HOMOLYSIS OF T-BUTYL 7-NORBORNENE- AND NORBORNANE- PERESTERS

THE QUESTION OF NONCLASSICAL FREE RADICALS: DECOMPOSITION OF T-BUTYL 7-NORBORNENE- AND NORBORNANE- PERCARBOXYLATES

by

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
May 1967

DOCTOR OF PHILOSPHY (1967)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: The Question of Nonclassical Free Radicals: Decomposition of T-Butyl 7-Norbornene- and Norbornane- Percarboxylates

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NUMBER OF PAGES: ix, 103

SCOPE AND CONTENTS:

There is only one unambiguous report in the literature of anchimeric assistance by the π-bond in a free radical reaction. It was the purpose of this work to investigate the possibility of such acceleration in the thermal homolysis of 7-norbornene peresters. Two such t-butyl peresters, the isomeric syn- and anti-7-norbornene percarboxylates as well as t-butyl 7-norbornane percarboxylate, were prepared and their decomposition was studied by kinetic methods and product analysis.

The homolysis of 7-norbornene peresters is shown to occur with rate-determining perester 0-0 bond rupture, the transition state of which may be a hybrid of radical and polar structures. A low order of anchimeric acceleration may also assist the decomposition of the syn compound.

The pK_a values for syn- and anti- 7-norbornene- and 7-norbornane- carboxylic acid are reported.

Acknowledgment

I wish to express my sincere appreciation to Dr. J. Warkentin who suggested this problem and gave helpful advice and assistance, without which this work could not have been completed.

I also wish to thank the Government of Ontario for financial assistance in the form of an Ontario Graduate Fellowship, 1964-66.

To my wife, Sheila, I owe my deepest gratitude for her encouragement, patience and invaluable assistance during the preparation of this manuscript.

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Introduction and Historical

(A) Neighbouring group participation in carbonium-ion reactions

A recent review article [1] defines neighbouring group participation as the behaviour of substituents that do besides their regular steric and electronic effects " ... influence a reaction by stabilising a transition state or intermediate by becoming bonded or partially bonded to the reaction centre". If the bonding occurs in the transition state of the rate determining step, the reaction rate increases, often quite dramatically, and the neighbouring group is said to provide anchimeric assistance [2].

Participation of neighbouring groups in ionic reactions is a well established phenomenon of physical organic chemistry. One of the earliest examples is that by Roberts and Kimball [3], who proposed the bridged bromonium-ion intermediate to explain the trans addition of bromine to olefins. Bartlett and Swain [4] studied sulfur-participation; they showed that β,β'-dichloroethyl sulfide (mustard gas) reacts with the rate-determining formation of the ethylenesulfonium ion.

Winstein and co-workers [5] proved that neighbouring groups are responsible for the overall retention of configuration observed in many solvolytic reactions, as first suspected by Hughes and Ingold [6]. A series of papers by Cram [7-10] dealt with aryl participation.

The word "anchimeric" assistance was coined by Winstein [11] to denote the formation, in the rate-determining step of a nucleophilic displacement reaction, of a bridged "nonclassical" [12-15] carbonium-ion in which the charge resides in delocalised molecular orbitals. Since this species is mesomeric, and because of the Evans - Polanyi principle [16], anchimeric assistance should result in significant rate-acceleration besides the usual retention of configuration [17].

A wide range of carbonium-ion systems have been investigated for the possibility of anchimeric assistance [1,18]. Some of these, especially the bicyclic norbornene [2,19,20], camphenilyl [21], and apoisobornyl [22] derivatives provide some of the most dramatic examples of anchimeric rate acceleration.

For example, Winstein, Woodward, and co-workers [19] found that the relative rates of acetolysis of anti-7-norbornenyl tosylate, syn-7-norbornenyl tosylate, and 7-norbornyl tosylate are $10^{11}:10^{4}:1$ respectively. Also, anti-7-norbornenyl tosylate was found to acetolyse 25 times faster than the exo - 2 - tosylate isomer, both reacting with almost complete retention of configuration [19,20].

These facts would be difficult to explain without assuming partial bond formation between the double bond [23] and the developing homoallylic carbonium-ion center in the transition state, i.e. anchimeric assistance by the double bond, that is facilitated by the geometry of the bicyclic molecule.

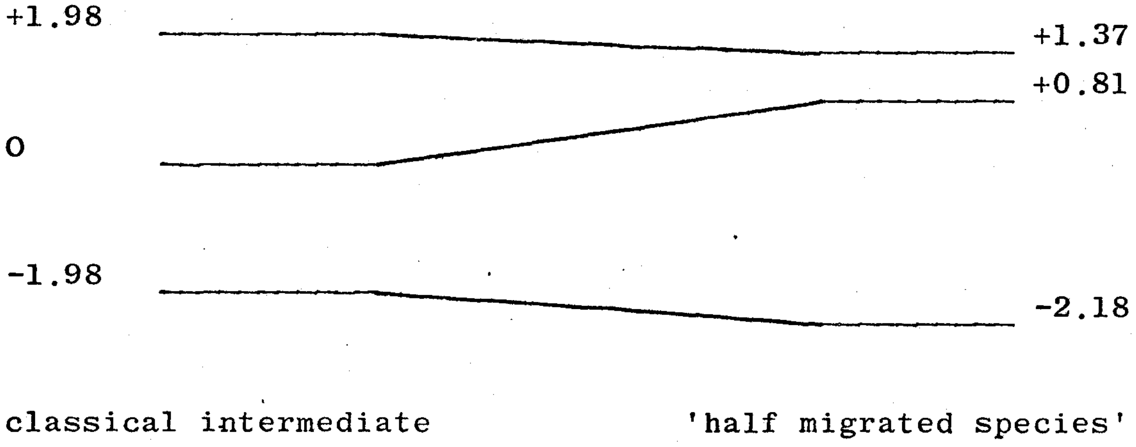
Other systems exhibit only small, or often practically no, rate enhancement [17,24] and the only legitimate claim for anchimeric assistance is based on the stereochemistry of the reaction. It was H.C. Brown who pointed out that this is not sufficient and proposed that "... the question of carbonium-ion structure should be reopened to ascertain whether or not certain of the ions now assigned bridged or nonclassical structures may not be better represented as equilibriating pairs" [17].

(B) Neighbouring group participation in free radical reactions

The intense activities of the last 15 years in the field of carbonium-ion reactions provided a strong stimulus for many attempts to observe neighbouring group participation in free radical reactions. The best authenticated, and to date the only, examples of anchimeric assistance in a radical reaction were reported by Martin and co-workers [25,128], who discovered that the introduction of o-phenylthio-, o-methylthio-, or o-vinyl-substituents (such as o-(2,2-diphenylvinyl and o-fluorenylidene) into tert-butyl perbenzoate causes an up to 10^4-fold increase in the rate of its thermal decomposition, but that the introduction of a p-methylthio substituent causes only a 3-fold increase [26].

A priori, a free radical species, because of the extra electron, should be less dependent on electron supply from its surroundings than is a carbonium-ion. That it is also less stable was shown by the molecular orbital calculations of Zimmerman and Zweig [27].

They considered the case of an 1,2-alkyl shift in a carbonium-ion, free radical, or a carbanion reaction of a saturated system. The rearrangement may proceed through a classical transition state or intermediate, or through a so-called 'half migrated species' with three-carbon molecular orbitals. The calculated energy levels of both types of intermediates, in units of β, are as follows:



In the case of a carbonium-ion reaction the two electrons of the ion may occupy the lowest energy MO of the 'half migrated species', which lies 0.20 β below the lowest energy sp^3 orbital of the classical ion, thus accounting for the widespread occurance of nonclassical carbonium-ions. But for the radical, the extra electron must occupy the next lowest available anti-bonding orbital, which makes the nonclassical free radical energetically less favoured by 0.41β (i.e. $2x(-0.20)+0.81$). Depending on the choice for the value of β [28,29], this makes the formation of the 'half migrated' free radical endothermic by 6-20 kcal/mole. These calculations are admittedly crude, involving several assumptions, but are claimed to be qualitatively in the right direction.

1) alkyl and aryl participation

In keeping with the theoretical conclusions of Zimmerman and Zweig, it is found that alkyl group migrations in radicals are extremely rare, and take place only with polyalkylated compounds (relief of steric strain).

Kharasch and co-workers [30,31] established that the di-tert-butylcarbinyl radical rearranges with migration of a methyl group. From the product mixture of the vapour phase photobromination of 2,2,4,4-tetramethylpentane a 72%-yield of 2-bromo-2,3,4,4-tetramethylpentane was obtained.

Aryl-group migrations are much more common, although they are always only partial and no evidence of a cyclic bridged intermediate has been found so far. As we have seen, the analogous carbonium-ion reactions are thought to proceed through the bridged phenonium-ion intermediate (recent data by H.C. Brown make this conclusion highly doubtful, at least for some symmetrical cases [17]).

Most frequently, investigations in this field involve neophyl-type free radicals [32-36,39,47]. Urry and Kharasch [32] investigated the cobalt(II) chloride catalysed reaction of β,β - dimethylphenethyl chloride (neophyl chloride) with a Grignard reagent (phenylmagnesium bromide), in which the neophyl radical is generated. Approximately half the monomeric products of the reaction were shown to derive from phenyl migration. Winstein and Suebold [33] confirmed this, using the tert-butyl peroxide - initiated decarbonylation of β-phenylisovaleraldehyde to generate the neophyl radical. Over 90% of the theoretical amount of CO evolved in about 5 hours, and a 70% yield of an approximately 1:1 mixture of tert-butylbenzene and isobutylbenzene was obtained.

Urry and Nicolaides [35], in their article concerning the mechanism of free radical aryl migrations, made two important observations. First, they found that the migratory aptitudes of the phenyl and p-tolyl groups are practically the same, which is unlike that in ionic rearrangements [37,38]. Secondly, the di-tert-butyl peroxide initiated decarbonylation of α,α-dimethyl-β-phenylpropionaldehyde produced no tert-butylbenzene, which is one of the expected products of aryl participation in the transition state. These facts are very difficult to reconcile with the hypothesis of an aryl-bridged free radical species.

The most convincing argument against neighbouring group participation in free radical aryl migrations has been presented by Suebold [36]. It is based on the variation of product ratios in the rearrangement of the neophyl radical, when the initial concentration of β-phenylisovaleraldehyde is varied, and will be discussed in more detail under "The Detection of Anchimeric Assistance".

2) participation in bicyclic systems (especially norbornane, norbornene)

In 1960, when nonclassical carbonium-ions were very fashionable, DePuy and Story [40] wrote as follows: "The norbornane system has been one of the most fruitful of all arrangements of atoms for the study of reaction mechanisms. Derivatives of this system exhibit some of the best examples of anchimeric assistance, transannular interactions.... Indeed, most of the common principles of organic reaction mechanisms could be well illustrated by the reactions of variously substituted norbornanes".

This statement is not exaggerated, for much of the evidence, both for and against anchimeric assistance, in carbonium-ion as well as free radical reactions, comes from studies on the bicyclo [2.2.1] heptanes and their unsaturated derivatives.

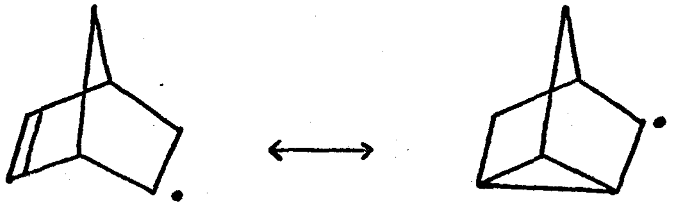
There are several reasons for this:

a) the unusual C6-C1-C2 angle [45] allows facile interactions, such as Wagner-Meerwin rearrangements [46], tricyclic product formations [47], increased endo H-H repulsion, and shielding of the endo side [48], to take place.

b) the stereochemical course, the products of reaction are relatively easily identified; chromatographic [42], NMR [41] and other [43,44] methods are available to distinguish between exo, endo, tricyclic, etc. products

c) the proximity of the π-orbital of the C2 double bond to a C7 carbonium-ion or free radical center provides the best conditions for homoallylic π-participation [19].

Roberts and co-workers [49] were the first to suggest the possible existence of a resonance-stabilised norbornene free radical intermediate (i)



(i)

It was postulated in order to explain the fact that norbornene reacts faster than norbornane with N-bromosuccinimide in carbon tetrachloride, and that tert-butylbenzene (which also has a homoallylic π-system) is entirely unreactive. The above results should not be taken as proof of the existence of (i), because alternative pathways, not investigated, may have been responsible for the products observed. Indeed, all subsequent investigations by several groups, with the possible exception of the work by Wilt and Levin [50], have indicated that (i) and its saturated analog do not form.

Dupont, et al [51] studied the addition of the trichloromethyl radical, generated by acetyl peroxide from carbon tetrachloride or chloroform, to camphene and norcamphene (bicycloheptyl derivatives with an exocyclic double bond). Only the product of addition to the exocyclic double bond was isolated in both cases; no rearrangements occurred at all.

The free radical addition of HBr to 2-bromo-2-norbornene [52], in pentane and under ultraviolet light, afforded a 2:1 mixture of trans 2,3-dibromonorbornane and exo-cis-2,3-dibromonorbornane. Lack of rearrangement and predominant cis addition of HBr exclude any participation either by the C1-C6 σ-bond or by the second bromine atom (subsequent to the addition step).

In the free radical halogenation of norbornane, Kooyman and Vegter [48] were able to isolate only very small amounts of 7-halogen substituted products (only 2% when Cl_2, 0% when SO_2Cl_2 was the halogenating agent); exo-2-halonorbornane was always the major product. In competitive reactions, where cyclohexane and norbornane competed for a limited amount of the halogenating agent, the rate ratio, $k_{cyclohexane}/k_{norbornane}$, was always greater than one. These findings exclude both anchimeric assistance and formation of a nonclassical free radical after the rate determining step.

Two more conclusions, both relevant to the present investigation, can be reached from the above data:

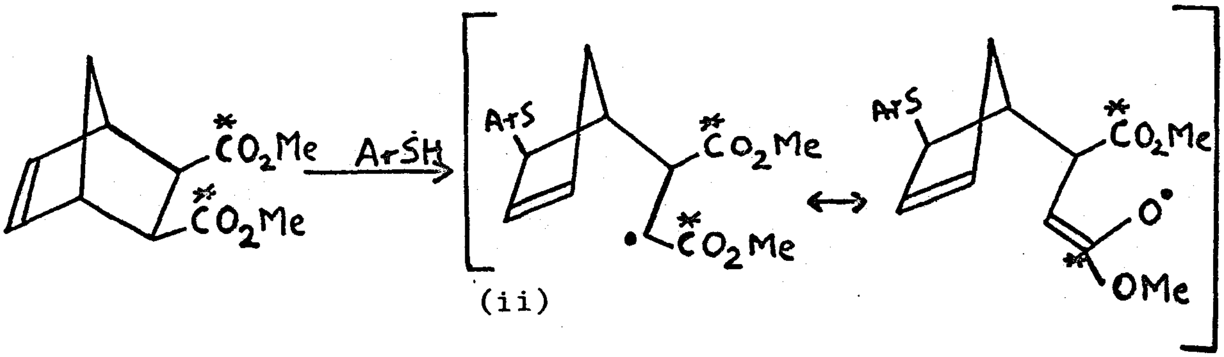
a) the 7-norbornyl radical is very difficult to form. This is due, no doubt, to the effect of the C1-C7-C4 angle-strain on the formation of a planar radical center. This can also be seen readily from the reactivity of $CH_3\cdot$ towards the methylene groups of cyclic hydrocarbons, which is in the following order; cyclohexane $>$ cyclopentane $>$ cyclobutane [53]

b) norbornyl free radicals do not easily undergo Wagner-Meerwein rearrangements [57]. Even the high temperature (250-290°C) thermal decomposition of 2,2 -bis-azocamphane produces only a small amount of isocamphane [54], the product of the Wagner-Meerwein rearrangement of the camphyl radical.

