PHOTOCHEMISTRY

AND

THERMOLYSIS OF THE 1,1-DIPHENYLINDENE SYSTEM

PHOTOCHEMISTRY AND THERMOLYSIS OF THE 1,1-DIPHENYLINDENE SYSTEM

By

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ABSTRACT

1,1-Diarylindenes rearrange when heated or irradiated to give 1,2- and 2,3-diarylindenes. Three 1,1-diarylindenes were synthesized and used in an attempt to probe the transition states for phenyl migration in both the ground and excited state. The three indenes synthesized were: 1-(p-bromophenyl)-1-phenylindene, 1-(p-cyanophenyl)-1-phenylindene and 1-(p-methoxyphenyl)-1-phenylindene.

On direct irradiation, the migratory aptitudes were $-C_6H_4CN$-p, 98%; $-C_6H_4OCH_3$-p, 95%; and $-C_6H_4Br$-p, 86%. On heating (258°C) the following aptitudes were found: $-C_6H_4CN$-p, 82%; $-C_6H_4OCH_3$-p, 48%; and $-C_6H_4Br$-p, 53%. The products were synthesized independently, and the product ratios obtained upon reaction were measured from the n.m.r. of mixtures, and by v.p.c. A charge transfer mechanism was put forward to explain the preference for migration of the substituted group in the excited state. Such charge transfer contributions are known to increase the rates of quenching in donor-acceptor pairs. A radical-type transition state was postulated as being present in the ground state migration. The rate constant for excited state rearrangement was calculated to be 4.9×10^9 sec^{-1}.

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INTRODUCTION

PART I: GENERAL

One of the more rapidly expanding areas of chemistry is the field of organic photochemistry. It may be defined as the study of the effect of light on organic compounds (compounds of carbon). Since ancient times, photochemical reactions of organic materials have been known. The early Greeks recognized that dyestuffs fade when left in the sunlight. Both Planck and Einstein attempted in their own way to understand the processes involved when a chemical compound reacts because of photoirradiation. The important preliminary investigations in the experimental science of organic photochemistry were performed by Ciamician and Silber[1], about 1900. They showed that chemists can expect many modes of behaviour from organic compounds upon irradiation. The four decades from 1900 to 1940 gave rise to many theoretical concepts. During this period, Einstein discovered that in order for a compound to react photochemically, a light absorption process must occur. The quantum yield concept was proposed and the Franck-Condon principle was developed.

During the period from 1940 to 1958 emphasis was on gas phase photochemistry. This was primarily because many organic photochemical reactions yielded complex mixtures which were difficult to separate and analyze. Separation of the products and determination of their structures became possible with the appearance of modern techniques and instrumental methods.

Recently, photochemists have become interested in the mechanisms of photochemical reactions. They now attempt to describe the exact reaction pathway of molecules from the initial light absorption to the final product formation. Spectroscopy has helped the photochemist to define and describe processes that result in light absorption and energy dissipation of excited

electronic states. Thus both physical and spectroscopic principles have been applied to organic molecules.

Organic molecules normally occupy the electronic state of lowest energy. This so called "ground state"[†] molecule, upon exposure to ultraviolet light or visible light of suitable wavelengths, is promoted to an "excited state"[†] (an electronic state of higher energy). Generally speaking, photochemists study the nature of these excited states.

A brief study of the basic theory of excited state photochemistry will be undertaken prior to a discussion of the migratory aptitudes in the excited state.

PART II: EXCITED STATE THEORY

The absorption of light energy by organic compounds in the visible and ultraviolet region involves promotion of electrons in σ (sigma), π (pi) and n-orbitals[#] from the ground state to higher energy states. These higher-energy states are described by molecular orbitals that are vacant in the ground state and are called antibonding orbitals. The antibonding orbital associated with the σ bond is called the σ^* orbital and that associated with the π bond is called the π^* orbital.

The generalized shapes of σ, σ^*, π and π^* orbitals are shown in Figure 1, where solid lines refer to σ and π bonding orbitals and dashed lines refer to σ^* and π^* antibonding orbitals. The dots represent atomic centers. The electronic transitions that are involved in the ultraviolet

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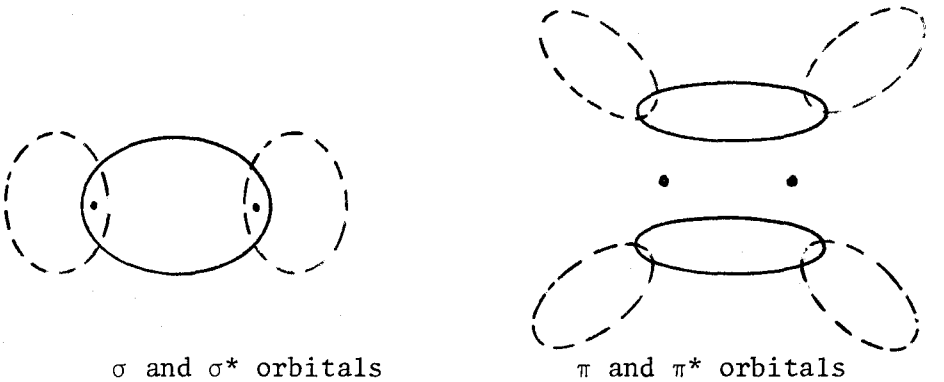
[†]All photochemical terms used but not defined in this thesis can be found in reference 2.

[#]Many molecules contain electrons that are not directly involved in bonding; these are called nonbonding or n electrons and are mainly located in atomic orbitals of oxygen, sulfur, nitrogen and the halogens.

and visible regions are of the following types: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The energy required for the $\sigma \rightarrow \sigma^*$ transition is very high; thus compounds in which all valence shell electrons are involved in single bond formation, such as saturated hydrocarbons, show absorption in the vacuum ultraviolet region.



σ and σ^* orbitals π and π^* orbitals

Figure 1. Electron densities associated with molecular orbitals.

Compounds containing nonbonding electrons on an atom such as oxygen or sulfur are capable of showing absorptions owing to $n \rightarrow \sigma^*$ transitions. These transitions are of lower energy than $\sigma \rightarrow \sigma^*$ transitions. An example of $n \rightarrow \sigma^*$ transition is shown by methyl alcohol, $\lambda_{max.}^{vapour}$ 173 mμ[3]. Transitions to antibonding π^* orbitals are associated only with unsaturated centers in the molecule. These latter transitions are of still lower energy requirement and occur at longer wavelengths. A ketone, such as acetone, exhibits an absorption of low intensity around 279 mμ which is attributed to an $n \rightarrow \pi^*$ transition and an absorption of high intensity around 189 mμ which is attributed to a $\pi \rightarrow \pi^*$ transition[3]. The $\pi \rightarrow \pi^*$ transitions are of intermediate energy, possessing absorptions usually between those of $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. The general relative electronic excitation energies for these transitions are shown in Figure 2.

Light absorption by an olefin, such as ethylene, results in the pro-

motion of one electron from the bonding π level to the essentially anti-bonding π^* level. Two possible spin configurations may be produced. If the electronic excitation occurs with complete retention of electron spin, the excited state is called a singlet state. If, on the other hand, excitation occurs with resultant spin inversion, the excited state is called a triplet state. Direct excitation to the triplet excited state, an excited state with spins unpaired, is a quantum mechanically forbidden process, and population of the triplet excited state usually results from some secondary process.

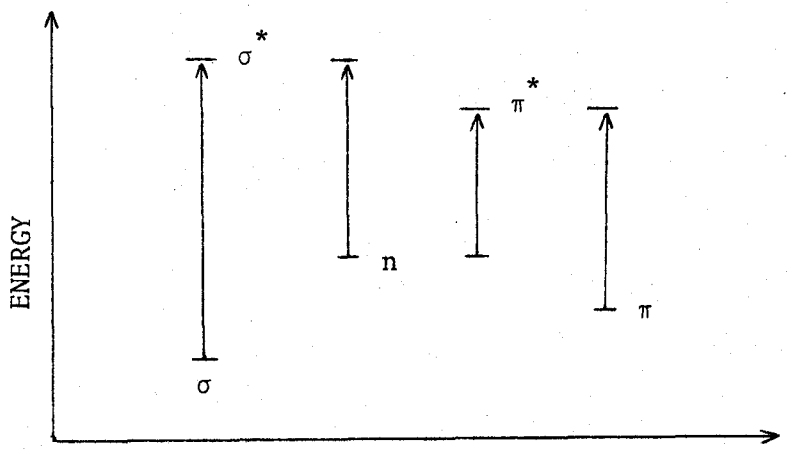
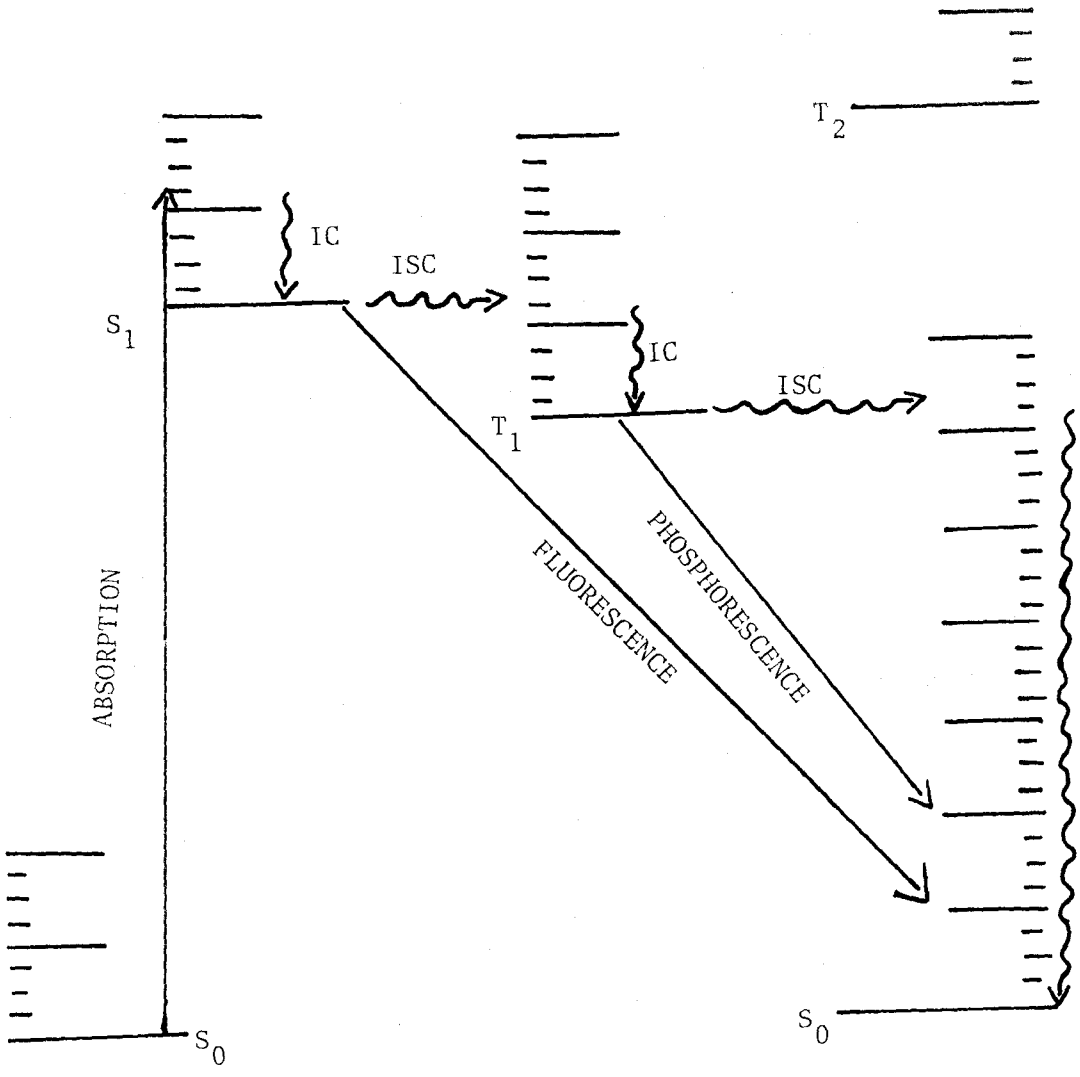


