $\underline{D}$ 1.4911]. Treatment of the dichloride IIc with potassium *t*-butoxide in refluxing *t*-butyl alcohol (66) gave *syn*-7-chloronorbornene (Ic): $\underline{n}^{20}$ $\underline{D}$ 1.4984 [lit. (69) $\underline{n}^{25}$ $\underline{D}$ 1.4920]. Catalytic reduction of *syn*-7-

chloronorbornene (69) gave 7-chloronorbornane (IIe): $\underline{n}^{20}\ \underline{\underline{D}}$ 1.4770 [lit. (69) $\underline{n}^{25}\ \underline{\underline{D}}$ 1.4878].

anti-7-Chloronorbornene (IVb) was prepared from *anti*-7-norborneneol (IVc) and thionyl chloride (67): $\underline{n}^{22}\ \underline{\underline{D}}$ 1.4950 [lit. (67), $\underline{n}^{25}\ \underline{\underline{D}}$ 1.4937]. Similarly, 7-norbornadieneol (Vc) and thionyl chloride gave 7-chloronorbornadiene (Vb) (70): bp 46-48° (11 mm); $\underline{n}^{22}\ \underline{\underline{D}}$ 1.5099 [lit. (70) bp 77.5° (63 mm), $\underline{n}^{25}\ \underline{\underline{D}}$ 1.5050]. 7-Chloronorbornadiene also gave 7-chloronorbornane (IIe) on catalytic reduction (71).

Photolysis of 7-chloronorbornadiene (Vb) (72) using acetophenone sensitizer gave 7-chloroquadricyclane (VIIb): $\underline{n}^{22}_{\underline{\underline{D}}}$ 1.5076.

Chlorocyclohexane (VIc) was purchased from the Baker Chemical Company.

Norbornenyl-1-carbinol (XIa) was prepared by the method of Wilt, *et al.* (65): bp 52-56° (0.1 to 0.3 mm) [lit. (65) bp 46-48° (0.15 mm)].

Norbornenyl-1-carbinyl chloride (XIb) was prepared from alcohol XIa and thionyl chloride. A solution of XIa (2 g, 0.0161 mol) in ether (15 ml) containing 1.72 g (0.017 mol) of triethyl amine, was cooled to 0° in an ice bath. Thionyl chloride (2.02 g, 0.017 mol) was added dropwise with stirring. The volatile material was removed under reduced pressure and the flask slowly

heated to 120°, while reducing the pressure to 20 mm. The distillate was collected, washed with 10% sodium carbonate solution, and dried (Na_2SO_4) giving 365 mg (15.8%) of XIb, homogenous by glpc (Carbowax 10'x1/8"): nmr (CCl_4) δ 6.0 (m,2,-C<u>H</u>=C<u>H</u>-), 3.8 (s,2,-C<u>H</u>$_2$Cl), 2.88 (m,1,bridgehead) and 2.0-0.95 ppm (m,6,methylenes).

Hydrogenation of XIb in ether over palladium on charcoal catalyst gave norbornyl-1-carbinyl chloride (XII): nmr (CCl_4) δ 3.56 (s,2,-C<u>H</u>$_2$-Cl), 2.25 (m,1, bridgehead), and 1.8-1.1 ppm (m,10,methylenes).

Both XIa and XII were purified by preparative glpc (SE-30, 10'x3/8").

(iii) <u>Cycloalkanes</u>

The structures of all compounds described in this section are given in Chart I, page 77. Norbornane (IIf) was purchase from the Aldrich Chemical Company. Cyclohexane (VIa) was purchased from the Fisher Scientific Company. Photolysis of 2,5-norbornadiene (Va) using acetophenone sensitizer (73) gave quadricyclane (VIIa): $\underline{n}^{22}$ $\underline{\underline{D}}$ 1.4841 [lit. (73) $\underline{n}^{26.5}$ $\underline{\underline{D}}$ 1.4830]. Bicyclo [3.2.0] hepta-2,6-diene (VIII) was obtained from the photolysis of cycloheptatriene (X) (Shell Development Corp.) (74): bp 100° (760 mm); $\underline{n}^{22}$ $\underline{\underline{D}}$ 1.4728 [lit. (74) bp 97-98° (760 mm), $\underline{n}^{22}$ $\underline{\underline{D}}$ 1.4728].

Lithium aluminum hydride reduction of *anti*-7-

chloronorbornene (IVb) (75) gave tricyclo [2.2.1.$0^{2,7}$] heptane (IX): nmr (CCl_4) δ 2.8-0.95 ppm (m).

(iv) Acyclic Halides

All of these compounds were prepared directly from the corresponding alcohol or *via* rearrangement of a cyclopropylcarbinol. The reaction of thionyl chloride with 4-methyl-1-pentanol (Aldrich Chemical Co.) gave 1-chloro-4-methylpentane: bp 120-122°; $\underline{n}^{20}$ $\underline{D}$ 1.4180 [lit. (76) bp 125-126°]. Treatment of 2-methyl-4-penten-2-ol (Aldrich Chemical Co.) with concentrated hydrochloric acid gave 2-chloro-2-methyl-4-pentene: bp 34° (50 mm); $\underline{n}^{22}$ $\underline{D}$ 1.4255 [lit. (77) bp 44° (90 mm), $\underline{n}^{14}$ $\underline{D}$ 1.4284]. Similarly, 2-methyl-2-pentanol (Aldrich Chemical Co.) and concentrated hydrochloric acid gave 2-chloro-2- methylpentane: bp 112-113°; $\underline{n}^{22.5}$ $\underline{D}$ 1.4125 [lit. (78) bp 110-111° (734 mm), $\underline{n}^{20}$ $\underline{D}$ 1.4126]. Treatment of 2-pentanol (Eastman Chemical Co.) with thionyl chloride gave 2-chloropentane: $\underline{n}^{22.5}$ $\underline{D}$ 1.4060 [lit. (78) $\underline{n}^{20}$ $\underline{D}$ 1.4079].

Cyclopentylcarbinyl chloride was prepared from cyclopentylcarbinol (Aldrich Chemical Co.) by the method of Richie and Hill (79): $\underline{n}^{22}$ $\underline{D}$ 1.4558.

Treatment of cyclopropylcarbinol (Aldrich Chemical Co.) with thionyl chloride (3) gave cyclopropylcarbinyl chloride: bp 85-86°; $\underline{n}^{22}$ $\underline{D}$ 1.4350 [lit. (3) bp 87-89°; $\underline{n}^{25}$ $\underline{D}$ 1.4332],

cyclobutyl chloride: bp 84-85°; n^{22} D 1.4360 [lit. (3) bp 82-83°, n^{25} D 1.4332] and allylcarbinyl chloride: bp 75-76° [lit. (3) bp 75-75.4°]. These three compounds were purified by distillation and preparative glpc (15'x3/8" Carbowax).

The reaction of cyclopropylmethylketone (Aldrich Chemical Co.) and methylmagnesium iodide (80) gave dimethylcyclopropylcarbinol: bp 121-122°; n^{20} D 1.4342 [lit. (80) bp 122°, n^{25} D 1.4312]. Treatment of dimethylcyclopropylcarbinol with Lucas reagent gave 1-chloro-4-methyl-3-pentene: bp 129-130°; n^{25} D 1.4446 [lit. (81) bp 134° (750 mm), n^{20} D 1.4458]. The treatment of cyclopropylmethylcarbinol (Aldrich Chemical Co.) with Lucas reagent (82) gave 1-chloro-3-pentene: bp 107-108° [lit. (82) bp 107-108°] and 2-chloro-4-pentene: n^{22} D 1.4230 [lit. (82) $n^{18.5}$ D 1.4233]. These were purified by preparative glpc (10'x3/8" Carbowax). Dicyclopropylcarbinol (Aldrich Chemical Co.), when treated with phosphorous trichloride (83), gave 1-chloro-4-cyclopropyl-3-butene: bp 60° (8 mm); n^{22} D 1.4773 [lit. (83) bp 60-62° (12 mm)].