The addition of mercaptans to olefins has been shown to be a free radical chain process [54]. By using norbornene and norbornadiene as the olefin, the nature of the intermediate free radical was ascertained in considerable detail.

Cristol, et al [57,58] allowed norbornene to react with p-thiocresol, but the sole 1:1 addition product was exo-2-thiocresoxynorbornane. Therefore the intermediate cannot be a carbon-bridged radical. It cannot be a sulfur-bridged species either, because the stereochemistry of addition to 6-chloroaldrin (a 2-chloronorbornene derivative) was found to be predominantly cis [58].

Berson and Jones [56] employed endo-and exo-cis-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride and their dimethyl esters, labelled in the carbonyl carbons. It was thought that this system may form a mesomeric radical more easily, since the properly located carbonyl group might stabilise the transition state for rearrangement, as in (ii)

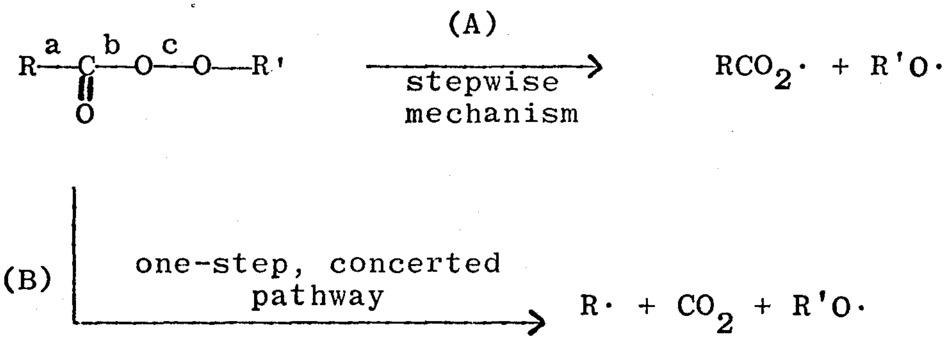


(ii)

The very sensitive isotope dilution technique (±0.5%) was used to follow the course of the reaction, but no rearrangement could be detected.

Addition of p-thiocresol to norbornadiene led predominantly to the rearranged nortricyclene derivative, but Cristol and co-workers [55] showed, by a kinetic argument similar to that used by Suebold [36] in the neophyl system, that the product ratio was dependent upon the initial concentration of p-thiocresol and that classical radicals were therefore involved rather than a nonclassical radical.

The thermal decomposition of norbornene and norbornane tert-butyl peresters is another well studied reaction. Bartlett and co-workers [59-63] established that the decomposition of peresters is rather delicately balanced between two alternative mechanisms:

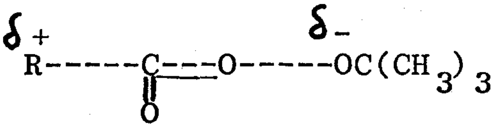


$$R\overset{a}{—}\underset{\overset{\|}{O}}{C}\overset{b}{—}O\overset{c}{—}O—R' \xrightarrow[\text{stepwise mechanism}]{(A)} RCO_2\cdot + R'O\cdot$$

$$\xrightarrow[(B)]{\text{one-step, concerted pathway}} R\cdot + CO_2 + R'O\cdot$$

In general, path (B) is followed when the radical R· is of the stable type (tert-butyl, benzyl). The transition state for such a decomposition requires that rotation around bond (b), in addition to the stretching of bonds (a) and (c), be restricted because of the developing double bond character between C and O. This fact is reflected in the magnitude of the activation parameters for the decomposition. An essentially quantitative yield of CO_2 and the absence of acids amongst the reaction products is also indicative of a concerted pathway.

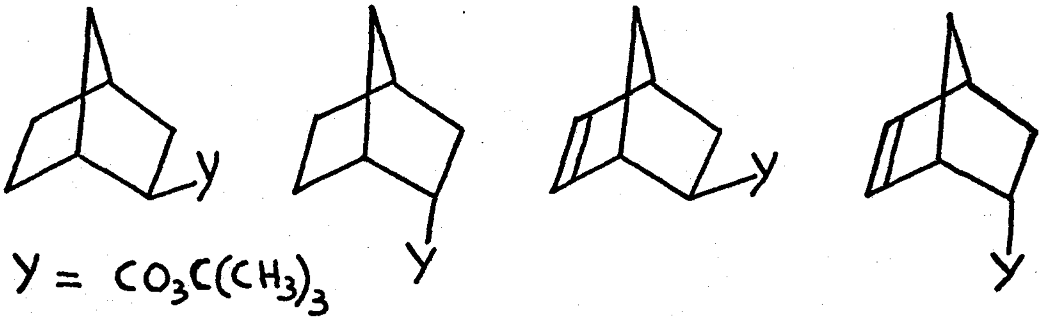
If R· is norbornyl or norbornenyl, and if it is stablised by σ- or π- participation, the perester would be expected to decompose by a concerted mechanism, and at a rate appreciably greater than, say, tert-butyl cyclohexane percarboxylate [63]. Even if the rate determining step does not lead to a mesomeric (bridged) R·, one may still have a cationic-type anchimeric assistance [63] which increases the importance of the polar contribution structure (iii) at the transition state [61]:



$$\overset{\delta +}{R}\text{-----}\underset{\underset{O}{\|}}{C}\text{---}O\text{-----}\overset{\delta -}{O}C(CH_3)_3$$

(iii)

The predictions of Kooyman and Vegter [48], as well as those of Zimmerman and Zweig [27], were confirmed when it was found that the following four peresters



all decomposed by a concerted path but without any significant rate enhancement or rearrangement of the bicyclic skeleton [63-65].

Induced decomposition [66,67] -- attack by the products of the 'spontaneous' fission of the O—O bond on the starting perester -- which can complicate the kinetics of perester pyrolysis, was shown to be too unimportant to have masked the effect of anchimeric assistance.

The results of Hart and Chloupek [68], who investigated the decomposition of the closely related diacyl peroxides of exo- and endo-norbornene-5-carboxylic acids and of exo- and endo-norbornane-2-carboxylic acids, also make it unnecessary to postulate anchimeric assistance in the homolysis of these compounds. The exo/endo rate ratio for the unsaturated diacyl peroxides was 1.04, nowhere near the value of 156 obtained by Roberts and Bennett [69] in the solvolysis of the corresponding chlorides. From the exo norbornene diacyl peroxide a lactone (15%) was produced, which may have derived from a nonclassical radical formed after the rate determining step. However, the structure of this lactone was not determined. Therefore, the assumption that it derived from a nonclassical radical is quite speculative.

Wilt and Levin [50] reached a different conclusion concerning anchimeric assistance in the formation of the 7-norbornene radical. They decomposed several cyclic aldehydes, amongst them

(a) bicyclo[2.2.1]hept-2-ene-anti-7-carboxaldehyde
(b) bicyclo[2.2.1]hept-5-ene-endo-2-carboxaldehyde
(c) bicyclo[2.2.2] oct-2-ene-endo-5-carboxaldehyde.

All aldehydes, except (a), lost CO in the presence of di-tert-butyl peroxide with extreme difficulty. While a comparative study of the decomposition of (a) and its syn isomer was not made, the above fact suggested to them anchimeric assistance in the free radical decomposition of 7-substituted norbornene derivatives.

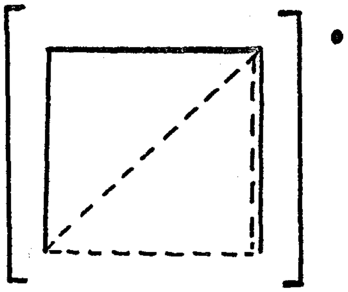
Anchimerically assisted hydrogen abstraction by the tert-butoxy radical at C7 of norbornadiene was considered by Story [70] to be the rate determining step in the Cu(I) catalysed reaction of norbornadiene with tert-butyl perbenzoate. Later he disproved this mechanism using norbornadiene deuterium-labelled at C2 [71], thus casting doubts upon the importance of anchimeric assistance in the free radical reactions of norbornadiene.

The present thesis is concerned with the preparation and thermal decomposition of both the syn- and anti-tert-butyl bicyclo[2.2.1]hept-2-ene-7-percarboxylates, as well as the saturated perester. It is shown that the homolysis of the anti perester is without anchimeric assistance, although the possible existence of a nonclassical free radical, formed in the product determining step(s), cannot be excluded. Decomposition of the syn perester is assisted by participation of the neighbouring double bond.

3) the cyclopropylcarbinyl radical

The methyl cyclopropyl radical has been studied in the hope that it would generate a nonclassical radical analogous to the methylcyclopropyl cation postulated by Roberts and co-workers [72] to explain the kinetics and products of solvolysis of methylcyclopropyl derivatives.

Vapour phase photochlorination experiments by Roberts, et al [73] and by Walling and Fredericks [74] with methyl-^{13}C-cyclopropane as the substrate, led to two products only; cyclopropylmethyl chloride and 4-chloro-1-butene. No cyclobutyl chloride formed, and no scrambling of the ^{13}C-label occurred. It was concluded therefore that a bicyclic, bridged radical intermediate (iv) does not form in the reactions of the methylcyclopropyl radical:



(iv)

However, Hart and Cipriani [75] observed that cyclopropyl acetyl peroxide decomposed much faster than alkyl diacyl peroxides usually do. The diacyl peroxides $CH_3COOOCOR$, where R is cyclohexyl, cyclopentyl, or cyclobutyl, all decompose at approximately the same rate. Cyclopropyl acetyl peroxide, on the other hand, decomposes at a rate 55-times faster than cyclohexyl acetyl peroxide.

This acceleration is mainly due to a decrease in the activation energy of the reaction (approximately 1.5-2.0 kcal/mole) and must mean that the methylcyclopropyl radical has a means of electron-delocalisation that is not available to the methylcyclohexyl radical.

It is not entirely clear what the nature of this delocalisation effect is. It clearly is not the formation of a bridged radical similar to (iv). The main product of the reaction was cyclopropyl carbinyl cyclopropyl acetate (56%). The yield of CO_2 evolved was about 15% lower, than it is usual for many diacyl peroxide decompositions. This is contrary to the expectation that anchimeric assistance should lead to an increased amount of stretching of the R-CO bond as well as the O-O bond at the transition state.

(C) The detection of anchimeric assistance

There are several reliable criteria of anchimeric assistance in a free radical reaction, the most important being a substantial increase in the rate of the reaction. Of course, it first has to be shown that the reaction proceeds by a free radical mechanism. Bartlett and co-workers [61,63,78] proved that tert-butyl peresters, with the exception of the persulfonates and tert-butyl trichloromethyl percarboxylate, decompose by a homolytic mechanism. The peresters were found to initiate chain polymerisations [77], Galvinoxyl, and the Hammond-Soffer reagent [76] were found to be effective scavengers. Product composition depended on the type of solvent (e.g. cumene, chlorobenzene) used.

The persulfonates and the trichloromethyl perester are derivatives of very strong acids; an acid catalysed ionic mechanism was found to be responsible for their exceptional behaviour.

1) the kinetics of the reaction

As was already mentioned, resonance stabilisation of the transition state of a rate determining step manifests itself in an increased reaction rate. But the question of just how much rate increase is required before anchimeric assistance is invoked is of fundamental importance and lies at the bottom of the current controversy of nonclassical versus equilibriating classical intermediates.

It is customary to compare acceleration of a free radical reaction due to a given structure with that in a carbonium-ion reaction, usually solvolysis. This presumes that anchimeric assistance in the carbonium-ion reaction is known to occur, which is not always beyond doubt. The main reason for our selection of the 7-substituted norbornene peresters to investigate anchimeric assistance was the fact that in the solvolysis of the 7-norbornene tosylates and chlorides there unquestionably is a strong anchimeric acceleration.

Acceleration of the rate of perester decompositions is often caused by factors other than neighbouring group participation at the transition state:

(a) acceleration due to acid catalysis

(b) induced decompositions

(c) change of mechanism.

Acid catalysed ionic decomposition is not commonly encountered, and is only present when the perester $RCO_3C(CH_3)_3$ was prepared from a strong acid RCO_2H (e.g. CCl_3CO_2H).

Induced decomposition is almost always a complicating factor in the kinetic analysis of perester reactions. Bartlett and Nozaki [66,67] were the first to recognise that the inconsistency of the rate data obtained from the thermal decomposition of benzoyl peroxide was caused by attack on the starting peroxide by $C_6H_5CO_2\cdot$, one of the products of the 'non-induced' cleavage of the peroxide. This leads to a chain reaction, which can only be analysed mathematically if the predominant chain termination step is known. For a comparatively simple process, such as the reaction of benzoyl peroxide in benzene at 60-100°C, this step may be determined. However, tert-butyl perester decompositions are more complicated. In general, one can only demonstrate the presence or absence of induced decompositions by changing the initial concentration of the perester, adding various scavengers, or changing the solvent, and noting what effect these changes produce on the rate of the reaction.

Another effect that has to be taken into account is that the mechanism of the reaction may change from one compound to another even within a closely related series of compounds. The kinetics of the decomposition of a series of tert-butyl peresters of the general formula $RCO_3C(CH_3)_3$, reported by Bartlett and Hiatt [59], very eloquently illustrates this point. With R = CH_3, in C_6H_5Cl, the half-life of the reaction (extrapolated to 60°C) was $t_{\frac{1}{2}} = 5.0 \times 10^5$ minutes. A change to R = $C(CH_3)_3$ caused a decrease in the half-life to $t_{\frac{1}{2}} = 300$ minutes. The only explanation that can be offered for this drastic change is that the two compounds followed a different mechanistic pathway; one was concerted, the other non-concerted.

Several criteria of mechanism have been used in the study of perester decompositions. A quantitative yield of carbon dioxide, and an enthalpy of activation of between 23-33 kcal/mole [59] are thought to be highly indicative of a concerted process. A low carbon dioxide yield, and the presence of products arising from $RCO_2\cdot$ demand an at least partially non-concerted mechanism.

The Hammond-Soffer reagent has been widely employed to trap the $RCO_2\cdot$ radical. It should be pointed out that this reagent often gives inconclusive results, especially when it only produces a partial reduction in the carbon dioxide yield. Bartlett has shown [63] that while the reagent $I_2/CCl_4/H_2O$ is a highly effective scavenger for $ArCO_2\cdot$, it is much less so for the $RCO_2\cdot$ radical.

A definitive test, for a concerted as opposed to a non-concerted radical process, is the (C^{12}/C^{13}) kinetic isotope effect which so far has not been applied to the thermal decomposition of peresters. In a concerted loss of carbon dioxide the ($^{k}C^{12}/^{k}C^{13}$) ratio would be expected to be between 1.02 and 1.04 (i.e. a primary C^{12}/C^{13} kinetic isotope effect)[79]. For a non-concerted process only a 'secondary mass effect'[80] is observed whose magnitude is ($^{k}C^{12}/^{k}C^{13}$) = 1.006-1.007.

2) the activation parameters

The magnitude of the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, in a given solvent, reflect the stability and geometry of the transition state. Hence a comparison of their values for a series of compounds of the same type (e.g. peresters) can give some useful information about anchimeric assistance.

There is a considerable controversy about the significance of empirical relationships between the activation parameters for a series of related reactions[81,82], but it is beyond the scope of the present work.

Experimentally, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are determined from the fundamental equation (1) of the transition state theory[83]

$$k = (KT/h)\exp(-\Delta F^{\ddagger}/RT), \qquad (1)$$

where T = obsolute temperature, K = Boltzman constant, k = rate constant, h = Planck constant, R = gas constant, and $\Delta F^{\ddagger}$ = free energy of activation.