Figure 2. Schematic electronic excitation energies.

The Jablonski Diagram (Figure 3) is a pictorial representation of the energy transitions that result from the simple absorption by a molecule of ultraviolet radiation. The molecule is excited to one of the excited singlet electronic states (S_1 or S_2) and through a series of radiationless transitions called internal conversions, it decays to the excited singlet state of lowest energy. Generally, resulting transitions occur from this lower energy excited singlet level. The whole excitation process requires less than 10^{-12} sec. The molecule may then decay to the ground electronic



IC ≡ internal conversion

ISC ≡ intersystem crossing

Figure 3. The Jablonski Diagram.

state by emitting radiation called fluorescence in a time of 10^{-9} sec. The molecule may also undergo crossing to the first excited triplet state (T_1). This radiationless transition which requires less than 10^{-9} sec. is called intersystem crossing. The first excited triplet state is generally of lower energy than the first excited singlet state. Since singlet-triplet conversions are low probability transitions, the triplet state is longer lived than the singlet state. After a time period which may vary anywhere from 10^{-6} sec. to several minutes, the triplet state may decay to ground state by a radiative process called phosphorescence, whereby a photon of light is emitted. Both excited singlets and excited triplets can decay to the ground state by radiationless processes. These processes result because of collision with solvent, with the vessel walls or with other molecules. The observation of phosphorescence depends upon the limiting of other modes of deactivation to the molecule by freezing the compound from which phosphorescence is expected into a rigid matrix at low temperatures so that collisional deactivation is prevented[4,5].

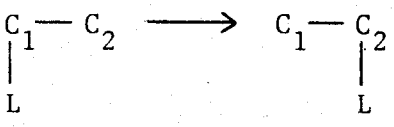
The energy-wavelength relationship is given by

$$E = 2.86 \times 10^4/\lambda$$

where E is the energy in Kcal/mole, and λ is the wavelength in millimicrons (1 mμ = 10^{-7} cm). Thus to excite 1,1-diphenylindene to its π - π^* singlet state requires 96.2 Kcal/mole of energy or light of 297 mμ wavelength.

PART III. MIGRATORY APTITUDES

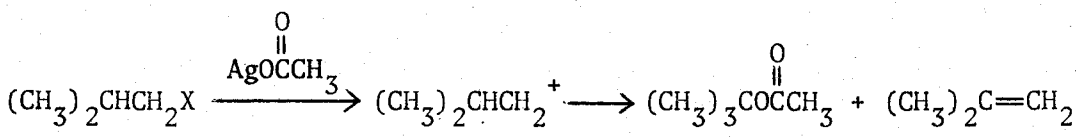
In an intramolecular reaction a group moves from one atom to another in the same molecule. A large number of intramolecular rearrangements can be described as resulting from so-called 1,2-shifts wherein the migrating group L goes from C_1 to C_2. In some reactions, the molecule may contain



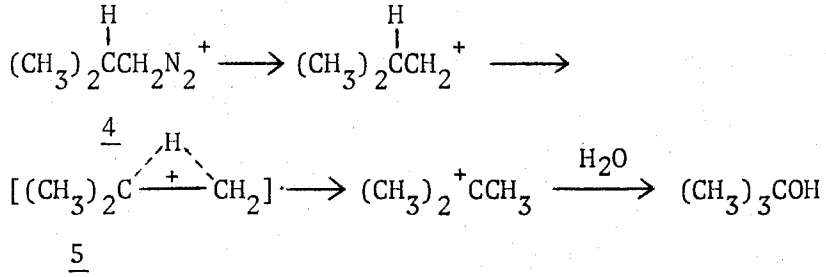
several groups which geometrically have equal chances of migrating. These reactions permit a direct study of relative migratory aptitudes of the groups, i.e., the relative tendencies of the substituted groups to shift from their original carbon atom of attachment to the adjacent carbon atom. The migrating group L may go from C_1 to C_2 via four different reactive intermediates: carbonium ion, carbanion, free radical and carbene intermediates.

1. Migratory aptitudes in carbonium ion rearrangements.

As early as 1872, Linneman[6] demonstrated hydrogen migration in the reaction of isobutyl halides 1 with silver acetate to form tert-butylacetate (2) and isobutene (3).

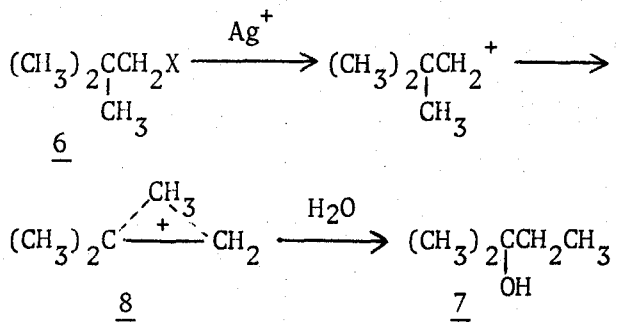


Cannel and Taft[7] studied the decomposition of the diazonium ion 4 in water to give tert-butanol. They postulated the presence of the hydrogen bridged carbonium ion 5.

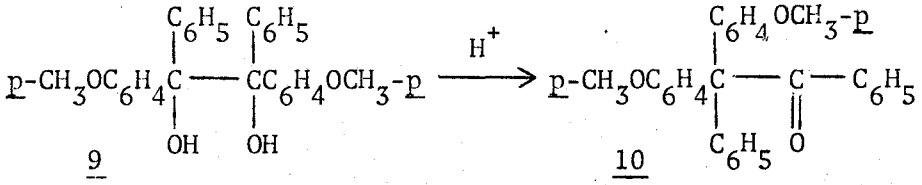


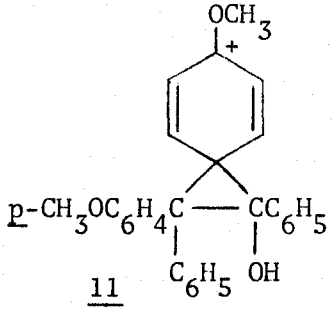
Likewise, 1,2-alkyl group migrations are plentiful in carbonium ion

rearrangements. The rearrangements of neopentyl halides 6 to isopentanol 7 were postulated by Dostrovsky and Hughes[8] as proceeding through the intermediate carbonium ion 8.



Another reaction shown to involve a carbonium ion intermediate is the pinacol rearrangement. Bachmann and Ferguson[9] studied the migratory aptitudes of substituted phenyl groups in the pinacol rearrangement of symmetrical glycols such as compound 9 to the ketone structure 10. They found a 500-fold preference for p-methoxyphenyl migration versus phenyl migration and postulated the intermediacy of structure 11. This structure allows for resonance stabilization of the carbonium ion by the methoxy substituent.



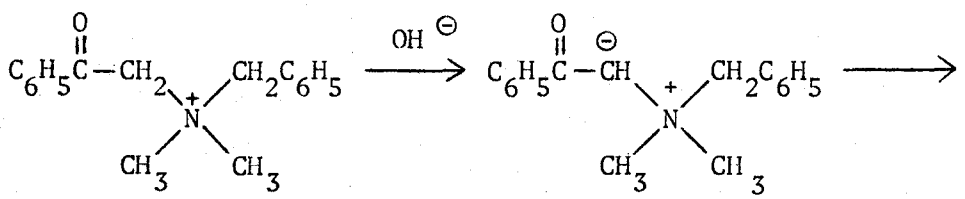


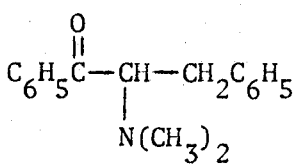
Extensive reviews of rearrangements involving carbonium ions have

been provided by Wheland[10] and Pocker[11].

2. Migratory aptitudes in carbanion rearrangements.

A number of 1,2-rearrangements are initiated by carbanion formation. The Stevens rearrangement[12] involves migration of an alkyl group from a quaternary ammonium to an adjacent carbanionic center.





STEVENS REARRANGEMENT

The work of Zimmerman[13] on the rearrangement of 2-phenyl-2-p-tolylpropyllithium (12) showed an eleven-fold preference for the product 13 of phenyl migration over the product 14 of p-tolyl migration. He postulated the presence of the half-migrated species† 15 and 16 and noted that the phenyl rearrangement intermediate 15 should be of lower energy than the p-tolyl migration intermediate 16, since in the latter, electron delocalization toward the p-position of the migrating ring is inhibited by the presence of the methyl group.

