IDENTIFICATION AND DECAY KINETICS OF o-XYLYLENES

IDENTIFICATION AND DECAY KINETICS OF PHOTOGENERATED o-XYLYLENES

By

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ABSTRACT

The thesis consists of two parts, which have been combined in the Introduction and Discussion sections.

Part A. Isoindenes

Transient isoindenes absorbing in the 400-550 nm range have been observed in the flash photolysis of a series of 1,1-diarylindenes. They have been studied by ultraviolet spectroscopy, low temperature nmr, chemical trapping, and flash photolysis techniques. Irradiation of 1,1,3-triphenylindene at 254 nm in cyclopentane at -70°C gives an orange solution (λ_{max} 478 nm) which contains 1,2,3-triphenylisoindene whose methine and vinylic proton resonances in the nmr occur at 4.45 and 6.80 ppm respectively. Reaction of 1,2,3-triphenylisoindene with 4-phenyl-1,2,4-triazoline-3,5-dione at -70°C, gave a Diels-Alder adduct. The isoindene formed 1,2,3-triphenylindene quantitatively on warming to 20°C. The kinetics of the 1,5-hydrogen shift by which a series of isoindenes rearrange to stable indenes were studied by flash photolysis. The transient decay was first order, and rate constants (deoxygenated hexane, 20°C) are: 1,2-diphenylisoindene, 36 s^{-1}; 1-phenyl-2-p-cyanophenylisoindene, 14 s^{-1}; 1-phenyl-2-p-bromophenylisoindene, 27 s^{-1}; 1-phenyl-2-p-methoxyphenylisoindene, 44 s^{-1} and 1,2,3-triphenylisoindene, 1.21 s^{-1}. Kinetic isotope effects of k_H/k_D = 3.7 and 6.5 for the decay of 1,2,3-triphenylisoindene and 1,2-diphenylisoindene (2-H and 2-D) respectively show that the H- shift is rate determining. The 1,5-hydrogen shift in 1,2-diphenylisoindene has E_a = 13.1 kcal/mol and $\Delta S^{\circ\ddagger}$=-9.0 eu, and in 1,2,3-triphenylisoindene has E_a = 11.8 kcal/mol and $\Delta S^{\circ\ddagger}$ = -19.6 eu. The ground state energy of isoindene relative to indene is estimated to be 20 kcal/mol, which is compared with theoretically calculated values.

Part B. o-Xylylenes

o-Xylylene derivatives have been generated in the flash photolysis of four indan-2-ones. Thus, 1,1,3,3-tetramethylindan-2-one gives 7,7,8,8-tetramethyl-o-xylylene while 1,1-dimethylindan-2-one gives 7,7-dimethyl-o-xylylene. Both these transients decay (thermally and photochemically) by a 1,5-hydrogen shift to yield alkyl isopropenylbenzenes. The rates of thermal decay are 0.002 s^{-1} and 0.038 s^{-1}, for the tetra- and dimethyl compounds respectively, at ca. 20°C in deoxygenated hexane. The decay of tetramethyl-o-xylylene showed a kinetic isotope effect (k_H/k_D) of 5.4. Activation parameters were: E_a= 19 kcal/mol, $\Delta S^{\circ\ddagger}$= -7.7 eu (tetramethyl o-xylylene); E_a= 15.5 kcal/mol, $\Delta S^{\circ\ddagger}$=-13.9 eu (dimethyl-o-xylylene). Low temperature photolysis (-70°C, 254 nm) show absorption maxima at 350 nm, for the tetramethyl compound, and 360 nm for the dimethyl compound. Photolysis of 1,1,3,3-tetramethyl-4,5-benzindan-2-one gives the thermally stable 9,9,10,10-tetramethyl-1,2-naphthoquinodimethane, which decays photochemically to 1-isopropenyl-2-isopropylnaphthalene. A transient with a lifetime of about 1 μs could be observed in the flash photolysis of 1,1,3,3-tetramethyl-5,6-benzindan-2-one, which gives two photoproducts, 2-isopropyl-3-isopropenylnaphthalene and 3,3,4,4-tetramethylnaphtho[b]cyclobutene. The rates of thermal decay of the transients are consistent with thermochemical calculations. Spectroscopic evidence, together with theoretical calculations, indicates that the transients are twisted about the 'essential' single bonds of the non-aromatic ring, and cannot adopt the planar geometry necessary for the allowed suprafacial 1,5-H shift. This together with the photolability of the transients, suggests that the thermal decay may involve the previously unknown antarafacial 1,5-hydrogen shift.

ACKNOWLEDGEMENTS

The author thanks his research supervisor, Professor J.J. McCullough, for his guidance and encouragement, and Professor A.J. Yarwood and Dr. C. Manning for invaluable assistance with the flash photolysis experiments. It was a pleasure working with the other members of SS 467, Rod Miller, Keith MacInnis and Susan Vaitekunas. Thanks go to several faculty members and students for advice and stimulating discussions. Special thanks to Pauline Horridge for typing this manuscript. The author wishes to take this opportunity to thank the many interesting people encountered over the past few years in the university and elsewhere, who contributed to make his stay in Canada a pleasant and memorable one.

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INTRODUCTION

General

Organic photochemistry is the study of the interaction between compounds of carbon and electromagnetic radiation, generally in the near ultraviolet (200-400 nm) and visible (400-800 nm) regions. Examples of this interaction include photosynthesis, vision, bioluminescence, action of sunlight on organic environmental pollutants, and photochemotherapy. Hence, this is an area of wide applicability, deserving systematic study.

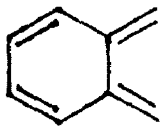
In order to react photochemically, a molecule should initially absorb light and thereby become promoted to a state of higher electronic energy, an "excited" state. Then, it may undergo a chemical transformation.

Considerable current interest has been focused on the detailed mechanisms of photoreactions. The technique of Flash Photolysis[1] developed by Nobel laureates Norrish and Porter has made a substantial contribution in this direction. In this technique, a reactant is irradiated with an intense flash of light, of duration shorter than that of ensuing reactions to be studied. The spectroscopic properties and concentrations of the resulting transient (intermediate) species can then be measured as a function of time, using physical methods of observation. Though originally applied solely for the study of free radicals in the gas phase, currently, the greatest activity is in organic reactions in solution. In principle, the investigator should observe the electronic excited states, free radicals, and all other intermediate stages in the photochemical transformation. In practice, this is rarely attained, due to short lifetimes, weak absorptions, and overlapping spectra. Some applications of this technique will be described in subsequent sections.

The next section reviews some recent work on o-xylylene and its derivatives. The last two sections deal with the two techniques used in the present work to generate derivatives of o-xylylene.

Biradicaloid hydrocarbons

o-Xylylene (1) can be represented as a resonance hybrid of the structures 1a - 1c, and it is considered to be a biradicaloid hydrocarbon. The adjective biradicaloid[2] is used to describe "those molecular geometries at which a simple molecular orbital picture of the species shows two approximately nonbonding molecular orbitals containing a total of two electrons in the ground state, irrespective of the nature of their distribution in the ground state".



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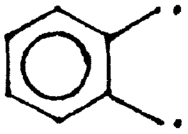
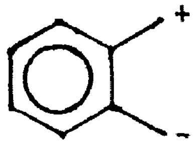


1a



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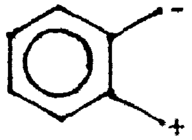
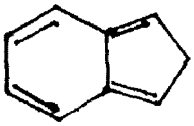


1c

In the Huckel molecular orbital approximation, o-xylylene has a HOMO-LUMO gap equal to 0.59 β (cf. butadiene, 1.24 β)[3]. Such biradicaloid species serve as good models for biradicals, which are an important class of intermediates in many thermal and photochemical reactions. Most molecules in the excited state possess biradicaloid geometries (e.g., the twisted form of ethylene), and at the time they return to the ground state, they would be expected to possess the same geometry, thus influencing the nature of the final products.[2]

There has been considerable recent interest in the structures and properties of o-xylylene and the related isoindene (2).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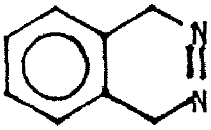
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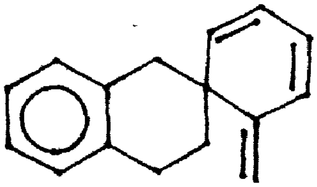
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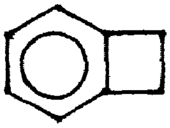
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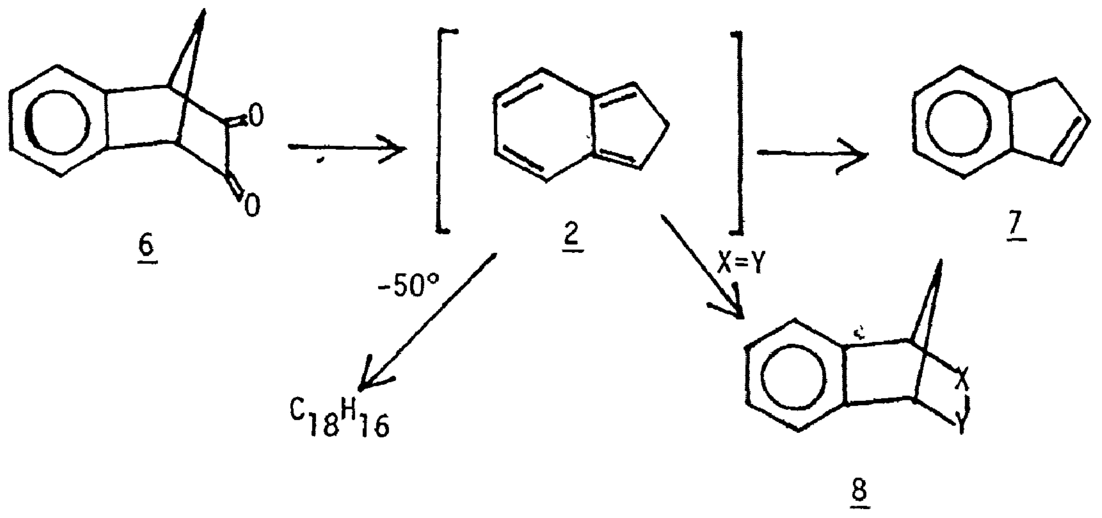
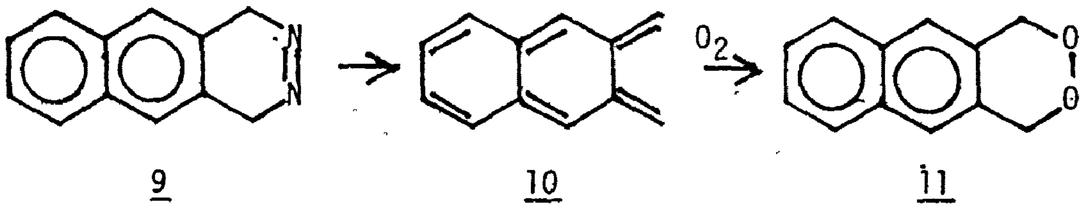
Theoretical calculations[4] on 1 show considerable biradical character at the terminal methylene groups. Michl and Flynn[2] generated 1 in an EPA (diethyl ether, isopentane and ethanol in a volume ratio of 5:5:2, respectively) matrix at 77K by the irradiation of 1,4-dihydrophthalazine (3). Its electronic spectra were accounted for by semiempirical π-electron calculations. It did not show a half-field electron paramagnetic resonance spectrum, indicating that it is a ground state singlet. It dimerised rapidly when the matrix softened, giving 4. Irradiation of 1 at -196° gave benzocyclobutene (5).

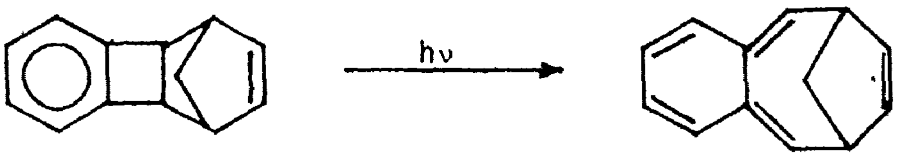
Isoindene (2) has not yet been isolated in a matrix. However, experiments to utilise the diketone 6 to generate isoindene in matrix isolation studies are currently in progress.[5] 6, upon irradiation at 254 nm, produced indene (7) in 70% yield. Irradiation in the presence of N-methyl maleimide gave the endo-adduct of type 8. Irradiation at -50° suppressed the formation of indene at the expense of dimerisation of the isoindene nucleus.[5]



The observation of naphthoquinodimethane 10 was first reported[6] in 1976. Thus, Gisin and Wirz[6] irradiated 9 in a rigid EPA matrix at 77K to give 2,3-naphthoquinodimethane (10). Its absorption spectrum (λ_{max} = 541 nm) and lack of emission were accounted for by theoretical calculations. Irradiation of 9 in the presence of air, produced the dioxin 11.



Some other types of reactions used to generate these biradicaloid species in matrix isolation studies, are the photochemical ring-opening of the benzocyclobutene 12[7], dehalogenation of the dihalide 14[8], and photolysis of o-xylene.[4g]



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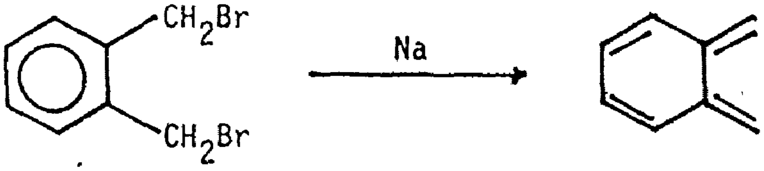
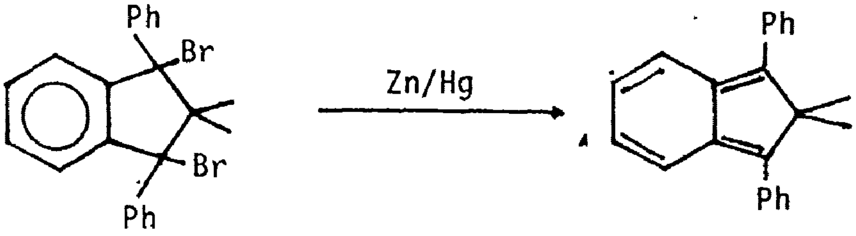


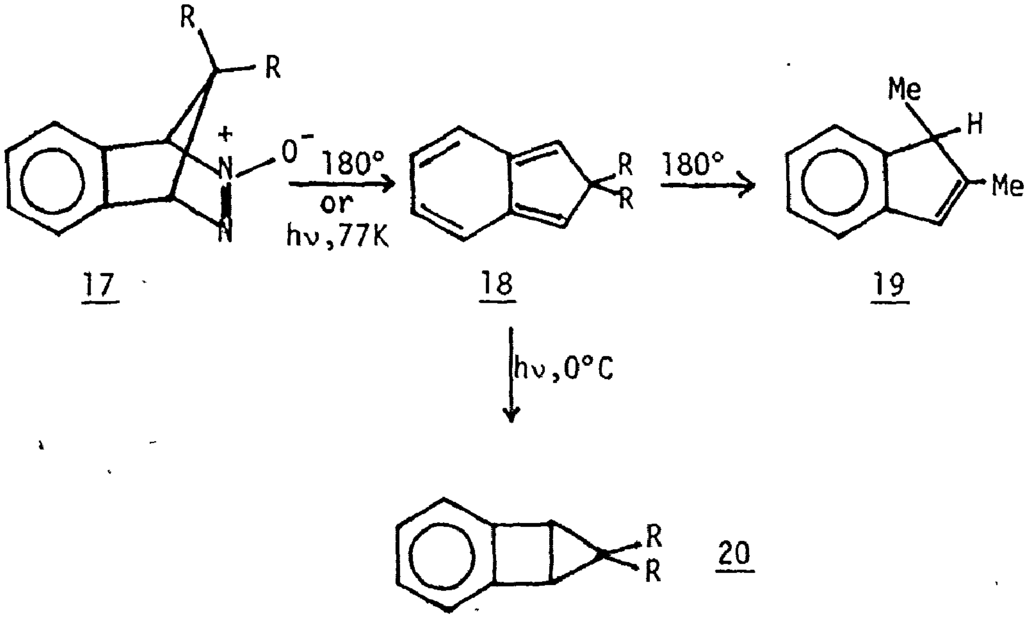
14 1

Some o-xylylenes have been isolated at ambient temperatures. Alder and Fremery[9] synthesised 1,3-diphenyl-2,2-dimethylisoindene (16) by the dehalogenation of 15. 16 was purified by distillation.

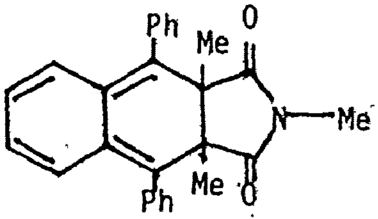


15 16

Michl, Dolbier and their co-workers[10] have studied 2,2-dialkylisoindenes of the type 18, which were synthesised by the thermolysis or photolysis of azoxy compound 17. 18 (R=Me) was indefinitely stable at room temperature in EPA solution. It aromatised by methyl migration at higher temperatures. Irradiation (λ > 285 nm) of 18 at temperatures below



0°C resulted in the benzobicyclopentene 20, which reverted to 18 upon warming to 20°. The stability of the 2,2-dialkylisoindenes indicate the higher activation energy for alkyl migration, compared to hydrogen. Jones and Kneen[11] have synthesised several sterically stabilised o-xylylenes of the type 21, where the phenyl substituents lie orthogonal to the o-xylylene system where they provide steric rather than conjugative stabilisation.



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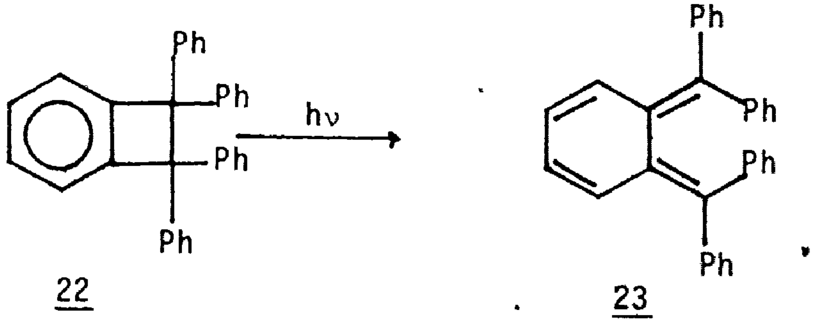
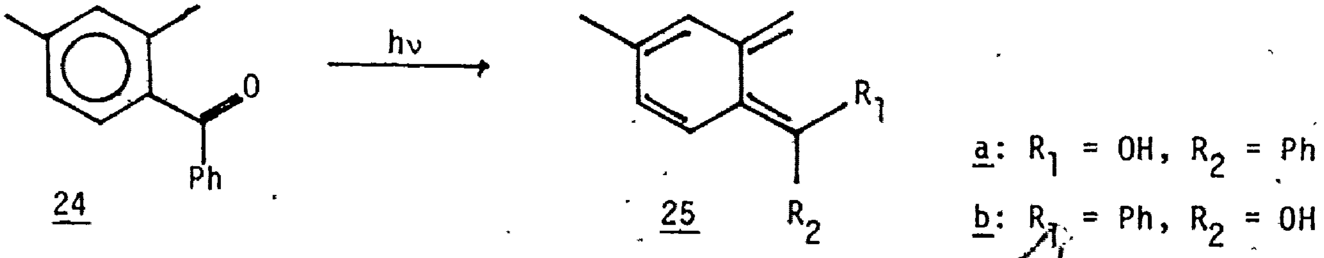
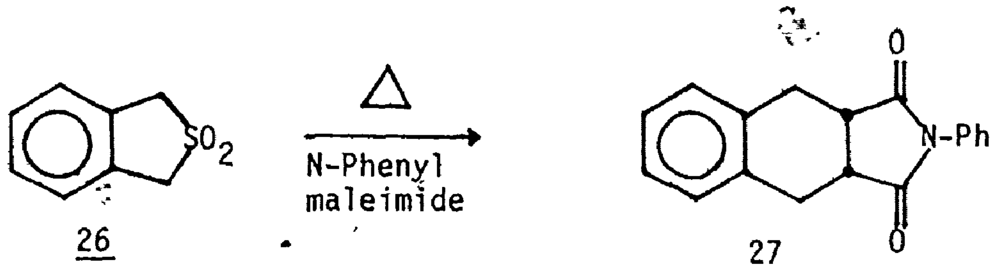
Flash photolysis has been used in detecting transient o-xylylenes. Quinkert et al.[12] observed the transitory 7,7,8,8-tetraphenyl-o-xylylene (23) in the flash photolysis of the benzocyclobutene (22). 23 cyclised rapidly to 22 (τ = 36 μs at 23°C).



Porter and Tchir[13] studied the photoenolisation of ortho-alkyl-substituted benzophenones by flash photolysis, and were able to observe the enol 25 arising from intramolecular hydrogen abstraction in the ketone excited state. 25a decayed to 24 with a lifetime of 3.9 s (ca. 20°C).



Chemical trapping has been widely used to indirectly show the intermediacy of o-xylylenes in various reactions. Thus, thermolysis of the sulfone 26[14], and irradiation of the styrene 28[15] and the benzophenone 30[16] in the presence of dienophiles, give rise to the adducts 27, 29 and 31 respectively.



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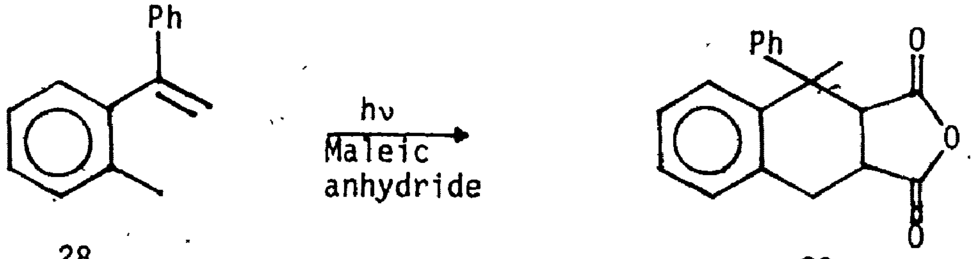

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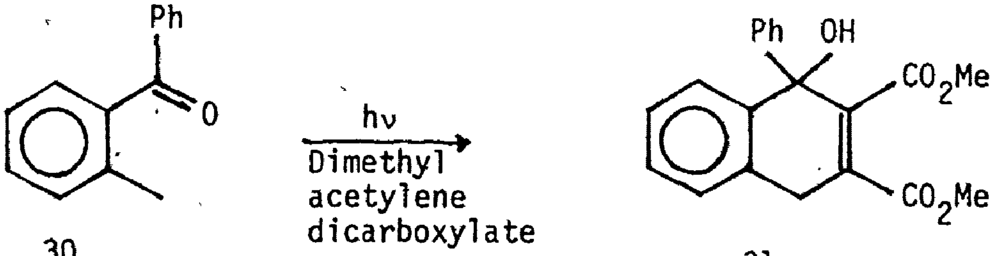

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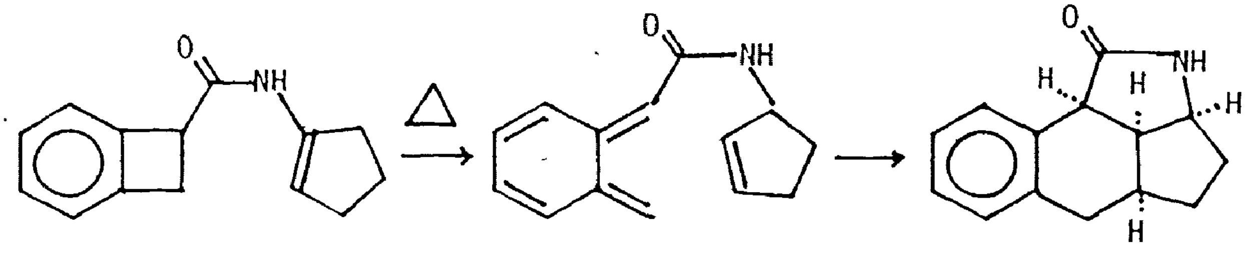
31

Two other major routes to o-xylylenes are the photodecarbonylation of indanones, and the rearrangements of the indene system. These two routes have been used in the present study, and will be discussed in detail in the next two sections of the introduction.

The synthetic utility of o-xylylenes is exemplified in the work of Oppolzer.[17] o-Xylylenes generated in situ. by the thermolysis of benzocyclobutenes have been used to synthesise condensed ring systems, with stereochemical control, via $(\pi^{4}s + \pi^{2}s)$ processes.[29]



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33

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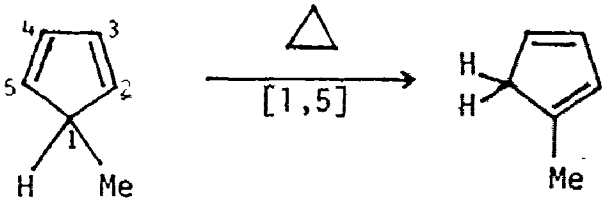
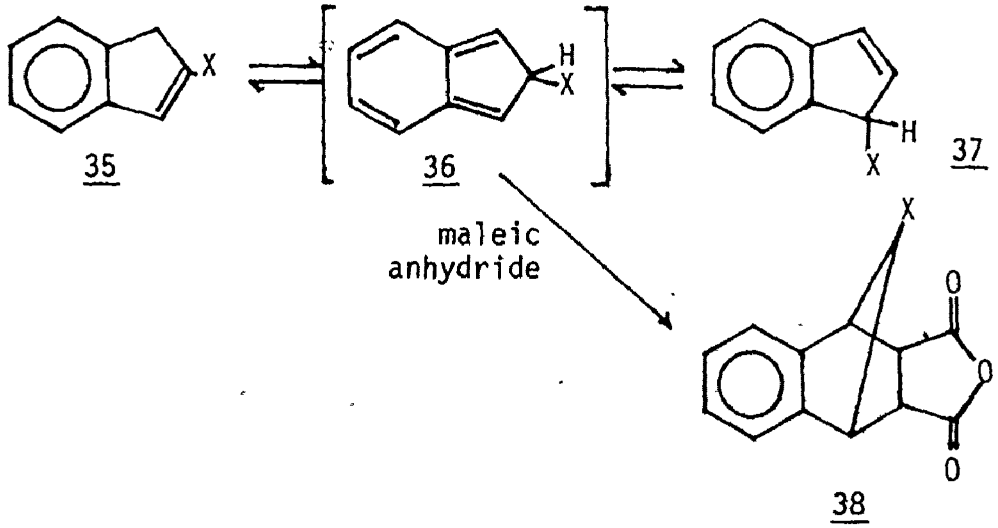
Rearrangements of the indene system

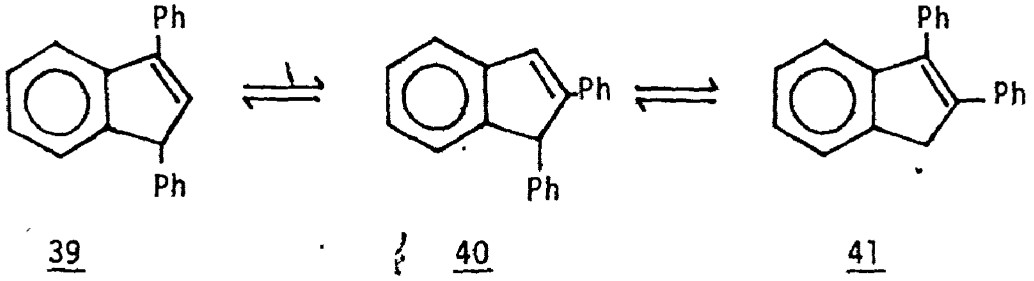
A sigmatropic reaction of order [i,j] is defined as the migration of a σ-bond, flanked by one or more π-electron systems, to a new position whose termini are (i-1) and (j-1) atoms removed from its original bonded loci, in an uncatalysed intramolecular process. For example, the rearrangement of 5-methylcyclopentadiene to 1-methylcyclopentadiene is a [1,5] sigmatropic shift.