Since $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, equation (1) may be rewritten as (2)

$$k = (KT/h)\exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R), \qquad (2)$$

in which $\Delta H^{\ddagger}$ = enthalpy of activation, and $\Delta S^{\ddagger}$ = entropy of activation.

Dividing equation (2) by T and taking its logarithm one obtains equation (3)

$$\log_{10}(k/T) = \log_{10}(K/h) + \Delta S^{\ddagger}/2.303R - \Delta H^{\ddagger}/2.303RT \qquad (3)$$

Therefore from a plot of $\log_{10}(k/T)$ versus $(1/T)$ both parameters may be determined.

In general, the magnitude of the enthalpy of activation depends on the strength of the bond(s) being broken at the transition state, the extent of electron delocalisation, and possible electrostatic interactions between polar transition state and solvent. However, solvents can also exert a strong influence on the entropy of activation [81]. Thus great caution is required in the interpretation of activation parameters in solution. A negative entropy of activation indicates that the entropy of the system has decreased during passage from the ground state to the transition state. This can mean that the number of possible orientations or internal degrees of freedom of the reacting molecule has been decreased, that solvent molecules became "frozen" at the transition state, or that both factors are important.

Series of compounds are known in which there is a general relation between enthalpy of activation and entropy of activation [59,80,81]. Bartlett and Hiatt [59] found that the tert-butyl peresters $RCO_3C(CH_3)_3$ constitute such a series. They showed that in chlorobenzene, a structural change which led to a decrease of enthalphy of activation also caused a decrease of entropy of activation.

This relationship was thought to reflect the fact that a lowering of the energy of activation for a given perester has to occur together with some steric restrictions at the transition state. An empirical relationship was worked out according to which any perester can be assigned a number, ranging from 0 to 3, that denotes the number of bond rotations which are unhindered in the ground state but which become "frozen" at the transition state.

Once the value of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is determined for a new perester, there may be a strong temptation to use this relationship as a proof of mechamism. But a compound that falls within the "zero rectangle" of Bartlett and Hiatt, for example, does not necessarily decompose by a non-concerted mechanism. There is no theoretical justification for this correlation, and the range of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values that places a given compound in one of the "rectangles" is somewhat arbitrary.

3) product studies

Anchimeric assistance in free radical reactions necessarily involves the formation of a nonclassical intermediate. The product forming steps of this intermediate may include rearrangements, although rearranged products do not prove intermediacy of a nonclassical free radical. They may arise from classical radical intermediates in rapid equilibrium, where the nonclassical structure is only the transition state for their interconversion. Rearranged products provide an argument for anchimeric assistance only when a significant rate acceleration is also observed.

An elegant argument, based on product studies, against the presence of a nonclassical neophyl radical in the thermal decarbonylation of β-phenylisovaleralehyde was presented by Suebold [36]. The ratio of isobutylbenzene to tert-butylbenzene, the two main products of the reaction, was observed to increase as the initial concentration of the aldehyde decreased.

This observation is not compatible with the existence of a bridged neophyl radical but is consistent with a scheme involving classical free radicals:

$$R_1CO\cdot \xrightarrow{k_1} R_1\cdot + CO$$

$$R_1\cdot + R_1CHO \xrightarrow{k_2} R_1H + R_1CO\cdot$$

$$R_1\cdot \xrightarrow{k_3} R_2\cdot$$

$$R_2\cdot + R_1CHO \xrightarrow{k_4} R_2H + R_1CO\cdot$$

where R_1 = Ph $C(CH_3)_2CH_2$–, and R_2 = $(CH_3)_2\dot{C}CH_2Ph$.

Using the steady-state approximation, equation (1) can be derived

$$d(R_2H)/d(R_1H) \approx (R_2H)/(R_1H) = (k_3/k_2)/(R_1CHO) \qquad (1)$$

If a cyclic intermediate which could react at either of two sites with R_1CHO were present, the ratio R_1H/R_2H should be independent of the concentration of the hydrogen-donor R_1CHO.

This method of product analysis was applied successfully by Cristol and co-workers [55] to the addition of p-thiocresol to norbornadiene. The ratio of 1:1 addition products, tricyclic/norbornene, was found to vary considerably with the concentration of ArSH, thus disproving that a bridged radical intermediate could have been responsible for the products formed.

Product analyses by several groups of investigators attest to the fact that the free radical analog of the

Wagner-Meerwein rearrangement of the norbornane system is very uncommon [48,51,52,84]. Norbornene and norbornadiene radicals may rearrange [55,85], but the determining factor in these rearrangements is the greater thermodynamic stability of the tricyclic nucleus and not a nonclassical radical intermediate.

Wilt and Levin [50] were unable to support their suggestion that 7-norbornene carboxaldehyde decarbonylates with anchimeric assistance because the product mixture was extremely complex.

4) stereochemical evidence

The stereochemical consequence of anchimeric assistance in many carbonium-ion reactions is retention of configuration at the reaction center. In several cases the existence of nonclassical ions was claimed, mainly on the basis of this result. However, equilibriating classical ions may equally well account for the stereochemistry of these reactions.

The stereochemical course of free radical reactions is often very difficult to follow because they may undergo many product-forming reactions such as disproportionation, rearrangement, elimination, induced reactions.

The chain addition of HBr to 1-bromo or 1-methyl cyclohexene is one reaction where a nonclassical free radical was at one time thought to be present. A bromine-bridged cyclic intermediate radical was proposed by Goering and co-workers [86] on the ground that the existence of a classical radical with bromine in the axial position was unlikely. Further investigation [87-89] revealed that the thermodynamic stability of axial and equatorial bromine was about the same in these radicals. Also, as the lifetime of the radical increased stereospecificity drastically decreased, indicating a conformation-equilibrium of the initially formed classical radical.

Experimental Section

(A) General discussion

The 7-norbornene carboxylic acids were eventually prepared by addition of CO_2 to the Grignard reagent from syn-7-bromonorbornene, and were separated as the methyl esters by fractional distillation.

Because of the highly toxic nature of 2,7-dibromonorbornane and syn-7-bromonorbornene [123], and of the low yields obtained from the Grignard reaction, the following alternative approaches to the acids were also examined:

(a) displacement by cyanide ion on anti-7-chloronorbornene and bis (anti-7-norbornenyl)- sulfite

(b) preparation of ethyl 3-cyclopentene 1,1-dicarboxylate from which ethyl 2,4-cyclopentadiene 1,1-dicarboxylate and ethyl norbornene 7,7-dicarboxylate might be synthesised.

Nucleophilic displacement by method (a) could not be accomplished but preliminary work indicated that approach (b) might be successful. A new method of preparation of ethyl 3-cyclopentene 1,1-dicarboxylate is reported.

The saturated acid was prepared by catalytic hydrogenation of syn-7-carbomethoxy norbornene, followed by hydrolysis.

The peresters were synthesised in good yields from the acid chlorides by standard methods.

Thermal decompositions of the peresters were carried out in bromobenzene solutions. The rate of decomposition was followed by several methods:

(a) measuring the volume of CO_2 evolved

(b) a N.M.R. -method, used for the first time in monitoring a perester decomposition

(c) attempts to use I.R. -analysis or iodometric titration were unsuccessful.

Extent of induced decompositions, also the concerted or stepwise nature of the homolytic process were tested.

The complex product mixtures were analysed whenever possible. However, the majority of the 15-20 products obtained from each perester could not be identified. Material balances were incomplete; non-volatile products accounted for 70-80% of the starting weight of perester.

Acid dissociation constants (pK_a) for the three carboxylic acids were determined.

(B) Purification of solvents

Bromobenzene, cumene, and pentane were obtained as practical or reagent grade chemicals from the Eastman, Matheson, or Eastern companies. They were purified by shaking, first with portions of concentrated sulfuric acid until the acid layer no longer became colored, and then, successively, with distilled water, 10% sodium carbonate, and distilled water again. After standing over Analar calcium chloride and phosphorous pentoxide, the solvents were then fractionated from anhydrous sodium carbonate through a 2 ft. Vigreux column. The boiling points of the fractions used were: bromobenzene, 154.2°C; cumene, 152.2°C; pentane, 35.6°C; all uncorrected.

Pyridine (Fisher reagent grade) was purified by refluxing over barium oxide for 3 hours and fractionation through a 2 ft. Vigreux column. The fraction boiling at 114-115°C was collected and stored over sodium hydroxide.

Dimethylsulfoxide (Crown Zellerbach Corp.) was dried over calcium hydride (Metal Hydrides, Inc.) and was fractionated under vacuum.

Solvents for chromatography were bulk chemicals from various sources and were fractionated before use.

Carbon tetrachloride was dried over anhydrous calcium chloride and distilled before use.

Dry tert-butyl alcohol was prepared by first refluxing technical grade (Anachemia Chemicals Ltd.) tert-butanol with sodium (2g per 100ml alcohol), for two hours, then distilling. The fraction boiling at 81-82°C was collected.

(C) Preparation of compounds

All melting and boiling points are uncorrected. Melting points were determined using a Gallenkamp block apparatus or a simple oil bath.

Infra-red spectra were measured on a Beckman I.R.5 spectrometer using sodium chloride cells or potassium bromide wafers. Nuclear magnetic resonance spectra were determined on a Varian A.60 spectrometer. The N.M.R. samples were scanned in carbon tetrachloride with tetramethylsilane or hexamethyldisiloxane as internal standard.

Vapour phase chromatographic analyses were carried out using an Aerograph, Model A-700, instrument with a 20' x 3/8", SE-30, silicone gum rubber on Chromosorb W (60-80 mesh) column supplied by the manufacturer.

Mass spectra of compounds were obtained from a Hitachi-Perkin-Elmer RMU-6A mass spectrograph.

Spinning band distillations were carried out with a Podbielniak, Model No. 3073, apparatus.

Microanalyses were performed by Alfred Bernhardt, Max Planck Institut, Mülheim, Germany.

1) Preparation of the acids RCO_2H, where R = 7-norbornyl, syn- and anti- 7-norbornenyl.

Preparation of 2,7-dibromonorbornane

The procedure of Kwart and Kaplan [44] was followed, with some modifications.

Norbornene was used as received from Aldrich Chemical Co.

A 2-liter 3-necked flask, equipped with mercury - sealed stirrer and condenser, was immersed in an ice-salt bath and was charged with a solution of 120 g norbornene (1.26 mole) in 600 ml carbon tetrachloride and 102 g (1.26 mole) dry pyridine. To the cold solution 204 g bromine (1.26 mole), dissolved in 250 ml carbon tetrachloride, was added dropwise in approximately 3 hours to maintain an internal temperature of 0^{o} to 5^{o}C throughout the reaction.

The product mixture was filtered to remove pyridinium bromide, was washed successively with 6N hydrochloric acid (200 ml) and water (300 ml), and was dried over anhydrous calcium chloride. Solvent and volatile products were removed by fractional distillation and the residue (165.0 g), a high boiling (above 110^{o}C at 13 mm) viscous liquid, was used in the subsequent elimination step without further purification.

Vapour phase chromatographic analysis of this residue was difficult because of its very high boiling point. However, it was found to be a mixture of mainly two closely related compounds, in the approximate ratio 4:1 which corresponds, very closely, to the 2,7-dibromonorbornane/trans-2,3-dibromonorbornane product ratio observed by Kwart and Kaplan [44].

Preparation of syn-7-bromonorbornene [44]

A solution of potassium tert-butoxide was prepared by adding 30.0 g (0.75 mole) of potassium to 600 ml dry tert-butyl alcohol in a 2 liter 3-necked flask equipped with a condenser, mercury-sealed stirrer, dropping funnel, heating mantle, and kept under nitrogen atmosphere.

To this hot solution 175.2 g (0.69 mole) of the 2,7-dibromonorbornane/trans-2,3-dibromonorbornane mixture was slowly added. The resulting mixture was refluxed for 14 hours, after which it was allowed to cool to room temperature and was poured onto approximately its own volume of water.

The two layers was separated, the water layer extracted with ether, and the combined extract was dried over sodium sulfate. Evaporation of solvent and tert-butanol, at atmospheric pressure, gave an almost black oil which was vacuum-distilled in a spinning band distillation apparatus. Only the fraction boiling at 71-73°C/15 mm Hg was collected and used in the subsequent preparation of the acids. The yield of elimination product was 60.7 g (51%), somewhat higher than the 46% yield of syn-7-bromonorbornene, b.p. 68-70°C at 13 mm, reported by Kwart and Kaplan [44].

No impurities (such as 2-bromo-2-norbornene) could be detected by V.P.C.-analysis (at 250°C) of the above product.

Preparation of syn- and anti- 7-norbornene carboxylic acid

A mixture of syn- and anti- 7-norbornene carboxylic acid (45 g) was prepared by repeated application of the procedure of Sauers [90,91].

The 40%-yield reported by Sauers, based on syn-7-bromonorbornene, was not obtained in any of these preparations. This is partly due, no doubt, to the fact that it is extremely difficult to achieve a slow dropwise addition of the bromoalkene solution over a long period of time (30 hours) without a specially designed dropping funnel.

A cyclic Grignard reactor [93,94] was also set up. It is recommended for the preparation of acids from alkyl bromides that show a high tendency to couple with the Grignard reagent. However, each cycle produced only a very small conversion to the acids, and the overall yield did not improve.

The only other product isolated from the Grignard reaction mixture is a neutral material, the components of which are not known at the present time.

Separation of syn- and anti- 7-norbornene carboxylic acid

Ethereal diazomethane was prepared from N-nitrosomethylurea and aqueous KOH according to the procedure described by Vogel [92].

Esterification of the norbornene acids (45 g) was carried out by addition of small portions of ethereal diazomethane to the acid mixture, dissolved in ether, until nitrogen no longer evolved. After evaporation of solvent, only the mixture of methyl esters (40 g) remained. It was vacuum distilled at less than 1 mm in a spinning band apparatus.

The products collected, and the V.P.C analysis at 185°C, were as follows:

(a) a colorless liquid (16 g) b.p. 50-56°C; a mixture of syn- (90%) and anti- (10%) ester

(b) an intermediate fraction (12 g) b.p. 56-60°C; contained approximately equal amounts of syn- and anti- ester.

(c) a yellow colored residue (11 g). It was made up of three components: the syn- ester (80%), the anti ester (5%), and another less volatile ester (15%). This third component was assumed to be the vinyl ester, 2-carbomethoxy norbornene, on the basis of its N.M.R. spectrum (only one olefinic proton).

The impure methyl esters were fractionated two more times to provide anti-7-carbomethoxy norbornene, of greater than 99% purity, and syn-7-carbomethoxy norbornene that contained 2.5% of the anti isomer.

Saponification of the esters, by stirring overnight at room temperature with a two-fold excess of aqueous KOH, followed by acidification and extraction with ether gave the corresponding acids in quantitative yield.

Anti-7-norbornene carboxylic acid had m.p. 69-71°C (lit. [50,90] 70-73°C, 71-73°C) and the following N.M.R. absorption pattern (τ, in deuterochloroform, relative to hexamethyldisiloxane): 3.92 (2H), olefinic, triplet; 6.94 (2H), bridgehead, six lines; 7.56 (1H), bridge, five lines; 8.12 (2H), methylene, multiplet; and 8.98 (2H), methylene, multiplet.

Corresponding values for the syn carboxylic acid were as follows: m.p. 97-99°C (lit. [90] 91-96°C) and N.M.R. peaks centered at 3.99 (2H), olefinic, triplet; 6.86 (2H), bridgehead, five or six lines; 7.65 (1H), bridge, three lines; 8.22 (2H), methylene, multiplet; and 8.96 (2H), methylene, multiplet.

Preparation of 7-norbornane carboxylic acid

Catalytic hydrogenation was carried out at 50 p.s.i. hydrogen pressure in a Parr low pressure apparatus.