No examples are given in the literature where cyanophenyl is compared with phenyl in a 1,2-intramolecular carbanion rearrangement; however, it is

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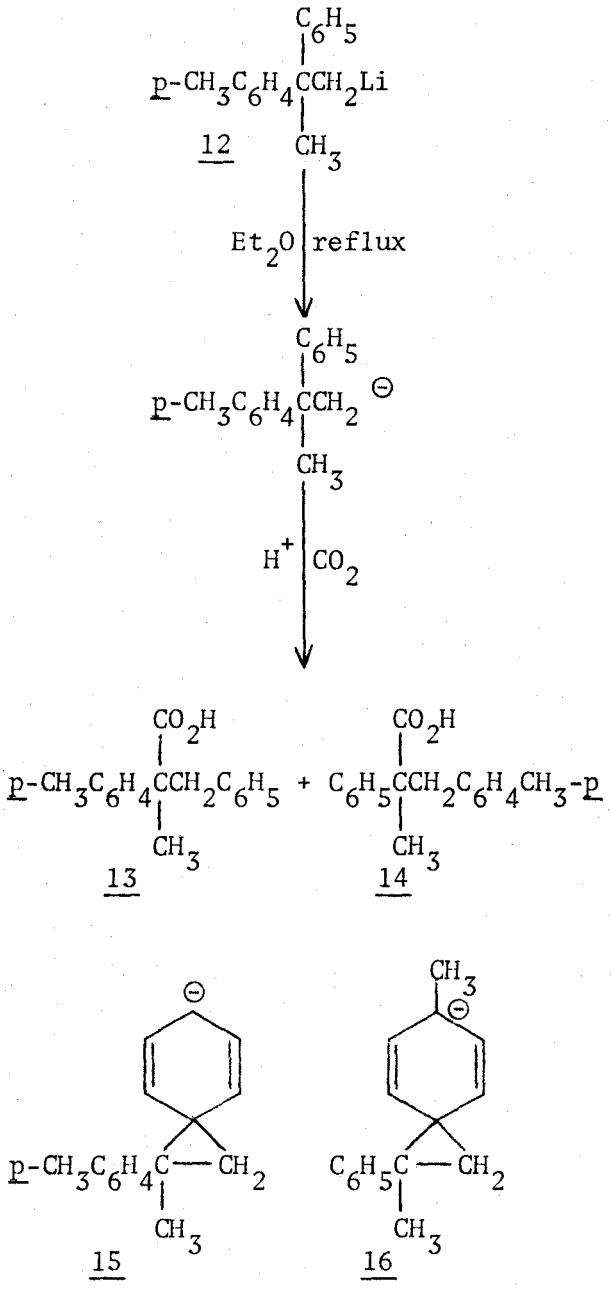
†Whether the half-migrated species was a transition state or intermediate was not stated by Zimmerman. Rather he said that in either event the half-migrated species approximates the transition state in geometry and parallels it in energy.



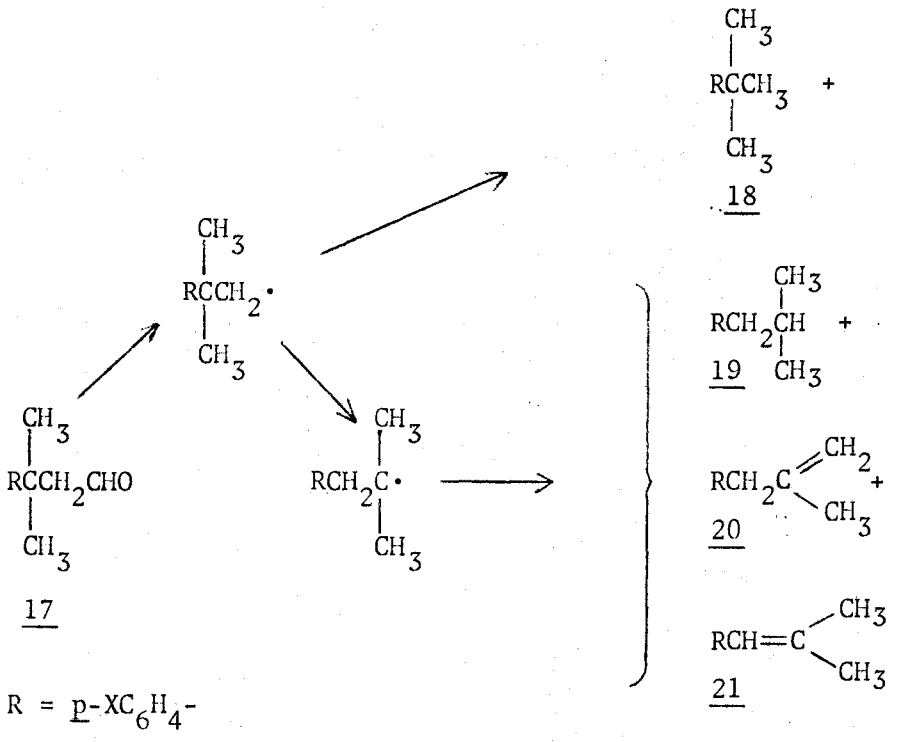
Rearrangement of 2-phenyl-2-p-tolylpropyllithium (12)

expected that the cyano substituent would readily accommodate the negative charge and hence cyanophenyl migration would be favoured.

A thorough study of 1,2-rearrangements involving carbanion intermediates has been done by Cram[14].

3. Migratory aptitudes in ground state free radical rearrangements.

The largest group of ground state free radical rearrangements are those involving aryl groups. Rüchardt[15] studied the peroxide catalyzed decarbonylation of aryl-substituted isovaleraldehydes 17. By observing the

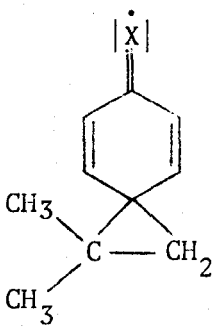


product ratio, when R was substituted phenyl, of the three compounds 19, 20 and 21 to compound 18 and comparing this ratio with the ratio observed when R was phenyl, Rüchardt was able to compare the relative rate of migration (k) of substituted phenyl versus phenyl. He observed a trend favouring migration of phenyl bearing electron withdrawing substituents (Table 1).

X	k
H	1.0
CH_3O	0.35
Br	1.79
CN	19

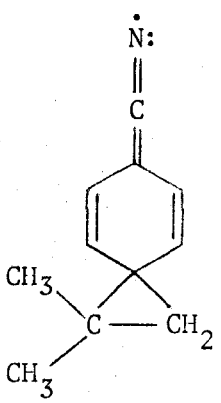
Table 1. Relative rate of migration (k) of substituted phenyl vs. phenyl (X = H) in rearrangement of decarbonylated isovaleraldehydes.

The rationale was that the electron withdrawing substituents were able to accommodate an additional electron and hence served to stabilize the transition state for migration. Structures 22 and 23 are two of the proposed stabilized transition states for migration.



22 X = Cl, Br

or



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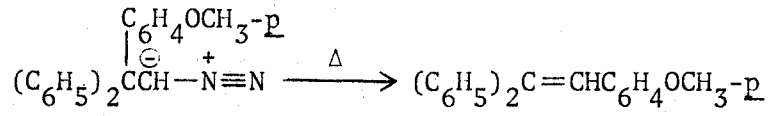
There is no unambiguous evidence that 1,2-hydrogen or alkyl group migrations occur in ground state free radical reactions.

4. Migratory aptitudes in carbene rearrangements.

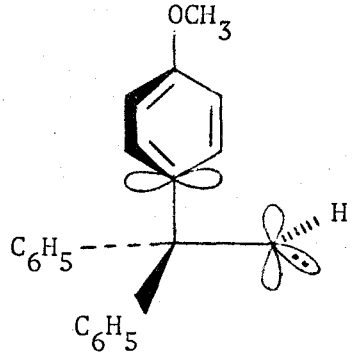
Little work has been done on migratory aptitudes in carbene rearrangements. Alkylcarbenes can undergo rearrangement, with migration of alkyl or hydrogen[16]. Zimmerman[17] in his study of the thermal rearrangement of 2-

anisyl-2,2-diphenyldiazoethane (24) found under all conditions of solvent and temperature that 24 rearranged, with an excess of anisyl migration over statistical, to give 1,1-diphenyl-2-(4-methoxyphenyl)ethylene (25).



24 25

The proposed migration step involved the anisyl group migrating with bonding to an electron deficient p orbital of the carbene as illustrated in structure 26. The electron donating methoxy substituent is thus able to stabilize the transition state for migration.



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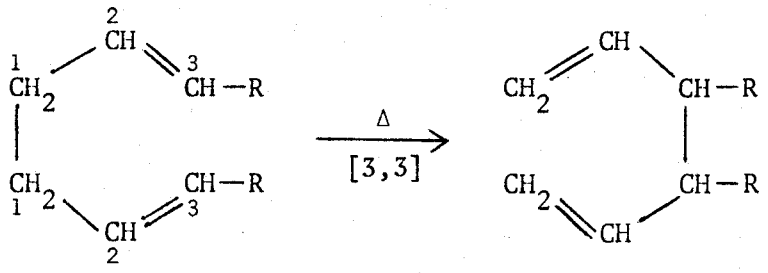
5. Migratory aptitudes in thermal, sigmatropic rearrangements.

In general, 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 uncatalyzed intramolecular process.

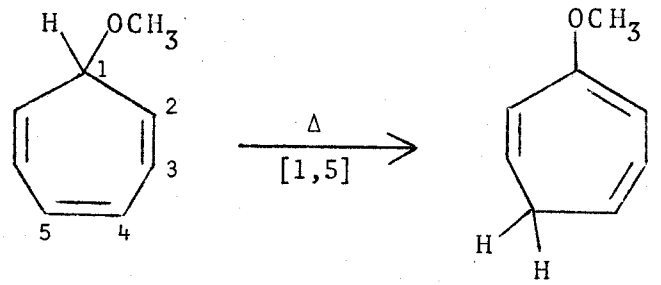
The Cope rearrangement is an example of a sigmatropic rearrangement of order [3,3][18].

Thermolysis of 7-methoxycycloheptatriene (27) results in a [1,5]



Cope rearrangement

sigmatropic shift [18] to form the triene 28.