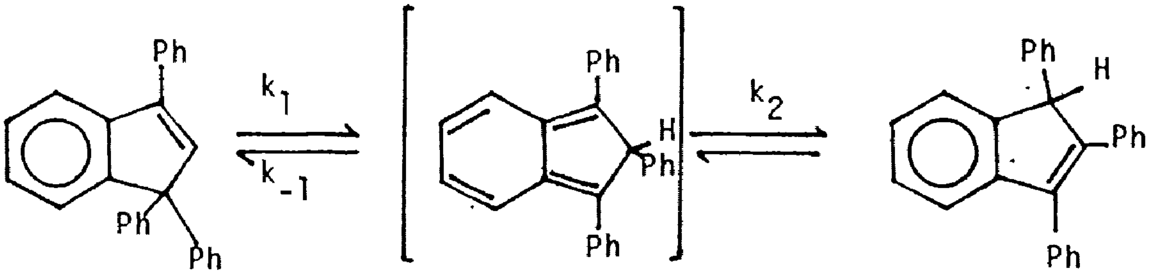
Invisible thermal rearrangements of indene were first revealed by Alder[18], who isolated the adduct 38 (X=H) in the thermal reaction between indene and maleic anhydride. A more comprehensive trapping study by Isaacs[19] showed that 2-deuterioindene 35 (X=D) produced a maleic anhydride adduct with ∿ 90% of the deuterium intact on the bridge methylene. These results are consistent with a mechanism where an isoindene intermediate 36 is formed from indene, by a formal [1,5] sigmatropic hydrogen shift.



The thermal rearrangements of phenyl substituted indenes were originally detected by Koelsch and Johnson[20] who equilibrated 1,3-, 1,2-, and 2,3-diphenylindene at 470°C.



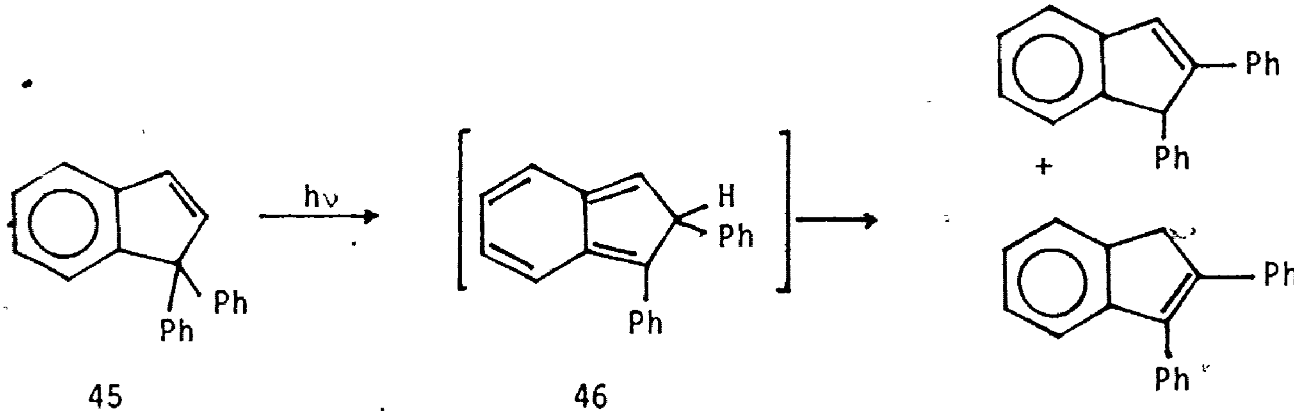
Miller[21] compared the migratory aptitudes of phenyl, hydrogen and methyl in the thermal rearrangement of these groups from the 1- to the 2-position of indene, and found them to be hydrogen > phenyl > methyl. Kinetic studies gave first order rates, unaffected by added acid, base, or free radical scavengers. The data were consistent with a sigmatropic shift, with $k_2 > k_{-1} > k_1$.



42 43 44

The migratory aptitude series was attributed to the greater bridging capability of hydrogen, compared to carbon, in the transition state leading to the isoindene.

McCullough[22] studied the photochemical rearrangement of 1,1-diphenylindene (45) to the two products 40 and 41 in the ratio 1:3. In this case,

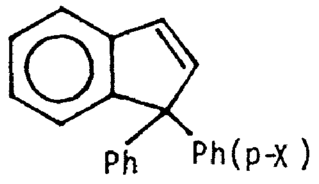


45 46 40 41

the postulated isoindene 46, which would form by an excited state phenyl migration, would further react by a thermal hydrogen shift to give the isolated products.

McCullough and McClory[23] studied the migratory aptitudes of substituted aryl groups in the diphenylindenes 47a-c in an attempt to probe the structure of the transition state leading to the isoindene. Both

ind and



47

a, X = Br

b, X = CN

c, X = OMe

The product mixture was treated with diethylamine in pyridine to convert the 1,2- to the 2,3-isomers, and the ratio, of products arising from p-X-phenyl migration to phenyl migration, was measured. In every case, preferential migration of the substituted phenyl group was noted (Table 1).

TABLE 1

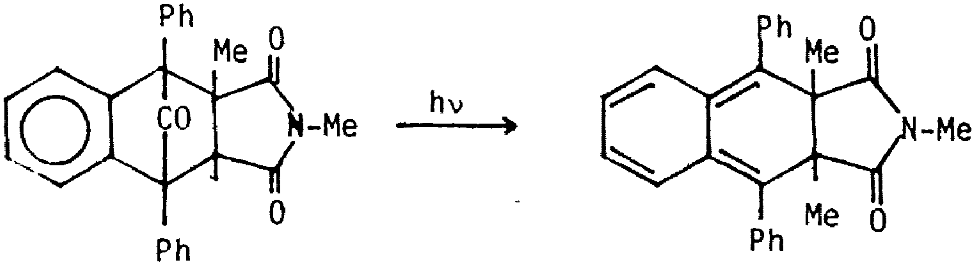
	X	Ratio (X-Ph/Ph)
Excited State	CN	98: 2
	Br	86:14
	OMe	95: 5
Ground State	CN	82:18
	Br	52:48
	OMe	50:50

Strikingly, the excited state process was more selective (favouring migration of p-X Ph) than the ground state process. These results were interpreted in terms of charge-transfer interactions which are more important in the excited state. Such interactions between the nonconjugated chromophores in the excited state of 47 could make the substituted group the better migrator.

The photochemical studies described above assume the intermediacy of isoindenes. Part of the present work is concerned with verifying this assumption.

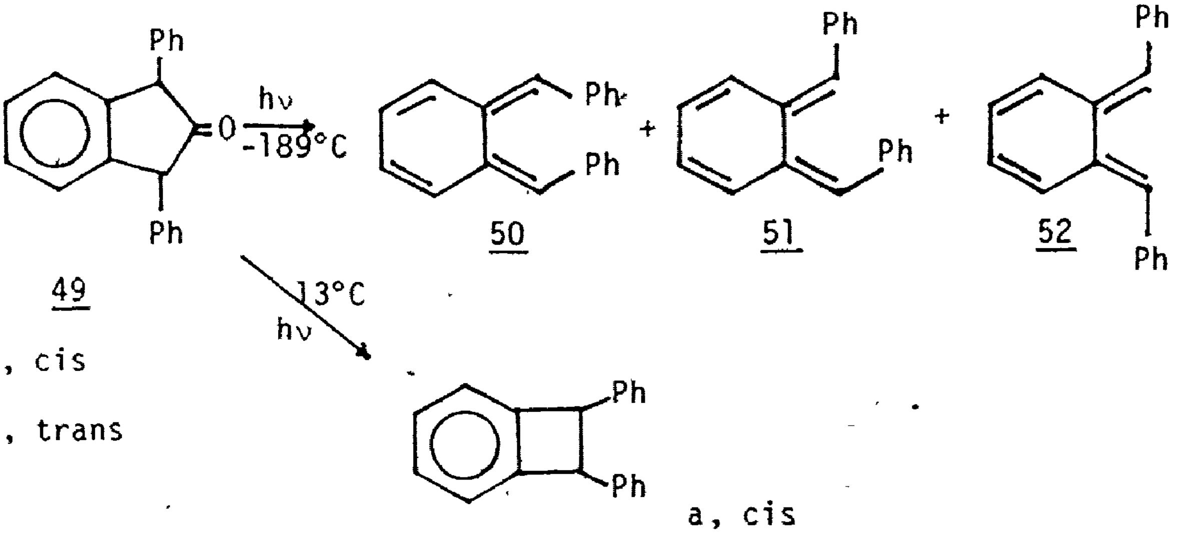
Photodecarbonylation of indan-2-ones

Irradiation of indan-2-one derivatives results in the efficient extrusion of carbon monoxide to give substituted o-xylylenes. For example, Jones and Kneen[11] prepared the stable o-xylylene 21 by photodecarbonylation of 48.



48 21

Quinkert et al.[24] irradiated the diphenylindan-2-ones 49a, b at -189°C giving 3 isomeric 7,8-diphenylsubstituted o-xylylenes 50-52. They found that under the reaction conditions 49a showed photostereomutation



49 50 51 52

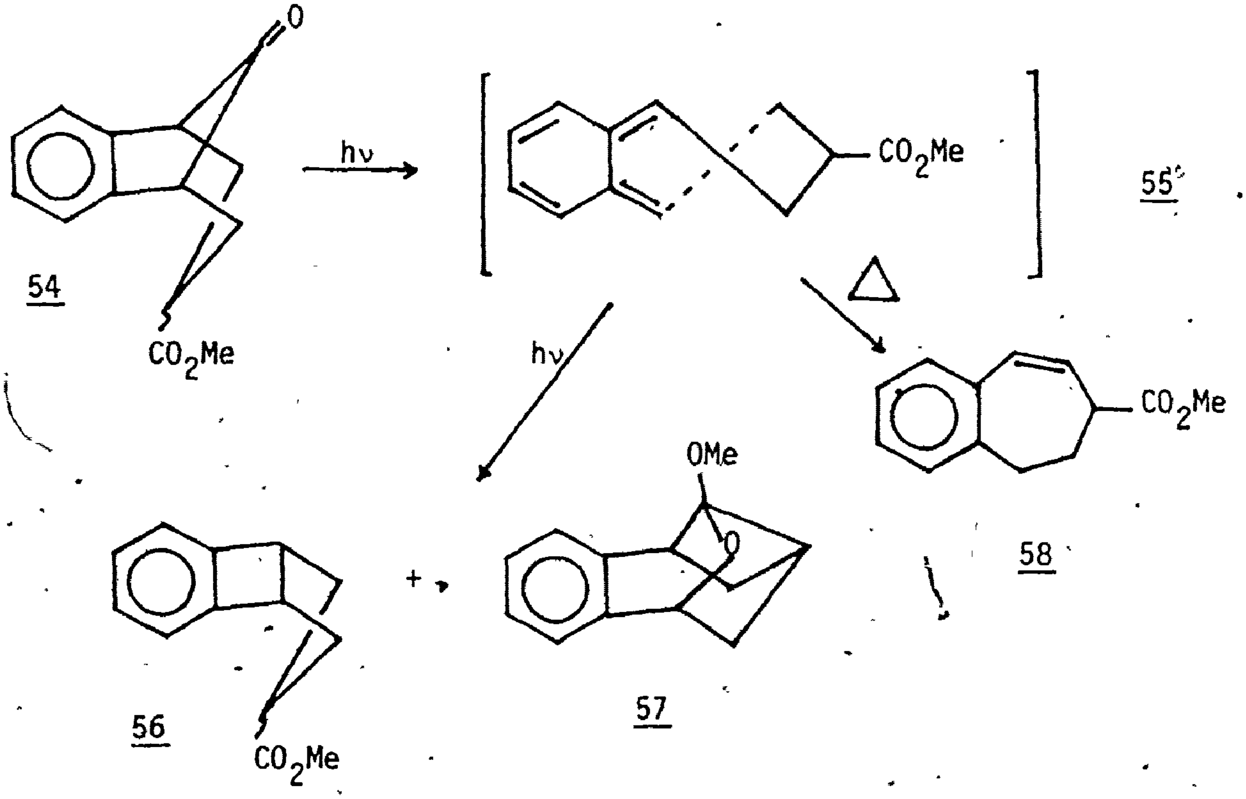
a, cis

b, trans

a, cis

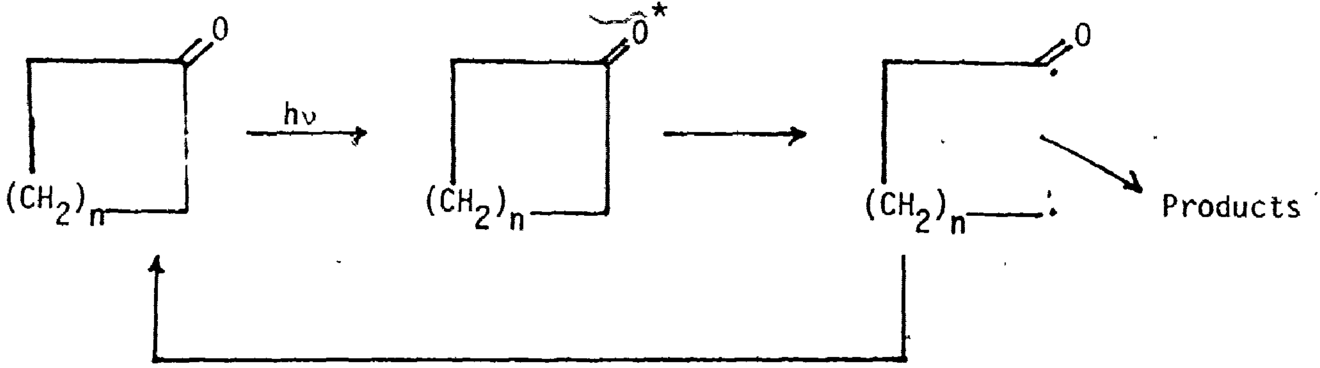
(i.e. cis-trans isomerisation). When the irradiation was performed at 13°C, a mixture of benzocyclobutenes 53a, b (formed by cyclisation of 50-52) were obtained. The product composition was unaffected by the presence of piperylene, a ketone triplet quencher. The observed non-stereospecificity did not necessarily indicate the non-concertedness of the decarbonylation since the isomerisation of 50-52 could not be ruled out. However, the fact that photostereomutation and photodecarbonylation in 49a result from the same singlet excited state, verified the stepwise nature of the CO elimination.

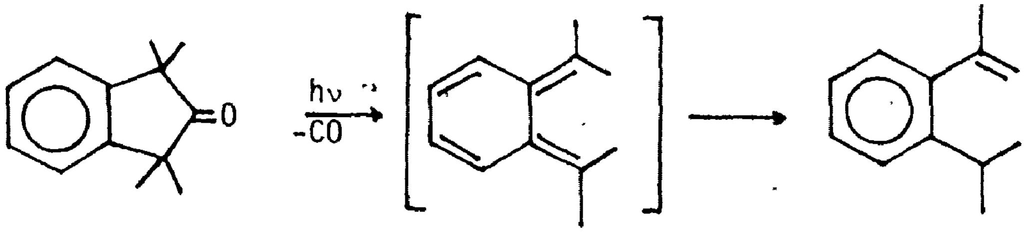
Weiss[25] prepared the twisted o-xylylene 55 by the photodecarbonylation of the benzobicyclo[3.2.1]octenone 54. 55 could be trapped as a one to one Diels-Alder adduct on irradiation of 54 in the presence of maleic anhydride. In the absence of a dienophile, it produced mainly 58 by 1,5 suprafacial



hydrogen shift. Studies at low temperatures showed that 56 and 57 formed by photochemical ring closure and cycloaddition respectively. Thus, the results showed that, in spite of twisting, the o-xylylene 55 did not exist as a biradical, and that its reactions were concerted ones governed by orbital symmetry.

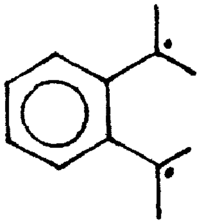
Mechanistically, photodecarbonylation is a consequence of α-cleavage of the excited ketone.[26] Thus, a ketone in its excited singlet or triplet state may homolytically rupture a C-C bond adjacent to the carbonyl function (α-cleavage) giving a radical pair. In the case of a cyclic ketone, a biradical is obtained. This may collapse to ground state ketone, or react by several possible routes which include hydrogen abstraction (intramolecularly, or from the solvent), loss of CO, and ring closure to an oxacarbene.[27] Starr and Eastman[28] studied the structural features facilitating the photodecarbonylation of cyclic ketones and found that β,γ-unsaturation and α-alkyl substitution enabled facile decarbonylation. 1,1,3,3-Tetramethylindan-2-one (59) meets both the above requirements and produces the styrene 61 in 95% yield.[28]





59 60 61

Part of the present work concerns the intermediate o-xylylene 60. Hence, it is opportune to discuss in greater detail, the work done by Starr and Eastman[28] on 59. These authors proposed that the intermediate was the biradical 62, which gave the styrene 61 by intramolecular hydrogen abstraction.



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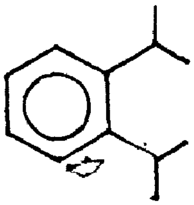
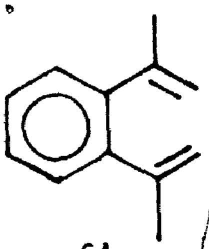


63



64

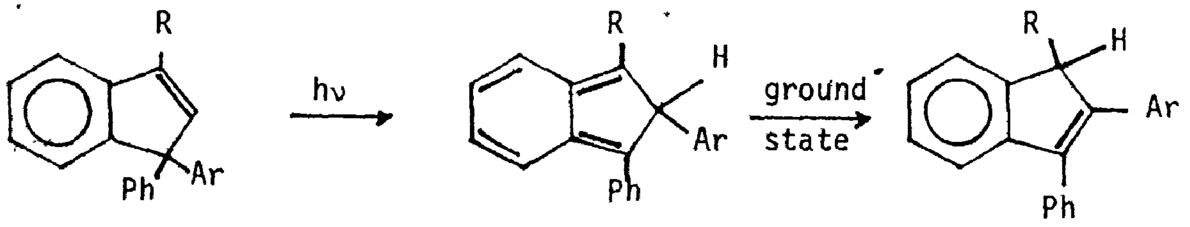
Thus, irradiation of 59 in tetrahydrofuran-d_8 showed no deuterium incorporation in the styrene, ruling out hydrogen abstraction from the solvent, by 62. Also, the absence of products such as 63 and 64 ruled out intermolecular processes, between two biradicals such as 62, or between 62 and the ketone, 59. The inability to observe the o-xylylene 60 was attributed to the fact that it either did not form at all, due to loss of aromatic resonance energy, or was short lived due to thermal or photochemical instability.

Part of the present work was initiated to verify the intermediacy of the o-xylylene 60, by the flash photolysis of the indanone 59.

RESULTS

PART A. ISOINDENES

The objectives of the work described were to characterise structurally and study the decay kinetics of transients (intermediates) which might be formed in the photolysis of 1,1-diarylindenes <u>65</u>. The general scheme would involve the intermediacy of the isoindene <u>66</u> (see pages 12-14).



<u>65</u> <u>66</u> <u>67</u>

<u>a</u>, R=H, Ar=Ph
<u>b</u>, R=Ar=Ph
<u>c</u>, R=H, Ar=Ph(p-CN)
<u>d</u>, R=H, Ar=Ph(p-Br)
<u>e</u>, R=H, Ar=Ph(p-OMe)

Scheme 1.

<u>Irradiation of 1,1,3-triphenylindene (65b)</u>

Photolysis of <u>65b</u> in hexane at 20°C caused polymeric material to precipitate on the walls of the vessel. However, when the photolysis was carried out at -70°C, in dilute solution, the only product isolated was that resulting from phenyl migration, i.e., 1,2,3-triphenylindene (<u>67b</u>). Yield, 78%.

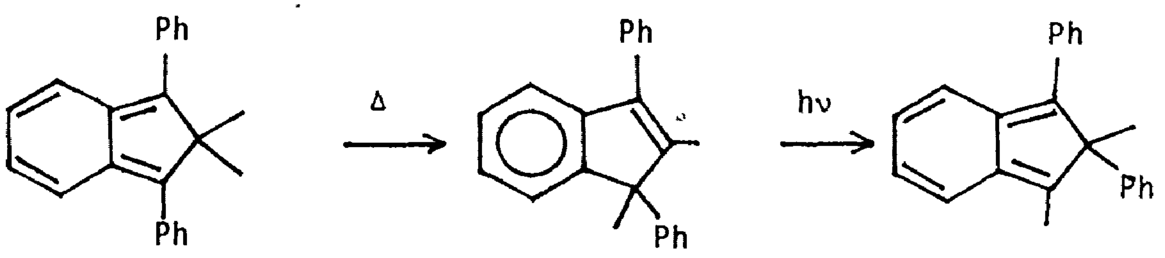
Structural evidence for the identity of the intermediates

(a) Electronic spectra

Flash photolysis of hexane solutions of the 1,1-diarylindenes (65a-e) (2 x 10^{-4}M) showed the presence of transients with lifetimes in the range 20-850 ms. The absorption of transients from 65a, c-e are similar, and are at 400-500 nm, while that from 65b absorbs at longer wavelength (400-550 nm) consistent with the additional conjugated phenyl group.

An electronic absorption spectrum of the transient from 1,1,3-triphenylindene (65b) was also obtained at -70°. Irradiation of 65b, with 254 nm light, in pentane at -70°C gave an orange solution with λ_{max} = 478 nm, which was attributed to the transient 1,2,3-triphenylisoindene 66b. The orange colour faded to yellow (λ_{max} = 440 nm) on warming to room temperature and the yellow colour bleached completely in 1-2 hours. The identity of the species responsible for the long-lived yellow colour is unknown at present. However, it had vinylic proton resonances in the nmr (see Figure 1), and its presence was noted in the flash photolysis of 1,1,3-triphenylindene (see kinetics section). Attempts to isolate or trap this species were failures. Some speculation on its identity is included in the discussion (p. 72).

For spectral comparison with 66b, a sample of 2,2-dimethyl-1,3-diphenylisoindene (16) was prepared. The NMR spectrum of the sample of 16 (see Experimental) showed more than one methyl resonance, and this was attributed to contamination by 68, formed by methyl migration[30] (Scheme 2). Irradiation of 68 in hexane produced a yellow colour which was stable for several hours at 20°C, under argon. Aerating the irradiated solution caused the yellow colour to decay in ca. 2h. It was attributed to 69,



16 68 69

Scheme 2.

formed from 68 by phenyl migration. The electronic spectral data for 66a, b, 16 and 69 are summarised in Table 2.

Table 2. Comparison of electronic spectra of isoindenes with model systems

Compound	Absorption λ_{max} (nm)	Emission λ_{max} (nm)
1,2,3-Triphenylisoindene (66b)[a]	478	572
1,3-Diphenyl-2,2-dimethylisoindene (16)	444	-[b]
1,2-Diphenylisoindene (66a)	-[c]	522
1,2-Diphenyl-2,3-dimethylisoindene (69)	448	555

[a] See Figure 1. [b] Blue fluorescence. [c] Absorbs in the range 400-500 nm.