The reaction vessel, charged with 4.4 g syn-7-norbornene carboxylic acid in 200 ml 95% ethanol and 2 g Matheson 5% Pd on powdered charcoal, was placed in the hydrogenation apparatus and the reaction was allowed to proceed for 5 hours at room temperature. Removal of catalyst and solvent, followed by vacuum sublimation at 80°C, gave a white crystalline solid; m.p. 73.5-75.0°C (lit.[44] 77.5-78.5°C).

Purity of the acid was determined from its mass spectrum. It was found to contain 2±1% of the unsaturated acid (m/e = 138). The N.M.R. spectrum of 7-norbornane carboxylic acid showed only two regions of absorption, ratio 3:8 (in deuterochloroform); a poorly resolved multiplet centered at 7.55τ due to the bridge and bridgehead protons and another methylene-proton multiplet centered at 8.58τ. No olefinic protons were detected.

2) Preparation of the peresters $RCO_3C(CH_3)_3$, where R = 7-norbornyl, syn- and anti-7-norbornenyl

Preparation of the acid chlorides

Technical grade thionyl chloride was purified by distillation first from quinoline (10 g per 100 g thionyl chloride) and then from boiled linseed oil (20 ml per 100 g thionyl chloride)[95]. The fraction boiling at 76°C was collected.

Preparation of the acid chlorides is illustrated by the following example. Anti-7-norbornene carboxylic acid (4.0 g, 0.029 mole) was added to 40 ml thionyl chloride and the reaction mixture was stirred overnight at room temperature. Evaporation of solvent at aspirator pressure followed by short path distillation of the residue provided 4.5 g (89%) anti-7-norbornene acid chloride.

The alternate procedure of refluxing the reaction mixture for 3 hours, which has been shown to cause exo-endo isomerisations in other related systems [64,65], was also tried. It was found to have no effect on the properties or rate of decomposition of the anti perester prepared from the acid chloride.

A recently discovered method of perester preparation [96,97] avoids the necessity of making the acid chlorides. This may prove to be an improvement for the norbornene system because norbornene acid chlorides are difficult to purify [50] and are prone to isomerisation during preparation [65].

Preparation of tert-butyl peresters

Tert-butyl hydroperoxide, b.p. 39-40°C at 13 mm and $n_D^{25} = 1.4000$ (lit.[99] $n_D^{25} = 1.3991$), was prepared by the method of Milas and Surgenor [98].

A typical perester preparation is that of tert-butyl anti-7-norbornene percarboxylate. A solution of 4.6 g (0.052 mole) tert-butyl hydroperoxide, 2.3 g (0.028 mole) pyridine, and 40 ml pentane -- in a 200 ml 3-necked flask -- was cooled in a ice-salt bath. To the cold solution 4.5 g (0.026 mole) acid chloride, dissolved in 50 ml pentane, was added dropwise in approximately 45 minutes. Stirring continued for an additional 2 hours, first at bath temperature (1 hour), then at room temperature.

Pyridinium hydrochloride was removed by filtration, the filtrate was washed with pentane, and the mother liquor was also washed with successive portions of 2.5% aqueous KOH (125 ml), 10% H_2SO_4 (100 ml), saturated Na_2CO_3 (50 ml), and water (100 ml). Evaporation of the solvent gave 5.1 g (92%) perester, a yellow oil.

Physical properties of the peresters

All three peresters are yellow oils, stable at room temperature, freezing point below 0°C.

Nuclear magnetic resonance spectra, in units of τ, refer to neat samples with hexamethyldisiloxane as internal reference ($\tau = 10.00$).

Intensity of IR absorption peaks is denoted by: w = weak, m = medium, and s = strong.

Tert-butyl 7-norbornane percarboxylate had index of refraction $n_D^{20} = 1.4676$; N.M.R. absorption peaks at 7.63 (3H, broad single line), 8.50 (8H, center of a broad multiplet), and 8.80 (9H, singlet); its IR spectrum (neat) had carbon-hydrogen stretching absorption at 3.41 μ(m) and at 3.50 μ(s), perester carbonyl at 5.64 μ(s), and tert-butyl absorption at 7.21 μ(w-m) and 7.31 μ(m).

Anal. Found: C, 68.07; H, 9.10

Calc. for $C_{12}H_{20}O_3$; C, 67.89; H, 9.50

Tert-butyl syn-7-norbornene percarboxylate had index of refraction $n_D^{24} = 1.4703$; N.M.R. absorption peaks at 4.08 (2H, triplet), 6.95 (2H, six lines), 7.60 (1H, three lines), 8.55 (9H, singlet), and 8.86 (4H, center of broad multiplet); its IR spectrum (neat) had carbon-hydrogen stretching absorption at 3.25 μ(w), 3.38 μ(w-m), and 3.47 μ(s), perester carbonyl at 5.64 μ(s), and tert-butyl absorption at 7.18 μ(w-m) and 7.31 μ(m).

Anal. Found: C, 68.66; H, 8.54

Calc. for $C_{12}H_{18}O_3$; C, 68.54; H, 8.63

Tert-butyl anti-7-norbornene percarboxylate had index of refraction $n_D^{20} = 1.4715$ ($n_D^{24} = 1.4688$); N.M.R. absorption peaks at 3.94 (2H, triplet), 7.00 (2H, six lines), 7.68 (1H, 3 lines), 8.50 (4H, center of broad multiplet), and 8.76 (9H, singlet); its IR spectrum (neat) had carbon-hydrogen stretching absorption at 3.30 μ(w), 3.42 μ(w-m), and 3.54 μ(s), perester carbonyl at 5.65 μ(s), at C=C stretching peak at 6.38 μ(w), and tert-butyl absorption at 7.21 μ(w-m) and 7.32 μ(m).

Anal. Found C, 68.13; H, 8.53

Calc. for $C_{12}H_{18}O_3$; C, 68.54; H, 8.63

3) Attempted synthesis of syn- or anti-7-norbornenyl cyanide, also of 7-norbornadienyl cyanide.

Nucleophilic cyanide ion displacement was attempted on the following norbornene or norbornadiene derivatives:

(a) anti-7-norbornenyl alcohol
(b) anti-7-chloronorbornene
(c) bis- (anti-7-norbornenyl)- sulfite
(d) 7-bromonorbornadiene

(a) Attempted cyanide displacement on anti-7-norbornenol

Some allylic alcohols undergo cyanide displacement directly [102] in the presence of strong acids. Since the allylic positions of anti-7-norbornenol alcohol are unreactive in ionic displacements, it was thought that a homoallylic displacement at C7 may occur instead.

Anti-7-norbornenyl alcohol was prepared by the method of Story [100].

Cuprous cyanide was synthesised from cuprous chloride, potassium cyanide, copper sulfate, and sodium bisulfite [101].

A 50 ml erlenmeyer flask was fitted with a condenser and 10 ml conc. HCl together with 2.7 g (0.030 mole) cuprous cyanide were placed in it. To the stirred suspension 3.0 g (0.027 mole) anti-7- norbornenol was added in small portions. Stirring continued for 5 hours at room temperature.

The mixture was then poured onto ice-water, the white precipitate was filtered off, and the aqueous layer was extracted with chloroform. Evaporation of the solvent provided 1 ml of a colorless liquid, b.p. 75-80°C at aspirator pressure.

The reaction product was found to be a mixture of at least two compounds, approximate ratio 2:1, by V.P.C. analysis. Its IR spectrum (neat) contained a broad hydroxyl absorption peak at 3.0 μ(s), carbonyl absorption at 5.8 μ(s), but no peaks in the alkyl nitrile region (4.3-4.6 μ). A qualitative test for nitrogen was negative.

(b) Attempted displacement on anti-7-chloronorbornene

Preparation of anti-7-chloronorbornene[103].

A solution of 20.4 g (0.185 mole) anti-7-norbornenol, 22.6 g (0.195 mole) thionyl chloride, and 15.9 g (0.191 mole) dry pyridine in 200 ml ethyl ether was refluxed for 10 hours after which the reaction mixture was poured onto water. The two layers were separated and the water layer was extracted with ether.

Evaporation of the ether and vacuum distillation of the residue from an 8" helices-packed column provided 14.3 g (70%) anti-7-chloronorbornene, b.p. 37-39°C/9 mm (lit.[104] 70.5-71.5°C/60 mm). The IR spectrum of the chloride matches that reported by Roberts and coworkers[105].

The displacement reaction in DMSO

Into a 250 ml 3-necked flask fitted with a condenser, a nitrogen inlet, and a dropping funnel 7.0 g (0.14 mole) sodium cyanide and 60 ml dry DMSO were placed. The stirred mixture was heated to 100°C and 9.1 g (0.071 mole) anti-7-chloronorbornene was added to it in approximately 15 minutes.

Stirring overnight at 100°C produced a deep brown solution which was poured on about five times its own volume of ice-water, the products were extracted with ether, and the extract was dried over sodium sulfate. Vacuum distillation of the residue on a helices-packed column afforded 2.3 g of a faintly yellow, oily liquid; b.p. 75-80°C at aspirator pressure.

The product was found to be a mixture of three compounds, ratio 1.0:2.4:4.4, by gas chromatography. One of the components, of relative peak area 2.4, was isolated and was shown to be anti-7-norbornenol, while the others were not separated. They had IR absorption (neat) at 4.48 μ(m) and 4.70 μ(m), characteristic of alkyl cyanides, also at 6.20 μ(w) and 6.38 μ(w) (C=C stretching vibrations).

Several other runs were carried out in the DMSO at various reaction temperatures. Increased temperature caused excessive blackening of the reaction mixture and further loss of yield, while at lower temperatures only partial conversion of the anti-7-chloronorbornene occurred.

The two alkyl cyanides were not further characterised; instead they were used directly in an attempted hydrolysis to the carboxylic acids.

Attempted hydrolysis of the alkyl cyanides to the carboxylic acids

Hydrolysis was carried out in an ethanolic KOH solution containing a 2-fold excess of KOH. The reaction mixture, kept under a nitrogen atmosphere, was refluxed for 48 hours. It was then concentrated to a small volume, water was added to it, and the resulting solution was extracted with ether. No organic acid could be isolated on acidification of the water layer.

From the ether layer two amides were obtained by fractional crystallisation. Both formed large, cubic crystals on recrystallisation from methanol, m.p. 203-205°C and 181-184°C respectively. Their IR spectrum was not noticeably different and contained peaks characteristic of primary amides [106], at 2.95 μ(s), 3.15 μ(s), 6.05 μ(s), and 6.18 μ(s).

Analysis of the N.M.R. spectra of the amides was made difficult primarily because they were only sparsely soluble in most organic solvents, and also because they were contaminated by one another. Nevertheless, the presence of the norbornene skeleton was indicated in both amides. Mass spectra of the two amides showed practically the same fragmentation pattern. The molecular ion peaks appeared at 137 mass units, as expected for norbornene amides.

(c) Attempted direct cyanide displacement on bis-(anti-7-norbornenyl)- sulfite

The previously unknown sulfite was obtained, inadvertly, instead of anti-7-chloronorbornene when thionyl chloride was added to an ethereal solution of excess anti-7-norbornenol and pyridine.

Preparation of bis- (anti-7-norbornenyl)- sulfite

Anti-7-norbornenol (3.0 g, 0.027 mole) and dry pyridine (2.3 g, 0.029 mole) were dissolved in 60 ml ether and placed in a 250 ml 3-necked flask. To this solution, stirred magnetically and kept under nitrogen, a 30 ml ethereal solution of thionyl chloride (1.8 g, 0.015 mole) was added in approximately 1 hour. Stirring, at room temperature, was continued for another hour.

Pyridinium hydrochloride was removed by filtration, the filtrate was washed with ether, and the ether solution was dried over sodium sulfate. On evaporation of the solvent and short-path distillation of the residue an almost colorless oil was obtained; b.p. 130-140°C/5 mm (oil bath temperature); yield 2.5 g (67%); and $n_D^{25} = 1.5178$.

The following peaks, characteristic of dialkyl sulfites [106], were present in the IR spectrum (neat): 7.50 μ(m), 8.24 μ(s), 8.34 μ(s), and 8.88 μ(m). Only the following types of protons, given together with their τ values and multiplicities, were detected by N.M.R. (carbon tetrachloride solvent, TMS internal reference): olefinic, 4.05(4H), triplet; bridge, 6.01(2H), one line; bridgehead, 7.32(4H), six lines; methylene, 8.21(4H), multiplet; and methylene, 8.90(4H), multiplet.

Anal. Found: C, 61.95; H, 6.97; S, 11.98

Calc. for $C_{14}H_{18}O_3S$; C, 63.12; H, 6.81; S,12.04

Attempted cyanide displacement on the sulfite in methanol

A 500 ml 3-necked flask was charged with 300 ml methanol, 20 ml water, and 25.0 g (0.384 mole) potassium cyanide. The stirred solution was refluxed and 5.0 g (0.018 mole) bis- (anti-7-norbornenyl)-sulfite, dissolved in 30 ml methanol, was slowly added to it.

The mixture was refluxed for 9 hours. It was then concentrated, 200 ml water was added to the concentrate, and the aqueous solution was extracted with ether.

Vacuum distillation of the extract provided no identifiable products.

(d) Cyanide displacement on 7-bromonorbornadiene in ethanol-water

Preparation of 7-norbornadienyl bromide

A quantitative yield of 7-norbornadienol was obtained by hydrolysis of its benzoate ester [107].

A 200 ml 3-necked flask was equipped with a mechanical stirrer, condenser, dropping funnel, and was charged with an ethereal solution (80 ml) of 7-norbornadienol (15.0 g, 0.139 mole) and pyridine (15.0 g, 0.165 mole). The stirred solution was cooled in an ice-salt bath and a solution of phosphorous tribromide (Matheson, 14.0 g, 0.0515 mole) in 100 ml dry ether was added to it in approximately 1 hour, after which the reaction mixture was allowed to warm to room temperature. It was poured on ice-water, the layers were separated, and the water layer was extracted with ether. The ether extract was dried over sodium sulfate and was distilled in vacuo. A colorless liquid, b.p. 78-80°C/23 mm and yield 16.0 g (67%), was obtained.

The product had the following N.M.R. absorption peaks (τ, hexamethyldisiloxane internal reference): 3.34(4H), olefinic, five lines; 5.73(1H), bridge, singlet; and 6.35(2H), bridgehead, triplet. Its IR spectrum (neat) showed the following absorption pattern (all peaks in μ units): 3.28(m), 3.36(s), 3.41(m), 3.48(w), 6.11(w), 7.16(m), 7.62(s), 7.97(s), 8.14(s), 8.28(m), 8.38(m), 8.98(m), 9.23(s), 9.46(s, broad), 10.56(s), 10.83(m), 11.42(m), and 11.82(s, broad).

The displacement reaction in ethanol-water

The reaction was carried out under conditions practically identical with those of Tanida and Hata[104], who proved that β-cyclopentadienylacrylonitrile is the unstable primary product in the reaction of 7-chloronorbornadiene with NaCN in ethanol-water.

There was no 7-cyanonorbornadiene detected in the reaction product of 7-bromonorbornadiene and NaCN.

4) Preparation of ethyl 3-cyclopentene 1,1-dicarboxylate

Preparation of a mixture of ethyl 2-vinylcyclopropane - and ethyl 3-cyclopentene - 1,1-dicarboxylates

A mixture of cis-1,4-dibromobutene-2 and the trans isomer was prepared from Matheson technical-grade 2-butene-1,4-diol by the method of Valette[109].

Malonate ion displacement on this mixture was carried out in dry ethanol [110] following the method of preparation of ethyl 3-cyclopentene 1,1-dicarboxylate described by Meinwald and co-workers [108]. The product, b.p. 95-105° at 1 mm, was found to be a 2:1 mixture of ethyl 2-vinylcyclopropane - and ethyl 3-cyclopentene - 1,1-dicarboxylate by V.P.C.-separation and identification of the components.