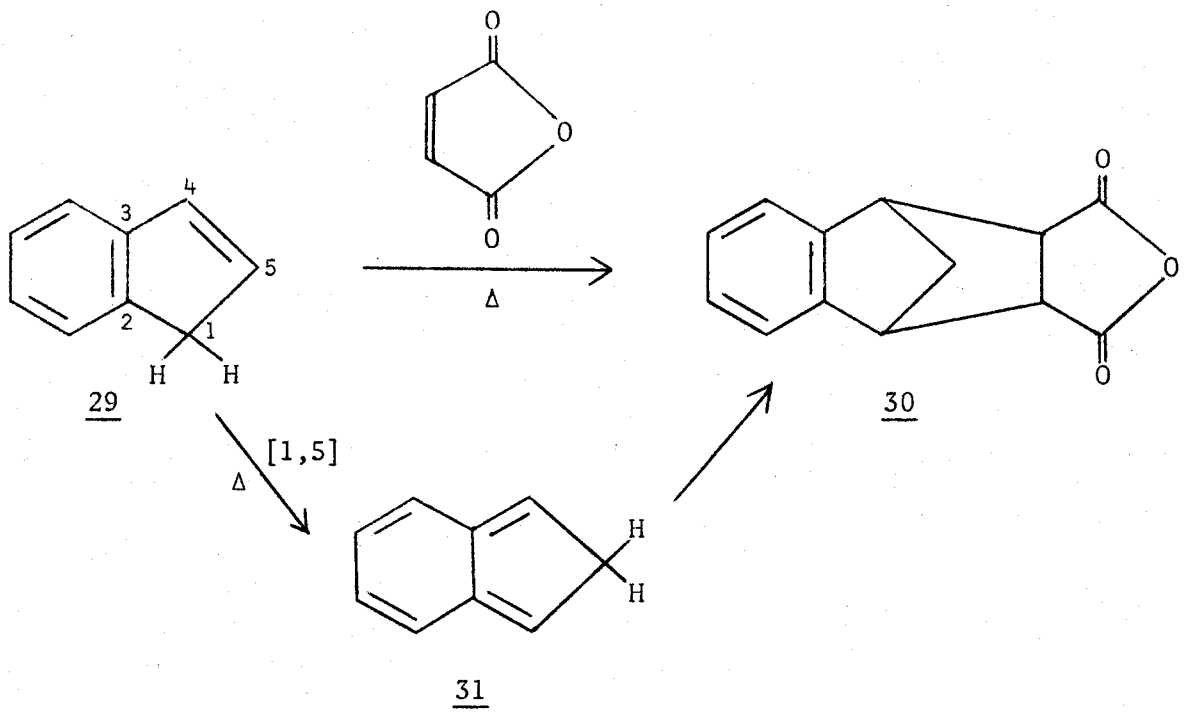
27 28

Since this thesis will be dealing with the indene system, a consideration of the migratory aptitudes involved therein is pertinent at this time.

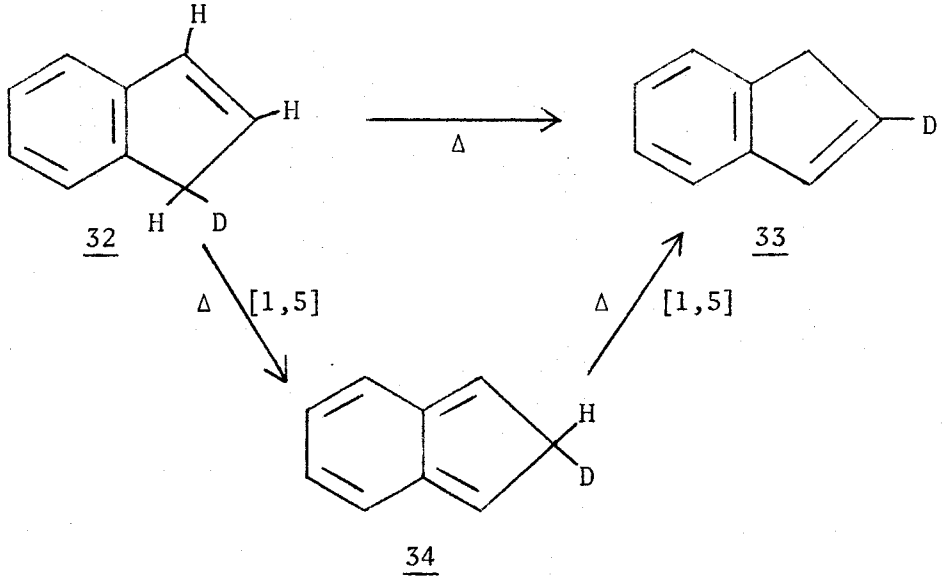
In his discovery of the ground state reaction between indene (29) and maleic anhydride resulting in the formation of the adduct 30, Alder[19,20] postulated the intermediacy of the isoindene structure 31. This was one of the first cases reported of a 1,2-hydrogen shift. (This may formally be called a [1,5] or [1,9] sigmatropic shift.)

Additional [1,5] sigmatropic shifts, relevant to the indene system, are mentioned below.

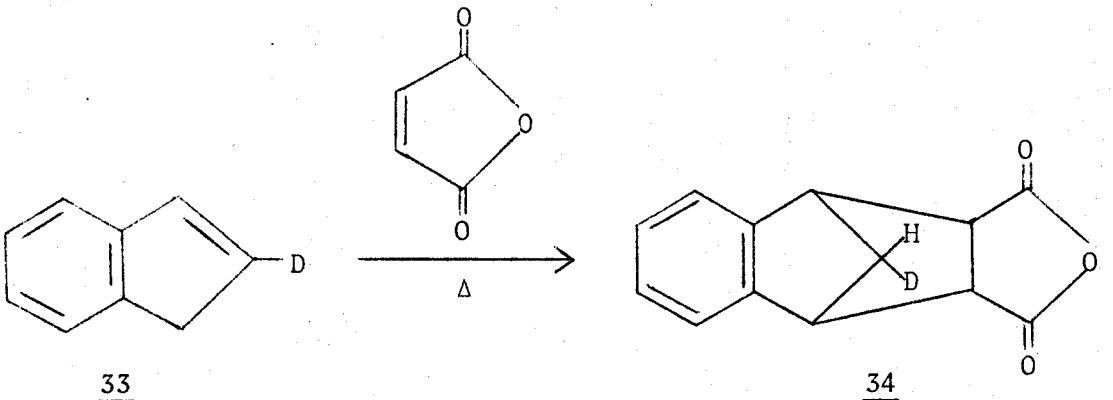
Roth[21] also discovered a 1,2-hydrogen shift in his study of the thermal rearrangement of 1-deuterioindene (32) to 2-deuterioindene (33). Again, [1,5] sigmatropic shift is postulated in the formation of the necessary



intermediate isoindene structure 34 with a similar subsequent shift resulting in formation of the product.

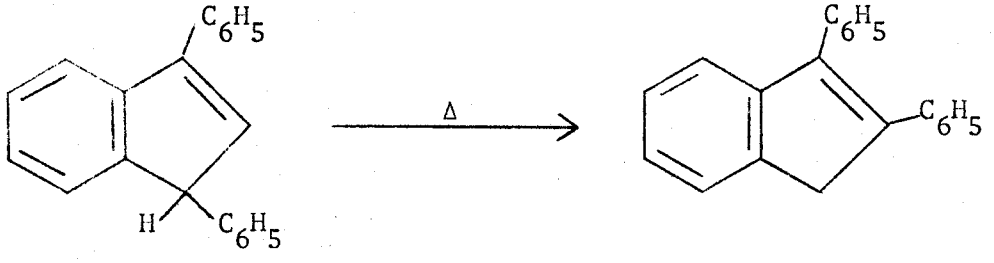


Also, Isaacs[22] was able to trap and identify the addition product 34 arising due to reaction between maleic anhydride and the isoindene intermediate encountered in the thermolysis of 2-deuterioindene (33).



33 34

Koelsch and Johnson[23] were the first to detect a 1,2-phenyl shift in the thermolysis of 1,3-diphenylindene (35) to 2,3-diphenylindene (36).



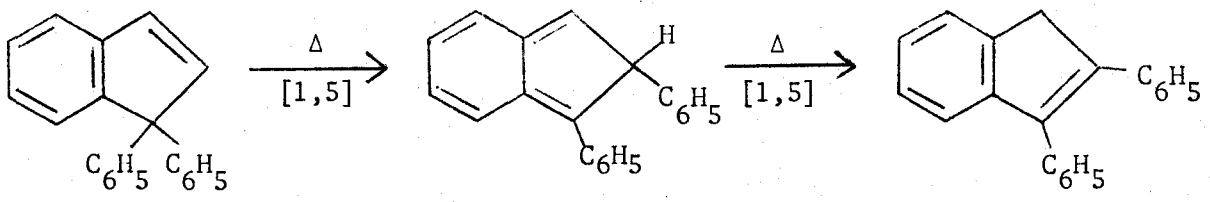
35 36

Miller[24,25] was the first to contrast and compare the migratory aptitudes of phenyl, hydrogen and methyl in the thermal rearrangement of these groups from the 1- to the 2- position of indene. Kinetic studies gave first order rate plots and showed an independence of k on the initial substrate concentration. Some of his findings are shown in Table 2. Addition of quinoline as an acid scavenger or degassing did not change the rearrangement rate. These data and the specificity for 1,2-rearrangement suggested

Reactant	Temp. (°C)	10^5 k,sec^{-1}	Migrating Group
1,1-diphenylindene	280	20.0	phenyl
1-methyl-1-phenylindene	300	8.0	phenyl
1-phenylindene	150	5.75	hydrogen
1,3-diphenyl-1-deuterioindene	150	9.0	deuterium

Table 2. Rate constants (k) for indene isomerizations in diphenyl ether solution[24,25].

a pair of intramolecular sigmatropic shifts involving an isoindene intermediate, i.e., the thermolysis of 1,1-diphenylindene (37) to 2,3-diphenylindene (36) was formulated as follows.

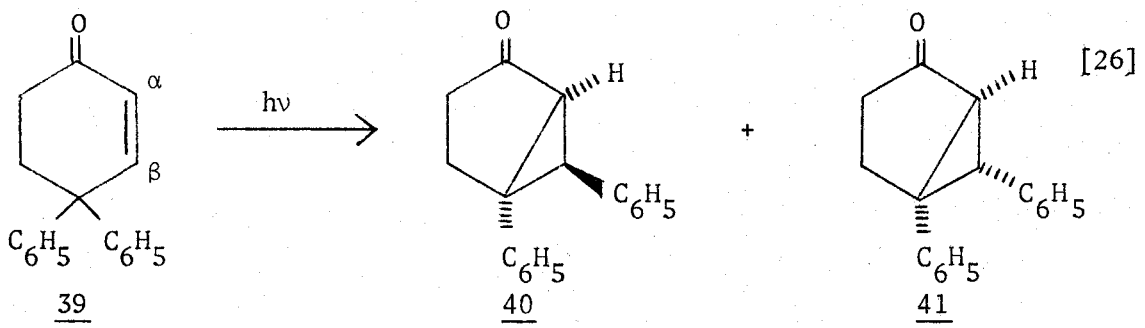


37 38 36

The results showed a migratory aptitude series hydrogen > phenyl > methyl. The rationale given[24] was one of transition state stabilization by the migrating group rather than by the group left behind. Hydrogen rearrangement in 1-phenylindene and phenyl migration in 1,1-diphenylindene involve different migrating groups but the same nonmigrating moiety, and the hydrogen again migrates much faster than phenyl. This large difference was attributed to the effective bridging capabilities of hydrogen in the transition state.