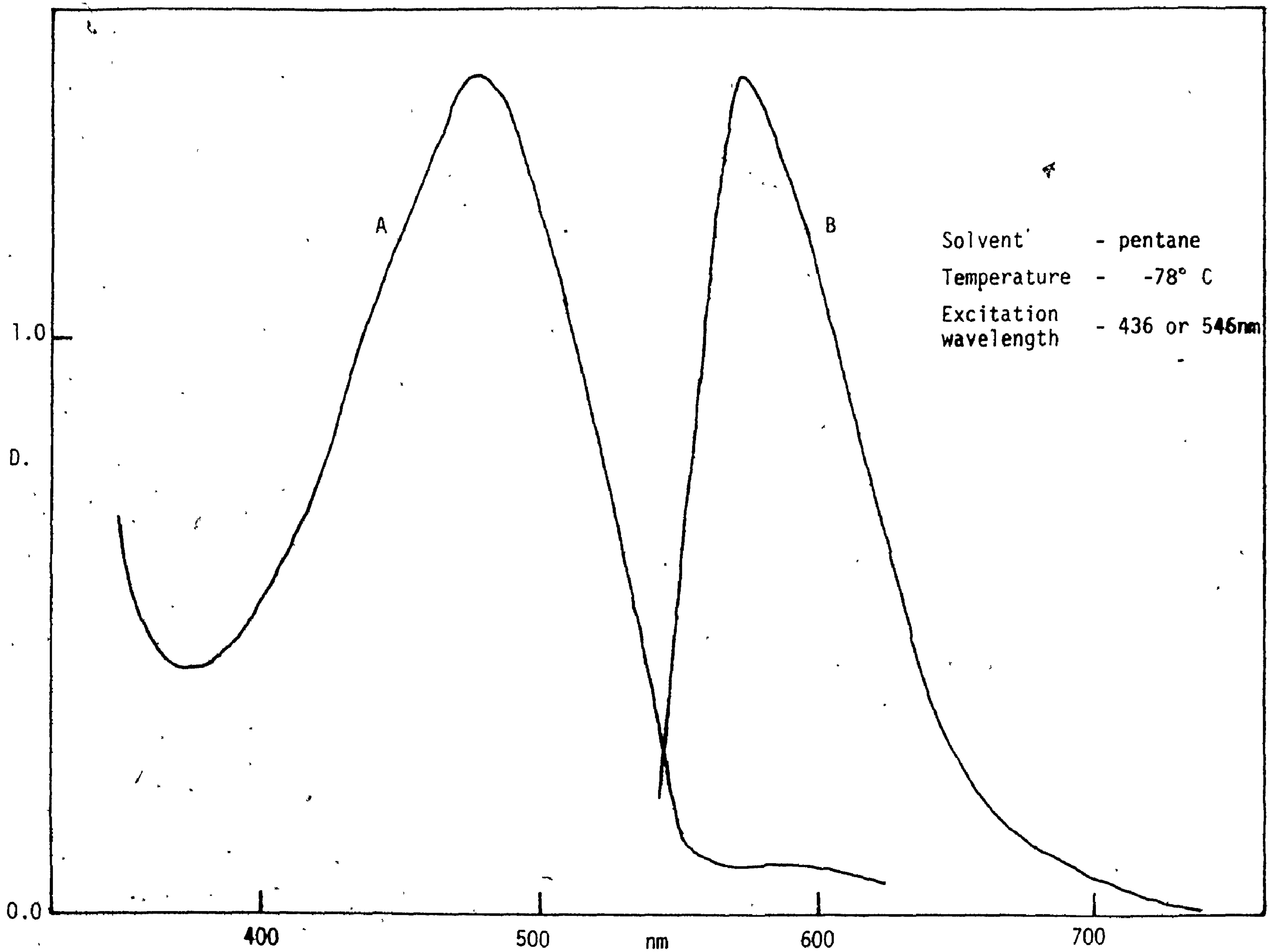


Figure 1, Visible absorption (A) and emmision (B) spectra of 1,2,3-triphenylisoindene.

(b) Nuclear magnetic resonance spectrum

Irradiation of 65b in cyclopentane at -70°C (in a quartz nmr tube) gave the orange colour described above. The proton nmr spectrum of this solution at -70°C is shown in Figure 2(A). In Figure 2(B) the spectrum of the same solution which had been warmed to 20°C and recooled to -70°C is shown. This contained reactant 65b and product 67b only; the absence of resonances H_B and H_C assigned to the transient isoindene will be noted. Figure 2(C) shows the spectrum of the transient solution from 2-deuterio-1,1,3-triphenylindene photolysis. While the methine resonances at higher field are absent, the singlet assigned to the four vinyl protons (H_B) at 6.80δ in the transient is unchanged. These changes are consistent with the presence of 66b in the low temperature spectra. The nmr spectrum of the 2,2-dimethylisoindene 16 also showed a broad singlet at -70°C at 6.90δ, attributed to the four vinylic protons. At room temperature, this resonance appeared as a complex multiplet, which simplified to a pattern similar to the vinylic proton resonance in 1,3-cyclohexadiene, on irradiation of the methylene protons in a decoupling experiment. Thus, these multiplets were assigned to the similar AA'BB' systems in 16 and in cyclohexadiene (see Figure 3).

(c) Trapping of isoindene 66b

Intermediate o-xylylenes and isoindenes have been trapped in several systems, by utilizing their reactivity in Diels-Alder reactions. However, in the photolysis of 1,1-diarylindenes, it was found that the better dienophiles such as maleic anhydride, acrylonitrile or acetylene dicarboxylic esters, acted as quenchers of the photochemical reaction, and attempts to trap the proposed isoindenes failed. The discovery that 1,2,3-triphenyl-

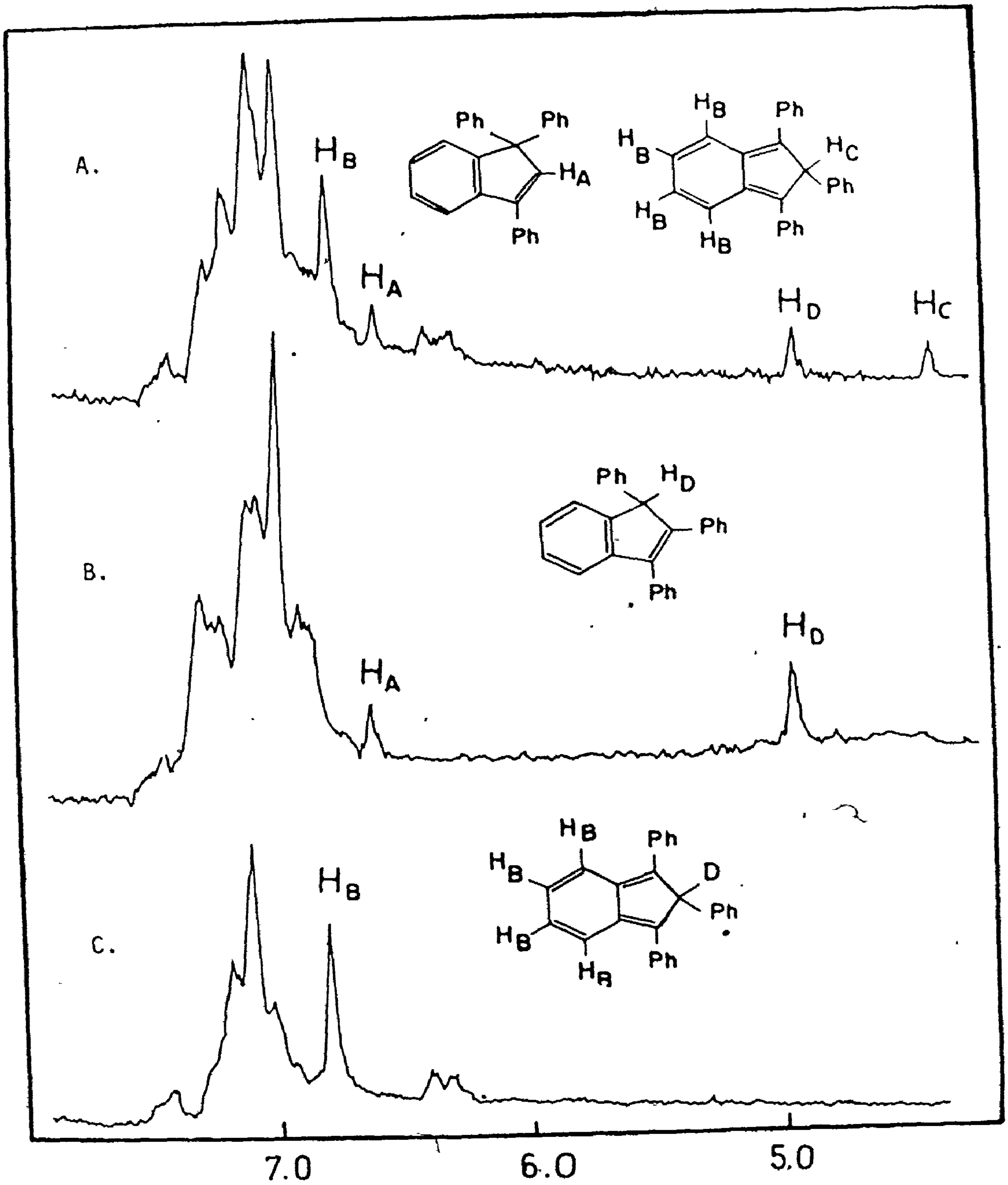


Figure 2. 100 MHz nmr spectra of <u>65b</u> irradiated in cyclopentane at -70^0 showing

A. reaction mixture immediately after irradiation

B. the same mixture after warming to room temperature and re-cooling to -70^0 and

C. reaction mixture immediately following a similar low-temperature irradiation of 1,1,3-tr[illegible]-2-D.

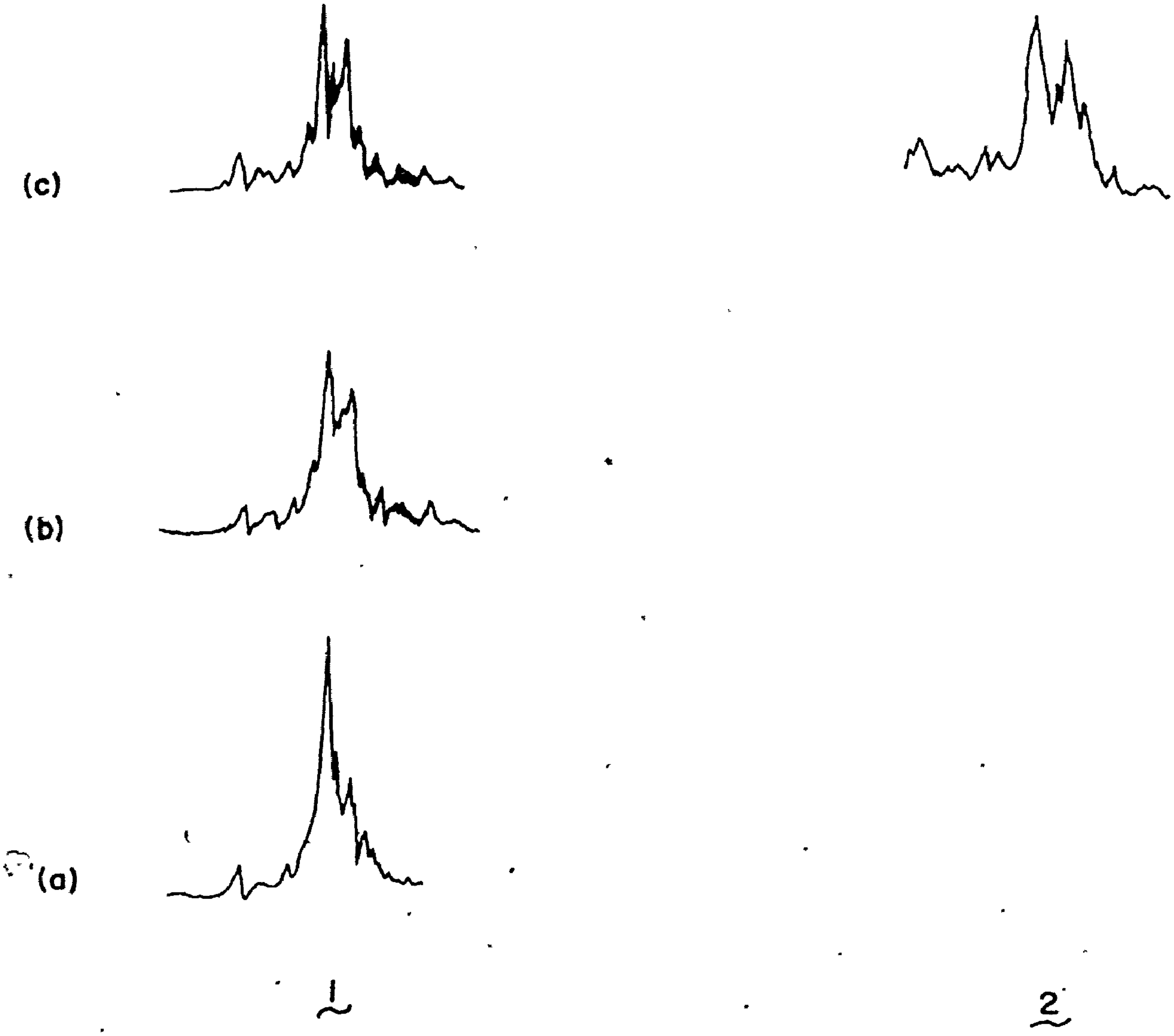
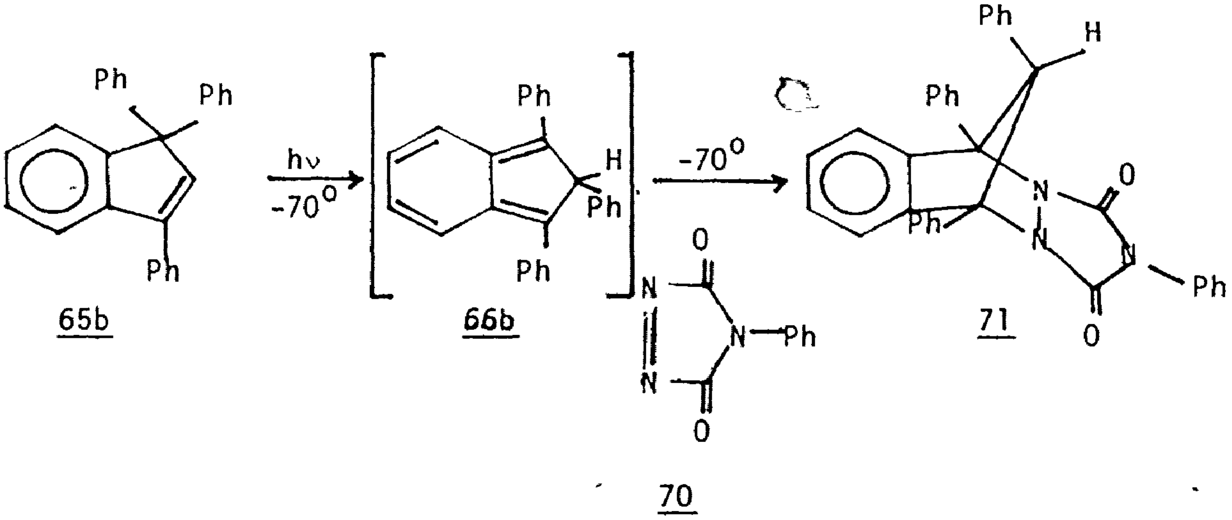


Figure 3. Comparison of the nmr signals of the olefinic protons in (1) cyclohexa-1,3-diene and (2) 1,3-diphenyl-2,2-dimethyl-isoindene.The decoupling of the methylene protons increases from (b) to (c). (a) is not decoupled.

isoindene was long-lived at -70°C suggested an alternative way of chemically trapping the intermediate. Thus, when a preirradiated solution of 1,1,3-triphenylindene (65b) in pentane was treated with the highly reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (70), at -70°C, an adduct assigned the structure 71 was obtained (Scheme 3).



Scheme 3.

The adduct 71 had mp 269°C. It showed infrared bands at 1787 and 1731 cm^{-1} (cyclic imide) and peaks in the mass spectrum at m/e 519(2) (parent ≡ $C_{35}H_{25}N_3O_2$), 344(100), 343(91) and 267(29). The last three would result from retro Diels-Alder fragmentation.

The ^{1}H nmr ($CDCl_3$) spectrum showed multiplets at 7.8-7.5δ (7 H), 7.4-7.2δ (10 H), and at 7.1-6.8δ (5 H). A doublet of doublets showed at 6.38δ (2 H, J = 8.0 and 2.0 Hz). A singlet at 4.08δ (1 H) is assigned to the methine hydrogen. The ^{13}C nmr spectrum ($CDCl_3$ or CD_2Cl_2) showed resonances at 157.5δ (C=O groups), at 127.9-123.3δ (aromatic system) and at 82.8δ and 80.1δ, under conditions of proton decoupling. On removal of the decoupling field, the resonance at 82.8δ remained a singlet while that at 80.1δ became a doublet. The former is assigned to the two bridgehead carbons, while the latter is assigned to the single carbon bridge.

The above results provide ample evidence for the identity of the transient from photolysis of 65b. Unfortunately, because of their shorter lifetimes, similar low temperature experiments did not allow characterization of the transients from 65a or 65c-e. It is assumed in the following section on kinetic spectroscopy, that the species whose absorption was monitored are the isoindenes analogous to 66b.

Kinetic studies

The lifetimes of the transients were determined by kinetic absorption spectroscopy (the transmittance of the solution in the region of the absorption by the transient was observed at times after the photolysis flash). All the transients in hexane solution disappeared by first order kinetics (in the photolysis of 65b an absorption due to an additional long-lived intermediate was present). The experimental conditions, lifetimes and rate constants are shown in Table 3. Usually the decay of the transient was monitored. However, the absorption of 67a from the photolysis of 65a could be distinguished easily from that of the transient and reactant. In this case it was found that the rate constant for the disappearance of transient 66a was within the experimental error of the rate constant for the appearance of the product 67a. It was shown that treatment of the 1,1-diphenylindene solution and the photolysis cell with either acid (3N H_2SO_4) or base (3N NaOH) prior to flash photolysis did not affect the decay times of the transients.

Table 3. Results of kinetic spectrophotometry

Expt[a]	Reactant	Wavelength monitored/nm	Transient lifetime/ms	Rate constants/s^{-1}
1	65a	450	28	36
2	65a	450	22	46
3[b]	65a	340	25	40
4	65b	475	850	1.21
5	65c	450	72	14
6	65d	450	37	27
7	65e	450	23	44

[a] All runs were in purified, deoxygenated hexane at 20°, except run 2 in which the solution was oxygen saturated.

[b] Appearance of product was monitored.

The nature of the rate determining step in the removal of the isoindene was investigated by studying the rate constants for the decay of 66a (2-D and 3-D) and 66b (2-D), relative to the non-deuterated species (see Table 4).

Table 4. Kinetic isotope effects in isoindenes 66a, b.

Structure	k (23.4°C) (s^{-1})	k_H/k_D
66a (2-H)	42	-
(2-D)	6.5	6.5
(3-D)	40	1.0
66b (2-H)	3.1	-
(2-D)	0.84	3.7

Further information on the nature of the species involved in the rearrangement can be deduced from measurements on the series of diphenylindenes 65a, c-e which involve different substituents on one of the phenyl rings. On irradiation of these indenes, the substituted phenyl group migrates (see p. 13). The first order rate constants observed for the decay of the isoindene in deoxygenated hexane at 20°C are shown in Table 3. Figure 4 shows the appropriate linear free energy plot, in which the logarithm of the decay rate constant for the substituted isoindene is plotted vs. σ^n. The σ^n values[31] are: H, 0.000; CN, 0.674; Br, 0.265; OMe, -0.111. The line shows a small negative slope (ρ = -0.6).

The rate constants increase with temperature as shown in Table 5, and may be interpreted in terms of the Arrhenius equation (Figures 5 and 6). The activation parameters are listed in Table 6.

Table 5. Variation of rate constants (k) with temperature (T).

i) 1,2-Diphenylisoindene (66a)

T (°C)	$k(s^{-1})$	$10^3/T(K^{-1})$	ln k
42.2	165.0	3.17	5.11
29.9	66.6	3.30	4.20
19.8	32.3	3.41	3.48
10.1	14.8	3.53	2.69
0.8	7.0	3.65	1.95

ii) 1,2,3-Triphenylisoindene (<u>66b</u>)

T(°C)	$k(s^{-1})$	$10^3/T(K^{-1})$	ln k
38.3	4.90	3.21	1.59
29.5	2.40	3.30	0.875
20.1	1.15	3.41	0.140
10.0	0.74	3.53	-0.301

Table 6. Activation parameters

Compound	E_a (kcal mol^{-1})	ln A	$\Delta S^{\circ\ddagger}$ (cal K^{-1} mol^{-1})
1,2-Diphenylisoindene (<u>66a</u>)	13.1±0.5	25.9±0.8	-9.0
1,2,3-Triphenylisoindene (<u>66b</u>)	11.8±1.0	20.6±1.7	-19.6

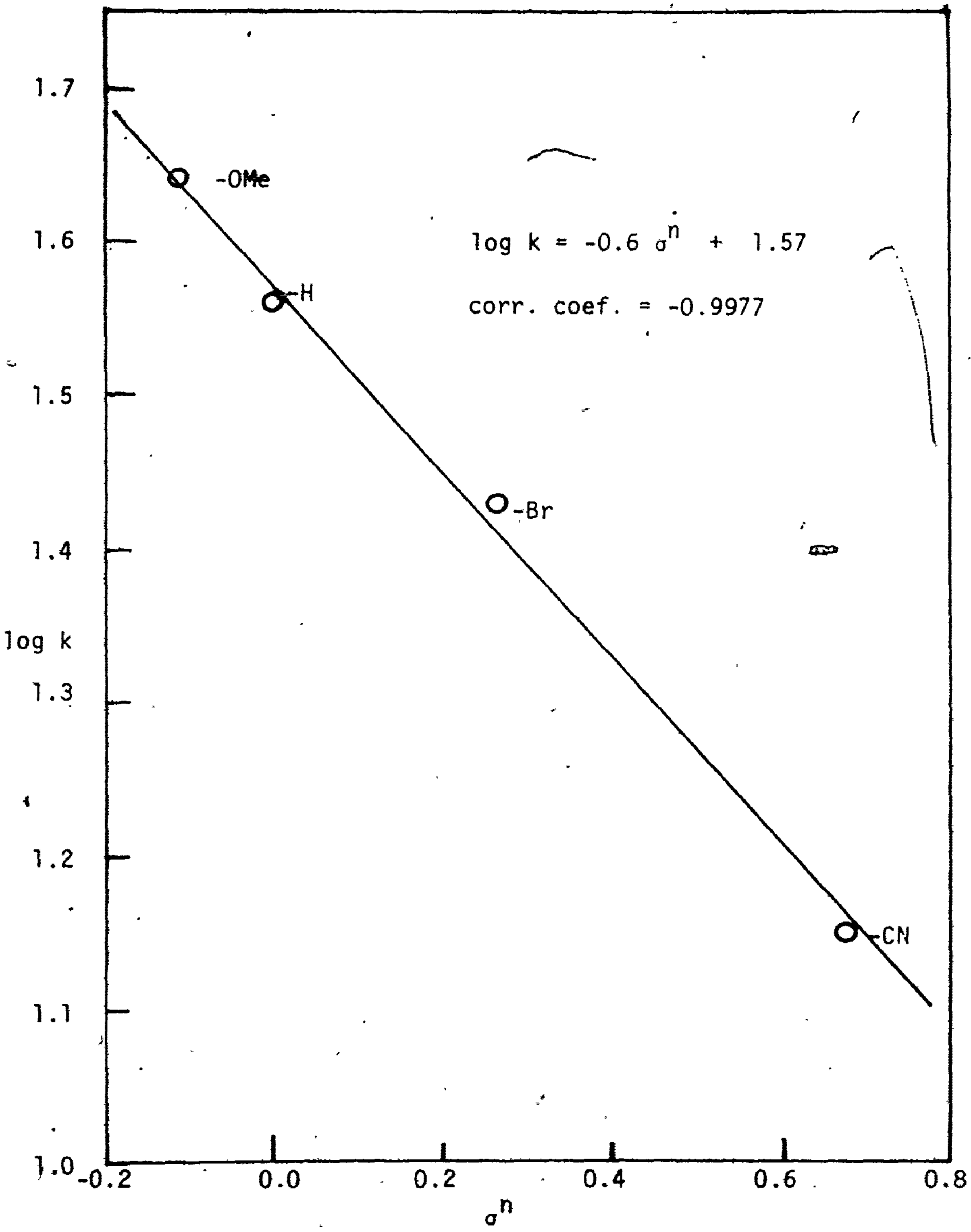


Figure 4. Correlation of rates of re-aromatisation of isoindenes <u>66e</u>,<u>a</u>,<u>d</u> and <u>c</u> with σ^n.

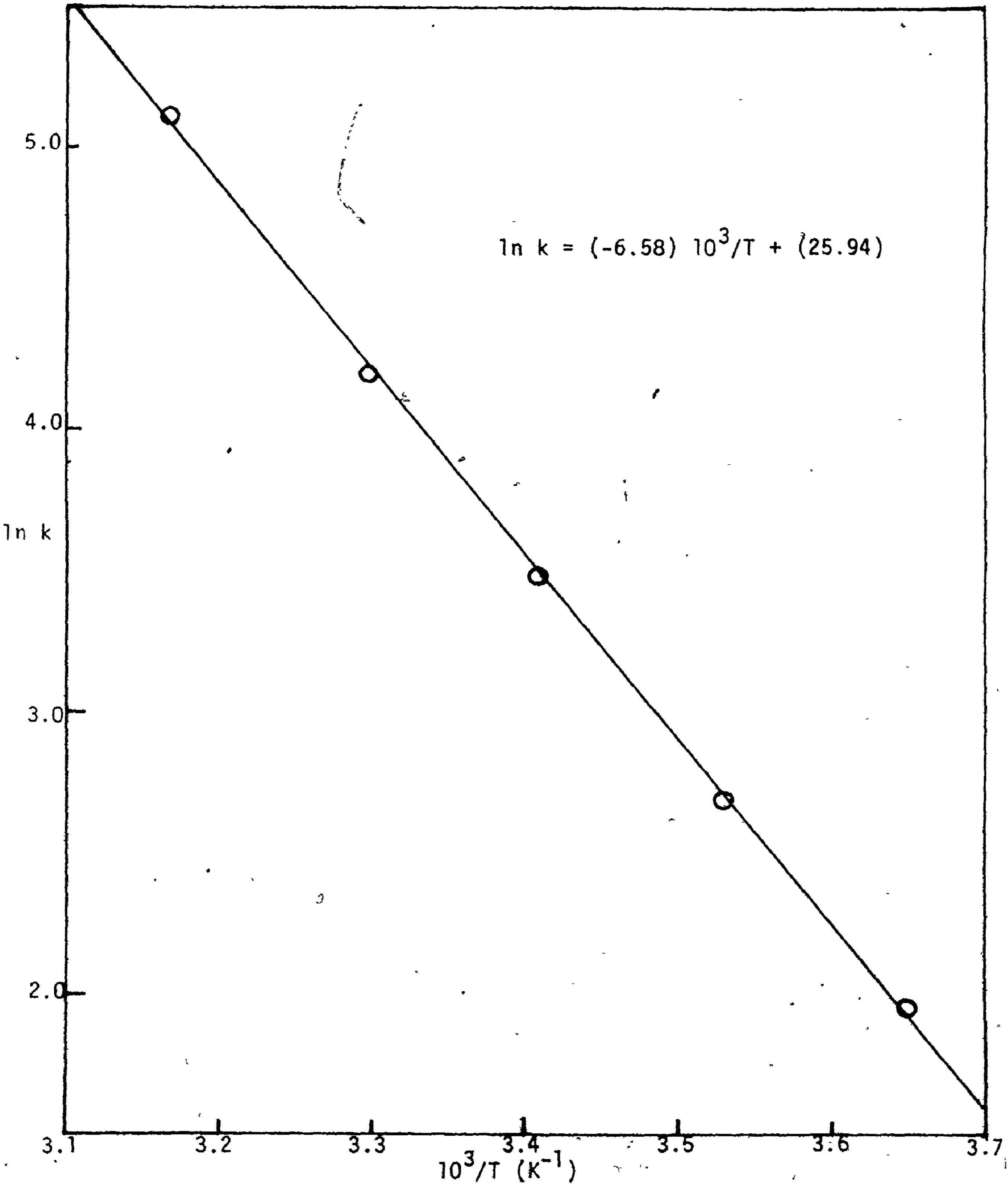


Figure 5. Arrhenius plot for the decay of 1,2-diphenylisoindene.