Ethyl 2-vinylcyclopropane 1,1-dicarboxylate showed N.M.R. signals at the following τ values: 4.66(2H), olefinic, multiplet; 4.88(1H), olefinic, multiplet; 5.85(4H), ethyl methylene, quartet; 7.48(1H), methylyne, quartet; 8.48(2H), cyclopropane methylene, multiplet; and 8.78(6H),methyl, triplet.

Pyrolysis of the mixture of ethyl 2-vinylcyclopropane- and ethyl 3-cyclopentene- 1,1-dicarboxylates

The pyrolysis apparatus, basically a Pyrex tube filled with glass helices and inserted into a cylindrical electric furnace, has been described by Lam [111].

The optimum pyrolysis temperature was found to be between 400-410°C.

A 2:1 mixture of the two 1,1-diesters (31.0 g) was pyrolysed at 400°C and carrier-gas flow (He) of 25 ml/min. in 1.1/2 hours. A dark liquid (25.7 g, 83%) was collected by condensing the vapours at dry ice-acetone temperature.

This liquid was fractionated on a spinning band distillation apparatus to obtain the following fractions:

(a) several products of undesirable rearrangements, combined weight 8.5 g (33%)

(b) 14.6 g (57%) of a new mixture of the two starting 1,1-diesters. The major component of this mixture was ethyl 3-cyclopentene 1,1-dicarboxylate

(c) 2.6 g (10%) ethyl 3-cyclopentene 1,1-dicarboxylate, b.p. 92-93^{o}C at 2.07 mm (lit.[108] 85.5-87.5^{o}C at 21 mm).

Ethyl 3-cyclopentene 1,1-dicarboxylate had N.M.R signals at τ 4.50(2H), singlet; 5.92(4H), quartet; 7.10(4H), singlet; and 8.84(6H), triplet which were assigned to the two olefinic, the ethyl methylene, the cyclopentene methylene, and the methyl protons, respectively.

<u>Anal</u>.	Found:	C, 61.97;	H, 7.52
	Calc. for $C_{11}H_{16}O_4$;	C, 62.25;	H, 7.60

(D) Kinetic studies

1) The CO_2-evolution method

The decomposition of tert-butyl 7-norbornenyl percarboxylate and tert-butyl 7-norbornyl percarboxylate, in bromobenzene, was followed by monitoring the evolution of

CO_2 in an apparatus of three main units:

(a) vacuum line and gas burette

(b) reaction flask and magnetic stirrer

(c) constant temperature bath.

Fig. 1 is a schematic diagram of the vacuum line, which was of the conventional type with a gas burette attached to it. Capillary tubing was used to minimise the non-thermostatted volume of the vacuum line. The areas around all joints were wrapped in glass wool. A Fisher volumetric burette, readable to ± 0.05 ml, was used. It was surrounded by a glass jacket through which thermostatted water was pumped from a Labline circulating bath. The burette was filled with mercury and was connected to a mercury reservoir.

The reaction flask and magnetic stirrer part of the apparatus, together with photographs of its units, have been adequately described by Warkentin[112].

Fluctuation of temperature of the heating fluid (light paraffin oil) was restricted to ± 0.05°C. Temperature was measured with a set of Fisher U.S.A. thermometers which had been calibrated by the Physical Chemistry Laboratory of the National Research Council of Canada.

Time was read with an accuracy of ± 5 seconds.

Nitrogen, used in de-gassing the reaction system, was purified by passage through two gas-scrubbing bottles

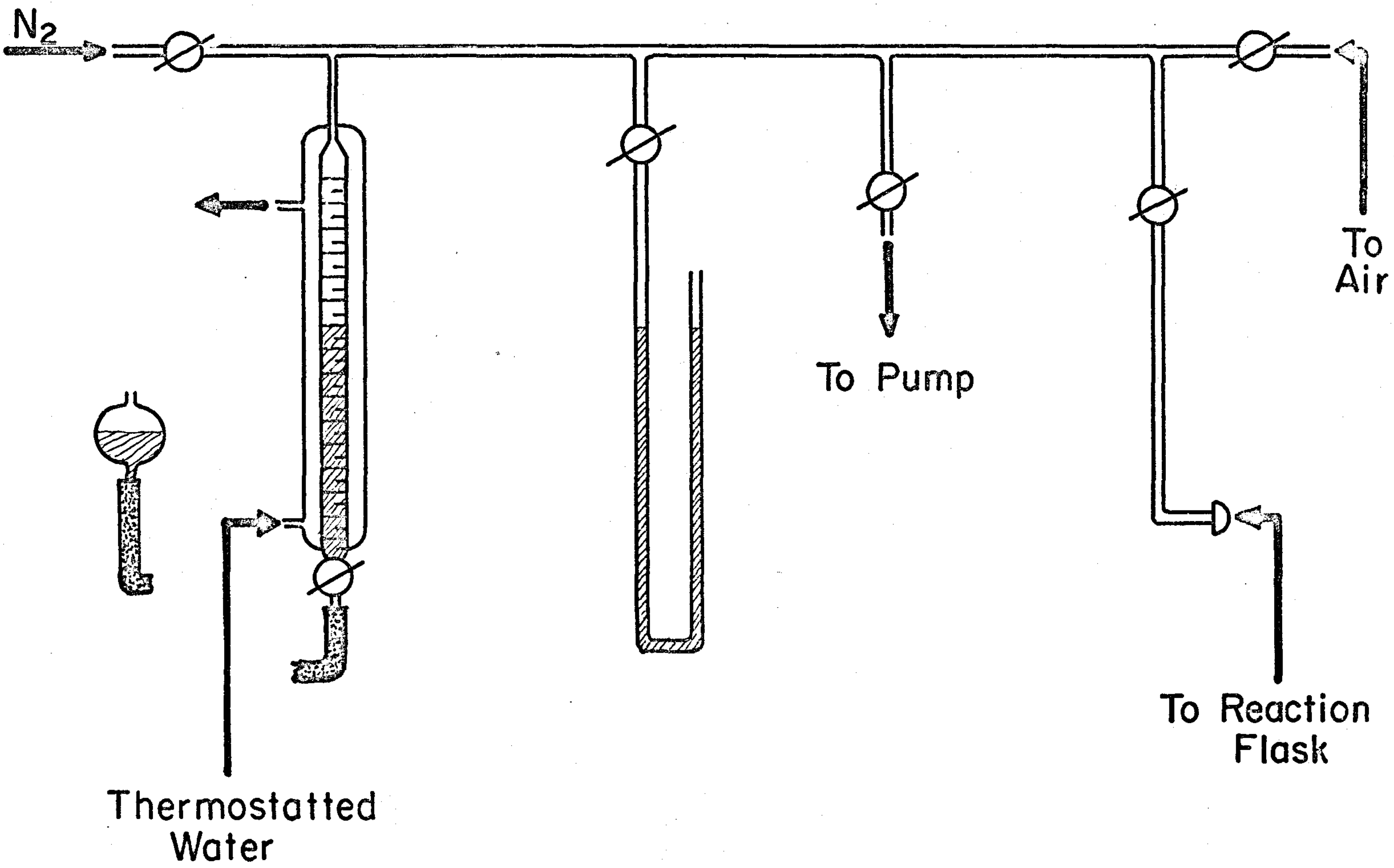


Figure 1. Apparatus for investigation of the kinetics of gas evolution.

of Fieser's solution [113], one of lead acetate solution and one of sulfuric acid, followed by a tube filled with KOH pellets.

Kinetic measurements were made on approximately 0.05 M solutions in bromobenzene. The solvent (50 ml) was placed in the reaction flask, the flask was attached to the vacuum line, followed by immersion in a dry ice-acetone bath. When the solvent was frozen the system was evacuated, then partially filled with nitrogen. The bromobenzene was then allowed to thaw in the partial vacuum. This freeze-thaw cycle was repeated two more times, after which the flask was lowered into the constant temperature bath.

Internal pressure of the closed system was adjusted to one atmosphere, stirring was started (1200-1400 r.p.m.) and, when solvent temperature reached equilibrium with the bath temperature, a weighed quantity of perester was injected. Volume readings were taken by adjusting the pressure to slightly less than one atmosphere and recording both reaction time and volume of CO_2 at the moment when the internal pressure equalled atmospheric again.

Since the pressure differential was never more than 2 mm, error due to imperfect liquid-vapour equilibrium should be small. This assumption was justified by the low value of 'chi-squared'[114] (0.01-0.03) calculated for each run.

The reactions followed clean first order kinetics. Reproducibility of rate constants was tested through the plot of k/T versus 1/T for each perester which gave excellent straight lines.

Reactions were followed to 'infinity', i.e. to practically complete decomposition. Together with the knowledge of Vo (volume-reading at t_o), this made it possible to determine directly the percentage of CO_2 that evolved during reaction.

2) The N.M.R. method

When tert-butyl syn-7-norbornene percarboxylate was decomposed in the CO_2-evolution apparatus, no CO_2 was detected. A new method of following the kinetics of its decomposition had therefore to be found.

Decomposition of the perester in an acetic acid solution containing excess KI and titration of the iodine liberated, against a standard solution of sodium thiosulfate, was the first such method attempted. The procedure of Traylor[115], with some minor variations, was followed. It proved to be unreliable, especially for data beyond one half-life of the reaction. The titration end-point was also often very difficult to find accurately, thus this method of kinetic analysis had to be abandoned.

It was found that the N.M.R. absorption pattern of the perester, in bromobenzene, changed in a regular fashion in the course of its homolysis. In particular, the triplet at 4.22τ gradually disappeared while a new singlet of increasing intensity appeared at 8.25τ. This new peak was shown to be due to acetone, one of the fragmentation products of the tert-butoxy radical[116].

A weighed amount of tert-butyl 7-norbornene percarboxylate (about 200 mg), a few drops of the internal standard hexamethyldisiloxane, and 1 ml bromobenzene were placed in a N.M.R. sample tube. The tube was immersed into a dry ice-acetone bath and the frozen solution was pumped down for 10 minutes after which the tube was sealed.

The sample tube was immersed in the heating bath thermostatted at the reaction temperature. It was withdrawn at regular intervals, the reaction stopped by quick cooling, and the N.M.R. spectrum was scanned at room temperature. The signals of acetone and of the standard were also integrated each time, usually five or seven times in succession, and the average values were used in calculating the rate constant.

A correction of one minute was added to the reaction time, recorded by the stopwatch, each time the solution was withdrawn from the bath. This correction is necessary to compensate for the finite time required for the tube and contents to reach the reaction temperature after each immersion. The one minute interval was established empirically by placing a thermometer in a thin-walled test tube that was immersed in the bath and noting the time it took for the thermometer to register the temperature of the bath.

The perester decomposed with good first order kinetics.

Accuracy of this method of kinetic analysis is limited by the degree of sensitivity of the instrument to small changes in the acetone peak-area. Sensitivity of the integral recorder of the A-60 instrument may be estimated to be ± 4-5%.

The main drawback of the N.M.R. method is that relatively large samples are required for the kinetic runs which may, in some cases, introduce serious concentration effects such as induced decompositions.

3) Attempted use of the IR-absorption method.

A commonly employed method [59,64] of following the rate of decomposition of peresters involves measurement of the decrease in length of the perester carbonyl absorption peak at 5.65 μ. Its great advantage is that it only requires a small amount of perester and that peak lengths can be determined to within ± 1%.

For the method to be applicable to the decomposition of a given perester, one of two conditions must be met:

(a) no decomposition product should absorb in the region scanned (5.5-5.8 μ). This usually restricts use of the IR method to peresters that decompose by a concerted pathway

(b) for a non-concerted process, the product that does absorb in the above frequency-region must be identified, its yield and rate of appearance accurately determined [64].

All three peresters prepared for the purpose of the present investigation decomposed by non-concerted processes. Also, the product mixtures obtained from their decomposition were too complicated for identification of any but a few individual components.

Thermal homolysis of tert-butyl anti-7-norbornane percarboxylate, in Fisher spectroanalytical grade cyclohexane and n-heptane, was followed by the IR-method. Liquid cells, 1.0 mm and also 0.5 mm in thickness, with NaCl windows were employed.

The reaction showed first order kinetics only up to approximately one half-life. For this, and the previously discussed reasons, no further use of the IR-method was made.

(E) Product studies

1) Measurement of CO_2 yield

Carbon dioxide yields were determined for two of the peresters; tert-butyl anti-7-norbornene percarboxylate and tert-butyl 7-norbornane percarboxylate, from the known values of the (a) number of moles of perester decomposed, and (b) number of moles of CO_2 evolved, using the $PV = nRT$ relationship.

Two different methods were employed to obtain values of V, the volume of CO_2 evolved. The first of these involved plotting gas-burette readings against reaction time and extrapolating the curve for V_o and V_∞. In the other method, the values of V_o and V_∞ were calculated employing a non-linear least squares computer program recently described by Singleton [117]. Agreement between the two methods was within ± 2%.

The accuracy of the CO_2 yield measurement is estimated to be ± 5%.

Mass spectroscopic analysis of a sample of gas taken from the gas burette revealed the presence of only carbon dioxide and nitrogen. No solvent, oxygen, or volatile organic products were detected.

2) Decomposition products from tert-butyl 7-norbornane percarboxylate

Since the kinetic measurements were made on dilute bromobenzene solutions (0.05M) of the perester, the first task after its complete decomposition was to effectively separate the small amount of products from a large volume of solvent. Solutions from four kinetic runs were combined and slowly distilled through an 8" x ½" helices-packed column under vacuum.

The solvent fraction was carefully redistilled from the spinning band apparatus and all fractions up to the boiling point of bromobenzene were collected. These fractions, b.p. 50-95°C, were combined and examined by N.M.R., V.P.C., and I.R. Acetone was the only product that could be identified. No tert-butanol was detected, although the tert-butyl group was found to be present both in the I.R. and N.M.R. spectrum of the mixture.

The residue, 1.16 g or 70% of the original weight of perester, was a yellow oily material which partially crystallized on cooling. It was chromatographed on a silica gel column made from a slurry of 200 g Matheson chromatographic-grade silica gel in pentane. The column was eluted with pentane (600 ml), 50% pentane-50% chloroform (500 ml), chloroform (500 ml), and methanol (600 ml). Two main groups of productswere obtained:

(a) compounds whose I.R. spectra indicate the presence of carbonyl groups. Total amount of these products was 0.54 g or 56% of the 7-carboxynorbornene present in the original perester. Together with the 40% yield of CO_2 this accounts for practically all the carbonyl of the parent perester

(b) products without carbonyl groups comprised the other half (0.54 g) of the fractions collected.

The main component (0.38 g) of group (a) proved to be 7-norbornane carboxylic acid, m.p. 69-74°C (lit.[44] 77.5-78.5°C). Its N.M.R., I.R. and mass spectrum matched that of the carboxylic acid from which the perester was made. Almost all the rest of this group (0.13 g) was a high-boiling viscous oil of dark brown color. The N.M.R. spectrum of this oil indicated the presence of the bicyclic ring system; it had multiplets at τ 7.58, 8.52, and 8.80. There were two carbonyl absorptions at 5.80 μ and 5.88 μ in the I.R. spectrum of the oil, suggesting that it was a mixture of at least two components.

Most of the compounds of group (b) could not be characterised with any degree of certainty. They may be divided into two sub-groups of compounds depending on the solvent that was used to elute them from the column.

The pentane-eluted fraction (0.14 g) was a colorless liquid, a mixture of at least three closely related compounds as indicated by its V.P.C. analysis at 250°C. All available evidence suggests that these compounds were combination products of the bromobenzene and the norbornyl radicals. The following I.R. absorption peaks, characteristic of aromatic carbon-carbon and carbon-hydrogen vibrations[106], were present: 3.30 μ(w-m), 3.51 μ(m), 6.24 μ(m), 6.40 μ(m), 6.8 μ(s), and 6.90 μ(s). No tert-butyl absorption was detected. In the N.M.R. spectrum of the fraction there were multiplets in the aromatic proton region (τ 2.88), in the bridge-bridgehead region (τ 7.16, 7.42, and 7.56), and in the bicyclic methylene proton region (τ 8.55). Two molecular ion peaks, at M_1 = 252 and M_2 = 250, of approximately equal height and an intense peak at m/e = 171 (i.e. M_1-81 or M_2-79) appeared in the mass spectrum of the mixture. By comparison, the natural abundance ratio of the bromine isotopes ^{79}Br:^{81}Br is 100:97.9 or almost 1:1[118].