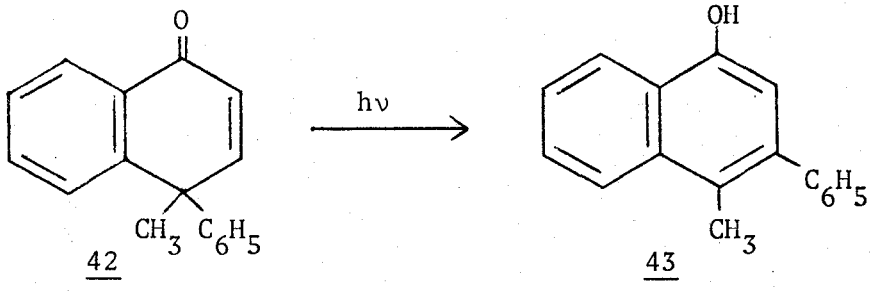
6. Migratory aptitudes in photochemical rearrangements

Zimmerman[26] was the first to show an excited state 1,2-migration of

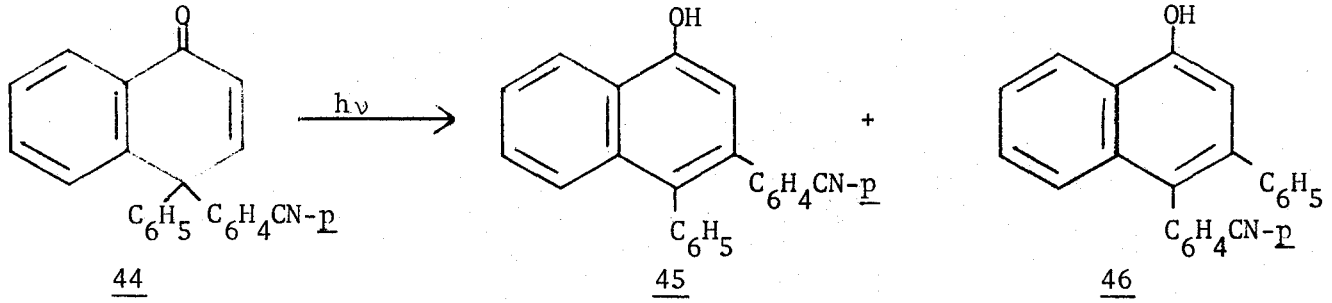


[26]

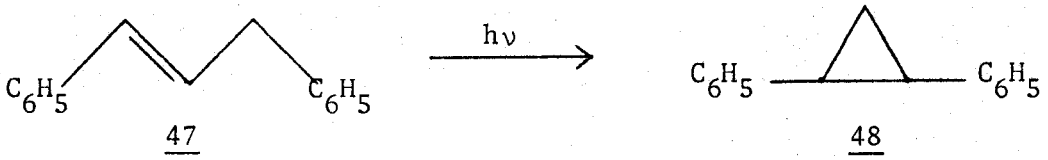
an aryl group to the β-position of an α,β-unsaturated ketonic grouping. The first photochemical migratory aptitude work was likewise performed by Zimmerman[27]. He observed exclusive phenyl migration upon photolysis of 4-methyl-4-phenyl-1(4H)-naphthalenone (42). Also he compared the migratory aptitude[27]



of phenyl versus p-cyanophenyl in the photolysis of 4-(p-cyanophenyl)-4-phenyl-1(4H)-naphthalenone (44). The product arising due to cyanophenyl migration, structure 45, was preferred in a 2:1 ratio over the product 46 arising as a result of phenyl migration.



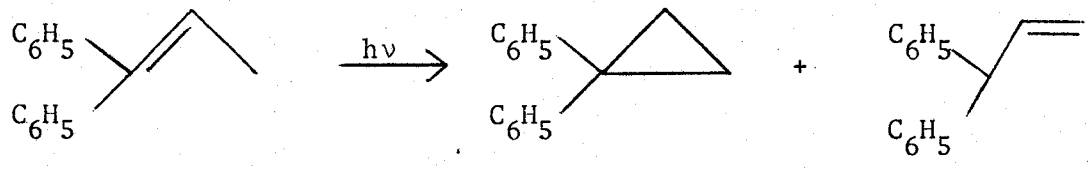
Griffin[28], in his photocyclization of 1,3-diphenylpropene (47) to the cyclopropane structure 48 in solution, found the first evidence for an excited state 1,2-hydrogen shift. Griffin[29] also discovered other

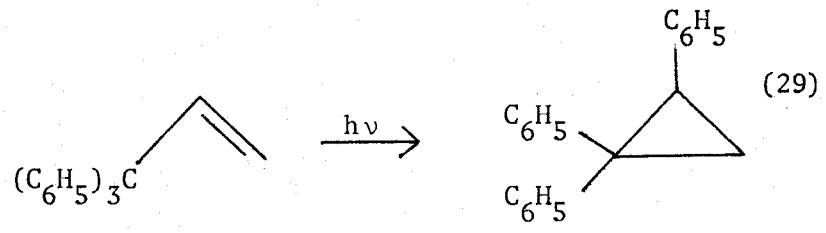


47 48

reactions wherein excited state 1,3-hydrogen and phenyl migrations occurred.

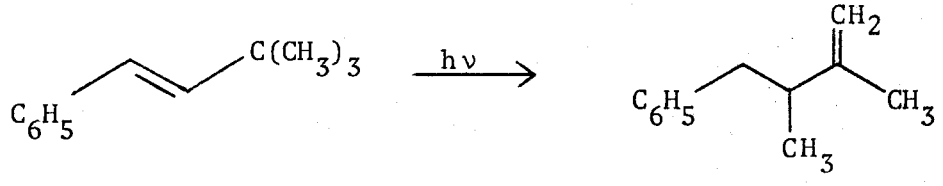
(29)





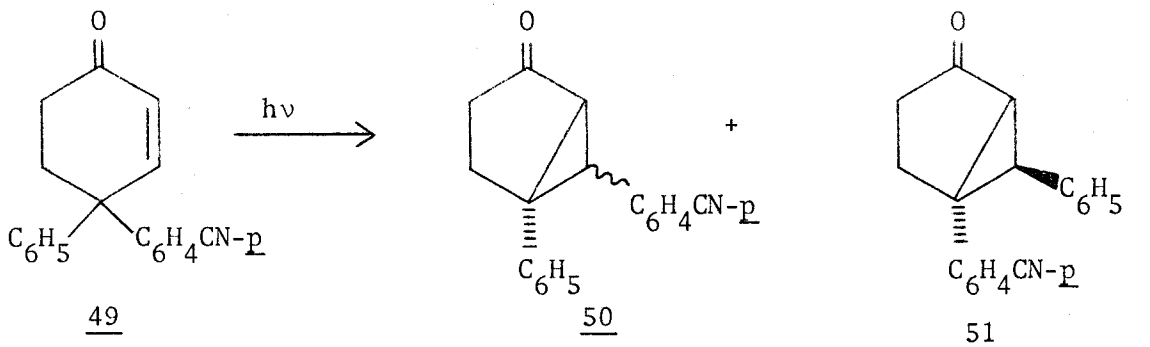
(29)

The first example of a photoinduced 1,2-methyl migration was discovered by Griffin[30] when he irradiated a mixture of cis- and trans-3,3-dimethyl-1-phenylbutene (47) and obtained compound 48 in which a methyl shift had occurred.



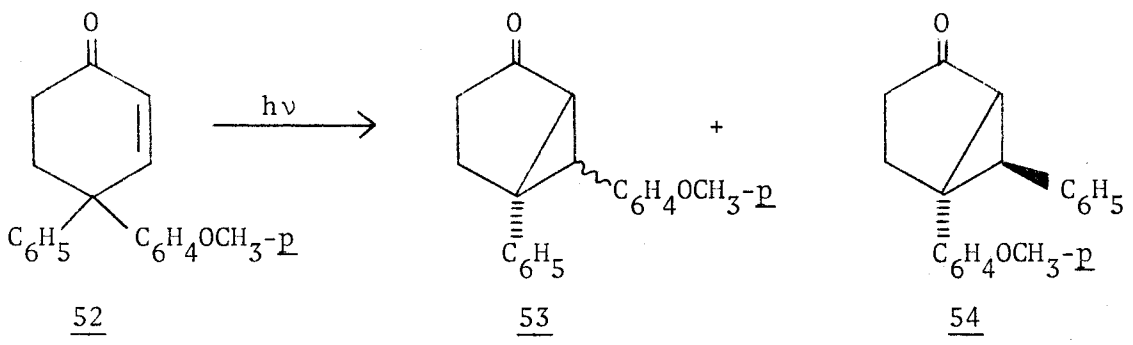
47 48

Zimmerman[31] made use of the migratory behaviour of p-methoxyphenyl and p-cyanophenyl to probe the excited state electron distribution in the 4,4-diphenylcyclohex-2-en-1-one system.