The action of phosphorous tribromide on 4-methyl-1-pentanol gave 1-bromo-4-methylpentane: bp 102-104° (150 mm) [lit. (84) bp 145-147°]. Treatment of cyclopropylcarbinol with 48% hydrobromic acid by the method

of Roberts and Mazur (3) gave cyclopropyl bromide, cyclobutyl bromide and allylcarbinyl bromide. These were purified by preparative glpc (15'x3/8" Carbowax) and identified by their nmr spectra.

(v) Derivatives of 1,2,3,4,7,7-Hexachloronorborn-2-ene

All of the compounds synthesized from 1,2,3,4,7,7-hexachloronorborn-2-ene (XIX) are outlined in Chart II, page 110. The Diels-Alder condensation of hexachlorocyclopentadiene (Aldrich Chemical Co.) and ethylene (Matheson), using the procedure of Wilcox and Zajacek (61), gave 1,2,3,4,7,7-hexachloronorborn-2-ene (XIX): bp 94-96° (0.1 mm); mp 38-39° [lit. (61) bp 113° (2-3 mm), mp 37.5-39°]. Reduction of XIX with zinc in acetic acid (61) gave 1,2,3,4-tetrachloronorborn-2-ene (XX): bp 66-74° (1-2 mm) [lit. (61) bp 74-77° (3 mm)] and 1,2,3,4,*syn*-7-pentachloronorborn-2-ene (XVIII): mp 58-59° [lit. (61) mp 59.2-59.8°]. Hydrogenation of XX in ethanol containing triethylamine over 5% palladium on charcoal catalyst gave 1,4-dichloronorbornane (XXVI): mp 78-79° [lit. (61) mp 78-79°]. Catalytic reduction of XVIII, in ethanol containing triethylamine, over 5% palladium on charcoal catalyst, gave 1,4,7-trichloronorbornane (XIII): mp 66.5-67° [lit. (62) mp 65-66°).

Reduction of 1,2,3,4,7,7-hexachloronorborn-2-ene

(XIX) with tri-*n*-butyltin hydride gave a mixture of *syn*- and *anti*-1,2,3,4,7-pentachloronorborn-2-ene (XVIII and XVII). Tri-*n*-butyltin hydride (85) (5 g, 0.0172 mol) was added to a solution of XIX (5 g, 0.0165 mol) in 15 ml hexane. The solution was sealed in an evacuated pyrex tube and heated at 100° (steam bath) for 30 hrs. The solvent was evaporated and the residue fractionated through an 8 cm glass-helicies-packed column. The following fractions were collected (0.1 to 0.3 mm):

#1 bp 103-106° }→ 4.5 g
#2 bp 106-116° }
#3 bp 116-124° }→ 4.4 g
#4 bp 124° }

Analysis by glpc (SE-30, 10'x1/8") showed that the last two fractions contained a single component. This was shown to be a tri-*n*-butyltin compound by nmr analysis. The first two fractions contained a 2:3 mixture of XVII and XVIII. A small amount of XIX was present as well as some of the tri-*n*-butyltin compound.

The mixture in fractions one and two was separated by preparative glpc (SE-30, 10'x3/8") giving pure XVIII: mp 58-59° [lit. (61) mp 59.2-59.8]; nmr (CCl_4) δ 4.23 (s,1,C_7-H) and 2.6-1.9 ppm (m,4,CH_2-CH_2) and pure XVII: mp 38.5-39°; nmr (CCl_4) δ 3.95 (m,1,J<1Hz,C_7-H) and 2.7-1.7 ppm (m,4,CH_2-CH_2).

A mixture of XVII and XVIII was quantitatively reduced in ethanol-triethylamine over palladium on charcoal

catalyst to give 1,4,7-trichloronorbornane (XIII) as the sole product: mp 66.5-67°; mixture mp 66.5-67°.

(vi) Derivatives of 1,2,3,4,5,7,7-Heptachloronorborn-2-ene

All of the compounds synthesized from 1,2,3,4-*endo*-5,7,7-heptachloronorborn-2-ene (XXI) are outlined in Chart IV, page 116. 1,2,3,4-*endo*-5,7,7-Heptachloronorborn-2-ene (XXI) was prepared by bubbling vinyl chloride (Matheson) through hexachlorocyclopentadiene at 200° (86). The reaction was stopped when the hexachlorocyclopentadiene was completely used up (glpc analysis, SE-30, 10'x1/8"). The product (XXI) solidified to give a white waxy solid: mp 120-140° [lit. (86) mp 125-136°]. Treatment of XXI with a hot solution of potassium hydroxide in ethanol (61) gave 1,2,3,4,7,7-hexachloronorborna-2,5-diene (XXII): bp 87-89° (0.1 mm); $\underline{n}^{23}\ \underline{D}$ 1.5498 [lit. (87) bp 128-145° (18 mm), $\underline{n}^{25}\ \underline{D}$ 1.5529]. Reduction of XXII in zinc and acetic acid, using the procedure of Wilcox and Zajacek (61), gave 1,2,3,4-tetrachloronorborna-2,5-diene (XXV): bp 50-60° (0.1-0.5 mm); $\underline{n}^{23}\ \underline{D}$ 1.5310; nmr (CCl_4) δ 6.73 (s,2,C$\underline{H}$=C$\underline{H}$), 3.13 (d,1,J=10Hz, *anti*-C_7-$\underline{H}$) and 2.91 ppm (d,1,J=10Hz,*syn*-C_7-$\underline{H}$). Reduction of XXV over 5% palladium on charcoal catalyst in ethanol-triethylamine gave 1,4-dichloronorbornane (XXVI) as the only reduction product: mp 78-79°; mixture mp

78-79°.

Reduction of XXII with one equivalent of tri-*n*-butyltin hydride, as described previously, gave only one reduction product (glpc analysis, SE-30, 10'x1/8"). This was separated from a small amount of unreacted XXII and the tri-*n*-butyltin residues by preparative glpc (SE-30, 10'x3/8"): $n^{23}D$ 1.5462. Analysis of this material on a 10'x1/8" carbowax column showed two partially separated components in the ratio of 32:68. Analysis of the mixture by nmr spectroscopy indicated 32% 1,2,3,4-*anti*-7-pentachloronorborna-2,5-diene (XXIV) and 68% 1,2,3,4-*syn*-7-pentachloronorborna-2,5-diene (XXIII): nmr (CCl_4) δ 6.77 (s,2,CH=CH in XXIII), 4.67 (s,1,C-7-H in XXIII), 6.50 (d,2,J=2Hz,CH=CH in XXIV) and 4.58 ppm (m,1,C-7-H in XXIV). The nmr spectrum of XXIII is in agreement with the published spectrum (62).

A mixture of XXIII and XXIV (25 mg) in ether was reduced over 5% palladium on charcoal catalyst at room temperature. The reduction products were identified by glpc (SE-30, 10'x1/8") using authentic samples as glpc internal standards. The mixture was quantitatively reduced to 29.1% 1,4-dichloronorbornane (XXVI), 33.4% 1,4,7-trichloronorbornane (XIII), 29.1% 1,2,3,4-*syn*-7-pentachloro-2-norbornene (XVIII) and a trace of 1,2,3,4-tetrachloro-2-ene (XX).