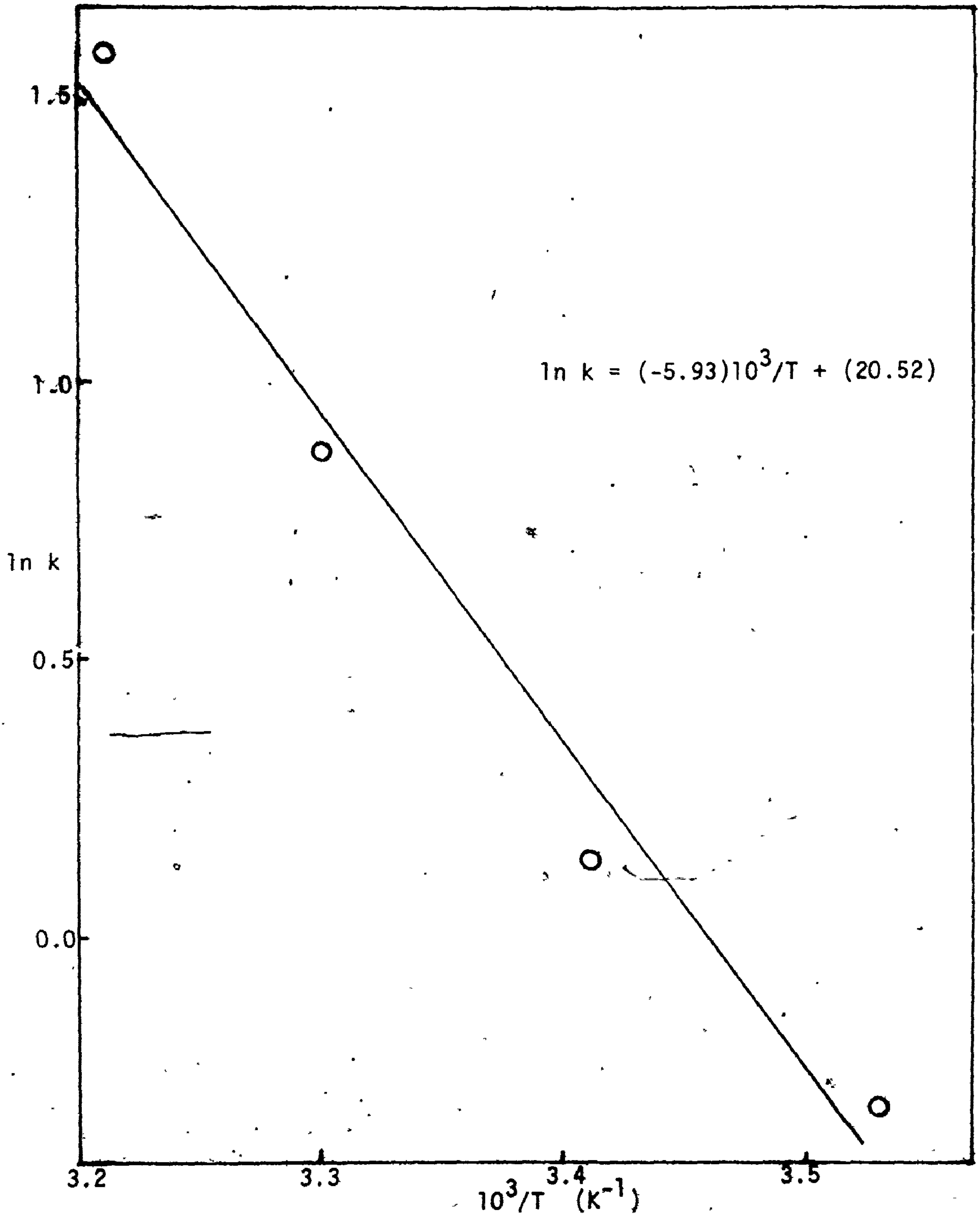


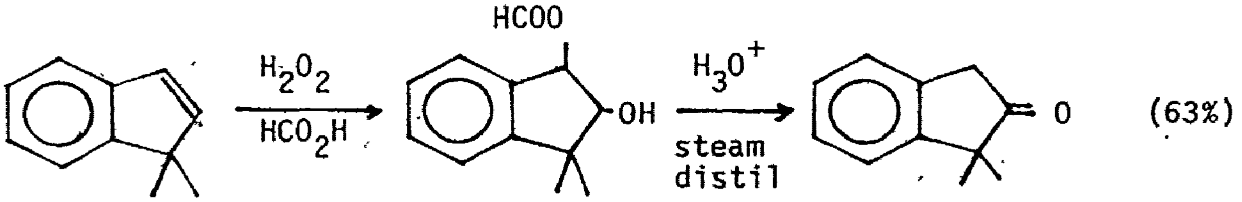
Figure 6. Arrhenius plot for the decay of 1,2,3-triphenylisoindene.

PART B. o-XYLYLENES

The objectives of the work described were to synthesise the indan-2-ones 59, 74, 80 and 86, study their photoproducts, and any intermediates that might be formed in their photolysis (see Table 7, p. 42 for the structural formulae of the compounds).

Synthesis of the ketones

1,1-Dimethylindan-2-one (74) was synthesised by the oxidation of 1,1-dimethylindene[32] using performic acid, yield, 63% (Scheme 4).

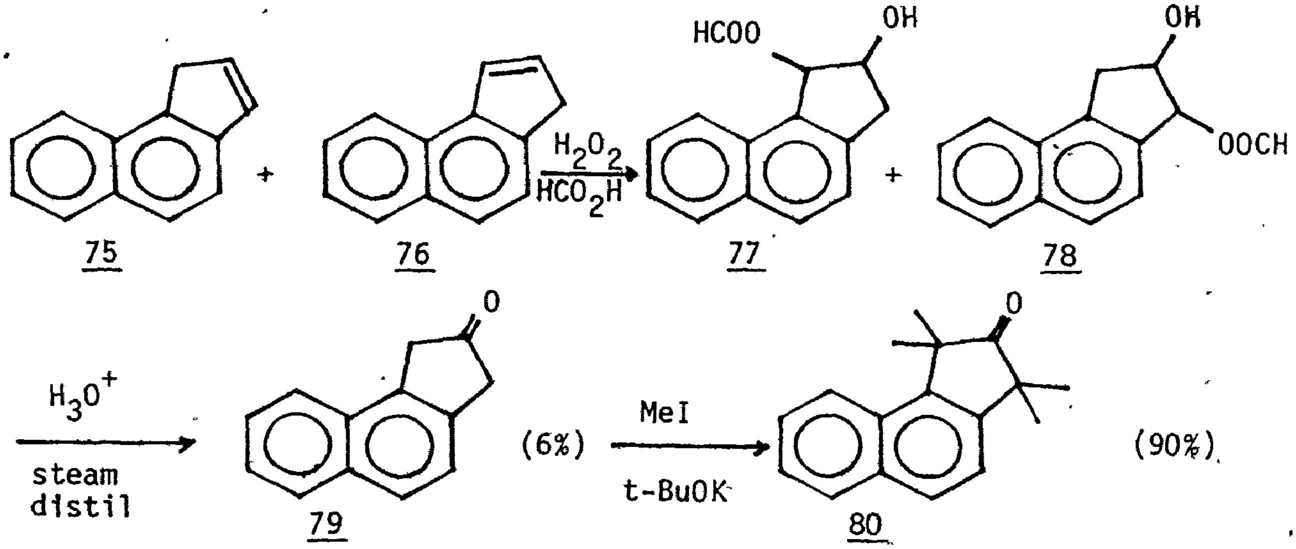


72 73 74

Scheme 4.

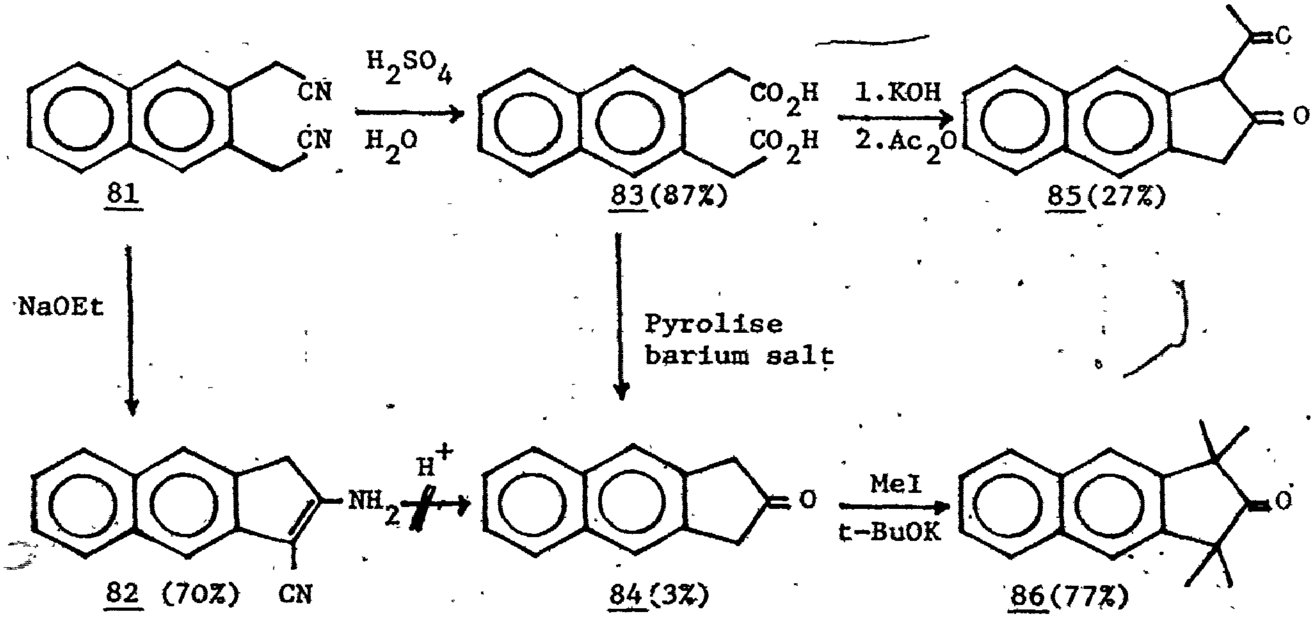
A similar oxidative procedure was used in the synthesis of 4,5-benzindan-2-one (79). Thus, a mixture of the isomeric benzindenes[33] 75 and 76 (50:50) was similarly oxidised to 79 in 6% yield (Scheme 5). Since the formation of the formate esters 77 and 78 appeared to be in reasonable yield, the low overall yield is probably due to the acid sensitivity of 79. The low volatility of 79 could also lower its recovery by steam distillation. 79 was methylated to the tetramethyl derivative 80 in 90% yield.

Due to the low yield in the oxidation of benzindenes, entirely different approaches to the synthesis of 5,6-benzindan-2-one 84 and its



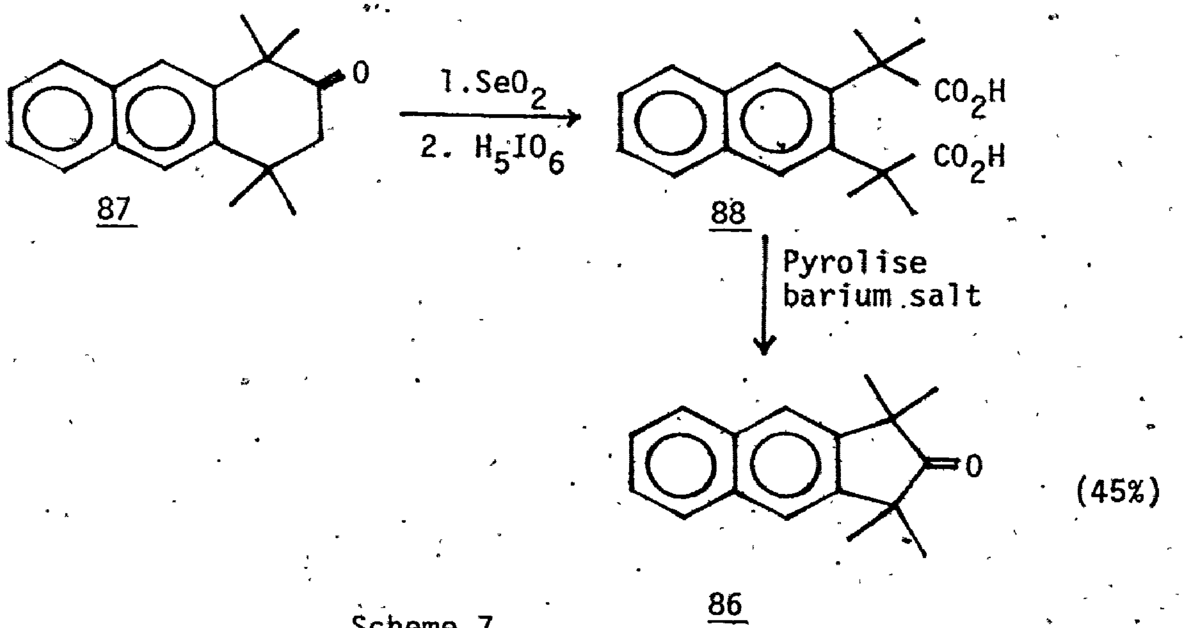
Scheme 5.

tetramethyl derivative 86 were investigated (Scheme 6). Naphthalene diacetonitrile (81)[34] was cyclised in 70% yield using sodium ethoxide. However, it was not possible to convert 82 to the desired ketone 84 by acid hydrolysis, due to the acid sensitivity of the latter. 81



Scheme 6.

was hydrolysed in 87% yield to the diacid 83. Based on the ready conversion of benzene-1,2-diacetic acid (potassium salt) to indan-2-one on treatment with acetic anhydride[35], the same procedure was applied to the naphthalene diacetic acid 83. Surprisingly the only product isolated was the acetyl derivative 85 of the desired ketone 84. The desired benzindanone 84 was finally synthesised by the pyrolysis of the barium salt of the diacid 83 under vacuum, in 3% yield. 84 decomposes on heating at 130°; hence the low yield is not surprising for a pyrolytic generation. Another reason for the low yield is that 84 was always accompanied by a large percentage of 2,3-dimethylnaphthalene in the crude sublimate from the pyrolysis.[36] This necessitated purification by chromatography on silica gel - a process which served to reduce an already low yield. 84 was methylated to give 86 in 77% yield. The tetramethylated ketone 86 was thermally stable. It melted sharply at 176°. This fact prompted a new route to 86 which did not require the intermediacy of the unmethylated ketone 84 (Scheme 7). Thus, the 2-keto-tetrahydroanthracene 87 was converted to the diacid 88 by the procedure of Barclay et al.[37] (The purification of 87, prior to this reaction,



Scheme 7.

involved chromatography in contrast to the simple literature procedure.[37] Hence its synthesis is reported in the experimental section.) Pyrolysis of the barium salt of 88 under vacuum resulted in the sublimation of relatively pure 86 in 45% yield.

Irradiation of the ketones

Based on the work of Starr and Eastman[28] (p.17) on 59, the photoproducts from 74, 80 and 86 were those expected. Thus, irradiation of the carbonyl group of 1,1-dimethylindan-2-one resulted in the formation of α,2-dimethylstyrene (90), cleanly, up to ca. 70% conversion of the ketone.

Irradiation of 1,1,3,3-tetramethyl-4,5-benzindan-2-one (80) produced a single product up to ca. 60% conversion, after which secondary products began to appear. Thus, irradiation was stopped at 60% conversion. The product was identified as 1-isopropenyl-2-isopropylnaphthalene (92).

1,1,3,3-tetramethyl-5,6-benzindan-2-one (86) was photolysed to give two products, 2-isopropyl-3-isopropenylnaphthalene (94) and 3,3,4,4-tetramethylnaphtho[b]cyclobutene (95). The product ratio varied with the time of reaction (Figure 7).

Flash photolysis

Flash photolysis of the ketones 59, 74 and 80 show transients (intermediates) absorbing in the range 300-400 nm. The transient from 86 absorbed from 390-540nm. These transients have been assigned the structures shown in Table 7, for reasons to be discussed later.

The first order rate constants for decay of the transients 60 and 89, determined by kinetic spectrophotometry are given in Table 8. The corresponding Arrhenius Plots are shown in Figures 8 and 9. Intermediate 91 survives indefinitely in the dark. It was found that the rates of decay

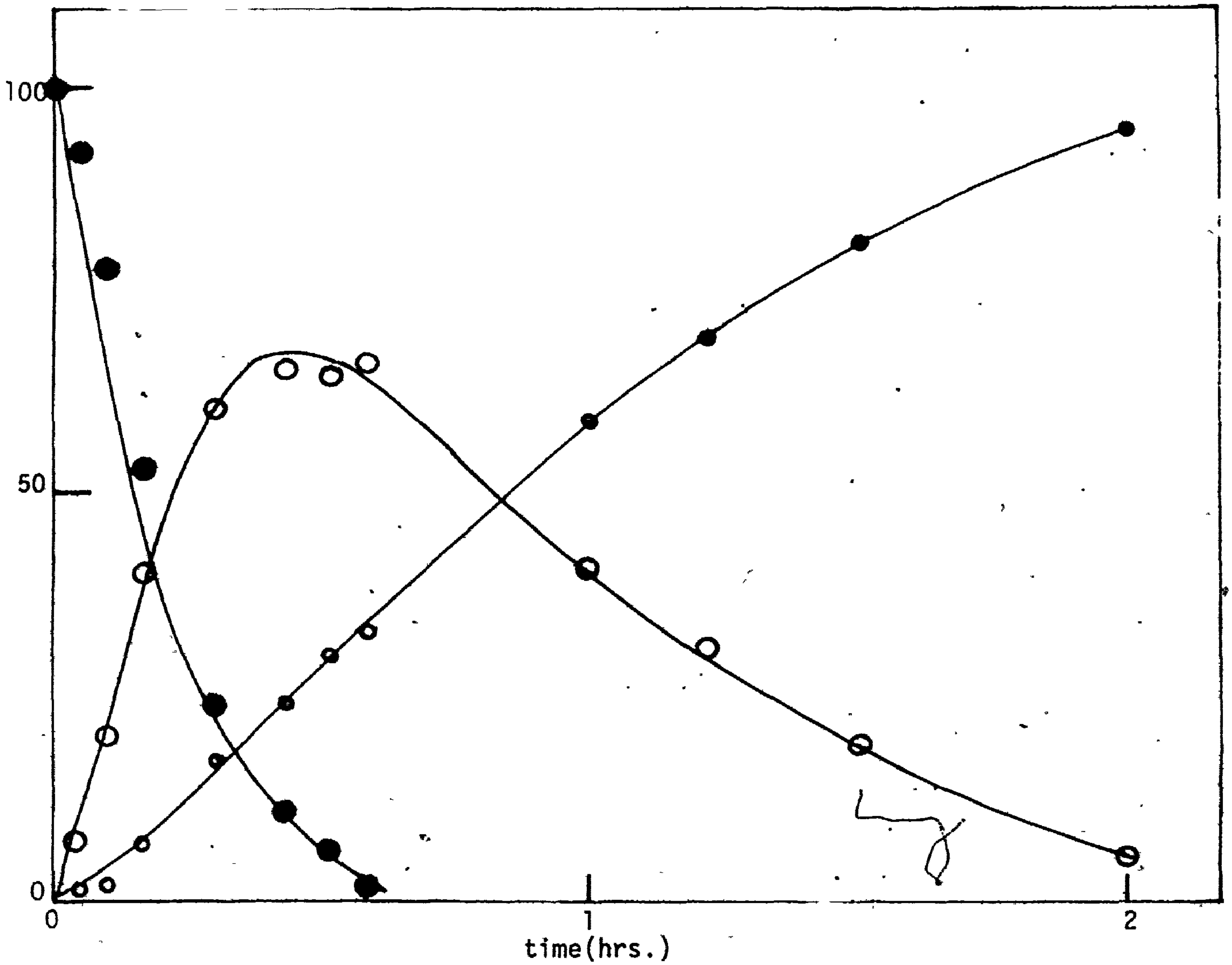


Figure 7. The generation of 2-isopropyl-3-isopropenylnaphthalene (○) and 3,3,4,4-tetramethylnaphthocyclobutene (◦) in the irradiation of 1,1,3,3-tetramethyl-5,6-benzindan-2-one (●), using RPR 3000A lamps. Aliquots were assayed by glc. It was assumed that the detector response was similar for all three compounds, and that the sum of their concentrations remained constant throughout the reaction. Initial ketone concentration, ca. 10^{-3}M.

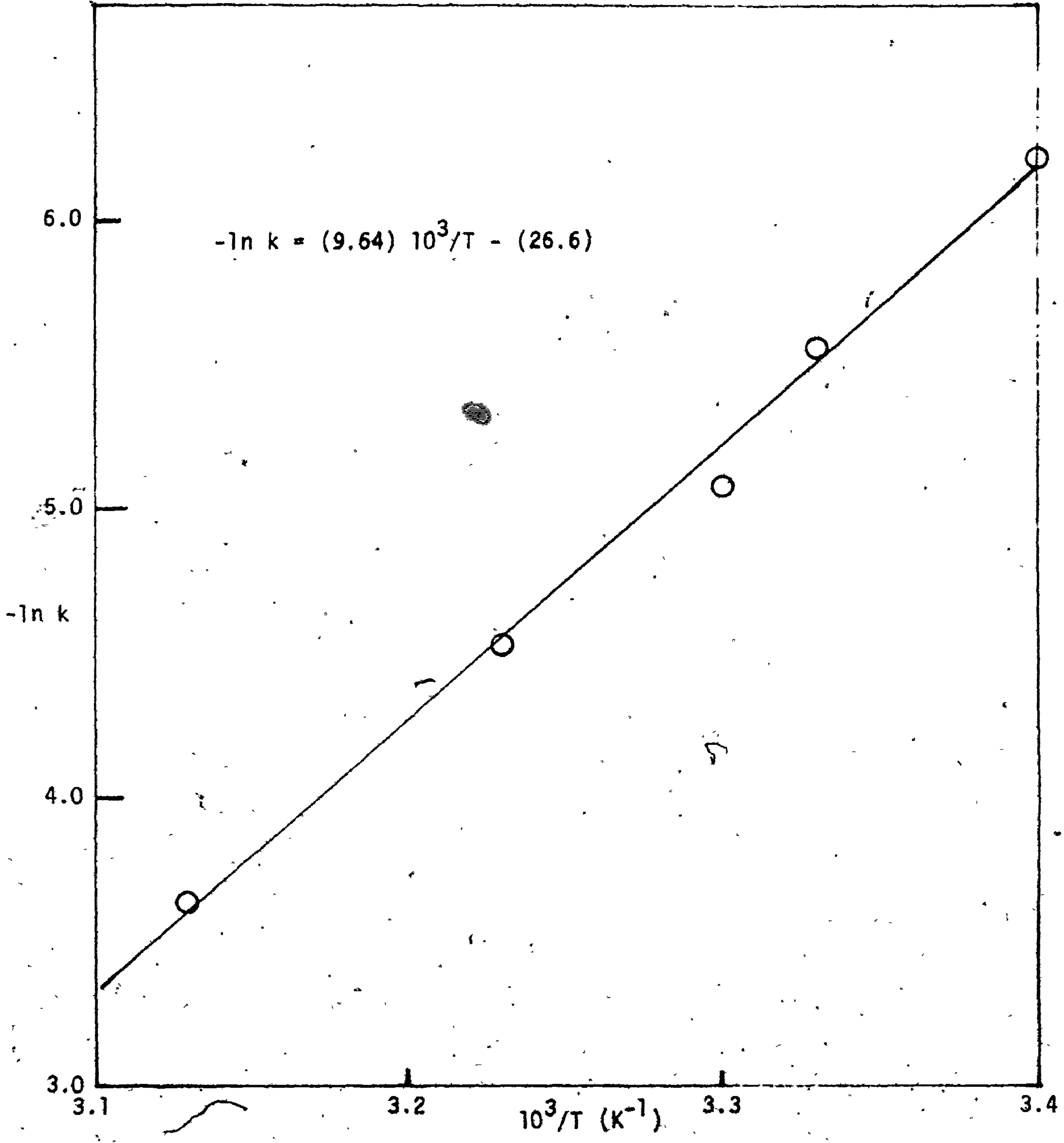


Figure 8. Arrhenius plot for the decay of 7,7,8,8-tetramethyl-o-xylylene.