49 50 51

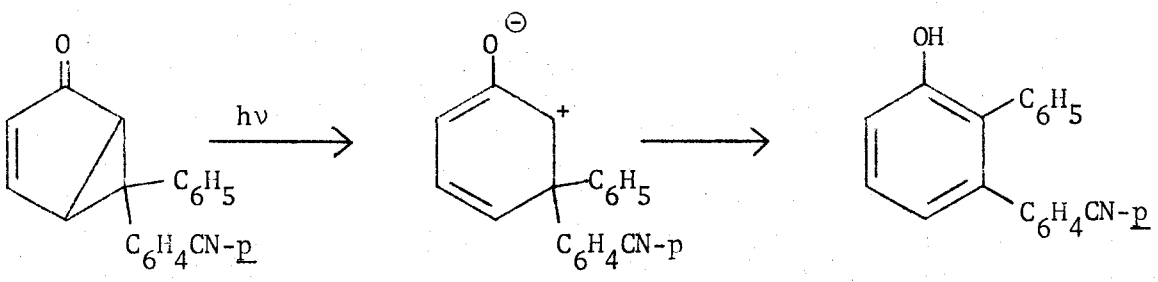
ratio 50:51 = 14:1



52 53 54

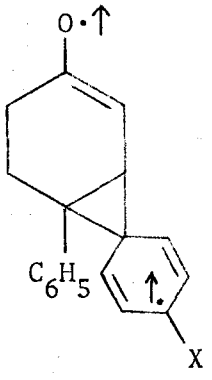
ratio 53:54 = 12.5:1

Irradiation of the cyclohexenones 49 and 52 gave rise preferentially to products of cyanophenyl and methoxyphenyl migration (structures 50 and 53 respectively). In an attempt to envisage the polarity of the product determining excited state in the rearrangements of the enones 49 and 52, Zimmerman[32] noted that irradiation of 6-p-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (55) gave a product 56 of phenyl migration. He invoked the



55 57 56

intermediacy of the zwitterionic species 57, wherein solely phenyl would be expected to migrate since in the migration step cyanophenyl could not accommodate the positive charge at the migration terminus. By similar reasoning, the model $^{+}C—C=C—O^{\ominus}$ was discarded as a possible intermediate moiety in the rearrangement of the enone 49 to 50 since the cyanophenyl would be required to migrate to a positively charged β-carbon. However, since irradiation of the enone 52 resulted in methoxyphenyl migration then $^{\ominus}C—C=C—O^{+}$ cannot be the model for the product determining excited state as the anisyl group would then be migrating to an electron rich migration terminus. Zimmerman thus postulated the product determining excited state in the photolysis of 49 and 52 as being represented by $\cdot C—C=C—O\cdot$ (structure 58).

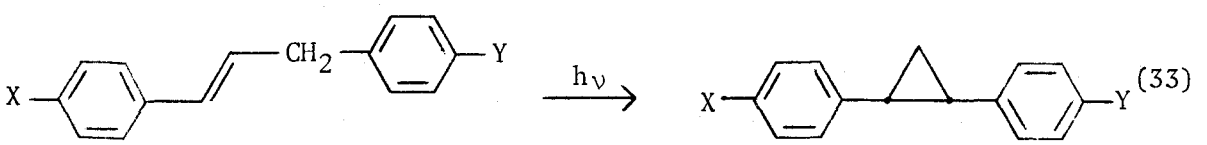


58, X = CN, OCH_3

In this way cyano could readily accommodate the extra electron in the migrating

phenyl (see for example structure 23). However, the preferred migratory aptitude of methoxyphenyl over phenyl was still not properly rationalized by this mechanism since Rüchardt[15] had shown phenyl to migrate preferentially over p-anisyl (Table 1) in the free radical rearrangement of isovaleraldehydes.

Recently, Hixson[33] determined substituent effects on aryl shifts in the photo-rearrangement of 1,3-diphenylpropenes to give 1,2-diphenylcyclopropanes. Decreasing the electron density at the migration terminus



(33)

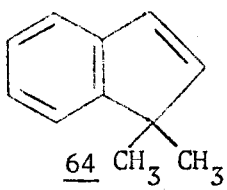
(X = CN; Y = H; 59) enhanced the rate of migration while an increased electron density at the same terminus (X = OCH_3; Y = H; 63) lowered the rate. When either a p-methoxy or p-cyano substituent was present on the migrating phenyl (X = H) the rate of rearrangement of the aryl group relative to that of the unsubstituted compound 62 was increased. The relative rates of migration are shown in Table 3.

		Relative rate of rearrangement
X = CN; Y = H	(59)	41
X = H; Y = OCH_3	(60)	13
X = H; Y = CN	(61)	3.8
X = Y = H	(62)	1.0
X = OCH_3; Y = H	(63)	0.04

Table 3. Relative rates of rearrangements of substituted 1,3-diphenylpropenes.

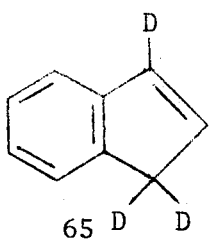
7. Migratory aptitudes in photochemical sigmatropic rearrangements.

McCullough[34] compared the migratory aptitudes of hydrogen, methyl and phenyl in his study of the photochemical behaviour of the indene system. 1,1-Dimethylindene (64) gave no detectable products of methyl migration and photolysis of 1,1,3-trideuterioindene (65) gave only starting material, thus ruling out deuterium (or hydrogen) migration.



64

$\xrightarrow{h\nu}$ no products of methyl migration

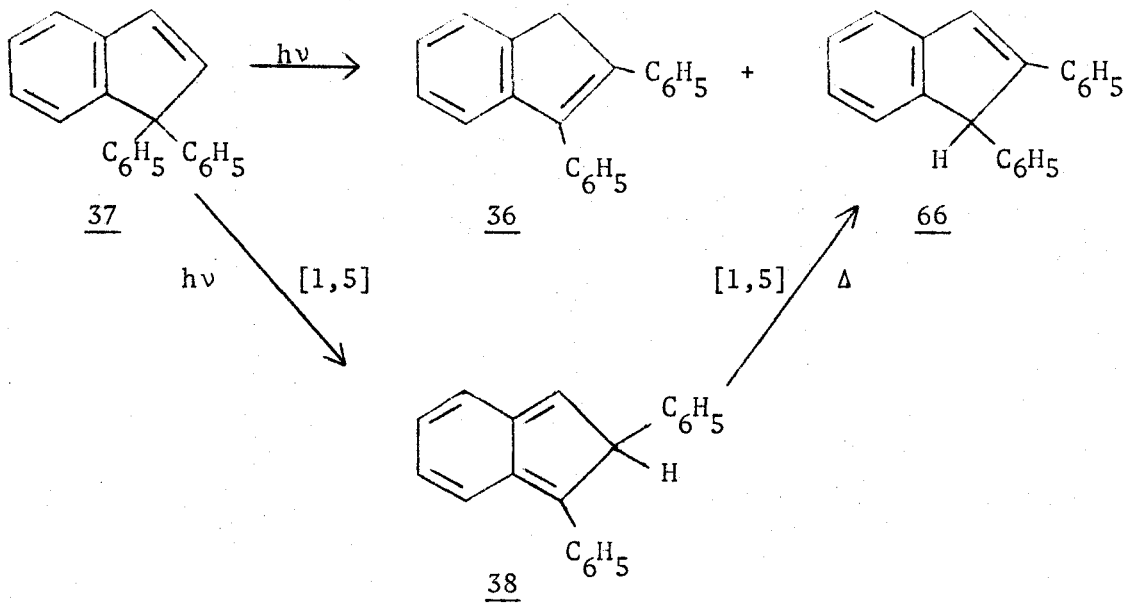


65

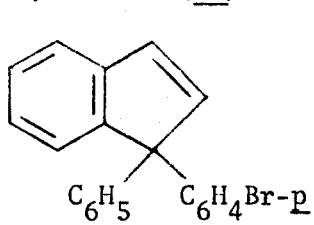
$\xrightarrow{h\nu}$ no deuterium shift

However, 1,1-diphenylindene (37) underwent efficient rearrangement on direct irradiation or on acetophenone sensitization, forming 2,3-diphenylindene (36) and 1,2-diphenylindene (66). Again (as in the thermolysis of 37), the isoindene intermediate 38 was postulated as being formed; however this time it arose due to an excited state [1,5] sigmatropic shift of phenyl. The isoindene species 38 could then undergo a ground state hydrogen shift, as described by Roth[21] for the thermolysis of 1-deuterioindene (32), to form the products 36 and 66.

However, as in the ground state thermolyses of the arylindenes, nothing was known about the transition state leading to the isoindene intermediate. Was a polar mechanism operating in the excited state reaction, or



was the transition state more diradical in nature? It was decided that a determination of the transition state structure for phenyl migration could be made by making a series of para-substituted phenyl derivatives. If for example the migrating phenyl bore some negative charge then surely its rate of migration would be enhanced by having a p-cyano or other electron withdrawing substituent on the phenyl ring. In this case it was expected that p-cyanophenyl would migrate preferentially with respect to phenyl. But to what degree would cyanophenyl predominate? By similar reasoning, a p-methoxyphenyl would be expected to migrate rather than phenyl if the migrating benzene ring bore some positive charge. Hence 1-(p-bromophenyl)-1-phenylindene (67), 1-(p-cyanophenyl)-1-phenylindene (68), and 1-(p-methoxyphenyl)-1-phenylindene (69) were synthesized in an attempt to answer the above questions.



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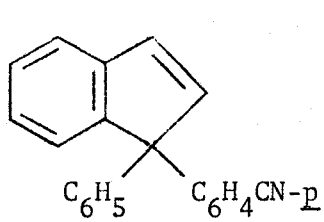
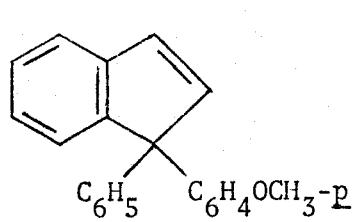


68



69

RESULTS

PART I. SYNTHESES

Starting Materials

It was hoped that 1-(p-bromophenyl)-1-phenylindene (67) could be the immediate precursor of the p-cyanoindene 68.