Reduction of 1,2,3,4-*endo*-5,7,7-heptachloronorborn-2-ene (XXI) over 5% palladium on charcoal catalyst in KOH-ethanol solution (62) gave 1-*endo*-2,4-*anti*-7-tetrachloronorbornane (XXVIII): bp 92-105° (0.1 to 0.5 mm); $\underline{n}^{22}$ $\underline{\underline{D}}$ 1.5342 [lit. (62) bp 122-124° (15 mm), $\underline{n}^{16}$ $\underline{\underline{D}}$ 1.5250]. A solution of XXVIII (4 g, 0.017 mol) in ethanol (10 ml) was added to solution of 0.5 g atom of sodium in 15 ml of ethanol and heated under reflux for 9 hours. The solution was poured into water, extracted with ether, and dried over anhydrous sodium sulfate. Analysis (glpc, SE-30, 10'x1/8") showed approximately one-half of XXVIII had reacted to give one shorter-retention-time component. This was separated by preparative glpc (SE-30, 10'x3/8") and shown to be 1,4-*anti*-7-trichloronorborn-2-ene (XIV): bp 59-65° (0.1 mm); $\underline{n}^{22}$ $\underline{\underline{D}}$ 1.5146; nmr (CCl_4) δ 6.24 (s,2,C$\underline{H}$=C$\underline{H}$), 3.83 (m,1,J<1Hz, C_7-$\underline{H}$) and 2.6-1.6 ppm (m,4,C$\underline{H}_2$-C$\underline{H}_2$).

Reduction of XIV (50 mg) in ether over 5% palladium on charcoal catalyst at room temperature gave 1,4,7-tricloronorbornane (XIII). This was purified by preparative glpc: mp 66.5-68°; mixture mp 66.5-68°.

(vii) Derivatives of 1,2,3,4,5,6,7,7-Octachloronorborn-2-ene

All of the compounds synthesized from 1,2,3,4,5,6,7,7-octachloronorborn-2-ene (XXIX) are outlined in Chart VI, pages 125 and 126. 1,2,3,4-*endo*,*cis*-5,6,7,7-octa-

chloronorborn-2-ene (XXIX) was prepared by heating a 1:2 mixture of hexachlorocyclopentadiene and *trans*-1,2-dichloroethylene in a sealed tube at 200° for 24 hours. Unreacted olefin was removed *in vacuo*. The residue solidified, and was crystallized from hexane: mp 192-196°; nmr (CCl_4) δ 4.95 (s); 70% yield.

A solution of XXIX (15 g, 0.041 mol) in 100 ml of ethanol containing 8.3 g (0.082 mol) of triethylamine was shaken with hydrogen over 5% palladium on charcoal catalyst until the uptake of hydrogen ceased. The catalyst was filtered from the solution and the ethanol distilled *in vacuo*. The residue was taken up in ether. The ethereal solution was washed with water, dried over anhydrous sodium sulfate and the ether evaporated. Analysis of the product mixture by glpc (SE-30, 10'x1/8") showed a mixture of six products, present in the following amounts (in order of their elution from glpc): 1,4,7-trichloronorbornane (XIII) (5%), 1,4,7,7-tetrachloronorbornane (XXXI) (trace), 1-*endo*,*cis*-2,3,4-tetrachloronorbornane (XXXIII) (6%), 1-*endo*,*cis*-2,3,4-*syn*- and *anti*-7-pentachloronorbornane (XXXIV and XXX) (36%) and 1,2,3,4-*endo*,*cis*-5,6-*syn*-7-heptachloronorborn-2-ene (XXXII) (53%). These were isolated as follows.

The reaction mixture was dissolved in hexane from which XXXII crystallized on cooling. Recrystallization from hexane gave a white crystalline solid: mp 104-107°; nmr (CCl_4) δ 4.68 (s,2,*exo*-2,3-hydrogens) and 4.36 ppm (s,1,C_7-H). Small samples of the following compounds were separated from the filtrate by preparative glpc (SE-30, 10'x3/8" column): 1,4,7-trichloronorbornane (XIII): mp 64-67°; mixture mp 66-67.5°; 1-*endo*,*cis*-2,3,4-tetrachloronorbornane (XXXIII): mp 83-85°; nmr (CCl_4) δ 4.49 (m,2,J<1Hz, *exo*-2,3-hydrogens) and 2.82-1.80 ppm (m,6,methylenes); approximately 1:1 mixture of 1-*endo*, *cis*-2,3,4-*syn*- and *anti*-7-pentachloronorbornane (XXXIV and XXX): nmr (CCl_4) δ 4.78 (m), 4.48 (m), 4.05 (m) and 2.92-1.74 (m).

The remainder of the filtrate was dissolved in 40 ml of ethanol containing potassium hydroxide (5 g) and heated under reflux for one hour. The reaction mixture was poured into water and extracted with ether. The ethereal extracts were dried over anhydrous sodium sulfate, and the solvent evaporated. The residue gave 1.5 g of volatile material when subjected to short path vacuum distillation. The two main components, present in 50:50 ratio, were isolated by preparative glpc (SE-30, 10'x3/8"). These were 1,2,4-*anti*-7-tetrachloronorborn-2-ene (XV): $\underline{n}^{24}$ $\underline{D}$ 1.5325; nmr (CCl_4) δ 6.21 (s,1,C$\underline{H}$=CCl), 3.92 (m,1,

J<1Hz, C_7-H) and 2.75-1.58 ppm (m,4,CH_2-CH_2); and 1,2,4-*syn*-7-tetrachloronorborn-2-ene (XVI): n^{25} D 1.5359; nmr (CCl_4) δ 5.90 (d,1,J=4Hz,CH=CCl), 4.09 (d,1,J=4Hz,C_7-H) and 2.5-1.9 ppm (m,4,CH_2-CH_2).

A 1:1 mixture of XV and XVI (50 mg) was dissolved in 20 ml of ether containing 1 ml of triethylamine and reduced over 5% palladium on charcoal catalyst. The mixture was quantitatively reduced to 1,4,7-trichloronorbornane (XIII). A small sample was purified by preparative glpc: mp 66.5-68°; mixture mp 66.5-68°.

A solution of XXXII (1 g) in ethanol (10 ml) containing triethylamine (2 ml) was reduced over 5% palladium on charcoal catalyst. The only reduction products were a 2:3 ratio of 1,4,7-trichloronorbornane (XIII) and 1-*endo*,*cis*-2,3,4-*anti*-7-pentachloronorbornane (XXX): mp 59-60°; nmr (CCl_4) δ 4.51 (m,2,J<1Hz,*exo*-2,3-hydrogens), 4.05 (m,1,J<1Hz,C_7-H) and 2.70-1.92 (m,4, CH_2-CH_2). These were purified by preparative glpc (SE-30, 10'x3/8" column).

When 1,2,3,4-*endo*,*cis*-5,6,7,7-octachloronorborn-2-ene (XXIX) was reduced as described above, except for the use of three equivalents of triethylamine, the product mixture consisted of 8.1% XIII, 10.8% XXXII, 69.5% mixture of XXX and XXXIV (mainly XXX), and 11.6% XXXII. This mixture was treated with KOH in ethanol as before. The product mixture from elimination was

mainly 1,2,4-*anti*-7-tetrachloronorborn-2-ene (XV). Small amounts of the following were isolated by preparative glpc: 1,2,4-trichloronorborn-2-ene (XXXV): n^{24}_D 1.5150; nmr (CCl_4) δ 6.06 (m,1,J<1Hz,C<u>H</u>=CCl) and 2.5-1.8 ppm (m,6,methylenes); 1,2,4,5,6-*syn*-7-hexachloronorborna-2,5-diene (XXXVI): nmr (CCl_4) δ 6.69 (s,1,C<u>H</u>=CCl) and 4.84 ppm (s,1,C_7-<u>H</u>); and 1-*endo*,*cis*-2,3,4-*syn*-7-pentachloronorbornane (XXXIV): mp 94-95.5; nmr (CCl_4) δ 4.78 (m,2,J<1Hz,*exo*-2,3-hydrogens), 4.48 (s,1,C_7-<u>H</u>) and 2.92-1.74 ppm (m,4,C<u>H</u>$_2$-C<u>H</u>$_2$).