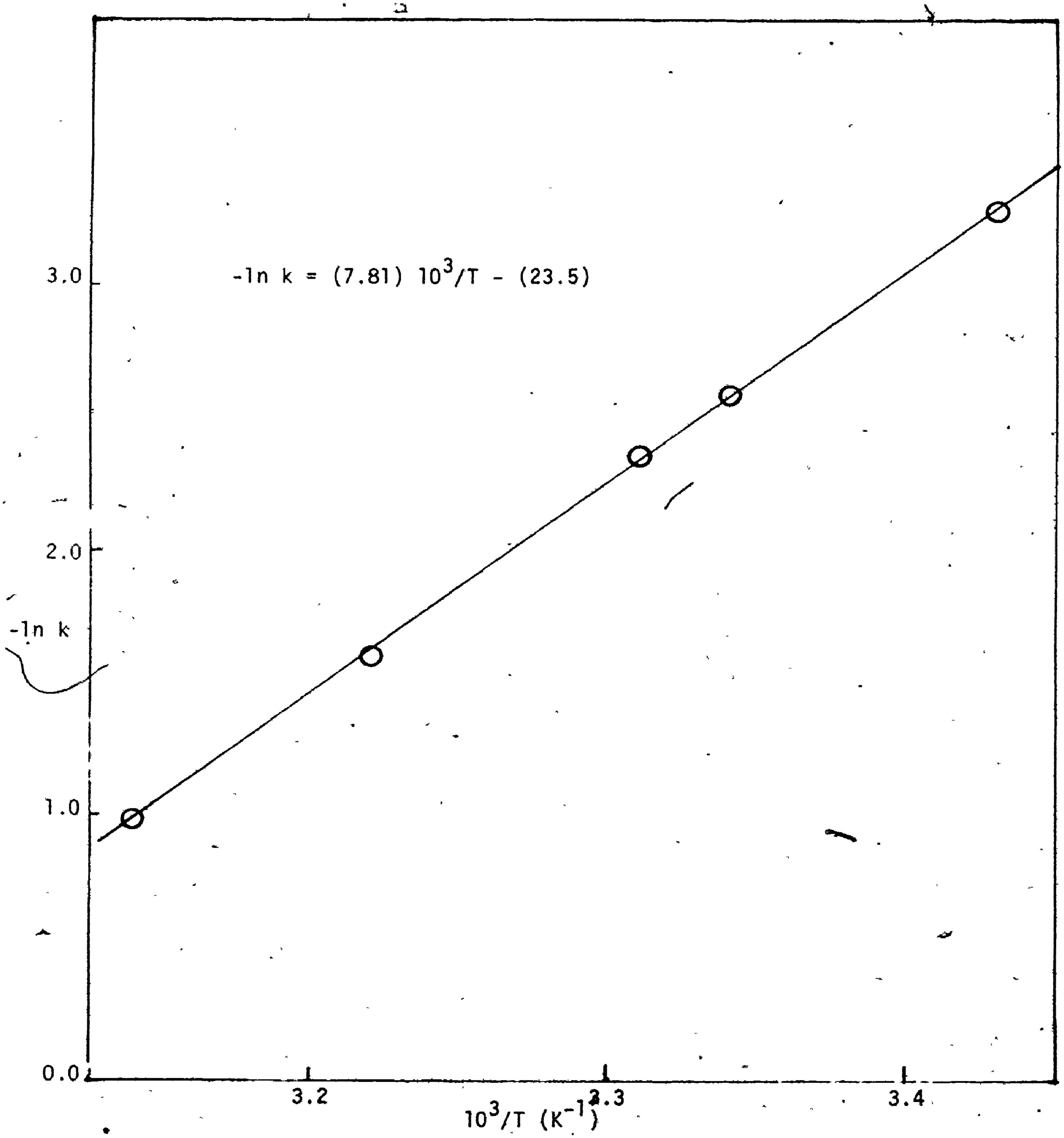


Figure 9. Arrhenius plot for the decay of 7,7-dimethyl-o-xylylene (89).

of the transients depend on the intensity of the light in the monitoring beam, i.e. that the transients are susceptible to secondary photolysis. Hence, the data refer to limiting values at low intensities of the monitoring beam. It was also shown that the decay rates did not change on the addition of acid or base.

To characterise the decay process for these transients, the hydrogen kinetic isotope effect and activation parameters were measured. These are in Tables 9 and 10 respectively.

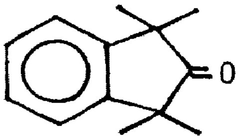
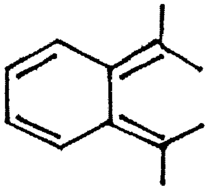
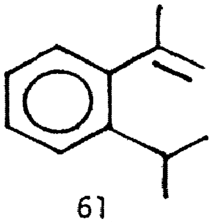
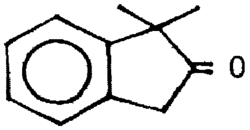
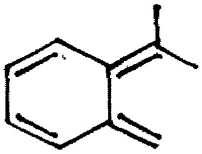
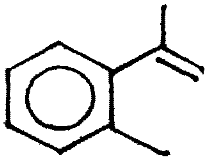
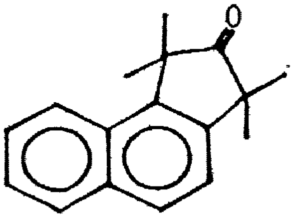
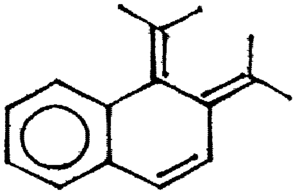
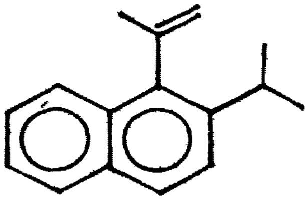
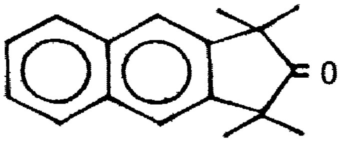
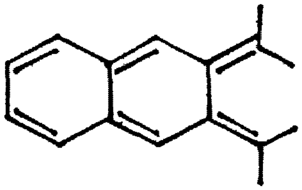
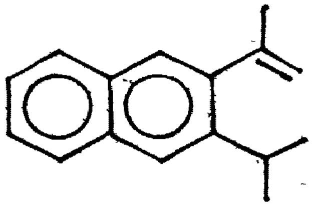
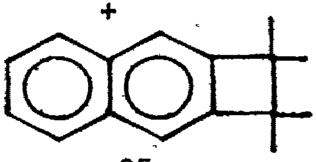
Spectral evidence for the identity of the intermediates

Since the intermediates were photolabile, in order to obtain a sufficiently high concentration of these species for obtaining an absorption spectrum, it was necessary to irradiate the ketones 59 and 74 through a filter which absorbed in the range 300-400 nm, while transmitting well at 254 nm. A $NiSO_4$ solution filter was used for this purpose, and by photolysis at -78°C it was possible to obtain the absorption spectra of 60 and 89. The emission spectra of these species were also obtained, and are shown in Table 7. Attempts to generate these intermediates in concentrations sufficient for nmr, failed.

Attempts to trap the intermediates 60 and 89

All attempts to trap the o-xylylenes 60 and 89 as Diels-Alder adducts, were failures. The dienophiles used were maleic anhydride, tetracyanoethylene and α-chloroacrylonitrile. In all cases, intractable material was obtained when the ketone (59 or 74) was irradiated in a solution containing the dienophile. Reasons for these failures are included in the discussion.

Table 7. Products and intermediates in the photolysis of indan-2-ones.

Indanone	Intermediate	Products isolated	λ_{max} (nm) absorption	emission[a]
 59	 60	 61	350	440
 74	 89	 90	360	430
 80	 91	 92	---[b]	372
 86	 93	 94 +  95	---[c]	?

[a] Excitation for 60, 89, and 91 was at 313,366, and334 nm, respectively.

[b] Maximum obscured by ketone absorption. Transient absorption tails to 360 nm.

[c] Absorbs in the range 390-540 nm.

Table 8. Variation of rate constants with temperature for the o-xylylenes

i) 7,7,8,8-Tetramethyl-o-xylylene (60)

T(°C)	$10^3k(s^{-1})^a$	$10^3/T(K^{-1})$	-ln k
21.2	2.01	3.398	6.21
26.9	3.86	3.333	5.56
29.6	6.22	3.304	5.08
36.2	10.8	3.233	4.53
46.1	26.2	3.133	3.64

ii) 7,7-Dimethyl-o-xylylene (89)

T(°C)	$10^3k(s^{-1})^a$	$10^3/T(K^{-1})$	-ln k
18.3	37.5	3.432	3.28
26.3	75.3	3.340	2.59
29.0	94.8	3.310	2.35
37.6	202	3.219	1.6
45.8	371	3.136	0.99

[a] Wavelength monitored, 366 nm. Filters used were Kodak CS 7-37, 3% neutral density and 366 nm interference.

Table 9. Kinetic isotope effect for the o-xylylene <u>60</u>

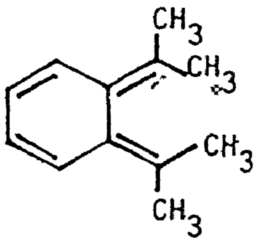
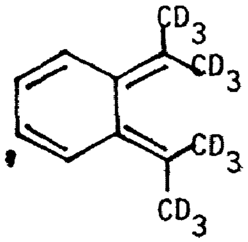
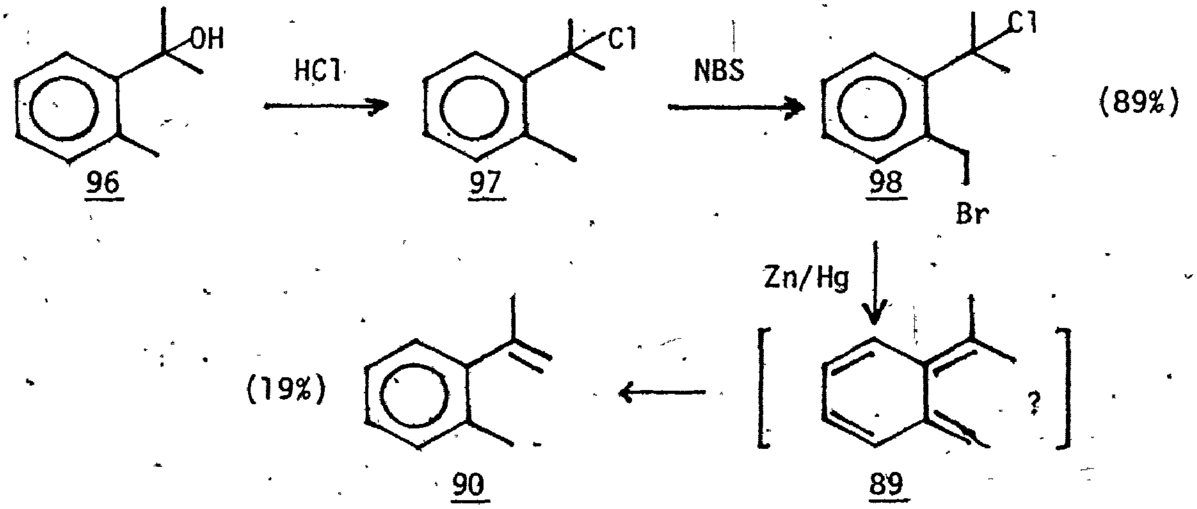
o-Xylylene	$k(s^{-1})$(38.5°C)	k_H/k_D
	0.0131	5.4
	0.00242	

Table 10. Activation parameters for the decay of o-xylylenes

Compound	E_a (kcal mol^{-1})	ln A	$\Delta S^{\circ\ddagger}$ (cal K^{-1} mol^{-1})
7,7,8,8-Tetramethyl-o-xylylene (<u>60</u>)	19.1±1.0	26.6±1.7	-7.7
7,7-Dimethyl-o-xylylene (<u>89</u>)	15.5±0.6	23.5±1.0	-13.9

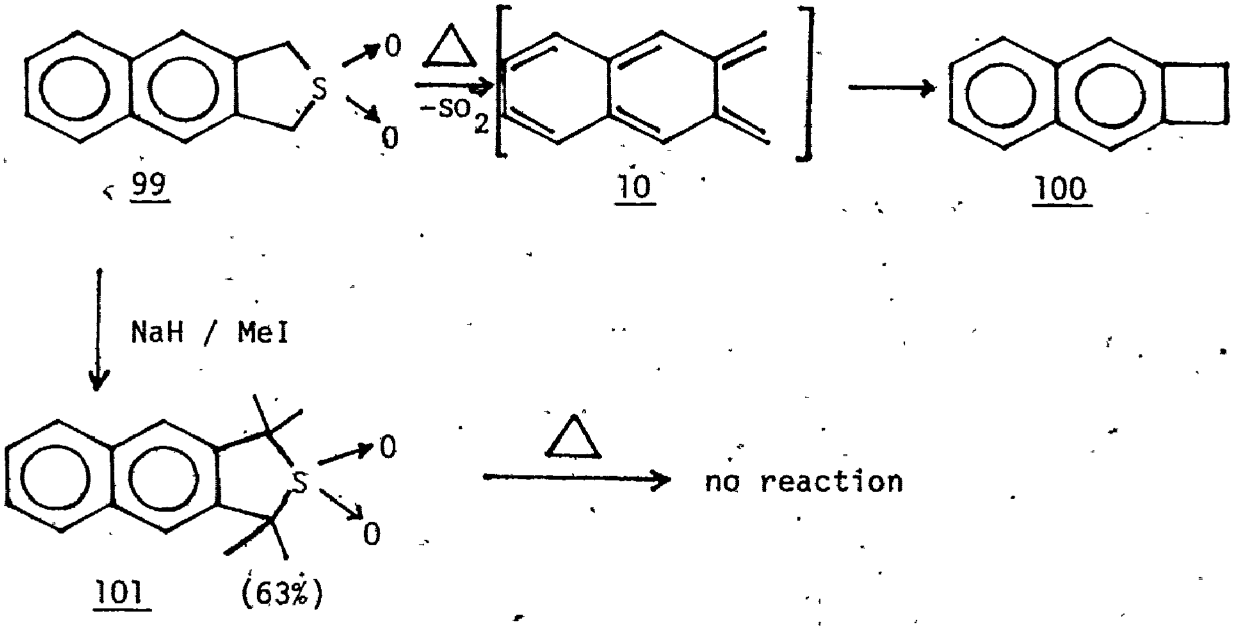
Attempts to thermally generate the intermediates

Since discovering that the o-xylylene intermediates were photochemically labile, it seemed convenient to find means of generating them non-photochemically. In such an attempt to generate the dimethyl-o-xylylene 89, (o-methylphenyl)dimethyl carbinol (96) was converted to the chloride 97 with dry HCl,[38] and brominated in the methyl group to yield the dihalide 98 in ca. 89% yield (Scheme 8). Treating the dihalide with zinc-amalgam produced the expected styrene 90 in 19% yield. It seems likely that this reaction proceeded via the xylylene. Similar dehalogenation reactions to give o-xylylenes are known (see p. 6).



Scheme 8.

Cava and co-workers[39] have synthesised the naphthocyclobutene 100 by pyrolysis of the sulphone 99 (Scheme 9). Since this reaction probably proceeded via 2,3-naphthoquinodimethane (10), it seemed worthwhile to pyrolyse the tetramethylsulphone 101 to generate the tetramethyl naphthoquinodimethane 93. 99 was methylated in 63% yield. However, the tetramethylsulphone 101 was stable to heat and to irradiation. Its thermal stability, though disappointing, correlated well with the thermal stability of the tetramethyl-5,6-benzindanone 86, which is a stable compound, compared to the much more reactive unmethylated derivative 84.



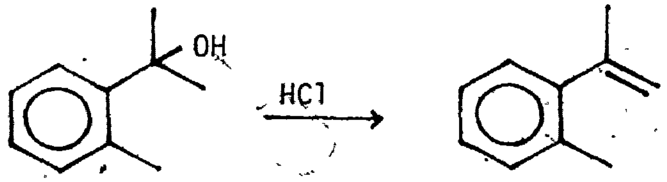
Scheme 9.

DISCUSSION

Identification of the photoproducts

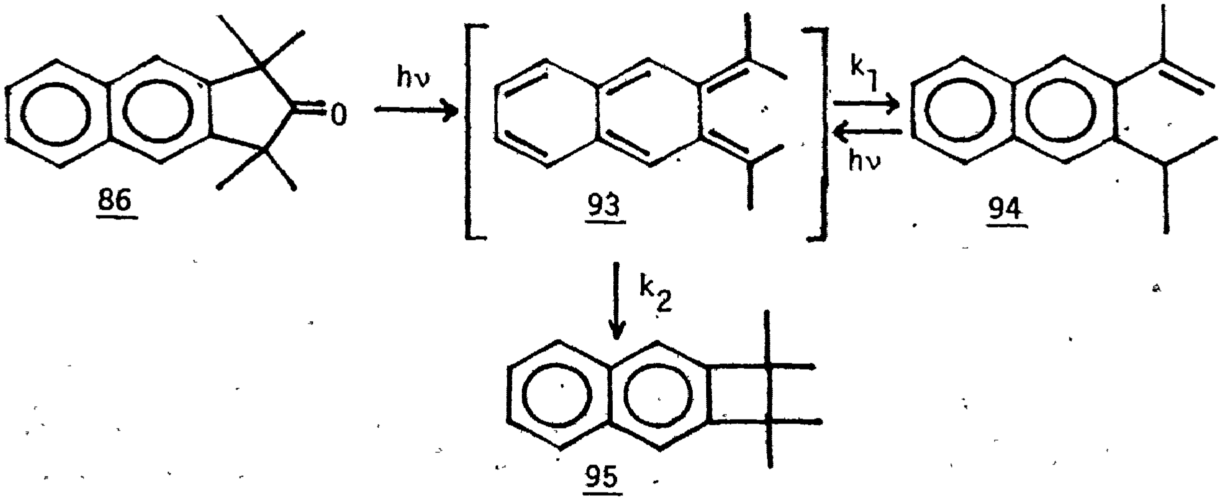
The irradiation of 1,1-diarylindenes has been shown to give products arising from the migration of an aryl group from the 1- to 2-position of the indene system.[22] Thus, the 1,1-diarylindenes 65a, c-e give 1,2- and 2,3-diarylindenes (p. 13), while 1,1,3-triphenylindene gives 1,2,3-triphenylindene upon photolysis.

The irradiation of indan-2-ones results in the loss of carbon monoxide. The most commonly encountered products are isopropenylalkylbenzenes, while in one case, a naphthocyclobutene was also formed. Thus, 1,1,3,3-tetramethylindan-2-one has been shown to give 1-isopropyl-2-isopropenylbenzene (61) as the only significant product (p. 17). Similarly, 1,1,-dimethylindan-2-one gives 1-methyl-2-isopropenylbenzene (90) which was independently synthesised by the dehydration of (o-methylphenyl) dimethylcarbinol (96). The nmr signals (see experimental) for the isopropenyl group of 90 were very similar to those of 1-isopropyl-2-isopropenylbenzene.[28] Both styrenes, 90 and 61, do not show characteristic styrene absorption in the ultraviolet due, presumably, to steric hindrance to coplanarity of the two chromophores. The absorption of 90 tails down to 300 nm, with log ε = 2.4 at 270 nm. A similar absorption is shown by α,2,4,6-tetramethylstyrene.[64]



96 90

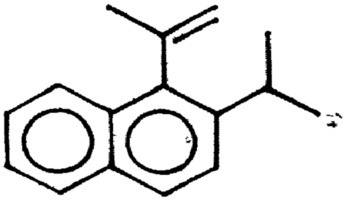
The benzindanone 86 gives two photoproducts; the styrene 94 and the cyclobutene 95. The variation of the ratio of these products with time (p.38) is consistent with Scheme 10, where the photolabile styrene is converted to the stable cyclobutene, and $k_1 > k_2$. There is precedence for the photochemical transformation of a styrene to an o-xylylene.[15]



Scheme 10.

(see the conversion of 28 to 29 on p. 9). The product ratio depends also on the wavelength of irradiation. Thus, flash photolysis of a solution of 86 showed ca. 3% conversion of the ketone, to the two products 94 and 95 in the ratio 3:2. This inconsistency with Figure 7 (p. 38) may be due to the fact that while the flash photolysis lamp irradiates down to 220 nm, the RPR 3000A lamps used to generate the products in Figure 4, emit only in the 280-340 nm range. The nmr data for the styrene 94 are shown in Table 11.

Irradiation of 1,1,3,3-tetramethyl-4,5-benzindan-2-one (80) gives 1-isopropenyl-2-isopropylnaphthalene (92) rather than the isomeric 1-isopropyl-2-isopropenylnaphthalene (102). The distinction between these two possibilities was made using spectral evidence. The nmr data for 92



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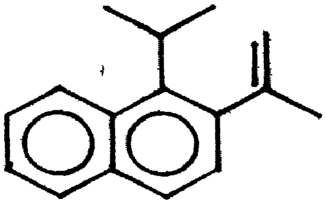


102

Table 11. Comparison of the proton nmr chemical shifts of the styrenes with model systems.

Compound	$\underline{HC}Me_2$	$\underline{Me_2}CH$	Me-C=	$=CH_2$
1-isopropyl-2-isopropenylbenzene (61)	3.17	1.20	2.02	5.14, 4.80
2-isopropyl-3-isopropenylnaphthalene (94)	3.22	1.27	2.10	5.18, 4.90
1-isopropenyl-2-isopropylnaphthalene (92)	3.30	1.12,1.27	2.08	5.42, 4.89
1-isopropylnaphthalene	3.62	1.31	-	-
2-isopropylnaphthalene	2.97	1.30	-	-

(Table 11) show that the two methyl groups of the isopropyl group are diastereotopic (i.e., chemically non-equivalent). This was verified by a spin-decoupling experiment. Irradiation of 92 at 3.30 ppm caused the pair of doublets at 1.12 and 1.27 ppm to collapse to a pair of singlets. Molecular models indicate that restricted rotation is more likely in 92, where the isopropenyl group is constrained to lie orthogonal to the naphthalene nucleus due to repulsion by the alkyl group and the peri-hydrogen, and also, free rotation of the isopropyl group is prevented. In 102, the isopropenyl group is able to rotate (though with some difficulty) and the methyl groups would therefore be equivalent. The u.v. spectrum is also consistent with the orthogonality of the two chromophores; only the naphthalene absorption is seen. Thus, while 94 absorbs to 355 nm, 92 absorbs only to 330 nm. In the nmr spectrum, one of the methyl groups, of the isopropyl group, is shifted upfield (by 0.15 ppm) due probably to shielding by the olefinic linkage, while one of the olefinic protons (the one nearer the peri-hydrogen) is shifted downfield due to deshielding by the ring current. The methine proton resonance is approximately the same in both 92 and 94. Comparison with the model isopropyl naphthalenes[40] indicate that the methine proton in 102 would resonate at lower field.

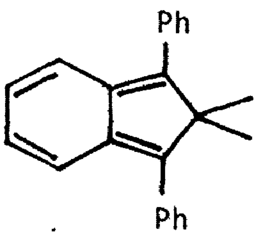
Identification of the o-xylylene type intermediates

The o-xylylene type intermediates that were generated by excited state phenyl migration and photodecarbonylation were identified mainly by their absorptions in the ultraviolet/visible region of the spectrum. Only in the case of 1,2,3-triphenylisoindene was it possible to employ a more diagnostic spectroscopic technique such as nmr and also chemical trapping. Since both these methods have been dealt with in fair detail in the Results section, this section will deal mainly with the results of absorption spectroscopy.

(a) Isoindenes

The absorption maximum of 1,2,3-triphenylisoindene (66b) occurs at 478 nm (p. 21) and hence shows a 34 nm red shift relative to the stable 1,3-diphenylisoindene 16. This red shift is more apparent in the emission spectra; 16 shows a bluish-green fluorescence while that of 66b is bright orange. Hence the presence of a phenyl group at the 2-position affects the spectral properties drastically, in spite of the fact that it is not conjugated (in the classical sense) with the isoindene chromophore. On the other hand, there is reasonably good spectral agreement between the transitory

1,2-diphenylisoindene (66a) and the more stable 69, both of which show identical phenyl substitution. Jones[30] has also observed a red shift in the 1,3-diphenylisoindene spectrum upon introducing substituents containing p-orbitals at the 2-position. Thus, the cyclic ketal 103 is a violet-red colour (λ_{max} 537 nm). The red-shift in 103 and 66b is consistent with a spiro-interaction ('spiroconjugation')[41] between the termini of the isoindene π-system and the acetal oxygen atoms or the sp^2 carbon atom attached to the spiro centre (Figure 10) respectively. The fact that the red shift is less in 66b compared to 103 is consistent with the lesser stereochemical rigidity of the phenyl group and the lesser substitution at the spiro centre of 66b. There is no precedence for similar changes in absorption spectra due to a spiroconjugated phenyl group. However the electron paramagnetic resonance spectrum of the mono-anion radical of 9,9'-spirobifluorene (104) is consistent with delocalisation of the odd electron over the perpendicular biphenyl systems.[42] This observation can be accounted for by spiroconjugation. Finally, it



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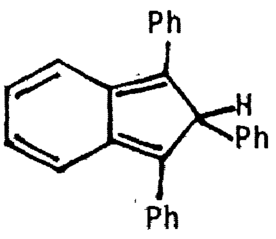
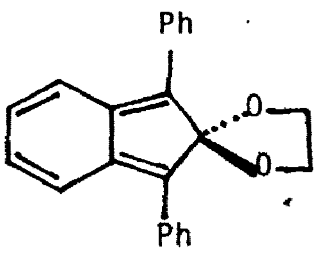


66b



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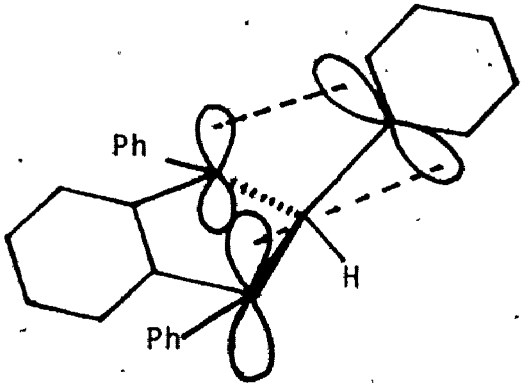
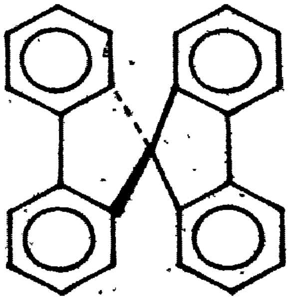


Figure 10. Spiroconjugation in 1,2,3-triphenylisoindene. (Some p-orbitals have been omitted for clarity.)

is noted that the "charge transfer interaction" invoked by McCullough and McClory (p. 13) to explain the greater selectivity of the excited state process in the rearrangement of substituted diphenylindenes,



104

could be related to spiroconjugation observed in the isoindene intermediates.