The chloroform-eluted fraction (0.35 g) was a yellow oil. It was shown to be a mixture of at least 13 compounds by V.P.C. analysis (200°C). Four of these compounds were sufficiently different from the others to permit collection of their vapours for the mass spectrograph. However, the mass spectra of these components were quite complicated and uninformative. The I.R. and N.M.R.

absorption pattern of the chloroform-eluted fraction was similar to that of the pentane-eluted mixture of compounds.

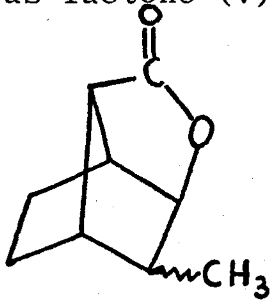
3) Decomposition products from tert-butyl syn-7-norbornene percarboxylate

The contents of one of the N.M.R. tubes was tested for the presence or absence of acetone and tert-butanol. Addition of acetone considerably increased the peak area τ 8.20, the rate of appearance of which was monitored in the decomposition. Thus in the N.M.R. method of kinetic analysis the evolution of acetone from the tert-butoxy radical was followed. Another strong signal was present at τ 8.85 (singlet), possibly due to a tert-butyl ether, but the OH proton signal of tert-butanol (τ 6.55 in bromobenzene) was absent.

The solvent was distilled off and the residue, weight 83% of that of the starting perester, was chromatographed. Silica gel chromatography proved to be entirely unsatisfactory. A new column was made from 200 g of a 50-50 mixture of celite and animal charcoal powder. A portion of the residue (0.492) was eluted from this column by the following solvents: cyclohexane (800 ml), 10% chloroform-90% cyclohexane (500 ml), 25% chloroform-75% cyclohexane (1600 ml), 40% chloroform-60% cyclohexane (800 ml), 50% chloroform-50% cyclohexane (600 ml), 70% chloroform-30% cyclohexane (1500 ml), 80% chloroform-20% cyclohexane (1000 ml), chloroform (900 ml), and benzene (600 ml).

Over 30 fractions of compounds were collected. Their I.R. spectrum indicated that they were various mixtures of mainly two carbonyl compounds, one absorbing in the lactone region (5.65 μ) and the other at 5.85 μ, and a number of minor components. The two carbonyl compounds were present in the residue before chromatography in the ratio of approximately 2:1.

None of the above compounds was positively identified, although there are strong indications that the major component was lactone (v) of formula $C_9H_{12}O_2$:



(v)

Its N.M.R. spectrum had a multiplet at τ 7.60, another multiplet at τ 8.38, and a singlet at τ 8.84 which may be assigned to the bridgehead and bridge protons, the methylene protons, and the methyl protons of the lactone, respectively. There were no spectral lines above m/e = 152 in the mass spectrum of the compound.

4) Product mixture from tert-butyl anti-7-norbornene percarboxylate

Decomposition of the perester in pentane, for the purpose of product studies, was hoped to facilitate isolation of practically all products.

A sealed heavy walled glass tube, containing 2.0 g perester dissolved in 20 ml pentane, was placed in a metal cylinder and was kept under 30 p.s.i. pressure. The metal cylinder and contents were heated at 110°C for 3 days in a muffle furnace.

Vapour phase chromatography of the residue (1.4 g), after evaporation of the solvent at atmospheric pressure, revealed that it was a complicated mixture of at least sixteen components. Six of these were collected in sufficient quantity for a mass spectroscopic examination. None of the components could be identified.

(F) Test for concerted or stepwise perester decomposition

The Hammond-Soffer reagent was employed to capture the $RCO_2\cdot$ radical that forms in a non-concerted perester decomposition.

A heavy walled and sealed reaction vessel, depicted in Fig. 2, was used in testing the homolysis of tert-butyl anti-7-norbornene percarboxylate. The reaction mixture was introduced through the side arm, was de-gassed, and the

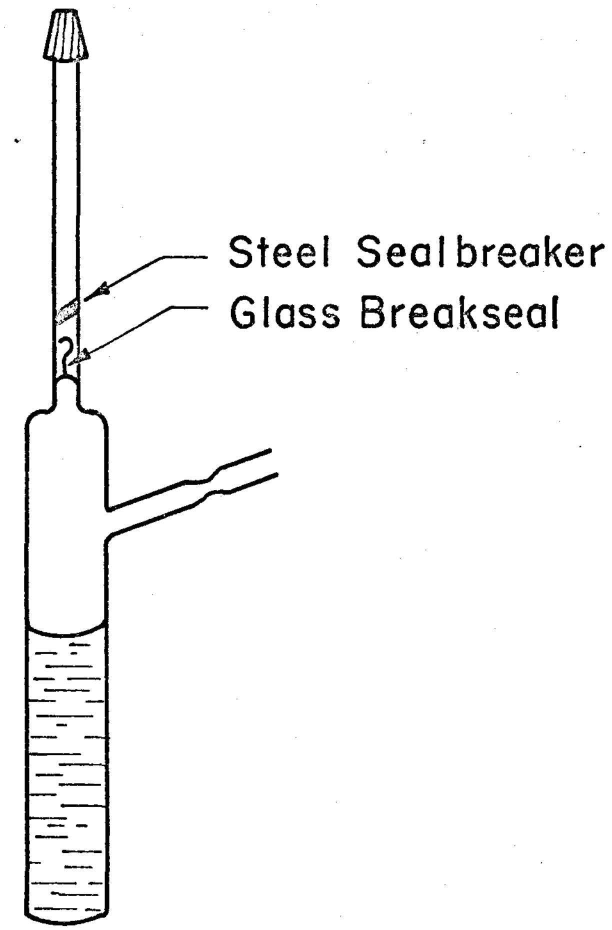


Figure 2. Reaction vessel for testing concerted perester decompositions.

vessel was sealed under vacuum. Decomposition was allowed to proceed for 24 hours at 105°C.

All volatile products were frozen out by immersing the sealed tube in a cooling bath kept at approximately -20°C. A weighed tube packed with Ascarite was attached, the break-seal was broken, and the system was left undisturbed for 4 hours before re-weighing the Ascarite-filled tube.

It was not necessary to test the homolysis of the saturated perester once the decomposition of the anti perester was found to be non-concerted.

(G) Determination of pK_a of RCO_2H, where R = 7-norbornyl, syn- and anti- 7-norbornenyl

The technique employed was that of Van Uitert and Haas [119]. A Radiometer-Copenhagen 4C pH meter, a saturated calomel electrode (Beckman) and low pH glass electrode (Beckman 41263) were used.

All measurements were made at 24.8 ± 0.1°C. The pH meter was standardized against a standard buffer solution (Beckman 3506). Titrations were conducted in an atmosphere of nitrogen.

Commerical grade dioxane was purified by refluxing over sodium and fractional distillation from a 1 meter Vigreaux column.

Standard solutions of perchloric acid (0.01N) and of sodium hydroxide (0.1N) were employed. The perchloric acid solution contained the necessary amount of $NaClO_4$ to maintain an ionic strength of 0.1 μ throughout the reaction.

The acid RCO_2H was dissolved in a solution of 50.0 ml purified dioxane and 50.0 ml 0.01N $HClO_4/NaClO_4$, and the 50% dioxane-50% water solvent composition was maintained throughout the titration by adding equal volumes of 0.1N sodium hydroxide and dioxane.

The error of this method of pK_a-determination is not greater than $\pm$ 1%.

(H) Treatment of data

1) Kinetic measurements

For the non-concerted homolytic decomposition of a perester, RCO_3R', the slowest step is the rupture of O-O -bond. The radicals $RCO_2\cdot$ and $R'O\cdot$ thus formed are relatively high energy species and rapidly undergo complex product-forming reactions. The first order rate constant for appearance of any one of the products is the rate constant for the first step. Of the many products formed, the ones most conveniently monitored were CO_2 and acetone.

For the process illustrated by the following equations (in which the slow first step is followed by a number of concurrent fast steps):

$$RCO_3C(CH_3)_3 \xrightarrow[slow]{k_1} RCO_2\cdot + (CH_3)_3CO\cdot$$

$$RCO_2\cdot \xrightarrow[fast]{k_2} R\cdot + CO_2$$

$$RCO_2\cdot \xrightarrow[fast]{k_3} P_1$$

$$(CH_3)_3CO\cdot \xrightarrow[fast]{k_4} \text{acetone} + CH_3\cdot$$

etc.,

the desired rate constant (k_1) may be obtained from the conventional first order rate expression

$$\log_e \frac{a}{(a-x)} = k_1 t$$

in which $a = \left[RCO_3C(CH_3)_3\right]^o$ is the initial perester concentration and $(a-x) = \left[RCO_3C(CH_3)_3\right]^t$ is the perester concentration at time t.

Following the concentration of, say, CO_2 instead, one obtains

$$b = \left[CO_2\right]^{\infty} \equiv (k_2/k_2+k_3+\cdot\cdot)a \quad \text{and}$$

$$(b-x) = \left[CO_2\right]^{t} \equiv (k_2/k_2+k_3+\cdot\cdot)a-x.$$

Therefore plotting 2.303 $\log_{10} \frac{b}{(b-x)}$ versus reaction time is equivalent to plotting 2.303 $\log_{10} \frac{a}{(a-x)}$ versus t, since the yield factor $(k_2/k_2+k_3+\cdot\cdot)$ cancels out regardless of the number of steps competing for the intermediate $RCO_2\cdot$ radical. Similar reasoning leads to the same result with $c = \left[\text{acetone}\right]^{\infty}$

or any of the products of perester decomposition.

In the N.M.R. method of following the reaction c and x are proportional to P_∞ and P_t respectively, where P_∞ is the integrated peak-area of acetone after completion of the decomposition and P_t is the peak-area at time t. Therefore,

$$\log_e \frac{P_\infty}{P_\infty - P_t} = k_1 t,$$

and the plot of P_t against t should obey the expression $P_t = P_\infty(1 - \exp(-k_1 t))$.

Similarly, for the CO_2-evolution method, b is proportional to V_∞ (gas burette reading at the end of the reaction) and x is proportional to V_t. Here, however, V_t has to be corrected for the fact that the initial mercury-level in the gas burette is seldom at 0.00 ml but at a finite value (V_o). Hence the rate expression becomes $V_t = V_o + V_\infty(1 - \exp(-k_1 t))$.

Values of P_∞ and V_∞ were determined directly for each run by allowing the reaction to proceed to practically complete decomposition, i.e. to at least five or six half-lives.

The experimental data were fed into a non-linear least squares Fortran IV program developed for use with the I.B.M.-7040 computer[117]. This program was designed to fit the data to the expressions derived above and calculate the best values of all parameters for a given kinetic run. In addition, the program calculated the standard errors for these parameters; e.g. for V_o, V_∞, and k_1 for a CO_2-evolution run, thus providing a convenient check on the accuracy of the experimental data.

The rate constants were also determined plotting V_t or P_t against reaction time from which $t_{\frac{1}{2}}$, the half-life for the reaction, can be obtained directly. The half-life of a first order reaction is related to its rate constant by the following expression:

$$t_{\frac{1}{2}} = \frac{\log_e 2}{k_1}$$

Agreement between rate constants calculated by the two methods was extremely good, within 1-3%, except when data up to only approximately two half-lives were fed into the program. This points out the main limitation of a least squares program; its accuracy sharply diminishes when the number of experimental points in the near-infinity region decreases.

The individual rate constants are estimated to be accurate to ±3% for the CO_2-evolution method and to ±3-5% for the N.M.R. method. Since usually only one rate constant was determined for a particular set of conditions, a statistical analysis of the accuracy of rate constants could not be carried out.

2) Calculation of activation parameters

Calculations were based on the equation

$$k = (KT/h)\ \exp.(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/T),$$

derived from transition state theory, where K is Boltzmann's constant, T is the reaction temperature in ^{o}K, h is Planck's constant, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation parameters.

Taking natural logarithms, and rearranging, the above equation becomes

$$\log_e k/T - \log_e K/h = \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT,$$

where R = 1.987 cal/degree/mole, and $\log_e K/h$ is equal to 23.759.

Therefore, a graph of $\log_e k/T$ against $-(1/T)$ should be a straight line, the slope of which is $\Delta H^{\ddagger}/R$, and the intercept of which is $23.759 + \Delta S^{\ddagger}/R$.

A computer program was again employed to calculate the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ from the experimental rate and temperature data.

A least-squares analysis of the probable error in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could not be carried out due to the limited number of kinetic runs available for each perester. The method of analysis developed by Petersen et al [120] was therefore employed, using the following equations:

$$\delta = 2\ R\alpha\left[T'T/(T'-T)\right] \text{ cal/mole, and}$$

$$\sigma = \delta\left[1/T + (T'-T)/2T'T\right] \text{ e.u.},$$

where δ and σ are the maximum probable error in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ respectively, R is the gas constant, α is the estimated fractional limit of error in k (the rate constant), and (T'-T) is the temperature interval within which the rate of decomposition of a given perester was measured.

3) Calculation of acid dissociation constants (pK_a)

The following equilibria are satisfied throughout the titration of a 50% dioxane - 50% water solution of a weak acid HA, in an excess of the strong acid $HClO_4$, against the strong base NaOH:

$$[H^+][OH^-] = K_w \qquad (1)$$

$$\frac{[H^+][A^-]}{[HA]} = K_a \qquad (2)$$

$$[HA] + [A^-] = L \qquad (3)$$

where K_w and K_a are the dissociation constants (in 50% dioxane - 50% water) of water and of the weak acid under investigation, and L is the known concentration of the weak acid. The object is to determine the value of K_a, which may be done conveniently following the method employed by VanUitert and Haas [119] in the determination of the dissociation constants of a number of inorganic complexes.

From expressions (2) and (3) L can be rewritten as (4)

$$L = \frac{K_a + [H^+]}{K_a}[A^-] , \qquad (4)$$

where both L and $[H^+]$ are experimentally measurable quantities, while $[A^-]$ cannot be determined directly. Therefore another expression has to be developed for K_a, in terms of measurable quantities.

Such an expression is that for P, defined by equation (5)

$$P = \frac{[HA]}{L} , \qquad (5)$$

i.e. for the fraction of undissociated acid that is present throughout the titration. Its value at any time during titration is determined in the following way:

(a) at the endpoint of the titration, when both the weak and the strong acid have been neutralised, the ion-balance is as shown by (6)

$$[H^+] + [Na^+] = [ClO_4^-] + [OH^-] + [A^-] \qquad (6)$$

or by expression (7), since $[Na^+] = [ClO_4^-]$ for all practical purposes

$$[H^+] = [OH^-] + [A^-] \qquad (7)$$

(b) at any time before the endpoint a modified expression (8) is valid

$$T + \left[H^+\right] = \left[OH^-\right] + \left[A^-\right] , \qquad (8)$$

where T is measurable, and is concentration of unreacted $HClO_4$ present in the solution after addition of each successive portion of NaOH

(c) from (1), (8) and (3) one obtains equation (9)

$$P = 1 - \frac{\left[H^+\right] + T - K_w/\left[H^+\right]}{L} . \qquad (9)$$

All quantities on the right hand side of equation (9) are experimentally measurable; $\left[H^+\right]$ is measured as the pH of the solution, T and L can be calculated since the total volume of the solution is accurately known, and K_w has been determined for a 50% dioxane-50% water solution [121].