A sample of XXXV was quantitatively reduced over 5% palladium on charcoal catalyst in ether - triethylamine as before to give 1,4-dichloronorbornane (XXVI): mp 77-79°; mixture mp 77-79° (glpc purification).

II Relative Rates of Reduction and Reduction Products

(i) Relative Rates

Relative rates were obtained by the method of Menapace and Kuivila (35). Relative rate constants were calculated using the equation of Ingold and Shaw (88) (equation [32]). This equation applies only when both

$$k_B/k_A = \frac{\log B_\infty - \log B_o}{\log A_\infty - \log A_o} \qquad [32]$$

competitors react by the same mechanism and, therefore, have the same kinetic order. Menapace and Kuivila (35) showed that this equation applies to trialkyltin hydride

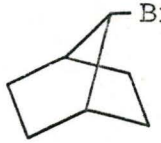
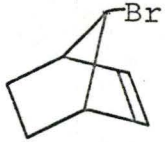
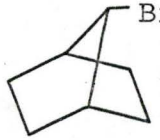
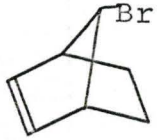
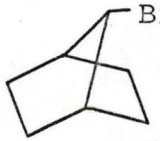
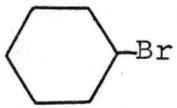
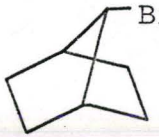
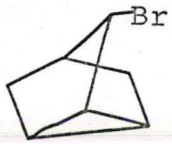
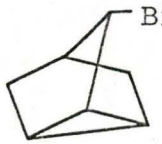
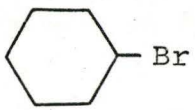
reductions by dtermining relative reactivities of two alkyl bromides at several concentrations. No noticeable drift in the relative rates with concentration was observed.

The halides (0.3 m mol of each, per ml of solvent) were allowed to compete in pairs for an insufficient amount of tri-*n*-butyltin hydride. Usually one-half mole of hydride was used per mole of halide. For most runs, hexane was used as solvent and *cis*- or *trans*-decalin was used as glpc internal standard. In some cases, decalin was used as solvent and hexane was used as glpc internal standard. The relative ratios of competitors before and after reaction, relative to the internal standard, were determined by glpc analysis. Integrations were performed either by manually cutting out the traces and weighing, or with an electronic, digital integrator. In all cases, a minimum of four integrations was obtained, and the results were averaged. Integrations were reproducable to ±2% or better.

The competitors and internal standard were placed in a vial, followed by solvent and hydride. Aliquots were sealed in evacuated pyrex tubes and kept in a constant temperature bath until the reaction was complete. Results of the individual competition experiments are given in Tables XX to XXIII.

TABLE XX

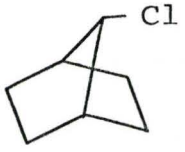
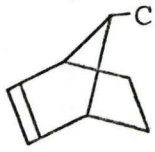
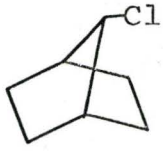
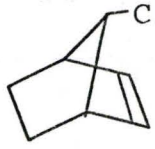
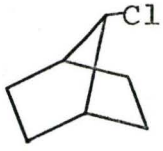
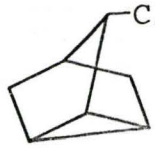
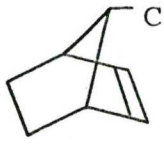
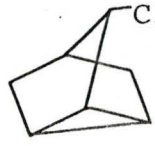
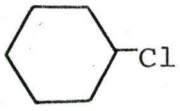
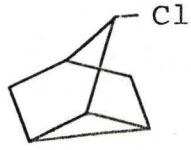
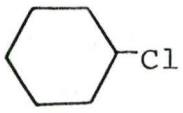
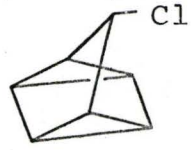
Relative Rates of Reduction of Cycloalkyl Bromides with Tri-*n*-butyltin Hydride

Entry	Competitor A	Competitor B	k_B/k_A (100°)	k_B/k_A (45°)	Average 100°	Average 45°
1			0.70 0.80	0.75 0.73	0.75 ±0.05	0.74 ±0.01
2			0.51 0.54 0.63	0.54 0.42 0.52	0.56 ±0.07	0.49 ±0.07
3			3.65	4.83 4.73		4.78 ±0.05
4			1.73	1.95		
5			2.26 2.11*	2.33 2.45*	2.19 ±0.08	2.39 ±0.06

* Calculated from entries 3 and 4.

TABLE XXI

Relative Rates of Reduction of Cycloalkyl Chlorides with Tri-*n*-butyltin Hydride

Entry	Competitor A	Competitor B	k_B/k_A	Average
1			1.53 1.46 1.48 1.48	1.49 ±0.04
2			2.86 3.12 3.29	3.09 ±0.23
3			8.24 7.91*	8.08 ±0.17
4			2.56	
5			0.30 0.30 0.28	0.29 ±0.01
6			2.06 2.14 2.01	2.07 ±0.07

* Calculated from entries 2 and 4.

TABLE XXII

Relative Rates of Reduction of Chloronorbornane Derivatives with Tri-*n*-butyltin Hydride

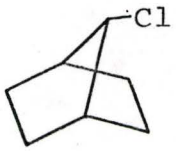
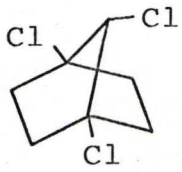
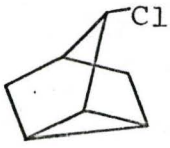
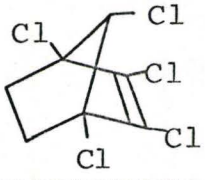
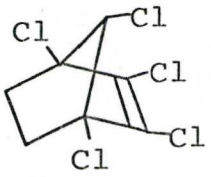
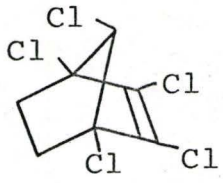
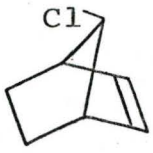
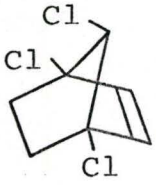
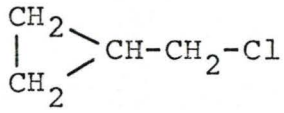
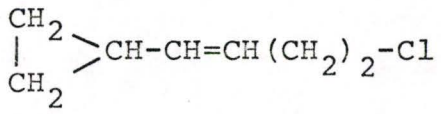
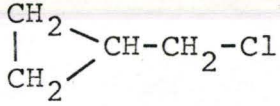
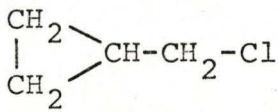
Entry	Competitor A	Competitor B	k_B/k_A	Average
1			1.09 1.07	1.08 ±0.01
2			19.8 17.3	18.5 ±1.2
3			1.89 1.84	1.87 ±0.03
4			11.2 11.3	11.3 ±0.1

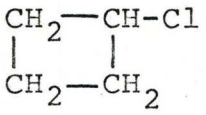
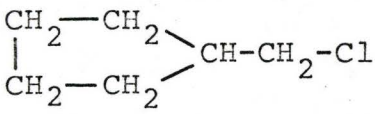
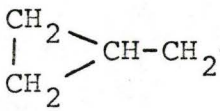
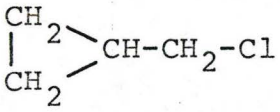
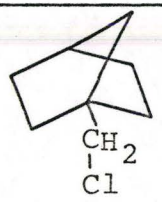
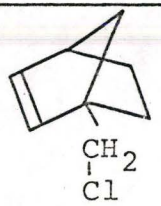
TABLE XXIII

Relative Rates of Reduction of Acyclic Alkyl Chlorides with Tri-*n*-butyltin Hydride

Entry	Competitor A	Competitor A	k_B/k_A	Average
1	$CH_2=CHCH_2CH_2-Cl$		1.78 2.12	1.95 ±0.17
2	$(CH_3)_2CH(CH_2)_2CH_2-Cl$	$CH_2=CHCH_2CH_2-Cl$	1.45 1.40	1.43 ±0.03
3	$(CH_3)_2CH(CH_2)_2CH_2-Cl$	$(CH_3)_2C=CHCH_2CH_2-Cl$	1.27 1.29	1.28 ±0.01
4	$(CH_3)_2CH=CHCH_2CH_2-Cl$		1.35 1.40	1.38 ±0.03
5		$CH_3(CH_2)_2C(CH_3)_2-Cl$	3.64 3.85	3.75 ±0.11
6		$CH_2=CHCH_2C(CH_3)_2-Cl$	3.60 3.40	3.50 ±0.10

Continued....