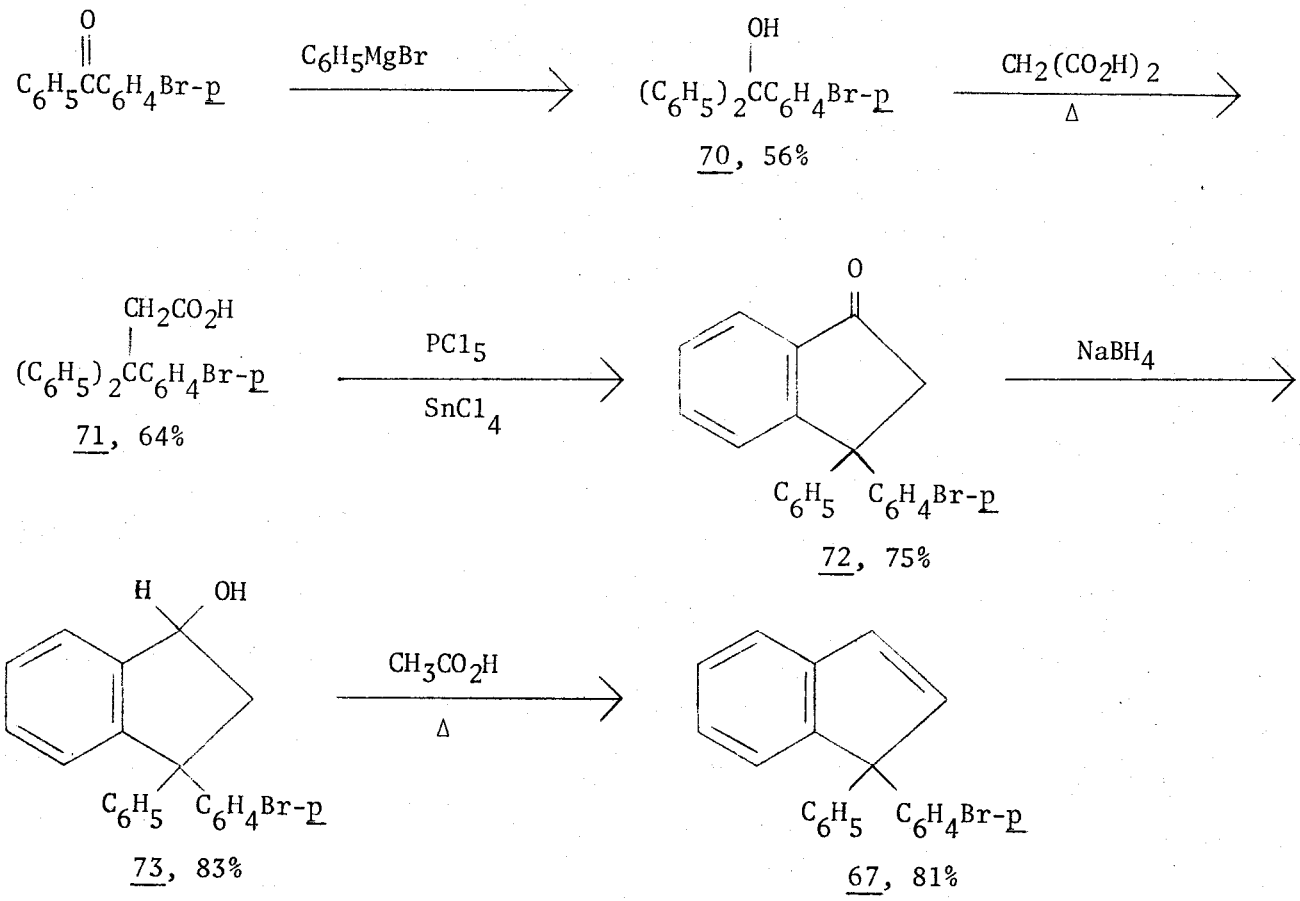
Thus 1-(p-bromophenyl)-1,1-diphenylcarbinol (70) was produced in 56% yield by the addition of phenylmagnesium bromide to p-bromobenzophenone. Addition of ketone to the grignard reagent gave a complex mixture of products and no carbinol.

3-(p-Bromophenyl)-3,3-diphenylpropionic acid (71) was obtained from the reaction of 70 with an excess of malonic acid, in 64% yield. The cyclic ketone 72 was synthesized, utilizing the method of Johnson[35], in 75% yield. Thin layer chromatography of the mother liquor after removal of compound 72 indicated the presence of many additional products, some of which could have arisen due to cyclization occurring on the p-bromophenyl ring.

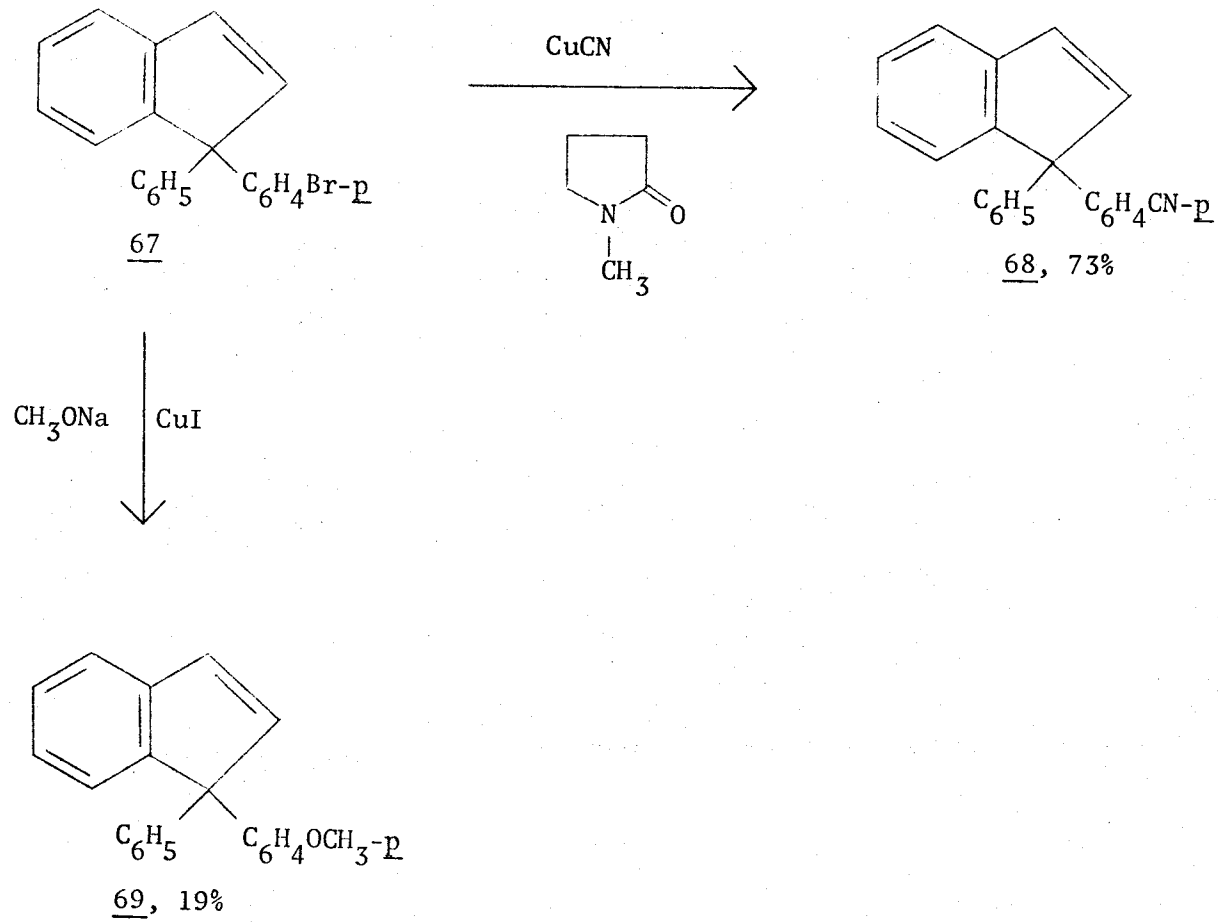
Reduction of the indanone 72 to 3-(p-bromophenyl)-3-phenyl-1-indanol (73) was achieved in 83% yield by reduction with sodium borohydride in ethanol according to the procedure of Brown and Jackman[36]. Compound 73 had a broad melting range between 120 and 170°C due to the fact that reduction gave a mixture of diastereomers.

Dehydration of the indanol 73 to 1-(p-bromophenyl)-1-phenylindene (67) was accomplished in 81% yield by treatment with p-toluene-sulfonic acid in acetic acid at reflux[36]. The AB quartet centered at 6.67 in the n.m.r.* was assigned to the two vinylic protons and the remaining thirteen protons absorbed at 6.95 to 7.40.

*All chemical shifts are reported as p.p.m. downfield from internal tetramethylsilane.



Scheme 1. Synthesis of 1-(p-bromophenyl)-1-phenylindene (67).



Scheme 2. Introduction of substituents.

The i.r. spectrum showed absorption at 695 and 820 cm^{-1} assigned to the bending vibrations of the olefinic C—H groups. The carbon-bromine stretching band was observed at 1075 cm^{-1} and the 1600 cm^{-1} peak was assigned to C=C stretching of the double bond conjugated to the benzene ring[37]. Scheme 1 illustrates the reaction steps involved.

The method of Newman[38], employing cuprous cyanide in 1-methyl-2-pyrrolidone as solvent, was utilized on 11.3 g of 67 to give 73% of the 1-(p-cyanophenyl)-1-phenylindene (68). The i.r. spectrum showed nitrile absorption at 2230 cm^{-1} and C=C stretching at 1600 cm^{-1}. The n.m.r. absorption showed an AB quartet at 6.76 attributable to the two vinyl protons and a thirteen-proton complex multiplet from 7.06 to 7.51.

Bacon and Rennison[39] discovered a method of converting aryl halides into alkyl aryl ethers. Cuprous iodide was the catalyst involved in the reaction of the halide with a three-fold excess of sodium alkoxide in 2,4,6-collidine as solvent. An important detail was that, after generation of the alkoxide from sodium and the appropriate alcohol, the excess of the latter was not evaporated before addition of collidine. Also the most favorable molar ratios found were C_6H_5X:NaOR:CuI = 1:3:0.5. Thus reaction of the p-bromoindene 67 with sodium methoxide in a refluxing collidine solution containing methanol yielded, following column chromatography, 1-(p-methoxyphenyl)-1-phenylindene (69) in 19% yield. The n.m.r. of 69 showed a three proton methoxy singlet at 3.77,and a four proton multiplet at 6.70-6.90 attributable to the two protons ortho to the methoxy substituent and to the two vinylic protons. There was also a complex eleven proton multiplet from 7.10 to 7.45. The i.r. bands at 1040 and 1245 cm^{-1} were assigned respectively to aliphatic and aromatic carbon-oxygen stretching. The C=C stretching was present at 1605 cm^{-1} while bands at 2840 and 2960 cm^{-1} were

attributed to symmetric and asymmetric C—H stretching respectively in the methoxy substituent. A majority of the starting material was found to have been reduced to 1,1-diphenylindene. Also it was not possible to either improve upon or duplicate the 19% yield as subsequent reactions gave only 10-15% of 69. Scheme 2 illustrates the formation of indenes 68 and 69.

Products

The procedure of Weiss[40] was utilized to synthesize the p-bromo-3-benzylidenephthalide (74) in 80% yield starting from phthalic anhydride and p-bromophenylacetic acid. The product, m.p. 174-176°C, showed a one proton singlet in the n.m.r. at 6.20. This peak was assigned to the vinyl proton. A complex multiplet at 7.20-7.80 integrating for eight protons was assigned to the eight aromatic hydrogens. The i.r. spectrum displayed aliphatic carbon-oxygen stretching bands at 1073 and 1267 cm^{-1}, C=C stretching at 1660 cm^{-1} due to the non-aromatic double bond and two strong absorption bands at 1765 and 1780 cm^{-1} due to carbonyl stretching.