(b) o-Xylylenes

The alkyl-substituted o-xylylene derivatives generated by photodecarbonylation show long wavelength absorption maxima at shorter wavelengths than the parent o-xylylene[2] (λ_{max} = 373 nm). This blue-shift, in spite of alkyl substitution, strongly suggests that their structures are non-planar, due to steric repulsion of the alkyl substituents, and are twisted about the "essential" single bonds[43] of the non aromatic ring. Inspection of models confirms that the large van der Waals repulsion between the "endo" allylic methyl groups in the planar geometry, is relieved most efficiently by ring puckering combined with a small conrotatory torsion of the isopropylidene groups. The configuration of the tetramethyl-o-xylylene 60 is shown in Figure 11.

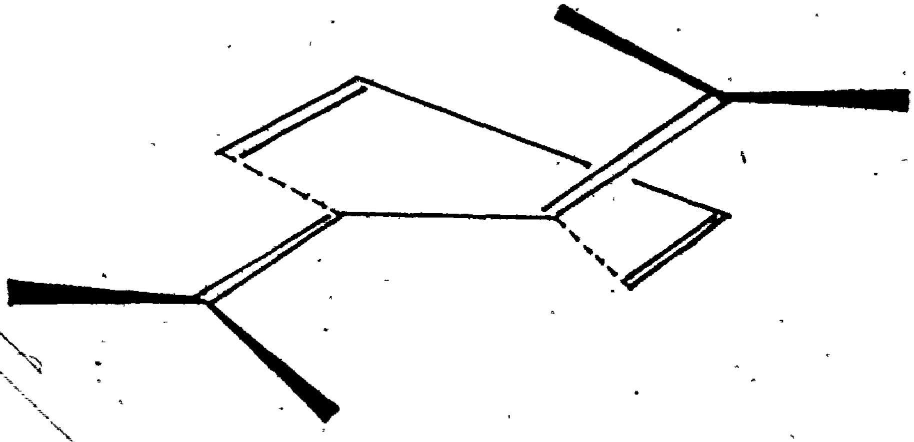


Figure 11. The configuration of 7,7,8,8-tetramethyl-o-xylylene.

Huckel molecular orbital (HMO) calculations[3] were performed to verify the effect of twisting on the HOMO-LUMO gap of o-xylylene. Since the resonance integral (G_{ij}) between adjacent p orbitals i and j varies with the angle between the orbitals (Θ_{ij}) as [44]

$$G_{ij}(\Theta) = G_{ij}(0) \, \mathrm{Cos}\, \Theta$$

(i.e. G decreases with increasing Θ), the effect of Θ on the HOMO-LUMO gap (and hence the absorption maximum) may be approximately ascertained. These calculations (Table 12) show the increase of the HOMO-LUMO with twisting consistent with experimental observation of a blue shift. Table 12 also shows that the π-electron stabilisation energies do not decrease appreciably with twisting, and that in general, 1,2-naphthoquinodimethane is the least biradicaloid species, while the 2,3-derivative the most.[2] This is consistent with the formation of a cyclobutene product in the latter case.

On the basis of twisting, one expects the absorption of the tetramethyl-o-xylylene 60 to resemble that of 1,1,8,8-tetramethyl-1,3,5,7-tetraene. The unmethylated tetraene absorbs at 304 nm.[45] Assuming that four methyl substituents would shift the maximum to 324 nm,[43] we find reasonable agreement between the noncyclic tetraene and the twisted cyclic compound 60, whose maximum is at 350 nm. Similarly, the tetramethyl 1,2-naphthoquinodimethane 91 whose maximum is obscured by the absorption of its precursor, the ketone 80, should resemble the styrene 105 which probably shows a maximum below 320 nm. The tetramethyl 2,3-naphthoquinodi-

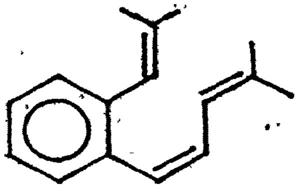


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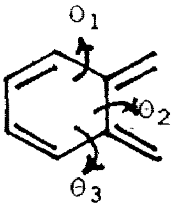
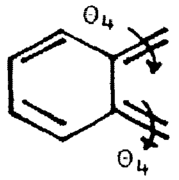
Table 12. The effect of twisting about the "essential" single bonds on the HOMO-LUMO gap (ΔE) and the π-electron energy (E_π) of o-xylylenes.



Structure	θ_1°	θ_2°	θ_3°	$\Delta E(\beta)$	$E_\pi(\beta)$
o-Xylylene	0	0	0	0.58992	9.95396
	15	30	15	0.61912	9.79072
	30	60	30	0.71044	9.39596
2,3-Naphthoquinodimethane	0	0	0	0.33874	15.53152
	30	60	30	0.38930	14.96240
1,2-Naphthoquinodimethane	0	0	0	0.72132	15.80206
	30	60	30	0.85838	15.26962

methane 93 absorbs at ca. 390-540 nm. This absorption is at shorter wavelengths than that of the unmethylated species 10, which is at 420-590 nm.[6]

An alternative mode of twisting was also considered in attempts to rationalise the absorption characteristics of the o-xylylenes. In this mode, the exocyclic methylene groups were twisted, while the ring was kept in a planar geometry (1d). These calculations showed that the HOMO-LUMO gap (ΔE) would decrease with twisting. For example, for $\theta_4 = 30°$, $\Delta E = 0.4926$. This would cause the absorption maximum to shift to longer



1d

wavelengths, in contrast to observations. Hence this form of twisting, if present, would be of little significance.

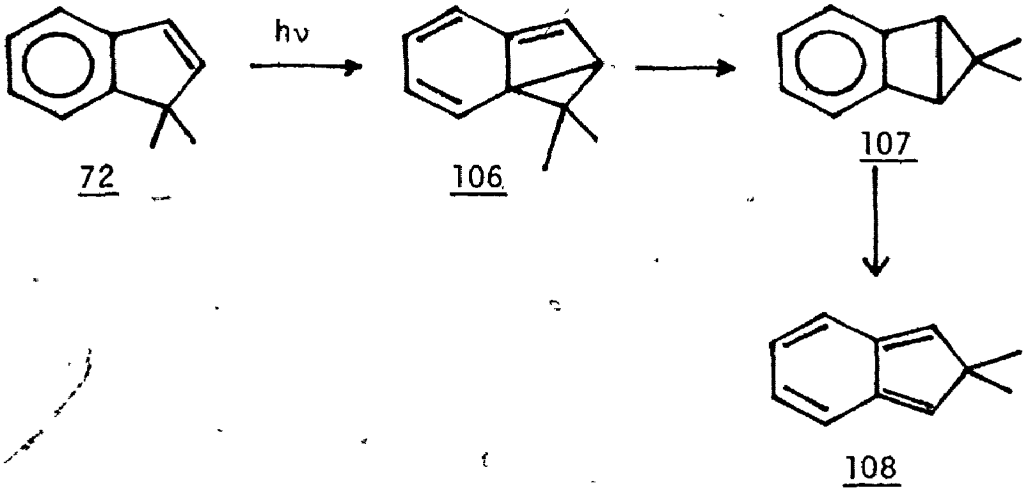
The inability to chemically trap any of the o-xylylenes generated by photodecarbonylation could be due to a variety of reasons. In general, tetrasubstituted dienes are not very susceptible to Diels-Alder trapping reactions, due to steric factors. The fact that the o-xylylenes are twisted, make them even less likely to be trapped. Since they are photolabile, it was not possible to build up an appreciable steady state concentration by low temperature photolysis, as was possible with triphenylisoindene. The use of filters to inhibit the photolysis of the o-xylylenes while not affecting the photolysis of the ketones, was attempted unsuccessfully. The irradiation of a solution of the ketone containing a dienophile usually gave rise to a large number of non-crystalline products indicating that even the photochemical generation of the o-xylylene may have been prevented by interference by the dienophile. For example, irradiation of the dimethyl or tetramethyl indanone in tetrahydrofuran containing an excess of maleic anhydride yielded an intractable mixture of products whose nmr seemed to indicate products derived from the solvent. When the solvent was changed to acetonitrile, only polymeric products were obtained. In another attempt, the dienophile 1-chloroacrylonitrile was used in tertiary butyl alcohol. The resulting product mixture showed nmr and i.r. signals consistent with oxetanes. One would expect the dimethyl-o-xylylene to be trapped more readily than the tetramethyl species, in spite of the shorter lifetime of the former, since steric hindrance and twisting is much greater in the tetramethyl compound.

Decay kinetics

All the o-xylylene type intermediates, encountered in the present work, decay to aromatic compounds, with an associated gain in resonance stabilisation energy. The mode of decay is usually a 1,5-sigmatropic hydrogen shift. In one case, however, cyclisation of the o-xylylene to a benzocyclobutene derivative was observed.

(a) Kinetic isotope effects

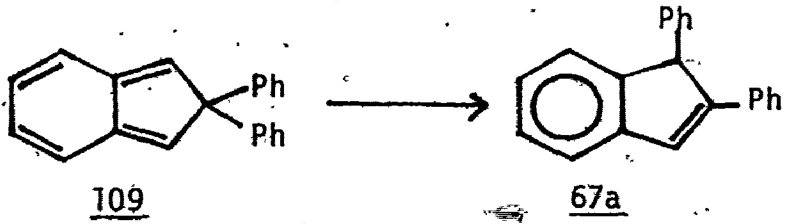
In several cases, the nature of the rate determining step in the removal of the isoindene was investigated by measuring the kinetic isotope effect for the decay process. 1,2-Diphenylisoindene and 1,2,3-triphenylisoindene show kinetic isotope effects of 6.5 and 3.7 respectively, and the 1,5-hydrogen shift is determining the kinetics of the decay of the isoindenes. The primary isotope effect is within the range of values observed in symmetry allowed, concerted, sigmatropic rearrangements.[46] Studies on 3-deuterio-1,1-diphenylindene showed that the secondary isotope effect is very small. These results on the kinetic isotope effect are especially important in view of the recent report on the skeletal rearrangement of 1,1-dimethylindene.[47] Irradiation of a dilute solution of 1,1-dimethylindene (72) at 0-10°C resulted in 2,2-dimethylisoindene (108) in 10-15% concentration relative to 72. This reaction is much less efficient than the phenyl migration of 1,1-diphenylindene, and has been proposed to proceed via an entirely different mechanism (Scheme 11).



Scheme 11

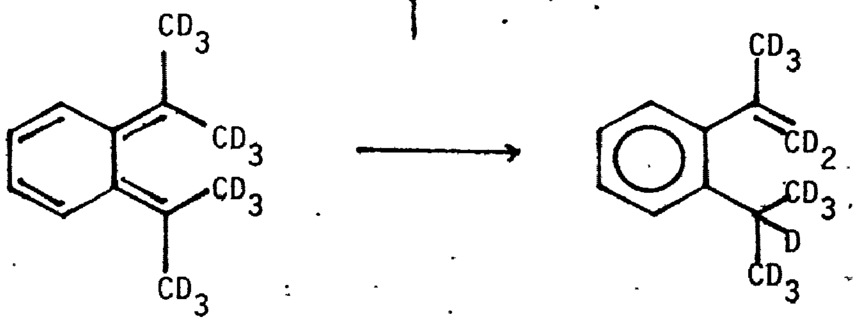
An initial photocyclisation to 106 is followed by a 1,3-sigmatropic alkyl shift to give 107, where aromaticity has been restored. The intermediate 107 then opens to the isoindene 108.

If a similar mechanism operates in the case of 1,1-diphenylindene, the transient observed in flash photolysis could be 2,2-diphenylisoindene (109), whose absorption may extend to 500 nm due to spiroconjugation of the two phenyl substituents with the isoindene chromophore. However, the decay of 109 to 1,2-diphenylindene (67a) would not show an isotope effect.



as high as 6.5, since secondary isotope effects are usually close to unity.[48]

Similarly, the kinetic isotope effect for the decay of the tetramethyl-o-xylylene 60 was 5.4, and showed that the decay process was not likely to be cyclisation to a benzocyclobutene, which is an alternative decay pathway. It is noted that the value of k_H/k_D in this case will have a substantial contribution from secondary effects, since the conversion of 110 to 111 involves the change in hybridisation at a carbon centre containing two deuterium atoms.[48] Assuming a secondary isotope effect of 1.2 per deuterium atom,[48] the total secondary effect would be 1.2^2, i.e. 1.4. No secondary isotope effect is expected to arise due to the other deuterium substituents, since the carbons they are bonded to do not change their hybridisation in the transition state for the deuterium shift. Hence, the primary isotope effect in 110 is ca. 5.4/1.4, i.e. 3.9. Similar reasoning shows that the secondary isotope effect for the cyclisation of 110 is expected to be unity.



110 111

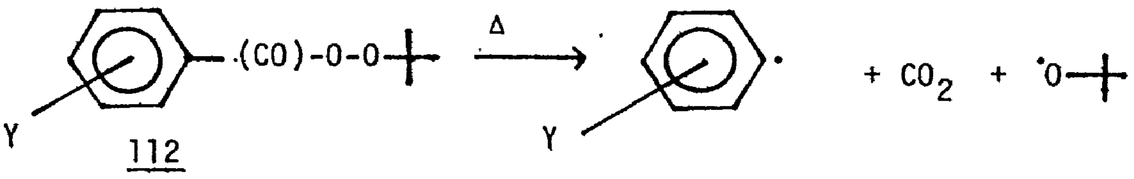
(b) Activation parameters

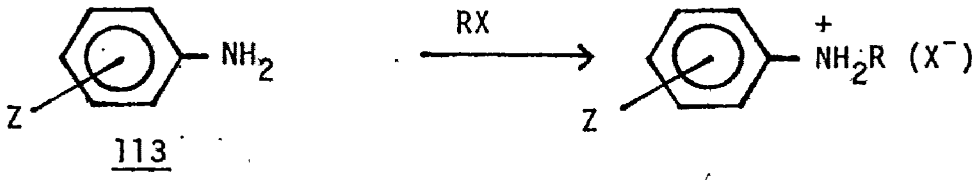
Activation parameters are also useful in characterising the decay process. Concerted reactions usually have low activation energies since there is no formation of free radicals or ions, and the bond making process commences before the bond breaking process is completed, thus lowering the energy of the transition state. Also, concerted reactions involve a great degree of order in the transition state, resulting in a decrease in entropy. The values of the Arrhenius parameters for 1,2-diphenylisoindene are $E_a = 13.1$ kcal mol^{-1} and ln A= 25.9. This corresponds to an entropy of activation, $\Delta S^{\circ\ddagger}$ of -9.0 cal K^{-1} mol^{-1} evaluated using $A = (eKT/h)e^{\Delta S^{\circ\ddagger}/R}$. The corresponding values for 1,2,3-triphenylisoindene are $E_a = 11.8$ kcal mol^{-1}, ln A = 20.6 and $\Delta S^{\circ\ddagger} = -19.6$ cal K^{-1} mol^{-1}. These values support a concerted mechanism for the 1,5-hydrogen shift. It is noted that the longer lived transient, 1,2,3-triphenylisoindene, has the lower activation energy, and its slow decay rate is due to a large negative entropy of activation. These values for the phenyl substituted isoindenes can be compared with the data on the 1,5-formyl shift in methyl substituted indenes. Field, Jones and Kneen[49] have reported $\Delta H^{\circ\ddagger} = 22.1$ kcal mol^{-1} and $\Delta S^{\circ\ddagger} = -11.4$ cal K^{-1} mol^{-1} for the 1,5-formyl shift in 1-formyl-1,3-dimethylindene in diphenylether solution. The results of Roth[50] on the hydrogen shift in 5H-perdeuteriocyclopentadiene give a value of $\Delta S^{\circ\ddagger} = -12$ cal K^{-1} mol^{-1}, while those of MacLean and Haynes[51] on the hydrogen shift in 1-methylcyclopentadiene and 1,5-dimethylcyclopentadiene yield values of -10 and -4 cal K^{-1} mol^{-1} respectively. Even more directly related to our work are the data of Miller and Boyer[21] on the H-shift in 1-phenylindene. They showed that the hydrogen-shift in diphenylether as a solvent had $\Delta S^{\circ\ddagger} = -2.3$ cal K^{-1} mol^{-1}. All the activation entropies are negative values, but the magnitudes differ markedly in the various molecules. All these molecules in which hydrogen shifts occur are effectively planar, yet the activation entropies are still very sensitive to the specific substitution in the system. It is possible that the large negative $\Delta S^{\circ\ddagger}$ for 1,2,3-triphenylisoindene is due to freezing of rotational motion in the substituent phenyl groups at the transition state.[53]

The methyl-o-xylylenes which have longer lifetimes than the isoindenes, show larger activation energies. The activation parameters are: 7,7-dimethyl-o-xylylene, E_a = 15.5 kcal mol^{-1}, $\Delta S^{\circ\ddagger}$ = -13.9 cal K^{-1} mol^{-1}; 7,7,8,8-tetramethyl-o-xylylene, E_a = 19 kcal mol^{-1}, $\Delta S^{\circ\ddagger}$ = -7.7 cal K^{-1} mol^{-1}. These activation energies are reasonable since E_a for a 1,5-hydrogen shift in 1,3-pentadiene[52] is 35.4 kcal mol^{-1}. The latter process lacks the driving force towards aromatisation, and its E_a is higher. It is noted that the large difference in $\Delta S^{\circ\ddagger}$ between the dimethyl- and tetramethyl-o-xylylenes could possibly be due to different types of transition states involved in the two cases. The conformation of the tetramethyl species is ideally suited for an antarafacial 1,5-hydrogen shift, and the formation of such a transition state would involve relatively little loss of entropy. The dimethyl-o-xylylene could decay via a suprafacial 1,5-hydrogen shift, resulting in greater entropy loss.

(c) Substituent effects

The structure of the transition state for the hydrogen-shift was further investigated using a series of substituted 1,1-diphenylindenes. The small negative slope (-0.6) of the line indicates that the transition state for the 1,5-hydrogen shift is electron deficient at C-2 of the five membered ring (the migration start), and that the migrating hydrogen has a slight "hydride ion" character. The extent of electron withdrawal from C-2 is rather small, as evidenced by the small negative value of ρ. This value of -0.6 is similar to ρ for the decomposition of t-butylperbenzoates (112) (-0.5 - -0.9),[31b] a reaction in which charged species are not formed, but much less than ρ for quaternarization of anilines (113) (-3.0 - -4.0).[31b]

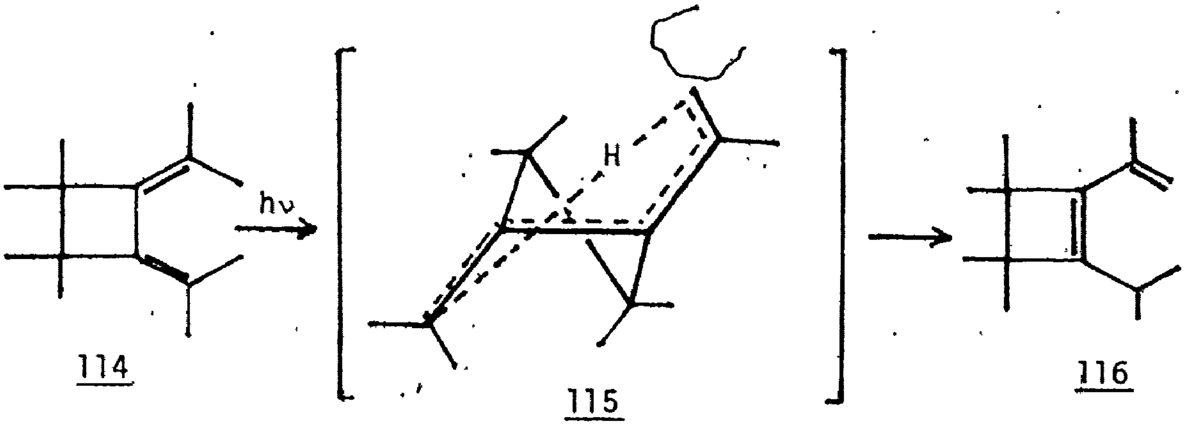




(R= 2,4-dinitrophenyl; X= Cl, F)

(d) Orbital symmetry considerations

In the proposed structures for the tetramethyl o-xylylenes, the molecule cannot adopt the planar geometry necessary for the symmetry allowed suprafacial 1,5-hydrogen shift, and it adopts a nearly ideal configuration for antarafacial 1,5-hydrogen transfer (see Figure 11, p.54). This suggests that the thermal decay may involve the previously unknown antarafacial 1,5-hydrogen shift which is a symmetry disallowed (forbidden) process.[29] The fact that the transient decay is accelerated on irradiation is consistent with the antarafacial 1,5-shift being a photochemically allowed process, for which there is precedence in the work of Kiefer and co-workers.[54] Thus, irradiation of the tetramethylallene dimer 114 resulted in the clean formation of the isomeric 116. It was suggested that geometrical constraints in



114 115 116

114 forced it to adopt a nearly ideal configuration for antarafacial 1,5-hydrogen shift, and that the reaction proceeded via 115.

Since a symmetry disallowed process is invoked in the present work, it is opportune to discuss some of the references to symmetry disallowed processes in the recent literature. Since the principle of the conservation of orbital symmetry in concerted reactions was postulated by Woodward and Hoffmann,[55] several workers have put forward alternative theoretical schemes to explain concerted reactions.[56] Another major development in the field was the realisation that some reactions apparently violated the Woodward-Hoffmann rules. It is stressed that all other factors being equal, the symmetry allowed process is favoured over the symmetry forbidden one. It is only when, for example, geometrical constraints make the symmetry allowed pathway of prohibitively high energy that the possibility of forbidden processes or diradical intermediates arises. Symmetry disallowed reactions have been explained in one of two ways. One recognises the role of orbital interactions other than frontier orbital interactions in stabilising the transition states of symmetry forbidden processes.[57] The other recognises the fact that when configuration interaction (CI) is considered in describing the electronic nature of molecules, and transition state complexes, one could account for low activation energy symmetry disallowed processes.[58]

Configuration interaction is important in compounds with low lying electronically excited states, such as those with extended π systems.

Biradicaloid compounds, which contain two approximately nonbonding MOs require configuration interaction to satisfactorily describe their electronic states.[2] Nonpolar biradicaloid species have three low-lying singlet states, each of which is described as a mixture of three electronic configurations,[2] shown in Figure 12. The lowest energy electronic configuration (G) has both electrons in the more bonding frontier orbital. The other two configurations are singly (S) and doubly (D) excited configurations. The lowest energy singlet state So, corresponds to an out-of-phase (G-D) combination of the two configurations G and D. The state S_1 corresponds to the configuration S, and the state S_2 to the combination (G+D). The relative energies of S_1 and S_2 depends on the HOMO-LUMO gap (ΔE). (As ΔE is very large, as in "normal" molecules, the ordering of energies is $S_0 < S_1 < S_2$, and S_0 and S_2 are well represented by pure G and D configurations, respectively.) Hence, as molecules become more biradicaloid, there is greater configuration interaction, and hence it is more likely that there is a low lying excited state of the right symmetry such that the energetic difference between forbidden and allowed processes is minimised.

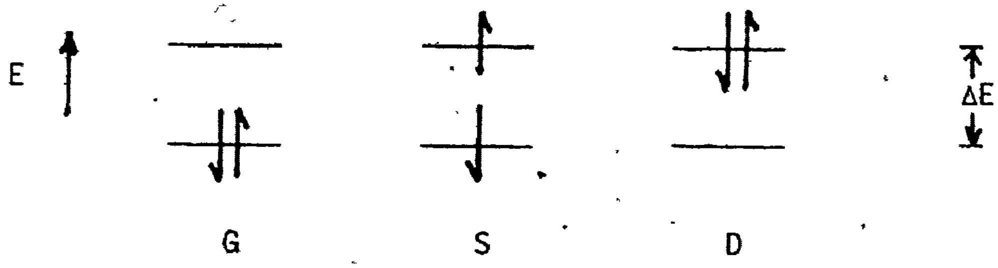
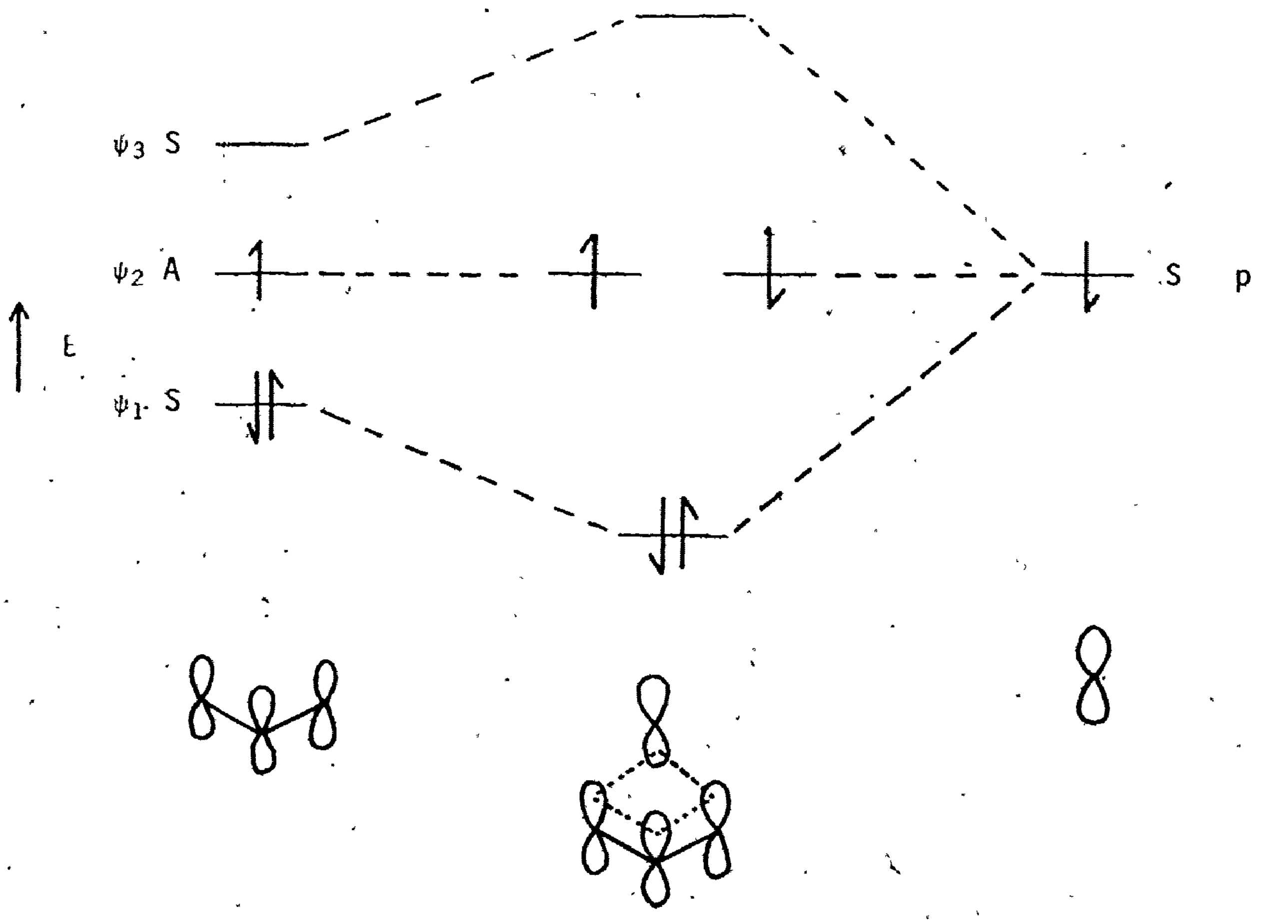


Figure 12. Three electronic configurations of a biradicaloid species.