TABLE XXIII (Continued.....)

Entry	Competitor A	Competitor B	k_B/k_A	Average
7	$(CH_3)_2CH(CH_2)_2CH_2$-Cl		0.28 0.34	0.31 ±0.03
8	$(CH_3)_2CH(CH_2)_2CH_2$-Cl		1.03 0.91	0.97 ±0.06
9		CH_2=$CHCH_2CH(CH_3)$-Cl	1.13 1.09	1.11 ±0.02
10	$CH_3(CH_2)_2CH(CH_3)$-Cl		1.18 1.31	1.25 ±0.06
11			2.31 2.84 2.39	2.52 ±0.30

(ii) Reduction Products from Monohalocycloalkanes

The structures of the reduction products described in this section are given in Chart I, page 77. Reduction of 7-bromo- and 7-chloronorbornane (IId and e), *syn*-7-bromo- and 7-chlornorbornene (Ib and c), *anti*-7-bromo- and 7-chloronorbornene (IVa and b), and bromo- and chlorocyclohexane (VIb and c) with tri-*n*-butyltin hydride gave the corresponding hydrocarbon products, norbornane (IIf), norbornene (Ia), and cyclohexane (VIa). These were identified by glpc using authentic samples as internal standards. The products from reduction of bromonortricyclane (IIIb) have been studied by Kuivila *et al.* (14). They found a 2:3 ratio of norbornene (Ia) to nortricyclane (IIIa). The same product ratio was observed in this study from both bromo- and chloronortricyclane (IIIb and c). The products described above were identified from glpc traces of the corresponding kinetic runs.

Gas-liquid partition chromatographic analysis of the product resulting from tri-*n*-butyltin hydride reduction of 7-chloroquadricyclane (VIIb) showed that neither quadricyclane (VIIa) nor 2,5-norbornadiene (Va) were present. The product was shown to be bicyclo [3.2.0] hepta-2,5-diene (VIII) by glpc, using an authentic sample as an

internal standard. Further proof of structure of the reduction product was obtained from a preparative scale reduction. 7-Chloroquadricyclane (VIIb) (444.6 mg) was dissolved in 5 ml of hexane, and 1.88 g of tri-*n*-butyltin hydride was added. The solution was sealed in an evacuated pyrex tube and heated in a bath at 100° for 48 hours. The hydrocarbon product was separated from the reaction mixture by preparative glpc (15'x3/8" Carbowax column). The nmr spectrum on the material obtained in this manner was identical to that of an authentic sample of bicyclo [3.2.0]hepta-2,5-diene (VIII).

The reduction of *syn*- and *anti*-7-bromonorbornene (Ib and IVa) was carried out using tri-*n*-butyltin deuteride. *syn*-7-Bromonorbornene (667 mg) was dissolved in 10 ml of hexane and 2 g of tri-*n*-butyltin deuteride (39) was added. This solution was sealed into an evacuated pyrex tube and heated at 51°C in a water bath for 8 days. The resulting 7-deuterionorbornene (IVd) was separated by preparative glpc (15'x3/8" Carbowax column). A similar experiment was carried out with *anti*-7-bromonorbornene. The reduction product in each case was shown (nmr) to be *anti*-7-deuterionorbornene (IVd).

The hydrocarbon tricyclo[2.2.1.$0^{2,7}$] heptane (IX) is a possible reduction product from 7-halonorbornenes

I (b and c) and IV (a and b). A 0.3 M solution of *syn*-7-bromonorbornene (Ib) in decalin containing 0.5 mole of tri-*n*-butyltin hydride was sealed in an evacuated pyrex tube and heated at 100° for 24 hours. Analysis of the hydrocarbon reduction products by glpc (10'x1/8" SE-30 columns) showed that norbornene (Ia) was the only reduction product. The rearranged product IX could not be detected, using conditions under which IX is stable and well separated from Ia. Amounts far less than one percent could have been detected. A similar experiment using 5 moles of tri-*n*-butyltin hydride per mole of Ib gave the same results. Analysis of products from kinetic runs on *anti*-7-bromonorbornene (IVa), *syn*- and *anti*-7-chloronorbornene (Ic and IVb) likewise showed that IX was not present.

(iii) Reduction Products from 1,4-*anti*-7-Trichloronorbornene

The products obtained from tri-*n*-butyltin hydride reduction of 1,4-*anti*-7-trichloronorbornene (XIV) are outlined in Chart VII, page 138. Tri-*n*-butyltin hydride (3 g, 0.0103 mol) was added to a solution of XIV (0.55 g, 0.0028 mol) in 5 ml hexane. The solution was sealed into an evacuated pyrex tube and heated at 100° for five days, then at 130° for 36 hours. Analysis of the reaction mixture by glpc (SE-30, 10'x1/8" column) showed

that the reduction was nearly complete. There were two main reduction products (approximate ratio 55:45) and two minor components.

The solvent was distilled and the reduction products were separated from the tin residues by short path vacuum distillation (0.1 mm). The two main products were purified by preparative glpc (SE-30, 10'x3/8"). These were 1,4-dichloronorbornene (XXXVII): nmr (CCl_4) δ 6.06 (s,2,C<u>H</u>=C<u>H</u>) and 2.42-1.70 ppm (m,6, methylenes) and 1,4-dichlorobicyclo[3.2.0]hept-6-ene (XXXVIII): nmr (CCl_4) δ 6.18, 6.15, 6.12 (s,2,C<u>H</u>=C<u>H</u>), 3.72 (m,1,J<1Hz,C<u>H</u>Cl), 2.76 (m,1,bridgehead), and 2.38-0.92 ppm (m,4,C<u>H</u>$_2$-C<u>H</u>$_2$). The minor components were not identified.

The nmr spectrum of XXXVII is in agreement with the published spectrum (62).

A 0.3 M solution of 1,4-*anti*-7-trichloronorborn-2-ene (XIV) in hexane was reduced with tri-*n*-butyltin hydride, using the same procedure as described previously for kinetic studies. The variation in product ratios with concentration of tin hydride (Table XIV, page 142) was determined by glpc analyses.

(iv) <u>Reduction Products from 1,2,4-*syn*- and *anti*-7-Tetrachloronorborn-2-ene</u>

1,2,4-*anti*-7-Tetrachloronorborn-2-ene (XV) (0.55 g, 0.0024 mol) was dissolved in 5 ml hexane and

tri-*n*-butyltin hydride (1 g, 0.0034 mol) was added. The solution was sealed into an evacuated pyrex tube and heated in a steam bath for 2 days. The solvent was distilled, and the reduction products separated from the tin residues by short path vacuum distillation. Analysis of the distillate by glpc showed one main component. This was purified by preparative glpc (SE-30, 10'x3/8") and identified as 1,4-*anti*-7-trichloro-norborn-2-ene (XIV) by comparison of its nmr spectrum with that of an authentic sample.