When $P = \frac{1}{2}$ and $T = 0$, relationship (10) holds

$$H^+ = K_w/\left[H^+\right] = L/2 \qquad (10)$$

Using equations (1), (2) and (7), equation (10) becomes

$$(K_a + \left[H^+\right])/K_a = 2$$

$$\text{or} \quad \left[H^+\right] = K_a, \text{ i.e. } pH = pK_a .$$

A computer program was employed to calculate the value of P for each separate pH-meter reading and corresponding total volume of solution. These P values were plotted against the pH readings and the pH at $P = \frac{1}{2}$ was taken to be the pK_a of the carboxylic acid.

The error of this method of pK_a determination is estimated to be $\pm$ 0.05 pK_a-units.

Results and Discussion

The results of Bartlett and co-workers clearly showed that the thermal decomposition of a tert-butyl perester, RCO_3R', tends to be concerted when the radical R· formed in the reaction is stabilized. It was expected that the 7-norbornenyl radical, formed by the decomposition of tert-butyl anti-7-norbornenyl percarboxylate, might be such a stabilized species. There was some indication [50] that a nonclassical 7-norbornenyl radical does exist, contrary to the conclusions of Zimmerman and Zweig from calculations on a so-called "half-migrated" radical.

It was hoped that the kinetics of and the products from the thermal homolysis of the three selected peresters might shed some light on the extent of stabilization of this elusive radical [48,71].

From the data of the present investigation two main conclusions can be reached;

(a) thermal homolysis of the 7-norbornene- and norbornane- peresters is non-concerted, i.e. the radical R· is not formed in the rate determining step,

(b) the norbornene double bond exerts a measurable influence on the transition state of the rate determining peroxide 0-0 bond fission.

(A) Rate determining oxygen - oxygen bond fission

In a concerted one-step perester homolysis the two radicals R· and R'O· form concurrently with CO_2. A quantitative yield of CO_2 is therefore indicative of a concerted mechanism, while a partial yield means that at least part of the reaction is non-concerted.

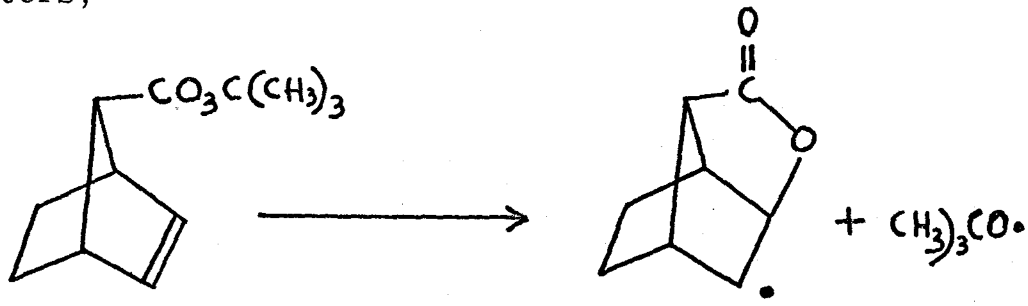
Table I lists the yields of CO_2 obtained by the CO_2-evolution method. The numbers are averages of three determinations, in bromobenzene at different temperatures, except in the case of the syn-perester where only one measurement was made.

Table I

YIELDS OF CARBON DIOXIDE IN BROMOBENZENE

Compound	% Yield of CO_2
tert-butyl anti-7-norbornene percarboxylate	52
tert-butyl syn-7-norbornene percarboxylate	0
tert-butyl 7-norbornane percarboxylate	40

There was no CO_2 evolved from the syn-perester, as anticipated from the results of Martin and De Jongh [64] who obtained only a low CO_2 yield from tert-butyl endo-2-bicyclo 2.2.1 hept-5-ene percarboxylate. Intramolecular attack by the carboxylate radical on the double bond, the process that was found to be responsible for the reduced CO_2 yield in the above compound, may be responsible for this. The process may also be a concerted one (vi), as will be seen from the discussion of activation parameters;



(vi)

The other two peresters reacted by a two-step mechanism. This was shown by decomposing tert-butyl anti-7-norbornene percarboxylate, in bromobenzene, in the presence of the Hammond-Soffer reagent. The yield of CO_2 was reduced to 6% which is negligible in view of the ±5% experimental error of the method used. A similar experiment was not carried out on the saturated perester because it would be difficult to see how its mechanism of decomposition would differ from that established for the anti-7-norbornene perester.

Since the two peresters that can theoretically provide π-electron assistance decompose by a rate-determining peroxide-oxygen bond fission, it must be concluded that in their homolysis there is no anchimerically assisted formation of the 7-norbornene radical. A more general statement, i.e. that formation of the 7-norbornene radical cannot be assisted anchimerically by the double bond, cannot be made at the present time. Further work, using systems such as the azonorbornenes or perhaps the norbornene tosylhydrazones where there are no two alternative radical pathways available, would be required before this problem may be answered.

It is interesting to compare the results of Table I with those of Martin and De Jongh. They obtained quantitative CO_2 yields from all 2-norbornene and 2-norbornane peresters, with the exception of the 2-endo norbornene perester discussed previously. Also, all four compounds decomposed by a concerted, but unassisted, formation of the 2-norbornane or 2-norbornene radical. These results suggest that there is a great deal of difference between the stabilities of the 2-norbornene and 7-norbornene radicals as well as between the 2-norbornane and 7-norbornane radicals. The reluctance of other norbornane and norbornene compounds to form C7 free radicals was also noted by Kooyman and Vegter [48], who explained it in terms of the highly strained Cl-C7-C4 bond angle.

(B) Polar contribution at the transition state of the homolytic O-O bond fission

The unsaturated peresters have rates and activation parameters different from those of the saturated compound, as can be seen from Tables II-VI:

Table II

RATE CONSTANTS FOR THE DECOMPOSITION OF TERT-BUTYL 7-NORBORNANE PERCARBOXYLATE

Solvent	Concentration, moles/liter	Temperature °C	$k \times 10^4 \sec^{-1}$
Bromobenzene	0.034	102.6	0.629 ±0.009*
Cumene	0.036	103.6	0.59 ±0.01
Bromobenzene	0.030	108.6	1.34 ±0.04
Bromobenzene	0.033	108.6	1.36 ±0.02
Bromobenzene	0.040	117.8	3.98 ±0.08

* errors in k were standard deviations obtained from the computer program.

Table III

RATE CONSTANTS FOR THE DECOMPOSITION OF TERT-BUTYL SYN-7-NORBORNENE PERCARBOXYLATE IN BROMOBENZENE

Concentration, moles/liter	Temperature °C	$k \times 10^4 sec^{-1}$
0.83	88.4	0.46 ±0.01
0.83	95.1	0.92 ±0.03
1.10	100.4	1.56 ±0.05
0.25	100.4	1.45 ±0.04
0.78	102.6	1.93 ±0.07

Table IV

RATE CONSTANTS FOR THE DECOMPOSITION OF TERT-BUTYL ANTI-7-NORBORNENE PERCARBOXYLATE IN BROMOBENZENE

Concentration moles/liter	Temperature °C	$k \times 10^4 sec^{-1}$
0.054	98.8	1.05 ±0.02
0.052	105.0	2.15 ±0.04
0.059	110.0	3.57 ±0.05

Table V

COMPARISON OF RATE CONSTANTS, IN BROMOBENZENE, AT 102.6°C

Compound	Concentration moles/liter	$k \times 10^4 \sec^{-1}$	Rate Factor
tert-butyl norbornane percarboxylate	0.034	0.628 ±0.009	1.00
tert-butyl syn-7-norbornene percarboxylate	0.78	1.93 ±0.07	3.08
tert-butyl anti-7-norbornene percarboxylate	0.05	1.63*	2.59

* rate constant calculated using data from plot of $\log_{10} k/T$ versus $1/T$

Table VI

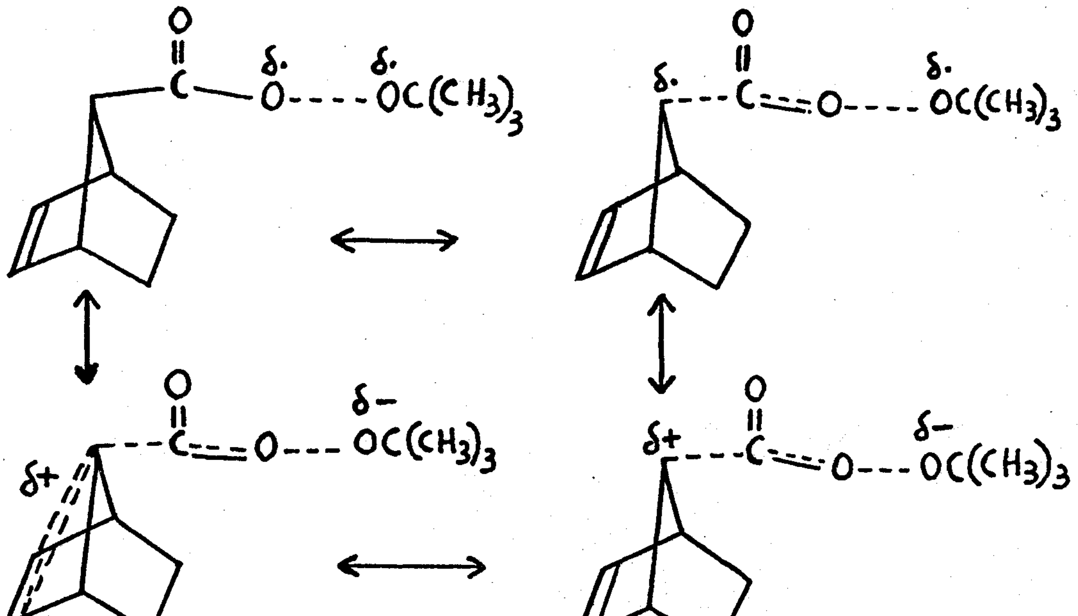
ACTIVATION PARAMETERS FOR PERESTER DECOMPOSITION IN BROMOBENZENE

Compound	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
tert-butyl 7-norbornane percarboxylate	33.6 ±1.3	11 ±3
tert-butyl syn-7-norbornene percarboxylate	26.3 ±1.9	-7 ±2
tert-butyl anti-7-norbornene percarboxylate	30.3 ±1.2	4 ±2

While the rates of decomposition are not significantly different (Table V) for the three peresters, their enthalpy of activation differ by as much as 7 kcal/mole and the entropies of activation by approximately 18 e.u.

Homolysis of the saturated perester is the slowest of the three; the enthalpy of activation is close to 35 kcal/mole and the entropy of activation is large and positive.

The anti-perester has a slightly faster rate of decomposition than the saturated compound and, apparently, lower activation parameters. This result could be accommodated if the transition state of its homolytic cleavage were a hybrid of radical and polar "contributing structures", depicted in (vii)



(vii),

in which the well-documented [2,19,20] positive charge-stabilizing ability of 7-norbornene is utilised. This polar contribution, first postulated by Bartlett [61,124] for some tert-butyl peresters whose R-groups can form resonance stabilized carbonium-ions, may ease attainment of a lower energy transition state without committing the system to continue toward heterolysis, especially in non-polar media, or full separation of the C-C bond. Such a transition state could achieve its lower $\Delta H^{\ddagger}$ only at the expense of increased order, that is by 'freezing out' rotation of the bond between carbonyl carbon and oxygen and by having a more rigid skeleton, which would explain the more negative $\Delta S^{\ddagger}$ for the anti-perester in comparison with that of the saturated compound.

Decomposition of the syn 7-norbornene perester is the fastest of the three; its activation parameters are also significantly different. Polar (cationic) contribution to the stability of the transition state cannot be solely responsible for these results because Winstein and co-workers [19] have shown that the rate of acetolysis of syn 7-norbornene tosylate is 10^6-times slower than that of the anti isomer. It is postulated that attainment of the lower energy transition state is brought about mainly by anchimeric assistance, i.e. by bonding interaction between perester O-O bond and π-electrons, and only partially by 'polar contribution'. The net accelerating effect of this additional factor is the sum of two opposing influences: (a) it lowers $\Delta H^{\ddagger}$, and (b) at the same time if further increases skeletal rigidity of the transition state (more negative $\Delta S^{\ddagger}$).

Participation of the olefinic double bond in homolytic O-O bond scission has been observed by several groups of investigators [64,128,129]. For example, Lamb and coworkers [129] reported that the rate of thermal decomposition of trans-γ-benzylidenebutyryl peroxide is 4.9 times faster (in 90% CCl_4-10% styrene) than that of δ-phenylvaleryl peroxide. Martin and Koenig [130] found even greater acceleration in the decomposition of some tert-butyl o-vinyl-substituted perbenzoates. Their results were shown to be compatible with homolysis through a transition state that has polar 'contributing structures'.

Induced decomposition reactions, that could effect the rates and activation parameters of individual peresters to a different degree, cannot be used to explain the results in Tables V-VI. It is generally agreed [64,65] that in cumene induced reactions are unimportant because the solvent is an effective scavenger for the tert-butoxy radicals. Yet the saturated perester decomposed in cumene only 16% slower than in bromobenzene, at similar concentrations. Also, when the initial concentration (in bromobenzene) of the syn-perester was decreased four-fold the rate constant at 100.4°C was lowered by only 7%.

(C) Perester decomposition products

Free radical reactions often produce complex product mixtures. It was not therefore surprising to find that both the volatile and non-volatile perester decomposition products were multi-component mixtures the constituents of which, with the exception of 7-norbornane carboxylic acid from the saturated perester, could not be identified. The nature of the rate-determining step, however, has already been established from other evidence for each perester and an exhaustive product study could not have provided much new information, except perhaps about whether or not the loss of CO_2 from $RCO_2\cdot$ was assisted by the double bond in one of the subsequent fast product-forming steps.

Among the several volatile products from each perester only acetone could be identified from its V.P.C. retention time, I.R. and N.M.R. spectrum. Tert-butyl alcohol was not detected.

The non-volatile product mixture of the saturated perester was relatively more simple than that of the others. If contained 39-mole percent 7-norbornane carboxylic acid as the only product positively identified. This, combined with the 40% yield of CO_2, accounts for the majority of the perester carbonyl. Some other products, described in the Experimental section, were only tentively identified.

The syn-perester decomposition products were also numerous. The majority of them showed I.R. absorption in the 5.6-5.7 μ region, suggesting that they were lactones. Careful chromatography using a 50% celite-50% animal charcoal column failed to separate these products.

Vapour phase chromatography indicated that the products from the anti-perester also formed a complex mixture.

(D) Alternate routes to the preparation of 7-norbornene carboxylic acids. The direction of ring enlargement of 1,1-dicarbethoxy-2-vinylcyclopropane

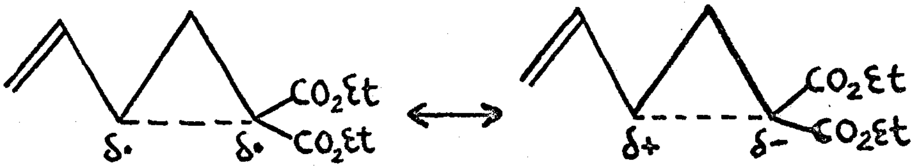
A mixture of syn- and anti- 7-norbornene carboxylic acid can be prepared, in a low overall yield, by the Grignard reaction on the extremely toxic syn-7-bromonorbornene. Several investigations have been made to find improved methods for the preparation of these two acids [104,122].

We first attempted cyanide ion displacement on anti-7-chloronorbornene and subsequent hydrolysis to the acids. This method, however, provided only a small amount of a mixture of two amides.

Another possible approach, that holds more promise, is the synthesis of 7,7-dicarbethoxy norbornene from 1,1-dicarbethoxy cyclopentadiene. As a first step towards this goal, a new method of preparation of 1,1-dicarbethoxy cyclopent-3-ene has been found which involves the vapour phase rearrangement of 1,1-dicarbethoxy-2-vinylcyclopropane.