Berson and Salem[57,59] have shown that in the 1,3-sigmatropic alkyl shift, the symmetry forbidden process is of lower energy, than the "diradical" process (non-concerted), due to transition state stabilisation by the interaction of the migrating p orbital with the subjacent bonding allyl orbital (ψ_1) (Figure 13). More directly



2s + 2s (thermally forbidden)

Figure 13. Orbital energies of the suprafacial 1,3-sigmatropic rearrangement transition state for the thermally forbidden mode.

related to our work are the theoretical calculations, of Bingham and Dewar,[60] of the activation energies for allowed and forbidden 1,5-hydrogen shifts. These workers used a MO theory in which CI with the first doubly excited configuration was included (MINDO/CI). The inclusion of CI was crucial, since the transition states of antiaromatic (symmetry forbidden) concerted reactions are biradicaloid, due to the fact that during an antiaromatic pericyclic reaction, the HOMO and LUMO must cross at some point, at or near the transition state.[60] The calculations were performed for the 1,5-shift in cis-piperylene (117 → 119), and showed that the activation energies for the suprafacial (allowed) and antarafacial (forbidden) shifts were 28.3 and 37.0 kcal mol^{-1} respectively. Hence we find that the difference in E_a is only 8.7 kcal mol^{-1}. The corresponding difference for the tetramethyl-o-xylylene 60 is expected to be less, due to the presence of low lying excited states. It is possible that for the 2,3-naphthoquinodimethane 93, the allowed and forbidden processes have very similar activation energies. On the other hand, the 1,2-naphthoquinodimethane 91 which is the least biradicaloid may have an unsurmountably large E_a, causing its thermal stability. These arguments support the feasibility of a symmetry forbidden process in the tetramethyl-o-xylylenes 60 and 93.

117 118 119

(e) Thermochemical calculations

Thermochemical calculations were performed to estimate the driving force towards aromatisation of the tetramethyl o-xylylenes. The method of group additivity[61] was employed (see Appendix). The results (Table 13) show that the enthalpy changes for conversion of 89, 60, 91 and 93 to their respective products are -30.4, -28.4, +3.2 and -48.2 kcal mol^{-1} respectively. These are consistent with the thermal stability of 91, and the very short lifetime of 93 . 93, which is the most biradicaloid species studied, has a large driving force to aromatise two rings. It could barely be observed at the detection limit of our instrument, ≈5 microseconds.

Table 13. Thermochemical calculations

Compound	ΔH_f	$\Delta\Delta H_f$
	(kcal/mol)	
7,7-Dimethyl-o-xylylene (89)	50.12	-30.4
1-Methyl-2-isopropenylbenzene (90)	19.70	
7,7,8,8-Tetramethyl-o-xylylene (60)	37.04	-28.4
1-Isopropyl-2-isopropenylbenzene (61)	8.64	
9,9,10,10-Tetramethyl-1,2-naphthoquinodimethane (91)	21.77	+ 3.2
1-Isopropenyl-2-isopropylnaphthalene (92)	24.92	
9,9,10,10-Tetramethyl-2,3-naphthoquinodimethane (93)	73.16	-48.2
2-Isopropyl-3-isopropenylnaphthalene (94)	24.92	

(f) Ground state energy of 1,2-diphenylisoindene

The activation energy data for the decay of the isoindenes are very interesting, in that they can be used with literature data to estimate, for the first time, the difference in energy between an isoindene and an indene. Miller and Boyer[21] report an activation energy of +33.2 kcal mol^{-1} for the thermal conversion of 1-phenylindene to the isoindene. One can obtain the ground state energy of the isoindene with respect to that of the indene from the difference in the activation energies of the forward and reverse reactions. The compound chosen to model the reverse reaction should have a phenyl group at the 1-position since Miller and Boyer[21] found that the substitution of a phenyl group for a hydrogen atom at the start position of an H-migration in the thermal reaction increases the rate by about 130 (due to the change in the conjugation of the phenyl group at the 1-position from nonconjugated in the reactant to conjugated in the isoindene, and so to conjugated in the transition state). 1,2-diphenylindene was chosen as the model compound, and it was assumed that the activation energy, E_a^{II} of Figure 14 for the thermal conversion of the diphenylindene, is the same as that measured by Miller and Boyer[21] for 1-phenylindene. This leads to a value of about 20 kcal mol^{-1} for the difference in the energies of 1,2-diphenylindene and 1,2-diphenylisoindene.

As the value reported above for the energy difference between the diphenylisoindene and the diphenylindene is the only value available that is based on experimental data, it was worthwhile to estimate that energy difference using other techniques. The experimental value was determined using hexane as a solvent. However, Miller and Boyer[21] have shown that the 1,5-hydrogen shift in 1-phenylindene does not depend on the identity of the solvent, in agreement with results on other 1,5-hydrogen shifts.[62]

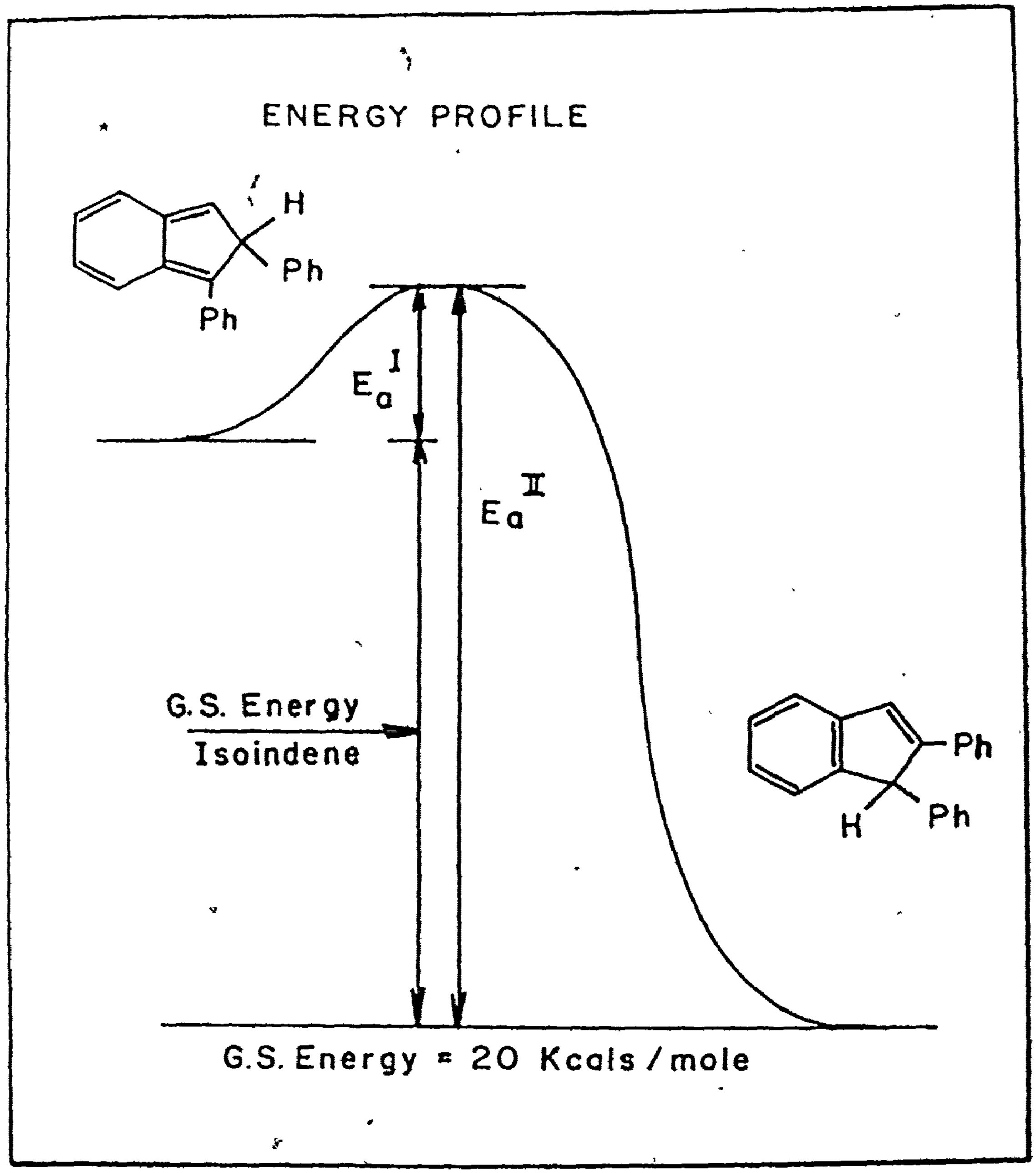


Figure 14. Energy verses reaction coordinate profile for the 1,2-diphenylisoindene to 1,2-diphenylindene conversion. E_a^{II} is the corresponding literature value[21] for 1-phenylindene conversion.

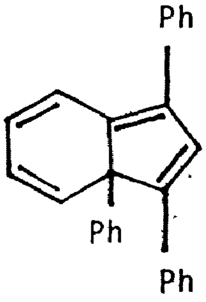
Thus the solvent, in this instance, appears to fill the role of merely occupying space, rather than being directly involved in the solvation of the reactant or the transition state. Accordingly, the techniques proposed by Benson[61,63] to estimate the differences in the enthalpies of species in the gas phase, using group additivity methods, might be relevant to the case of the isoindene-indene conversion in solution. Initially the standard enthalpy change at 298°K was estimated for the conversion of the unsubstituted indene to the isoindene from the values for the standard enthalpies of formation, 42.0 and 68.6 kcal mol^{-1} respectively. In this case all the group additivity values were available and the estimate led to a value of ΔH = 26.8 kcal mol^{-1}. Not all the group additivity values were available to estimate directly the standard enthalpies of formation of 1,2-diphenylindene and 1,2-diphenylisoindene, but one could estimate a value by assuming that $C-(C_d)_2(C_B)(H) \approx -1.5$ and $C-(C_B)_2(C_d)(H) \approx -1$. This approximation led to an estimate of 26 kcal mol^{-1} for the difference in enthalpies of 1,2-diphenylindene and 1,2-diphenylisoindene. The estimate from the group additivity method for calculating enthalpies of formation in the gas phase is thus in reasonable agreement with the value, 20 kcal mol^{-1}, calculated from the experimental data in solution. Part of the discrepancy could be due to the use of the activation energy of 1-phenylindene as a model for the diphenylindene thermal conversion. It would be expected that the activation energy of the diphenylindene thermal conversion would be greater than that for the 1-phenylindene conversion (because of the loss of conjugation of the phenyl group at the 2-position).

Other considerations

(a) The long-lived intermediate from 1,1,3-triphenylindene

Irradiation of 1,1,3-triphenylindene gave rise to a long-lived yellow coloured (λ_{max} = 440 nm) intermediate. Its presence was noted in flash photolysis and it showed vinylic resonances in the low temperature nmr spectrum. Attempts to isolate this species by low temperature chromatography of the photolysed products gave rise to a fast-moving yellow band, seperated from the 1,1,3- and 1,2,3-triphenylindenes. However, analysis of the yellow species (which turned to a colourless compound on warming) showed the starting indene, 1,1,3-triphenylindene. Attempts to trap this long-lived species using N-phenyltriazolinedione were failures.

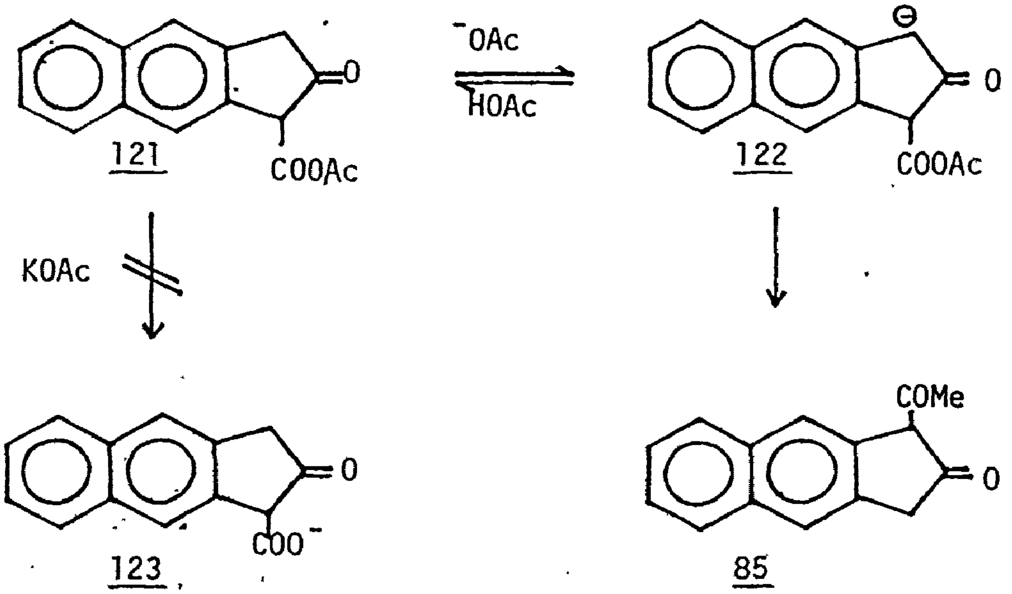
On this basis it is possible to speculate the structure of this species as 120, formed from 1,1,3-triphenyl~~indene~~ by a photochemical phenyl-shift. It is easy to see that it would rearomatise to 1,1,3-triphenylindene, at a rate much slower than the hydrogen shift of 1,2,3-triphenylisoindene.



120

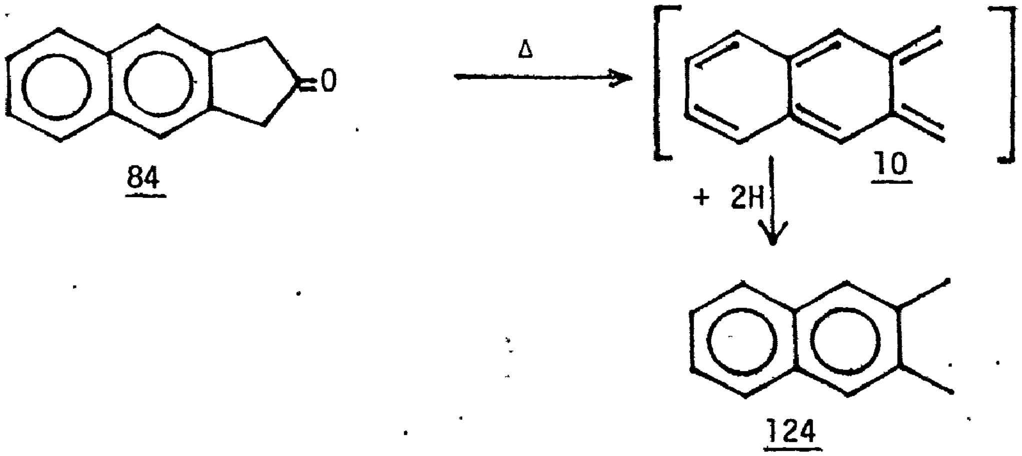
(b) Synthetic aspects

Most syntheses described in this thesis are quite straightforward, and will not be discussed here. However, the unexpected formation of 1-acetyl-5,6-benzindan-2-one (85) in the reaction of the dipotassium salt of naphthalene-2,3-diacetic acid (83) with acetic anhydride tempts one to postulate a mechanism based on the greater acidity of protons α to naphthalene, compared to benzene. (The corresponding reaction with benzene-1,2-diacetic acid yields indan-2-one.^{35}). Cyclisation of the dianhydride of 83 would yield the indanone derivative 121. This could react with acetate to



yield 123 (as was hoped!), or 122, by losing a proton α to the naphthalene ring. Intramolecular nucleophilic attack in 122, followed by ready decarboxylation of the β-keto acid formed, would yield the acetylated indanone 85. Alternatively, the desired indanone could have formed, and then reacted with acetic anhydride to yield 85.

The pyrolysis of the barium salt of naphthalene-2,3-diacetic acid gives 2,3-dimethylnaphthalene in addition to 5,6-benzindan-2-one. The former product probably arose by the decarbonylation of the indanone, which is thermally unstable. The resulting o-xylylene derivative could abstract



hydrogen atoms from the barium salt to yield dimethylnaphthalene. A similar generation of o-xylene from o-xylylene is known.[14]

The thermal instability of the indanone 84 and the analogous sulphone 99 in contrast to the thermal stability of the corresponding tetramethyl compounds 86 and 101 seem to indicate that tetramethylation confers stability towards the elimination of CO or SO_2. This is consistent with a concerted elimination reaction which would be a disrotatory process.[29] The methyl substituents would sterically hinder such a process.

Conclusion

These studies have shown that o-xylylenes, and the related isoindenes, can be generated as transients by aryl migration in the photolysis of suitable indenes and by photodecarbonylation of indan-2-ones. The transients can be investigated by various physical techniques (nmr and ultraviolet-visible spectrophotometry), and their lifetimes are in a range where the kinetics can be determined by flash photolysis experiments. Hence, the present work provides for the first time, compelling physical evidence for the intermediacy of o-xylylene type species in the photochemical phenyl migration in 1,1-diarylindenes and the photodecarbonylation of tetramethylindan-2-ones.

Activation energy studies have enabled the estimation of the energy difference between an isoindene and an indene, for the first time. Thus, 1,2-diphenylindene has been estimated to be only 20 kcal/mol lower in energy than 1,2-diphenylisoindene, indicating a moderate amount of resonance stabilisation in the isoindene system.

The tetramethyl o-xylylenes range from a thermally stable one to a very highly labile one with a lifetime of microseconds. This large difference in reactivity can be rationalised on the basis of their energies relative to stable products and the extent of their biradicaloid character.

EXPERIMENTAL

Materials

All solvents were reagent grade and were distilled before use. Hexane was purified by stirring for 24 h with fuming sulphuric acid (30% SO_3) followed by washing with water, sodium carbonate solution, and water. The hexane was dried over sodium sulphate and distilled. It showed negligible absorption above 240 nm (absorbance of 1 cm at 230 nm, 0.05). Tetrahydrofuran and benzene were distilled from lithium aluminum hydride. Tertiary butyl alcohol was distilled from calcium hydride.

1,1,3-Triphenylindene, 2-deuterio-1,1,3-triphenylindene and 2-deuterio-1,1-diphenylindene were prepared by the procedures of Miller and Boyer.[21] The diarylindenes (3c-e) were prepared as described.[23] 1,1,3,3-Tetramethylindan-2-one was synthesised by the procedure of Eastman and Starr.[28] The corresponding d_{12} compound was made similarly, except that CH_3I was replaced by CD_3I (99.5% D-Stohler Isotope Chem.). All the above materials had the reported melting points.

Photochemical and analytical methods

All photolyses were done under argon (Canadian Liquid Air, certified grade) in a Srinivasan-Griffin Photochemical reactor (Rayonet), unless otherwise stated.

Column chromatography was on silica gel (60-200 mesh), 'Baker Analysed' reagent grade, or alumina (Fisher certified, neutral, 80-200 mesh).

Analytical gas liquid chromatography (glc) was performed on a Varian-Aerograph Series 200 or a Tracor 560 dual column instrument with flame ionisation detectors. The columns used on the Varian instrument were (a) 5' x 1/8" of 10% Carbowax 20 M on 60/80 mesh Chromosorb W, and (b) 5' x 1/8" of 5% QF-1 on Chromosorb W. The Tracor instrument was used with a 6' x 1/6" column of 8% QF-1 on 80/100 Chromosorb W. The flow rate of the carrier gas (helium) was ca. 30 ml/min. Integration of glc peak areas were performed using a Varian Aerograph model 485 Electronic Digital Integrator.

Preparative glc was on a Aerograph Model 200 dual column instrument with thermal conductivity detectors. A helium flow rate of ca. 60 ml/min was used with a 5' x 1/5" column of 7% QF-1 on Chromosorb W.

Proton nuclear magnetic resonance (nmr) spectra were obtained at 100 MHz on a Varian HA-100 spectrometer or at 90 MHz on a Varian EM-390 spectrometer. ^{13}C nmr spectra were at 22.62 MHz on a Bruker WH-90 Fourier Transform Spectrometer. The solvent was chloroform-d, unless otherwise stated. The chemical shifts are δ values (p.p.m.) measured downfield from tetramethylsilane which was the internal standard.

Infra-red (i.r.) spectra were recorded with a Beckman IR-5 or a Perkin-Elmer 283 spectrophotometer. The solvent was spectrograde chloroform, unless stated otherwise. Ultraviolet spectra were on a Cary 14 spectrophotometer. Fluorescence spectra were taken using an Aminco Bowman Spectrofluorometer utilising a xenon-mercury lamp for excitation. Mass spectra were obtained using a CEC 21-110 mass spectrometer. Melting points (mp) were on a 'Kofler' Hot stage apparatus and are uncorrected. Temperatures are in °C.

Elemental analyses were by Galbraith Laboratories, Knoxville, Tennessee.

PART A. ISOINDENES

Irradiation of 1,1,3-triphenylindene (65b)

A solution of 1,1,3-triphenylindene (45 mg, 0.13 m mole) in hexane (150 ml) was irradiated at -78°C, under argon, with a Hanovia type L 100 watt mercury lamp in a centrally placed quartz immersion well. The latter was double walled, and the space between the walls was evacuated. The lamp was cooled with a current of air. The irradiation was continued for 15 min, and the resulting orange solution was warmed to room temperature and left for 3 hr. Analysis by glc on QF-1 at 220°C showed that 90% of the 1,1,3-triphenylindene had reacted, and a single product had been formed. The solvent was distilled and the mixture was chromatographed on 4.0 x 35 cm of silica gel, slurry-packed in hexane. Elution was with 10% benzene-hexane and 75 ml fractions were collected. Fractions 7-10 contained 1,2,3-triphenylindene, mp 132-134° (Lit^{65} 132-134°), from ethanol, yield 78%.

Attempt to isolate the 'long-lived' intermediate from 1,1,3-triphenylindene (65b)

The above irradiation was repeated for 10 min., the solution concentrated under vacuum at -10°C, and chromatographed at -5°C on 4 x 15 cm silica gel, slurry packed in hexane. Elution was with hexane containing a trace of ether and 40 ml fractions were collected. The yellow species was eluted first, seperated from 65b and 67b by 2 fractions. However, removal of solvent at -10°C yielded 1,1,3-triphenylindene.

Low-temperature NMR spectra

A solution of 1,1,3-triphenylindene (10 mg) in ca. 0.7 ml of cyclopentane was transferred to a quartz nmr tube (tube no. 703 PQ, Wilmad Glass

Co., Inc., Buena, N.J.). The ^{1}H nmr spectrum of the solution was run at -78° on the HA-100 spectrometer. The solution was then purged with argon for 10 min at room temperature, and was cooled again to -78° in a bath of ethanol. The ethanol was contained in a partly silvered, quartz Dewar, and was cooled with a "Flexi-Cool" refrigeration system (FTS systems, Inc., Stone Ridge, N.Y.). The cold sample was irradiated in the cooling bath for 40 min in a Rayonet Photoreactor, using 9 RPR 2537 Å lamps.

The sample was quickly transferred to the precooled probe of the spectrometer, and the spectrum of 1,2,3-triphenylisoindene was taken. Finally, after warming to room temperature, the spectrum of the product solution was obtained at -78°C. In all of the above, the singlet resonance of the solvent (cyclopentane) at 1.51δ served as reference and lock. The spectra of irradiated 2-deuterio-1,1,3-triphenylindene were obtained similarly. The spectra are shown in Figure 2.

Low-temperature visible absorption spectrum

A solution of 1,1,3-triphenylindene (3.0 mg) in cyclopentane (∿ 0.7 ml) was irradiated at -78° for 5 min, and described above for the nmr experiments. The irradiated solution was poured into a vacuum-jacketed absorption cell, of 4.5 cm path length containing 70 ml of isopentane at -78°C. The absorption spectrum was taken. The spectrum had λ_{max} = 478 nm, approximate log ε = 4.6 (see Figure 1).

Fluorescence spectra

A sample of 1,1,3-triphenylindene (or 1,1-diphenylindene) in cyclopentane in the nmr tube was irradiated as described for the absorption spectrum. The sample was kept at -78°C using the quartz dewar, normally used for phosphorescence spectra, which contained dry-ice-methanol. The fluorescence spectrum was obtained with the Aminco-Bowman Spectrofluorimeter.

Excitation was at 546 or 436 nm for triphenylindene and at 436 nm for diphenylindene.