Reduction of 1,2,4-*syn*-7-tetrachloro-2-norbornene (XVI) under similar conditions gave, as the main product, a compound with longer retention time (glpc, SE-30, 10'x1/8") than XVI. All other reactions of polychlorinated norbornane derivatives with tri-*n*-butyltin hydride gave reduction products with retention times smaller than those of the starting materials. The product from the reaction of XVI with tri-*n*-butyltin hydride was not identified.

(v) Reduction Products from *syn*- and *anti*-1,2,3,4,7-Pentachloronorborn-2-ene

The products obtained from reduction of *anti*- and *syn*-1,2,3,4,7-pentachloronorborn-2-ene (XVII and XVIII) with tri-*n*-butyltin hydride are outlined in Chart VIII, page 144. 1,2,3,4,7,7-Hexachloronorborn-2-ene (XIX) (2 g, 0.0067 mol) was dissolved in 6 ml of hexane and

5 g (2.5 mol/mol) tri-*n*-butyltin hydride was added. The solution was sealed in an evacuated pyrex tube and heated at 100° (steam bath) for 9 days. The solvent was evaporated and the residue fractionated through an 8 cm, glass-helicies-packed column. The following fractions were collected (0.1 mm):

#1	bp 60-66°	126 mg
#2	bp 66-72°	116 mg
#3	bp 72-82°	200 mg
#4	bp 82 104°	190 mg

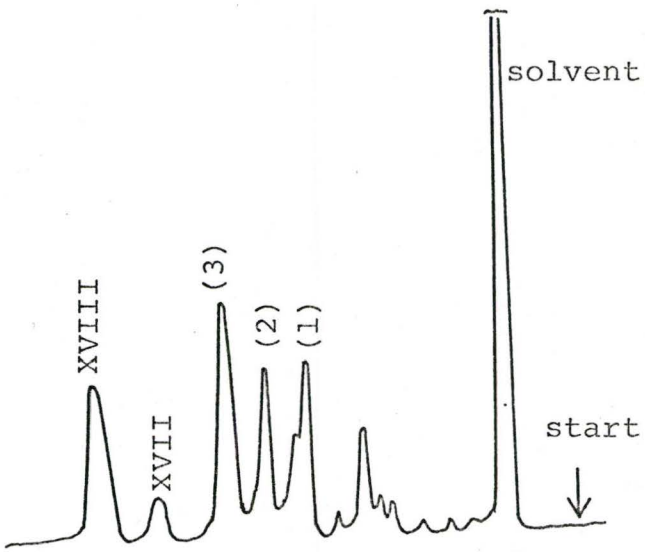
Analysis by glpc (SE-30, 10'x1/8") showed that the first three fractions were a mixture of reduction products. The fourth contained mainly tri-*n*-butyltin compounds.

As shown in Part I (v), reduction of XIX with 1 equivalent of tri-*n*-butyltin hydride gives only *anti*- and *syn*-1,2,3,4,7-pentachloronorborn-2-ene (XVII and XVIII). Small amounts of these were present in the reduction products obtained here. The other reduction products, which had shorter retention times, must arise from reduction of XVII and XVIII. A typical glpc analysis is shown in Chart XII.

The three main components (peaks 1,2, and 3, Chart XII) were separated by preparative glpc (SE-30, 10'x3/8"). The first consisted of a mixture of 1,2,3,4-tetrachloronorborn-2-ene (XX) (major component) and 1,2,4-

CHART XII

Gas-liquid Partition Chromatographic Analysis of Products from Bu_3SnH Reduction of 1,2,3,4,7-Pentachloronorborn-2-ene



anti-7-tetrachloronorborn-2-ene (XV): nmr (CCl_4) δ 6.21 (s,C<u>H</u>=CCl), 3.92 (m,J<1Hz,C_7-<u>H</u>) and 2.75-1.70 ppm (m,methylenes). The second component, obtained pure, was 2,5,6,7-tetrachlorobicyclo[3.2.0]hept-6-ene (XLII): nmr (CCl_4) δ 3.91 (m,1,J<1Hz,C<u>H</u>Cl), 2.98 (m,1,bridgehead), and 2.50-1.50 (m,4,$C\underline{H}_2$-$C\underline{H}_2$). The third component, also obtained pure, was 1,2,3,4-tetrachlorotricyclo[2.2.1.$0^{2,7}$]-heptane (XLIII): mp 80-81°; nmr (CCl_4) δ 4.01 (d,1,J=2Hz, C<u>H</u>Cl), 3.09 (m,1,bridgehead) and 2.30-1.42 ppm (m,4, $C\underline{H}_2$-$C\underline{H}_2$).

A 0.3 M solution of 1,2,3,4-*anti*-7-pentachloro-norborn-2-ene (XVII) in hexane was reduced with tri-*n*-butyltin hydride, using the same procedure as described previously for kinetic studies. The variation in product ratios with initial concentration of tri-*n*-butyltin hydride (Table XV, page 147) was determined by glpc analyses. Similar experiments (Table XVI, page 148) were carried out with 1,2,3,4-*syn*-7-pentachloronorborn-2-ene (XVIII).

(vi) <u>Reduction Products from *syn*- and *anti*-1,2,3,4,7-Pentachloronorborna-2,5-diene</u>

The products obtained from reduction of *syn*- and *anti*-1,2,3,4,7-pentachloronorborna-2,5-diene (XXIII and XXIV) with tri-*n*-butyltin hydride are outlined in Chart

IX, page 156. A solution of 1,2,3,4,7,7-hexachloronorborna-2,5-diene (XXII) (2 g, 0.0067 mol) and tri-*n*-butyltin hydride (4 g, 0.014 mol) in 10 ml hexane, sealed under vacuum into a pyrex test tube, was heated for three days in a steam bath. The solvent was distilled *in vacuo*, and the residue vacuum distilled at 0.1 mm. The following fractions were collected:

#1	100-105°	→ 0.50 gm
#2	105-112°	
#3	112-113°	
#4	113°	

Analysis by glpc showed that the last two fractions probably consisted entirely of tin adducts. These were not identified further. The first two fractions contained approximately 56% tin adducts, 19% *syn*- and *anti*-1,2,3,4,7-pentachloronorborna-2,5-diene (XXIII and XXIV), 10% 1,2,3,4-tetrachlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene (LV), 8% 1,2,3,5-tetrachloroquadricyclene (LIII) and 6% 1,3,4-trichlorotricyclo[2.2.1.$0^{2,7}$]hept-5-ene (LIV). The order of elution (SE-30, 10'x1/8") was LIV, LV, XXIII and XXIV, LIII, tin residues. Preparative glpc separation (SE-30, 10'x3/8") gave pure LV: nmr (CCl_4) δ 7.04-6.68 (m,2,C<u>H</u>=C<u>H</u>), 4.65-4.46 (m,1,C<u>H</u>Cl) and 3.75-3.50 ppm (m,1,bridgehead). Similarly, LIV was obtained pure: nmr (CCl_4) δ 6.99-6.78 (m,2,C<u>H</u>=C<u>H</u>), 4.45-4.26 (m,1,C<u>H</u>Cl) and 3.68-3.46 ppm (m,2,bridgehead hydrogens), as well as LIII:

nmr (CCl_4) δ 4.78 (d, 1/2,J=6Hz) 4.64 (d,1/2,J=6Hz), 4.15 (d,1,J=5Hz), 3.17 (d,1/2,J=16Hz), 2.94 (d,1/2,J=16Hz), 2.25 (m,1/2) and 2.05 ppm (m,1/2).