The probable mechanism of this pyrolytic rearrangement is worth a brief mention. Rearrangements of vinylcyclopropanes to cyclopentenes are generally considered to be concerted "valence isomerisations"[125] in which mixtures of cyclopent-2-enes and cyclopent-3-enes may be produced. Breslow[126] suggested that for some vinylcyclopropanes, which have substituents capable of stabilising a 1,3-diradical intermediate, the reorganisation of the molecule need not involve simultaneous bond making and bond breaking. His prediction was recently confirmed by Ketley et al[127] who found that the sole product in the vapour phase pyrolysis of 1,1-dichloro-2-vinylcyclopropane (at 200-275°) was 1,1-dichlorocyclopent-3-ene, a fact which strongly suggests a 1,3-diradical pathway for the rearrangement. Our result represents another example of a preferred 1,3-diradical mechanism in the pyrolysis of a suitably substituted vinylcyclopropane.

It seems also possible that the transition state for the observed direction of homolytic carbon-carbon bond fission is a resonance hybrid of radical and polar 'contributing structures', as in (viii),



(viii)

both of which are capable of further resonance-stabilisation.

(E) 7-norbornene- and norbornane- acid dissociation constants

The pK_a value of each carboxylic acid, in 50% dioxane-50% water, was determined to obtain some information about what kind, if any, of interaction exists between the olefinic π-electrons and the carboxylic function. It was already seen that in 7-norbornene perester decomposition the double bond exerts a measurable rate-accelerating effect. If the same type of interaction influenced acid dissociation, it would be expected to be acid weakening.

Table VII shows that the actual effect of the C=C bond is acid strengthening, especially when it is anti- to the carboxyl group:

Table VII

ACID DISSOCIATION CONSTANTS IN
50% DIOXANE-50% WATER

Acid	pK_a Value
7-norbornane carboxylic acid(a)	6.63 ±0.05*
syn-7-norbornene carboxylic acid	6.57 ±0.05
anti-7-norbornene carboxylic acid(b)	6.33 ±0.05

* the error of ±0.05 pK_a units is an estimated value

(a) the acid contained 2.2% of the syn-unsaturated acid

(b) the acid was contaminated by 2.6% of the syn-isomer

No satisfactory explanation for the above results is offered at the present time. It is likely that more could be learned about the apparent acid strengthening effect of the C=C bond by measuring the pK_a-values of some other norbornane- and norbornene- carboxylic acids, such as exo- and endo- bicyclo [2.2.1] hept-5-ene-2-carboxylic acid, etc.

In general, there is a scarcity of pK_a-data in 50%(v/v)dioxane-50% water available in the literature.

Summary

The tert-butyl peresters of syn- and anti-7-norbornene-, and of 7-norbornane-carboxylic acid were prepared and their thermal decomposition was studied by the CO_2-evolution and the N.M.R. techniques. It was shown that each compound decomposes by a mechanism in which the rate determining step is rupture of the perester 0-0 bond. Thus the present kinetic investigation cannot give an answer to the possible existence of a nonclassical 7-norbornene radical.

The rates and activation parameters of the unsaturated peresters are different from those of the saturated compound. It is suggested that at the transition state of the anti-perester the C7 carbon atom has some cationic character and that some overlap exists between its p-orbital and the π-orbital of the double bond. A more effective overlap is envisaged at the syn-perester transition state and it may be direct, nonclassical interaction between the π-electrons and the partially empty oxygen 2_p-orbital of considerably greater electronegativity.

Attempts were made to find alternative, more effective routes to the synthesis of 7-norbornene carboxylic acids.

The pK_a-values, in 50% dioxane-50% water, of syn- and anti- 7-norbornene and of 7-norbornane carboxylic acid were measured. The anti insaturated acid was found to be somewhat stronger than the other two which are of about equal acidity. This order of acidities is not readily interpreted in terms of interactions involving π-electrons either in the (ground state) acid form or in the acid anion.

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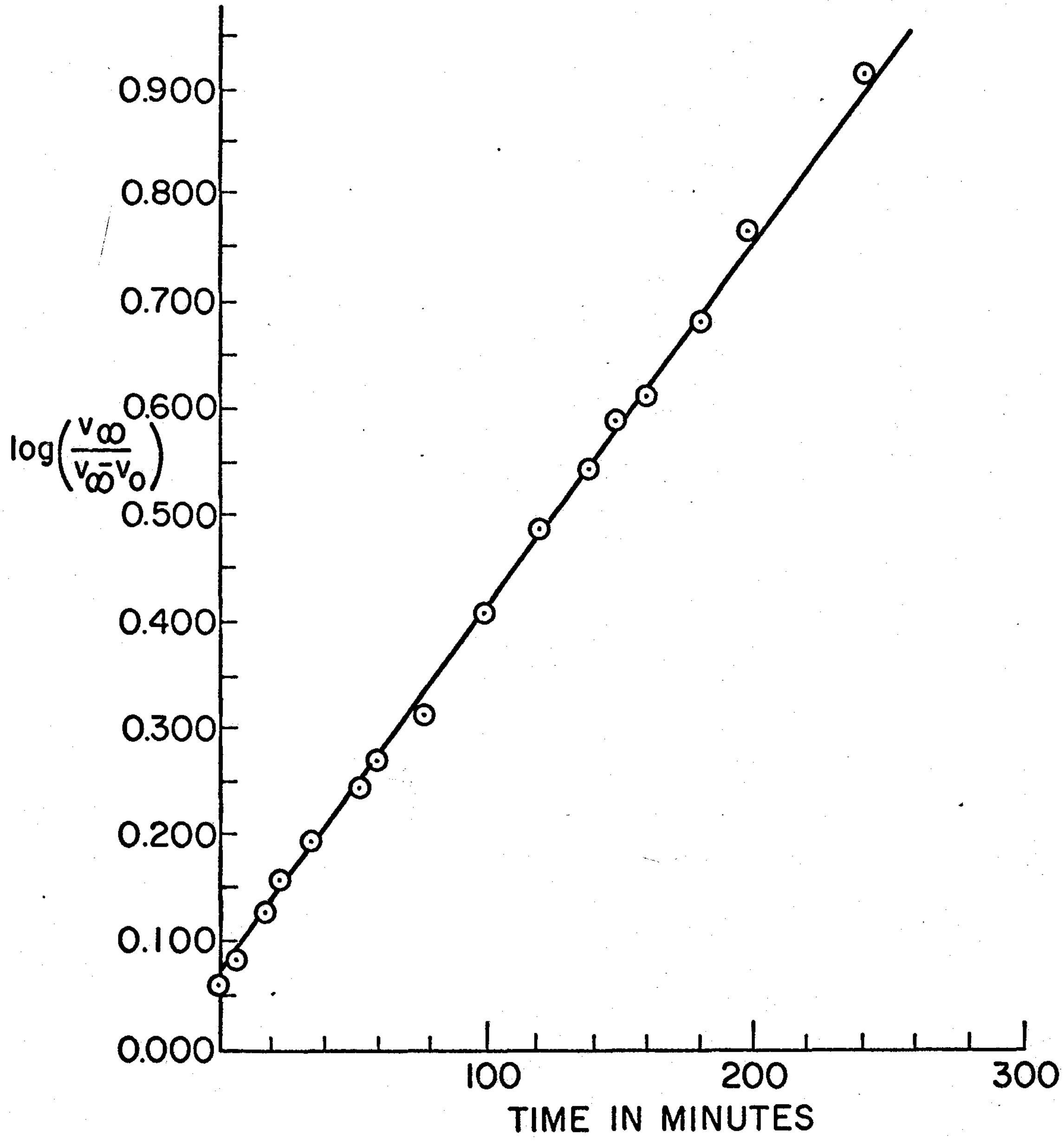

Figure 3. A representative plot of kinetic data obtained by the CO_2-evolution method (norbornane perester, in C_6H_5Br, 108.6°C).

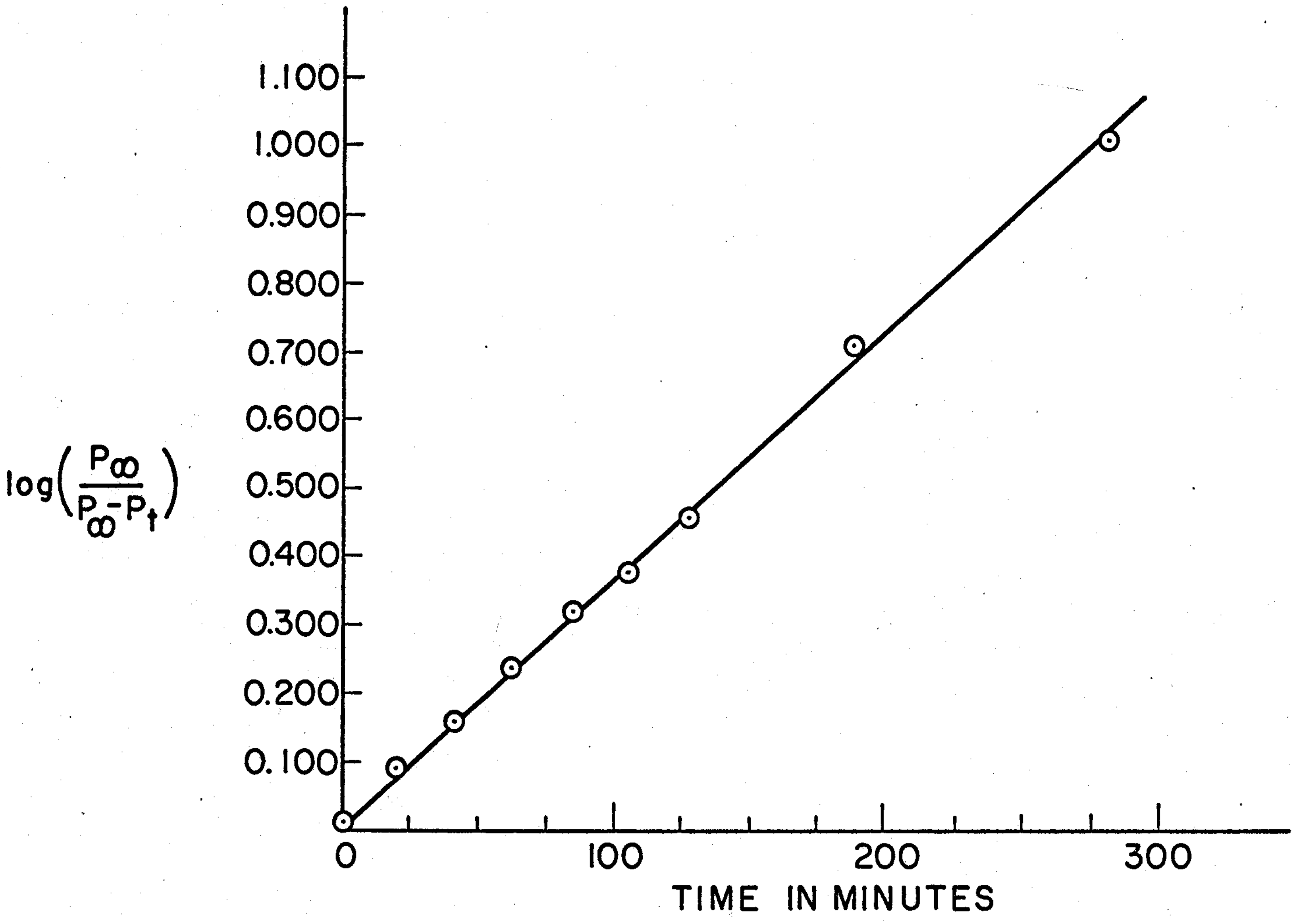

Figure 4. A representative plot of kinetic data obtained by the N.M.R.-method (syn norbornene peresters, C_6H_5Br, 100.4°C).

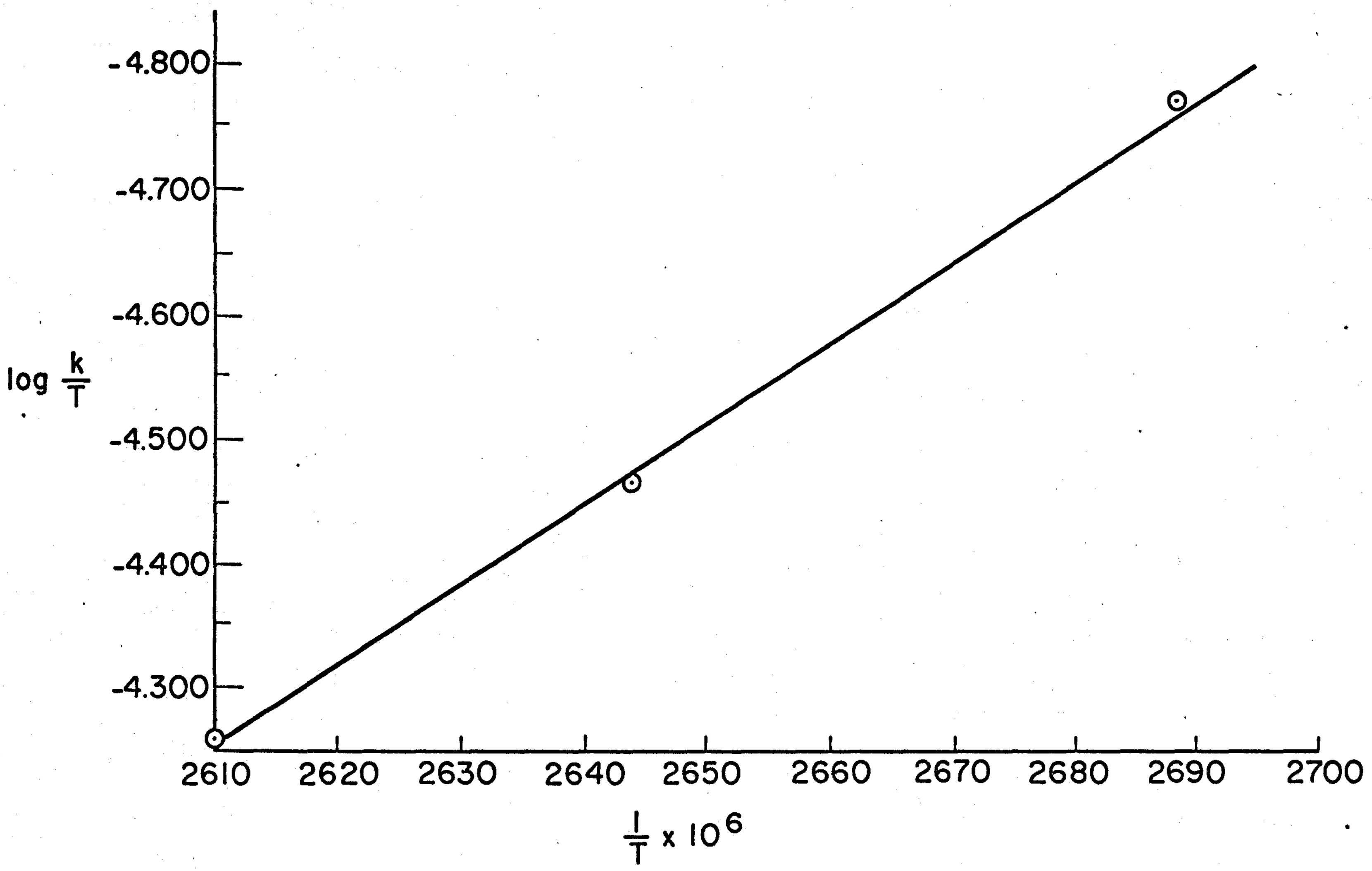

Figure 5. Representative graph of log(k/T) versus (1/T) for the decomposition of the anti-norbornene isomer (in C_6H_5Br).