Trapping of 1,2,3-triphenylisoindene (66b)

A solution of 4-phenylurazole (500 mg) in methylene chloride (25 ml) was cooled to -3°C and treated with 2.0 g of lead tetraacetate[66] (Alfa Inorganics, containing 10% of acetic acid). After stirring for 3 min, the red solution was cooled to -78°C. Triphenylindene (100 mg) in tetrahydrofuran (distilled from $LiAlH_4$) (125 ml) was purged with argon for 15 min, cooled to -78°C, and irradiated with the 100 W Hanovia lamp and vacuum jacketed immersion well described above, for 30 min. The cold solution of dienophile was then added, the mixture was kept at -78°C for 2 hr and then was warmed to room temperature. Evaporation gave a brown solid which was washed with successive 25 ml portions of water, 0.1 N HNO_3 and 0.1 N NaOH. The solid was dissolved in acetone, boiled with charcoal and filtered through celite. Evaporation and recrystallization from methanol gave white crystals (50 mg) mp 268-269°C. Anal. Found: C, 80.74; H, 4.78; N, 8.19.

$C_{35}H_{25}N_3O_2$ requires C, 80.90; H, 4.85; N, 8.09.

Attempt to trap the 'long-lived' intermediate from 1,1,3-triphenylindene

The above irradiation was repeated for 25 min, and the temperature was raised to -50°C, when the orange colour was bleached. To the resulting yellow solution which was recooled to -70°C was added the cold solution of dienophile (above) and the whole warmed slowly to room temperature. Removal of solvent yielded a pale brown solid which was partially soluble in methanol. The methanol extract contained essentially 1,2,3-triphenylindene while the residue did not melt at 360° and was highly insoluble.

Preparation of 1,3-diphenyl-2,2-dimethyl-isoindene (16)

This isoindene was prepared by the method of Alder and Fremery.[9] A yellow oil was obtained on evaporation of the filtered reaction mixture, as reported. This showed three methyl group resonances at 1.74δ, 1.70δ and 1.68δ (100 MHz, $CDCl_3$ solvent). In an attempt to purify 16 by distillation, it was heated to ca. 240°C at 10^{-4} torr, and the distillate (166-168°C) was collected. The nmr spectrum showed that the resonance at 1.70δ had disappeared completely, while those at 1.74δ and 1.68δ remained. The latter are attributed to 68 formed from 16 by a methyl group shift.[30] 68 was distilled giving a pale yellow viscous oil.

Irradiation of 1,3-diphenyl-1,2-dimethylindene (68)

A solution of 68 (4 mg) in 3 ml hexane was transferred to a 1 cm quartz cell, purged with argon, and irradiated in a Rayonet photoreactor using six RPR 2537 A lamps, for 2 min. The absorption and fluorescence spectra were obtained. Excitation was at 436 or 450 nm.

Flash photolysis

All flash measurements were made using cylindrical, jacketed Vycor cells of 25 cm path length and 50 ml capacity. Temperature control (± 0.1°) was achieved by circulating water or methanol using a Forma Scientific Inc. constant-temperature bath. Solutions of the various indenes (2×10^{-4}M) were deoxygenated using oxygen-free nitrogen immediately prior to being flashed.

An energy input of 750 J/flash was discharged through a cylindrical flash-lamp, 70 cm long and containing xenon at 100 torr, which was parallel to the long-axis of the photolysis cell. The excitation flash lamp had a half-life of 30 μ sec. The absorption spectra of the transients were obtained after a pre-determined delay. Light from the monitoring flash

(180 J) was dispersed in a medium quartz spectrograph (Hilger E 498.7) and recorded on photographic film (Ilford FP4).

Decay of the isoindene intermediates was followed quantitatively by monitoring the transmittance of the light filtered from a continuous xenon lamp (Oriel Corp., Model 6137) placed in front of the photolysis cell. A Jarrell Ash, Model 82-410 monochromator and a 1P 28 photomultiplier connected to a Biomation Model 805 Waveform Recorder permitted the recording of the transmittance at a particular wavelength as a function of time. The data were transferred from the Waveform Recorder to punched tape and processed on the CDC 6400 computer. The decays followed first order kinetics, and the rate constants were determined at temperatures in the range 0 to 40°C. The errors in the activation energy and the pre-exponential factor were propagated in the usual manner and were significantly greater than the precision of the data.[53,67]

Investigation of effect of acid and base on decay time

A stock solution (200 ml) of 1,1-diphenylindene in purified hexane (5 mg indene/100 ml) was prepared. This was divided into three equal portions. One of these was used as a control sample. The second portion was shaken with 3N H_2SO_4 (2 x 20 ml) separated, and dried. This was flashed in the usual cell which had been rinsed with 3N H_2SO_4 and dried. The third portion was similarly treated with 3N NaOH and flashed in a base-treated cell. Good first order decay plots were obtained from all three solutions. The rate constants (22°C, deoxygenated solution) were: control, 38 s^{-1}; acid treated, 35 s^{-1}; base treated, 35 s^{-1}.

PART B. o-XYLYLENES

Syntheses

1,1-Dimethylindan-2-one (74)

74 was synthesised according to the method of Horan and Schiessler.[68]

1,1-Dimethylindene[32] (10 g, 69 mmoles) was added dropwise to a solution of 30% hydrogen peroxide (10 ml, 96 mmoles) in 50 ml 90% formic acid at 50°C. The resulting red solution was stirred at 55°C for 6 hours. The removal of solvent under reduced pressure yielded a viscous red oil. This oil was added to a boiling solution of 7% sulphuric acid, steam was introduced and the steam distillate was collected in an ice-cooled receiver. The distillate (300 ml) was extracted using methylene chloride (2 x 60 ml), the extracts dried (Na_2SO_4) and concentrated giving 8 g yellow oil which was purified by vacuum distillation (49°C/0.1 torr). The yield of colourless liquid was 7 g (63%).

The u.v. absorption maxima (in 95% ethanol) occur at 274, 267 and 261 nm with extinction coefficients of 1160, 1060 and 720 respectively. The i.r. spectrum includes peaks at 1750 (strained carbonyl), 1377 and 1354 cm^{-1} (gem dimethyl). The nmr signals are at 7.14 (s, 4H) 3.38 (s, 2H) and 1.20 (s, 6H).

Anal. $C_{11}H_{12}O$ requires C, 82.46; H, 7.55. Found: C, 82.47; H, 7.50.

4,5-Benzindan-2-one (79)

The method used was the same as that for 74. Thus, a mixture (ca. 50%) of 4,5- and 6,7-benzindenes[33] (1g, 6 mmoles) in 10 ml CH_2Cl_2 was added dropwise to a solution of 30% hydrogen peroxide (1 ml, 9.6 mmole) in

15 ml 90%

8 hrs and concentrated under vacuum giving a pale brown solid (0.8 g), which was added to 150 ml boiling 7% sulphuric acid and steam distilled. The distillate (600 ml) was filtered giving 70 mg (6%) white crystals. Extraction of the filtrate with methylene chloride did not yield additional material. Recrystallisation from ethanol gave colourless needles of 79 melting at 112-113^{o}C (lit.[69] 112-113^{o}C).

The i.r. spectrum shows the carbonyl absorption at 1751 cm^{-1}. The nmr signals are at 3.70 (s, 2H); 3.80 (s, 2H) and 7.3-8.0 (m, 6H).

1,1,3,3-Tetramethyl-4,5-benzindan-2-one (80)

300 mg (7.7 mmoles) potassium and 5 ml (54 mmoles) dry tert-butyl alcohol in 10 ml dry tetrahydrofuran was heated to reflux under a nitrogen atmosphere till all the potassium had dissolved. The solution was cooled in ice, and to it was added, in rapid succession, 170 mg (0.93 mmoles) 79 in 5 ml tetrahydrofuran, and 1 ml (16 mmoles) methyliodide. The mixture was refluxed for 3 h, cooled, and added to 100 ml water, which was then extracted with methylenechloride (3 x 50 ml). The combined organic extracts were washed with 5% HCl and water, dried (anhyd. Na_2SO_4) and concentrated giving 270 mg crude 80 which was purified by recrystallisation from aqueous ethanol, giving colourless crystals. Yield, 200 mg (90%). An analytical sample was prepared by sublimation, mp 124-124.5^{o}C. The i.r. absorptions are at 1746 (carbonyl), 1382 and 1362 cm^{-1} (gem dimethyl). The nmr signals are at 8.2-7.3 (6H, m), 1.65 (6H, s), and 1.40 (6H, s). The u.v. maxima (log ε) in hexane: 272 (3.7), 279 (3.8), 291 (3.6), 308 (3.0), 314 (2.9), 322 (3.2).

Anal. $C_{17}H_{18}O$ requires C, 85.67; H, 7.61. Found: C, 85.91; H, 7.68.

2-Amino-3-cyano-5,6-benzindene (82)

The method of Moore and Thorpe was used.[70] 0.5 g (2.4 mmoles) naphthalene-2,3-diacetonitrile[34] in 20 ml 'super dry' ethanol, was heated to reflux under oxygen free nitrogen and 0.5 ml of a solution of 100 mg sodium in 2 ml dry ethanol was added. After 45 min at reflux, the mixture was cooled and filtered giving 400 mg yellow crystals. Recrystallisation from ethanol gave 350 mg yellow crystals, mp 260° (d.); yield 70%. The nmr signals (acetone-d_6) are at 3.77 (2H, s), 7.0 (2H, s), and 7.2-7.9 (6H, m). The i.r. absorptions included 3420, 3340, 3250 and 1650 (NH_2); and 2200 (CN) cm^{-1}. An analytical sample was obtained by sublimation, mp 260° (d.).

Anal. $C_{14}H_{10}N_2$ requires C,81.53; H,4.89; N,13.58. Found: C,81.43; H,4.91; N,13.54.

Naphthalene-2,3-diacetic acid (83)

5.2 g (25 mmoles) naphthalene-2,3-diacetonitrile in 25 ml each of sulphuric acid, acetic acid and water was refluxed for 45 min. The mixture was added carefully to 150 ml cold water and the resulting solid filtered and dried giving 5.7 g crude 8. Recrystallisation from aqueous ethanol gave 5.3 g colourless needles (87%), mp 220-237°C. Repeated recrystallisation did not improve the melting range. The nmr absorptions of the methylene protons are at 3.93 (in acetone-d_6). The i.r. signal appeared at 1705 cm^{-1}

with a shoulder at 1730 cm^{-1}.

Anal. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95. Found: C, 69.05; H, 5.06.

1-Acetyl-5,6-benzindan-2-one (85)

200 mg (0.82 mmoles) of the diacid 83 was converted to the dipotassium salt by titration with potassium hydroxide in methanolic solution, to a phenolphthalein end-point. Concentration under vacuum yielded the dry salt, which was added to 1.5 ml acetic anhydride (distilled from anhyd. NaOAc). The mixture was heated slowly to 105°C when it darkened considerably. The mixture was cooled, 15 ml water and 1 g calcium carbonate added and extracted with methylene chloride (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate, water, dried (Na_2SO_4) and evaporated giving 100 mg brown solid. Sublimation yielded 50 mg pale yellow solid, mp 115°-120°C; yield 27%. The i.r. spectrum shows a broad signal at 1750 cm^{-1}. The nmr signals are at 3.70 (2H, s), 2.27 (3H, s), 6.73 (1H, s), and 7.3-7.9 (6H, m). The mass spectrum showed $M^+ = 224$.

Anal. $C_{15}H_{12}O_2$ requires C,80.33; H,5.39. Found: C,80.45; H,5.40.

5,6-Benzindan-2-one (84)

0.5 g (2 mmoles) of diacid 83 was mixed intimately with 0.8 g (2.5 mmoles) hydrated barium hydroxide and a drop of water. The resulting paste was dried and heated to 400°C in a sublimation apparatus under 0.1 torr. The sublimate (90 mg) was essentially a mixture of 2,3-dimethylnaphthalene and the desired ketone 84. Its ketone content depended on the individual experiment, and varied from 25-75%. The sublimate from various runs (900 mg) was combined and chromatographed on 3.0 x 30 cm of silica gel. Elution with 25% benzene-hexane yielded 2,3-dimethylnaphthalene, while the indanone 84 was eluted with 25% ethyl acetate-hexane. 84 was further purified by sublimation yielding 120 mg colourless crystals mp 130°C (d.) (sealed capillary). Estimated yield ca. 3%.

The i.r. showed a signal at 1755 cm^{-1}. The nmr : 3.77 (s, 4H), 7.4-8.0 (m, 6H).

Anal. $C_{13}H_{10}O$ requires C, 85.69; H, 5.53. Found: C, 85.53; H, 5.66.

1,1,3,3-Tetramethyl-5,6-benzindan-2-one (86)

86 was synthesised by two different routes; (a) the procedure used was the same as that for 80. Thus, 90 mg (0.49 mmoles) indanone 84 was methylated using 0.5 ml (8 mmoles) methyliodide and 200 mg (5 mmoles) potassium in 5 ml tert-butyl alcohol /10 ml tetrahydrofuran. Sublimation of the crude reaction product yielded 90 mg (77%) of pale yellow crystals. Recrystallisation from acetone: methanol yielded colourless needles mp 176-177°C (sealed capillary). nmr: 1.43 (s, 6H), 7.4-8.0 (m, 6H). The i.r. showed 1745 (C=O), 1360 and 1380 (gem-dimethyl) cm^{-1}. U.V. maxima (log ϵ) in hexane: 319 (3.19), 304 (3.15), 294 (3.53), 283 (3.70), 272 (3.66), 262 (3.53).

Anal. $C_{17}H_{18}O$ requires C, 85.67; H, 7.61. Found: C, 85.97; H, 7.59.

(b) 650 mg (2.2 mmoles) diacid 88 and 880 mg (2.8 mmoles) hydrated barium hydroxide were mixed intimately with a drop of water, dried, and pyrolysed at 350°C in a sublimation apparatus under 0.1 torr. The crude sublimate (330 mg) was recrystallised from acetone: methanol yielding 240 mg (45%) colourless crystals, which were identical with those formed as described in (a) above.

1,1,3,3-Tetramethyl-1,3-dihydronaphtho[2,3-c]thiopene-2,2-dioxide (101)

10 g 50% NaH (0.2 moles) (Baker Chem. Co.) was washed with light petroleum and placed under 50 ml dry tetrahydrofuran in a nitrogen atmosphere. To this was added dropwise, 2 g (9.2 mmoles) sulphone 99[39] and 6 ml (97 mmoles) methyliodide in 300 ml tetrahydrofuran. The mixture was stirred at 20°C for 20 min and refluxed for 5 h. Excess NaH was destroyed using ice, and the solution concentrated under vacuum. The residue was dissolved in methylenechloride, washed with 7% HCl and water, dried (Na_2SO_4) and concentrated giving yellow crystals. Recrystallisation from benzene/ligroin yielded 1.6 g (63%) pale yellow crystals. Sublimation gave white crystals mp 190-192°C. The nmr: 7.4-8.0 (m, 6H), 1.73 (s, 12H). The i.r. shows 1375, 1390 (gem dimethyl), 1310, 1180, 1150, 1122 and 1102 (sulphone).

Anal. $C_{16}H_{18}O_2S$ requires C, 70.04; H, 6.61; S, 11.69. Found: C, 70.21; H, 6.71; S, 11.60.

Pyrolysis of the sulphones 99 and 101

100 mg of 99 or 101 in 10 ml n-butylphthalate was heated to 300°C. A thin stream of nitrogen was passed over the solution and then through 3 ml water so as to dissolve any evolved SO_2. With 99, the reaction mixture darkened while the water turned acidic (pH less than 2) and decolourised a dichromate solution. However, with 101, the reaction mixture remained clean and the tests for SO_2 proved negative. Sulphone 101 could be recovered from the reaction even after prolonged refluxing in n-butylphthalate (330°C).

2-Keto-1,1,4,4-tetramethyl-1,2,3,4-tetrahydroanthracene (87)

The method of Barclay et al[37] was used. Thus, naphthalene (32 g, 0.25 moles), 2,2,5,5-tetramethyltetrahydrofuran-2-one (35 g, 0.25 moles) and aluminium chloride (anhydrous, 68 g, 0.51 moles) in 250 ml carbon disulphide was stirred at 20° for 8 h. The lower viscous complex layer was added to ice, extracted with ether, dried (Na_2SO_4) and concentrated. Distillation of the residue under 0.1 torr yielded 20 g viscous oil (bp 140°-180°C). Chromatography on 15 x 9 cm silica gel was effective in purifying 87. Thus, elution with 20% benzene-hexane removed some impurities. The ketone 87 was eluted using 2% ethyl acetate-benzene. Removal of solvent and crystallisation from ligroin yielded 4 g (6.2%) colourless crystals mp 84-85°. (lit.[37] 84-85°).

o-Bromomethyl-(2-chloro-2-propyl)-benzene (98)

Dry HCl gas was passed over 1.5 g (10 mmoles) 2-(o-methylphenyl)-propan-2-ol[38] at 0°C for 0.5 hr until two layers seperated out. The lower layer was removed using a fine capillary and dried with $CaCl_2$. Dissolved HCl was removed by pumping for 10 min at 0.1 torr. The nmr showed the product to be 2-(o-methylphenyl)-2-chloropropane (97).[38] It was dissolved in 30 ml CCl_4 and 1.7 g (9.6 mmoles) N-Bromosuccinimide and 2 drops of bromine were added. The mixture was stirred at 20°C under nitrogen, while being irradiated by a 100 W tungsten lamp for 1 h. The resulting succinimide was filtered, and the filtrate was concentrated giving 2.2 g 98, as a pale yellow oil. (Yield from alcohol, 89%). The nmr shows δ 7.5-7.0 (m, 4H), 4.9 (s, 2H), 2.0 (s, 6H). The mass spectrum showed m/e: 246 (100), 248 (125), 250 (32) consistent with one chloro- and one bromo-substituent.

The reaction of 98 with zinc-amalgam

1.25 g mercury (6.2 mmoles) and 120 mg (1.8 mmoles) zinc under dry benzene and nitrogen were heated at reflux with a crystal of iodine until the purple colour had discharged. The mixture was cooled to 20°C and 100 mg (0.4 mmoles) dihalide 98 in dry benzene was added. After stirring at 20° for 10 min the solution was filtered and concentrated. Preparative glc on

QF-1 at 90° yielded 10 mg (19%) α,2-dimethylstyrene (90) (retention time, 2 min at 80 ml/min).

Steady State Photochemistry

Irradiation of 1,1-dimethylindan-2-one (74)

282 mg 74 in 20 ml purified hexane (0.09 M) contained in a quartz tube was purged with argon and irradiated using sixteen RPR 3000 Å lamps. A slow stream of argon was maintained through the solution throughout the entire irradiation. Aliquots were withdrawn periodically and assayed by glc on carbowax at 130°. The irradiation was stopped after 5 h when ca. 70% conversion to a single product was shown. The solution was concentrated and filtered through alumina (11 x 0.5 cm), giving 75 mg colourless oil, identical with the dehydration product from 2(o-methylphenyl)propan-2-ol by nmr, i.r. and retention time on glc.[71] Nmr: δ 7.11 (m, 4H), 5.16 (m, 1H), 4.82 (m, 1H), 2.29 (s, 3H), 2.02 (d, J=2Hz, 3H). The i.r. included peaks at 1645, 900 (terminal CH_2=), 1490 and 765 (ortho-disubstituted benzene ring).

Irradiation of 1,1,3,3-tetramethyl-4,5-benzindan-2-one (80)

A solution of 110 mg 80 in 70 ml purified hexane (6.6×10^{-3} M) contained in a pyrex tube, under argon, was irradiated using sixteen RPR 3000 A lamps, for 8 h. Assay by glc on QF-1 at 150°C showed ca. 80% conversion to a main product and ca. 5% of secondary product. The main product was isolated by preparative glc on QF-1 at 120°. (Retention time 6 min, at a flow rate of 60 ml/min) yielding 35 mg (36%) pale yellow crystals. Recrystallisation from 95% ethanol, followed by sublimation to a cold-finger condensor at -78°C gave an analytical sample mp 110°-112°. The nmr spectrum (CCl_4) shows 8.0-7.2 (m, 6H), 5.42 (m, 1H), 4.89 (m, 1H), 3.30 (septet, J=7Hz, 1H), 2.08 (triplet, J=1Hz, 3H), 1.27 (d, J=7Hz, 3H), and 1.12 (d, J=7Hz, 3H), i.r. (CCl_4): 1645, 1250, 1290, 1420, 880 cm^{-1}.

Anal. $C_{16}H_{18}$ requires C, 91.37; H, 8.63. Found: C, 91.40; H, 8.45.

Irradiation of 1,1,3,3-tetramethyl-5,6-benzindan-2-one (86)

115 mg 86 in 25 ml 7% benzene-hexane contained in a quartz tube was purged with argon and irradiated using sixteen RPR 3000 A lamps. Aliquots were withdrawn periodically and assayed by glc on QF-1 with temperature programming from 175° to 225°C. The irradiation was stopped after 6 h when ca. 98% conversion to two products was seen. The products were separated by preparative glc on QF-1 at 110°, with a flow rate of 35 ml/min. The retention times were 62 min and 72 min, for the two products, identified as 2-isopropenyl-3-isopropylnaphthalene (94) and 3,3,4,4-tetramethylnaphtho-[b]cyclobutene (95), respectively.

The styrene 94 was purified by preparative glc on QF-1 at 150°, giving 30 mg (30%) colourless oil. The nmr (CCl_4): 7.2-7.8 (m, 6H), 5.17 (m, 1H), 4.89 (m, 1H), 3.21 (septet, J=6Hz, 1H), 2.10 (d, J=1Hz, 3H), 1.27 (d, J=6Hz, 6H). The i.r.: 1635, 1421, 1285, 1245, 860 and 690 cm^{-1}. The u.v. spectrum in hexane showed essentially naphthalene type absorption, tailing to 355 nm. The high resolution mass spectrum showed the parent ion at 210.1395. $C_{16}H_{18}$ requires 210.1408.

Anal. $C_{16}H_{18}$ requires C,91.37; H,8.63. Found: C,91.41; H,8.59.

The cyclobutene 95 was recrystallised from aqueous ethanol giving 10 mg (10%) rhombic crystals, mp 91-93°. The nmr (CCl_4): 7.2-7.8 (m, 6H) and 1.33 (s, 12H). The i.r.: 1500-1400, 1375, 1370, 1290, 1250, 860, 690

cm^{-1}. The mass spectrum(60°C,80eV) showed prominent peaks at m/e 210 (parent) , 195 and 165 (loss of methyl groups).

Anal. $C_{16}H_{18}$ requires C,91.37; H,8.63. Found: C,91.20; H,8.76.

Low temperature absorption spectrum

A solution of 1,1,3,3-tetramethylindan-2-one (9 mg) in cyclopentane (0.7 ml), contained in a quartz nmr tube was purged with argon and cooled to -78° in a quartz dewar, normally used for phosphorescence spectra, which contained dry-ice-methanol. The dewar was immersed in a 0.45 M solution of $NiSO_4$, in 3N H_2SO_4, contained in a quartz beaker. The whole assembly was irradiated using eight RPR 2537A lamps for 2.5 h, and the sample was poured into a vacuum-jacketed absorption cell, of 4.5 cm path length containing 70 ml of hexane at -78°. The absorption spectrum was measured.

Flash Photolysis

The experiments were conducted as described in section A, except that the Biomation waveform recorder was replaced by a Hewlett-Packard model 7047 A X-Y recorder which facilitated the measurement of slower rates. The decay curves were obtained on chart and processed manually. Computation of the first order rate constants (k) was on the HP-3000 computor.

The effect of acid and base on decay time was studied as in part A, using a stock solution of 5 mg <u>1b</u> in 100 ml hexane. Good first order decay plots were obtained. The rate constants (36.4°, deoxygenated solution) were: control, 0.0131 s^{-1}; acid treated, 0.0126 s^{-1}; base treated, 0.0129 s^{-1}.

APPENDIX AND REFERENCES

APPENDIX

Additivity of group thermochemical properties[61]

A molecular property is considered to be composed of contributions due to groups. The nomenclature followed in the table identifies first the polyvalent atom and then its ligands. Thus C-$(H)_3(C)$ represents a C atom connected to three H atoms and another C atom, i.e. a primary methyl group.

Group values[61] for ΔH_f^o (standard states of ideal gas at 1 atm and 25^oC) in kcal/mol

Group	ΔH_f^o	Group	ΔH_f^o
$C-(H)_3(C)$	-10.20	$C-(C_d)(C)(H)_2$	- 4.76
$C-(H)_2(C)_2$	- 4.93	$C-(C_d)_2(H)_2$	- 4.29
$C-(H)(C)_3$	- 1.90	$C-(C_d)(C_B)(H)_2$	- 4.29
$C-(C)_4$	0.50	$C-(C_B)(C)(H)_2$	- 4.86
$C_d-(H)_2$	6.26	$C-(C_d)(C)_2(H)$	- 1.48
$C_d-(H)(C)$	8.59	$C-(C_B)(C)_2(H)$	- 0.98
$C_d-(C)_2$	10.34	$C-(C_d)(C)_3$	1.68
$C_d-(C_d)(H)$	6.78	$C-(C_B)(C)_3$	2.81
$C_d-(C_d)(C)$	8.88	$C_B-(H)$	3.30
$C_d-(C_B)(H)$	6.78	$C_B-(C)$	5.51
$C_d-(C_B)(C)$	8.64	$C_B-(C_d)$	5.68
$C_d-(C_B)_2$	8.00	$C_B-(C_B)$	4.96
$C_d-(C_d)_2$	4.60	$C_{BF}-(C_B)_2(C_{BF})$	4.80

C_d represents a double bonded C atom, C_B the C atom in a benzene ring and C_{BF} the C atom in a fused ring system such as naphthalene.

Non-next-nearest neighbour corrections[61]

Group	ΔH_f^o
Alkane gauche correction	0.80
Alkene gauche correction	0.50
Cis-correction	1.00[a]
Ortho- correction	0.57

[a] When there are two cis-corrections around one double bond, the total correction is 3.00.

Corrections to be applied to ring compound estimates[61]

Ring	ΔH_f^o
Cyclobutene	29.8
Cyclopentadiene	6.0
Cyclohexa-1,3-diene	4.8

Sample calculation

$$\Delta H_f^o\ (CH_3\text{-}CH\text{=}CH_2) = C\text{-}(H)_3(C_d) + C_d\text{-}(H)(C) + C_d\text{-}(H)_2$$

$$= -10.20 + 8.59 + 6.26$$

$$= \underline{4.65}\ \text{kcal/mol}$$

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