III Polarographic Reductions

Fisher Certified Grade N,N-dimethylformamide (DMF) was used as the solvent throughout. Eastman Kodak Co. White Label tetraethylammonium bromide or tetraethylammonium chloride was used as the electrolyte. A Sargent Model XV polarograph was used with a conventional H-type cell immersed in a water bath at 25°C. The capillary height was 60 cm. An Ag/Ag^+ electrode was used.

From a stock solution of 0.100 M tetraethylammonium bromide in N,N-dimethylformamide, a solution ($\simeq 10^{-4}$M) of alkyl bromide was prepared. Ten ml of this solution was placed in one side of the cell. Nitrogen, saturated with DMF, was passed through until all of the oxygen had been removed. In the other compartment of the cell, which was separated by a sintered glass disc, 20 ml of 0.100 M tetraethylammonium bromide in DMF was placed. The electrode was then immersed in this solution. Subsequent runs under the same conditions were reproducable to ±0.02 volt.

Half-wave potentials obtained in this manner are given in Tables XXIV and XXV.

TABLE XXIV

Half-wave Potentials Obtained Using
0.100 M Et_4N Br in DMF

Entry	Compound	$E_{1/2}$ (volts)	Average
1	$CH_3CH_2CH_2CH_2$-Br	-1.83 -1.84	-1.84 ±0.01
2	$CH_3CH_2CH(CH_3)$-Br	-1.88 -1.89	-1.89 ±0.01
3	CH_2=CH-CH_2-Br	-0.93 -0.94 -0.94	0.94 ±0.01
4	$PhCH_2$-Br	-0.82 -0.83	0.83 ±0.01
5	*m*-Br-$C_6H_4CH_2$-Br	-0.72 -0.70	-0.71 ±0.01
6	$(CH_3)_2CHCH_2CH_2CH_2$-Br	-1.88 -1.85	-1.87 ±0.02
7	CH_2=CH-CH_2CH_2-Br	-1.79 -1.80	-1.80 ±0.01
8	cyclo-C_3H_5-CH_2-Br	-1.80 -1.81	-1.81 ±0.05
9	cyclo-C_4H_7-Br	-1.96 -1.95	-1.96 ±0.01
10	3-Nortricyclyl-Br	-1.97 -1.97	-1.97 ±0
11	7-Norbornyl-Br	-2.06 -2.04	-2.05 ±0.01

TABLE XXIV (Continued....)

Entry	Compound	$E_{1/2}$ (volts)	Average
12	*anti*-7-norbornenyl-Br	-2.00 -1.99 -1.99 -2.00	-2.00 ±0.01
13	*syn*-7-norbornenyl-Br	-2.09 -2.10	-2.09 ±0.01

TABLE XXV

Half-wave Potentials Obtained Using 0.100 M Et_4N Cl in DMF

Entry	Compound	Half-wave Potentials					
		1st wave	Average	2nd wave	Average	3rd wave	Average
1	$PhCCl_3$	-0.48 -0.48 -0.51 -0.55	-0.51 ±0.03	-1.20 -1.26 -1.23 -1.26	-1.24 ±0.02	-1.57 -1.61 -1.61 -1.62	-1.60 ±0.02
2	CCl_4	-0.33 -0.32	-0.33 ±0.01	-1.31 -1.28	-1.30 ±0.02	-1.95 -1.95	-1.95 ±0
3	$CHCl_3$	-1.31 -1.29	-1.30 ±0.01	-1.94 -1.92	-1.93 ±0.01		
4	CH_2Cl	-1.95 -1.96 -1.97	-1.96 ±0.01				
5	$PhCH_2Br$	-1.56					
6	*n*-Bu-Br	-1.81 -1.82	-1.82 ±0.01				
7	*sec*-Bu-Br	-1.87 -1.86	-1.87 ±0.01				

(Continued.....)

TABLE XXV (Continued.....)

Entry	Compound	Half-wave Potentials 1st wave	Average	2nd wave	Average	3rd wave	Average
8	$PhCH_2$-Cl	-1.55					
9	Ph-Cl	-2.16 -2.16	-2.16 ±0				

SUMMARY

Many studies dealing with the rate of formation of free radicals have been complicated by charge polarization in the transition state. In this study, the tri-*n*-butyltin hydride reduction of alkyl halides was used to generate free radicals. The effect of polar substituents on tin hydride reductions was determined through a study of polarographic reductions. A rate factor of 9.5 per σ^* (polar substituent constant) unit was calculated to be operative in tin hydride reductions of acyclic bromides. For reduction of cycloalkyl bromides and chlorides where the bond angle at the reaction centre was less than the normal tetrahedral value, polar effects were found to be unimportant.

The relative rates of tin hydride reduction of several 7-bromo- and 7-chloronorbornane derivatives were determined in a search for homoallylic π-bond participation in the transition state. The relative rates of reduction of the bromides were correlated with bond angle strain at the reaction centre. For the chlorides, rate accelerations were observed when allylcarbinyl- or dicyclopropylcarbinyl radicals were generated. For these

compounds, the observed relative rates were corrected for bond angle differences at the reaction centre, in order to estimate the actual rate acceleration from such delocalization.

The stereochemistry of the product determining step was determined for reduction of *syn*- and *anti*-7-bromonorbornene. Reduction with tri-*n*-butyltin hydride gave *anti*-7-deuterionorbornene in both cases. The rate acceleration and stereoselective product formation was taken as strong evidence for non-classical character of the 7-norbornenyl free radical. Supporting evidence was obtained from polarographic reduction.

The synthesis of several polychlorinated norbornane derivatives has been described. The relative rates of tri-*n*-butyltin hydride reduction of the 7-chlorine atom in several of these compounds was determined. Large rate accelerations were observed and rearranged products were obtained from reduction. These were identified and the dependence of product ratios on the tri-*n*-butyltin hydride concentration was determined. The enhanced rates of formation were interpreted as evidence of delocalization in the transition state for free radical formation. Possible non-classical free radical intermediates were proposed and discussed in light of the products and product ratios obtained.

The accelerated rates of reduction of several acyclic halides could be attributed entirely to polar contributions in the transition state. No evidence for delocalization in the rate determining step was obtained.

REFERENCES

1. P.D. Bartlett, "Nonclassical Ions, Reprints and Commentary", Benjamin, Inc. 1965.
2. P. von Schleyer, J. Am. Chem. Soc., *86*, 1856 (1964).
3. J.D. Roberts and R.H. Mazur, *ibid*, *73*, 2509 (1951).
4. E. Renk, P.R. Schafer, W.H. Graham, R.H. Mazur and J.D. Roberts, *ibid*, *83*, 1987 (1961).
5. D.I. Schuster, Ph.D. Thesis, California Institute of Technology, 1961.
6. A.J. Rosen, Ph.D. Thesis, California Institute of Technology, 1961.
7. F.H. Seubold, J. Am. Chem. Soc., *83*, 231 (1961).
8. L.K. Montgomery, J.W. Matt and J.R. Webster, *ibid*, *89*, 923 (1967).
9. L.K. Montgomery and J.W. Matt, *ibid*, *89*, 934 (1967).
10. T.A. Halgren, M.E.H. Howden, M.E. Medorf and J.D. Roberts, *ibid*, *89*, 3051 (1967).
11. S.J. Cristol, G.D. Brindell and J.A. Reeder, *ibid*, *80*, 635 (1958).
12. S.J. Cristol, T.W. Russell and D.I. Davies, J. Org. Chem., *30*, 207 (1965).
13. J. Wilt and A.A. Levin, *ibid*, *27*, 2319 (1962).
14. C.R. Warner, R.J. Strunk and H.G. Kuivila, *ibid*, *31*, 3381 (1966).

15. L.E. Barstow, Tetrahedron Letters, 865 (1968).

16. M.E.H. Howden, Ph.D. Thesis, California Institute of Technology, 1964.

17. M.E.H. Howden and J.D. Roberts, Tetrahedron Suppl., *19*, 403 (1963).

18. W.A. Pryor, "Free Radicals", McGraw Hill Book Co., Inc., New York, N.Y., 1966, p. 170.

19. G.S. Hammond, J. Am. Chem. Soc., *77*, 334 (1955).

20. C.G. Overberger, M.T. O'Schaughnessy and H. Shalit, *ibid*, *71*, 2661 (1949).

21. C.G. Overberger and M.B. Berenbaum, *ibid*, *73*, 2618 (1951).

22. C.G. Overberger and A. Lebovits, *ibid*, *76*, 2722 (1954).

23. H. Hart and R.A. Cipriani, *ibid*, *84*, 3697 (1962).

24. E.S. Huyser and J.D. Taliaferro, J. Org. Chem., *28*, 3442 (1963).

25. D.C. Neckers and A.P. Schaap, *ibid*, *28*, 620 (1963).

26. J.C. Martin, J.E. Schultz and J.W. Timberlake, Tetrahedron Letters, 4629 (1967).

27. S.F. Nelson and P.D. Bartlett, J. Am. Chem. Soc., *88*, 137, 143 (1966).

28. J.R. Shelton, C.K. Liang and P. Kovacic, *ibid*, *90*, 354 (1968).

29. S.E. Scheppele and S. Seltzer, *ibid*, *90*, 358 (1968).

30. M.M. Martin and D.C. de Jongh, *ibid*, *84*, 3526 (1962).

31. P.D. Bartlett and D.M. Simon, *ibid*, *82*, 1753 (1960).

32. P.D. Bartlett and C. Rüchardt, *ibid*, *82*, 1756 (1960).

33. D.J. Trecker and J.P. Henry, *ibid*, *85*, 3204 (1963).

34. E.S. Huyser and G. Echegarary, J. Org. Chem., *27*, 429 (1962).

35. L.W. Menapace and H.G. Kuivila, J. Am. Chem. Soc., *86*, 3047 (1964).

36. E. Zador, Ph.D. Thesis, McMaster University, 1967.

37. H. Tanida, T. Tsuji and T. Irie, J. Org. Chem., *31*, 3941 (1966).

38. F.W. Evans, R.J. Fox and M. Szwarc, J. Am. Chem. Soc., *82*, 6414 (1960).

39. F.D. Green and N.N. Lowry, J. Org. Chem., *32*, 875, 882 (1967).

40. P.J. Elving and B. Pullman, Adv. Chem. Phys., *3*, 1, 14 (1961).

41. F.L. Lambert, A.H. Albert and J.P. Hardy, J. Am. Chem. Soc., *86*, 3155 (1964).

42. F.L. Lambert and K. Kobayashi, *ibid*, *82*, 5324 (1960).

43. J.W. Sease, P. Chang and J.L. Groth, *ibid*, *86*, 3154 (1964).

44. F.L. Lambert, J. Org. Chem., *31*, 4184 (1966).

45. A. Streitwieser, Jr. and C. Perrin, J. Am. Chem. Soc., *86*, 4938 (1964).

46. C.H. De Puy and P.R. Story, *ibid*, *82*, 627 (1960).

47. Reference 18, p.6.

48. R.W. Taft, Jr. in "Steric Effects in Organic Chemistry", ed. M.S. Newman, John Wiley and Sons Inc., New York, N.Y., 1956, Ch. 13.

49. H.C. Brown and J. Muzzio, J. Am. Chem. Soc., *88*, 2811 (1966).

50. A.C. Macdonald and J. Trotter, Acta Cryst., *18*, 243 (1965), *ibid*, *19*, 456 (1965).

51. G.S. Hammond and R.W. Todd, J. Am. Chem. Soc., *76*, 4081 (1954).

52. J.D. Roberts, L. Urbanek and R. Armstrong, *ibid*, *71*, 3049 (1949).

53. J.P. West and L. Schmerling, *ibid*, *72*, 3525 (1950).

54. E.C. Kooyman and G.C. Vegter, Tetrahedron, *4*, 382 (1958).

55. J. Wilt, G. Gutman, W.J. Ranus, Jr. and A.R. Zigman, J. Org. Chem., *32*, 893 (1967).

56. J.O. Halford, J. Chem. Phys., *24*, 830 (1956).

57. J. Warkentin and E. Sanford, J. Am. Chem. Soc., *90*, 1667 (1968).

58. A.P. Marchand and J.E. Rose, *ibid*, *90*, 3724 (1968).

59. D. Seyferth, H. Yamazaki and D.L. Alleston, J. Org. Chem., *28*, 703 (1963).

60. R.R. Sauers, Chem. and Ind., 176 (1960).

61. C.F. Wilcox, Jr. and J.G. Zajacek, J. Org. Chem., *29*, 2209 (1964).

62. C.K. Alden and D.I. Davies, J. Chem. Soc. (C), 700 (1968).

63. H.O. House, "Modern Synthetic Reactions", W.A. Benjamin, Inc., New York, N.Y. 1965, Ch. III.

64. J.D. Roberts and M.C. Caserio,"Basic Principles of Organic Chemistry", W.A. Benjamin Inc., New York, N.Y. 1964, p. 266.

65. J.W. Wilt, C.T. Parsons, C.A. Schneider, D.G. Schulternover, S.J. and W.T. Wagner, J. Org. Chem., *33*, 694 (1968).

66. H. Kwart and L. Kaplan, J. Am. Chem. Soc., *76*, 4072 (1954).

67. H. Tanida and T. Tsuji, J. Org. Chem., *29*, 849 (1964).

68. P.R. Story, *ibid*, *26*, 287 (1961).

69. J.D. Roberts, F.O. Johnson and R.A. Carboni, J. Am. Chem. Soc., *76*, 5692 (1954).

70. S. Winstein and C. Ordronneau, *ibid*, *82*, 2084 (1960).

71. H. Tanida and Y. Hata, J. Org. Chem., *30*, 977 (1965).

72. P.R. Story and S.R. Fahrenholtz, J. Am. Chem. Soc., *86*, 528 (1964).

73. G.S. Hammond, N.J. Turro and A. Fischer, *ibid*, *83*, 4674 (1961).

74. W.G. Daubin and R.L. Cargill, Tetrahedron, *12*, 186 (1961).

75. S. Winstein, A.H. Levin and K.C. Pande, J. Am.

Chem. Soc., *85*, 2324 (1963).

76. H.T. Clarke, J. Chem. Soc., 1699 (1913).

77. J. Colonge and P. Garnier, Bull. Soc. Chim. France, 436 (1948).

78. "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., 46th ed., 1965, p. C-450.

79. H.G. Richie and E.A. Hill, J. Org. Chem., *29*, 421 (1964).

80. M. Julia, S. Julia and R. Guegan, Bull. Soc. Chim. France, 1074 (1960).

81. J.W. Cornforth, R.H. Cornforth (Mrs.) and K.K. Mathew, J. Chem. Soc., 2539 (1959).

82. W. Kirmse, M. Kapps and R.B. Hager, Chem. Ber., *99*, 2855 (1966).

83. M. Hanack and H. Eggensperger, Liebigs Ann. Chem., *663*, 31 (1963).

84. F. Sorm and J. Arient, Coll. Czech. Chem. Comm., *15*, 175 (1950).

85. H.G. Kuivila and O.F. Beumel, Jr., J. Am. Chem. Soc., *83*, 1246 (1961).

86. H. Bluestone, U.S.P. 2, 676, 132 (Chem. Abs., *48*, 8474 (1954)).

87. H. Bluestone, U.S.P. 2, 925, 445 (Chem. Abs., *54*, 10,900 (1960)).

88. C.K. Ingold and F.R. Shaw, J. Chem. Soc., 2918 (1927).