The phthalide 74 was reacted with a five-fold excess of phenylmagnesium bromide according to the procedure of Allen[41] to give a 39% yield of 2-(p-bromophenyl)-3-phenyl-1-indenone (75), m.p. 151-152°C. The i.r. exhibited the following characteristic stretching bands: C—Br at 1080, C=C at 1610, and C=O at 1720 cm^{-1}. The n.m.r. displayed only aromatic complex absorption at 7.06-7.60.

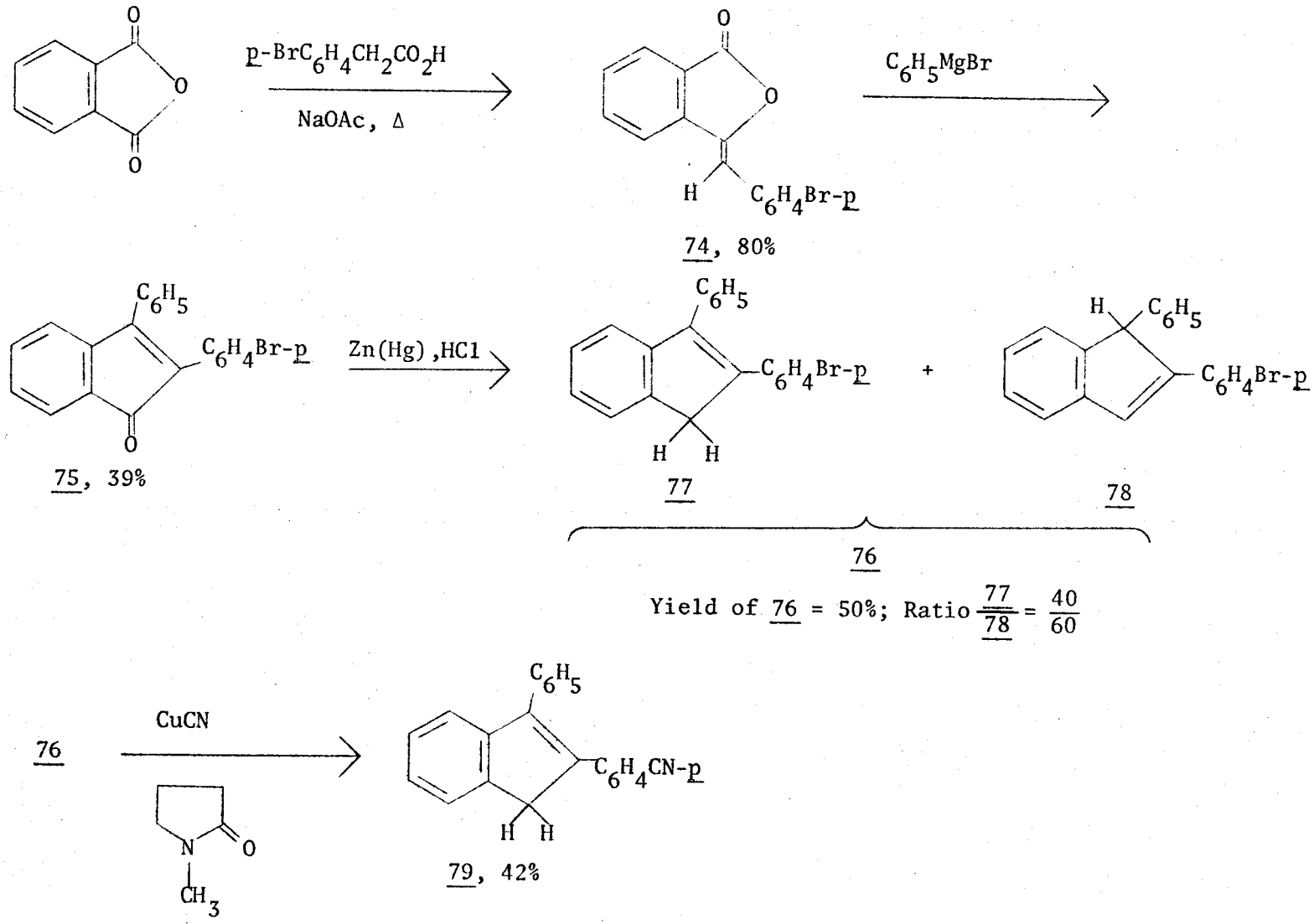
A Clemmensen reduction[42] utilizing a large excess of amalgam was employed on 75 to give a 50% yield of crude product 76 that showed two spots on t.l.c. and exhibited n.m.r. singlets at 3.84 and 4.87 in the relative ratio of 4:3 respectively. Column chromatography on alumina and elution with hexane

gave pure 2-(p-bromophenyl)-3-phenylindene (77) as colorless needles, m.p. 182-185°C. The n.m.r. showed a two proton singlet, at 3.84, assigned to the methylene protons and a thirteen proton complex multiplet from 7.00 to 7.60 due to the aromatic hydrogens. The infrared of 77 showed the following bands: out of plane aliphatic C—H bending at 705 and 828 cm^{-1}, C—Br stretching at 1080 cm^{-1} and C=C stretching at 1600 cm^{-1}. The singlet at 4.87 present in the n.m.r. of 76 was assigned to the methine proton of the less thermodynamically stable isomer 1-phenyl-2-(p-bromophenyl)-indene (78) and the crude reaction product 76 was estimated by n.m.r. to contain about 60% of this isomer and 40% of the isomer 77.

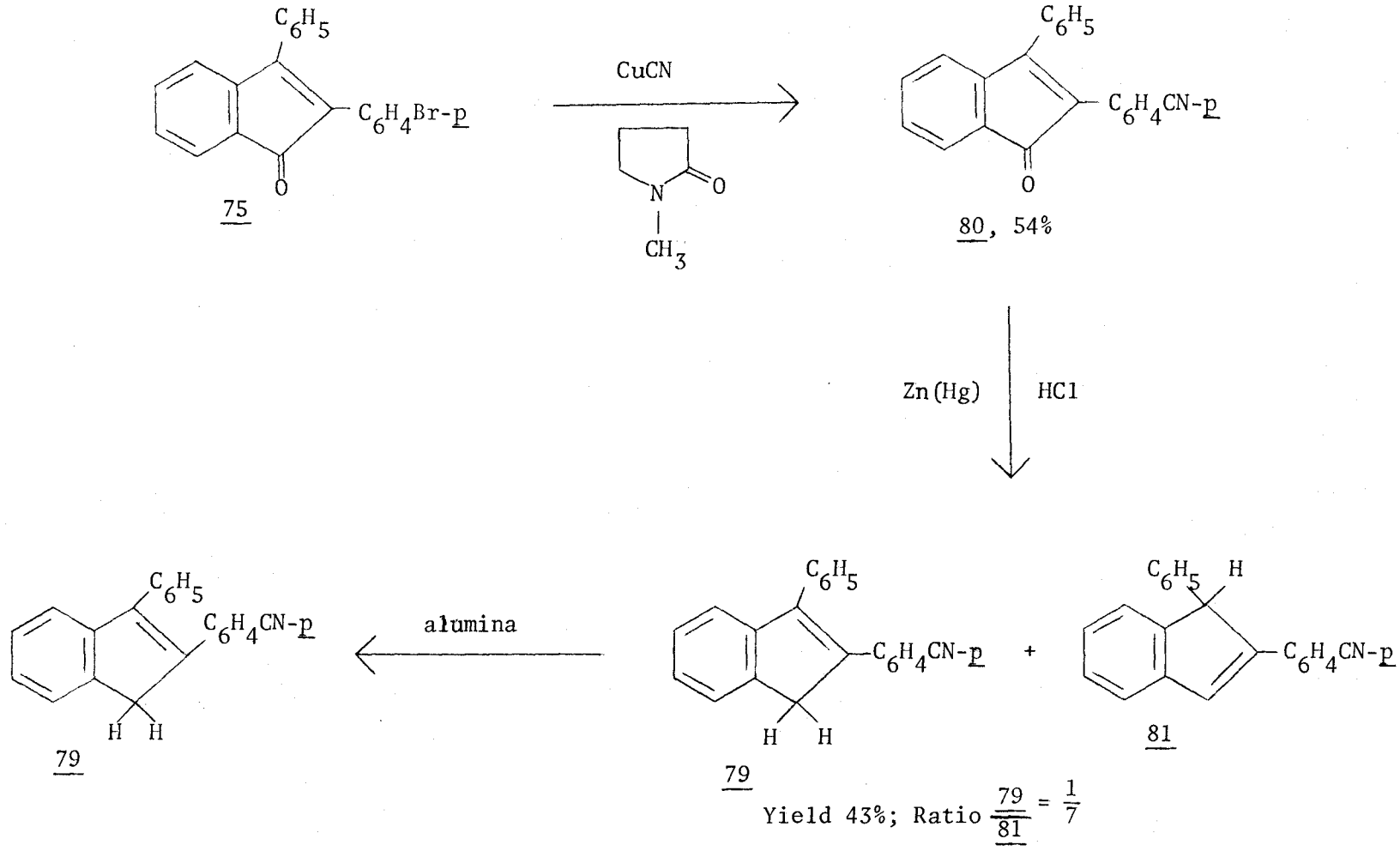
Conversion of 76 to 2-(p-cyanophenyl)-3-phenylindene (79) was achieved in 42% yield by the method of Newman[38] described previously in the synthesis of 68. The indene 79 was obtained as colorless needles, m.p. 214-216°C, and showed the following i.r. absorption: olefinic C—H bending vibrations at 698 and 835 cm^{-1}, C=C stretching at 1600 and C≡N stretching at 2225 cm^{-1}. The n.m.r. showed a two proton methylene singlet at 3.88 and a thirteen proton complex aromatic absorption at 7.02-7.60. Scheme 3 illustrates the steps involved in the synthesis of indene 79.

An alternate synthesis of compound 79 is shown in Scheme 4 wherein 2-(p-cyanophenyl)-3-phenyl-1-indenone (80), m.p. 147-148°C, was obtained in 54% yield by reacting the bromoindenone 75 with cuprous cyanide in the manner just described[38]. Compound 80 displayed the following i.r. bands: C=C stretching at 1610, C=O stretching at 1715 and C≡N stretching at 2230 cm^{-1}. A complex aromatic multiplet was seen at 7.10-7.62 in the n.m.r.

Reduction of 80 by the Clemmensen method[42] yielded an oil (43%) whose n.m.r. displayed singlets at 3.88 and 4.95. The singlet at 3.88 was



Scheme 3. Synthesis of 2-(p-cyanophenyl)-3-phenylindene (79).



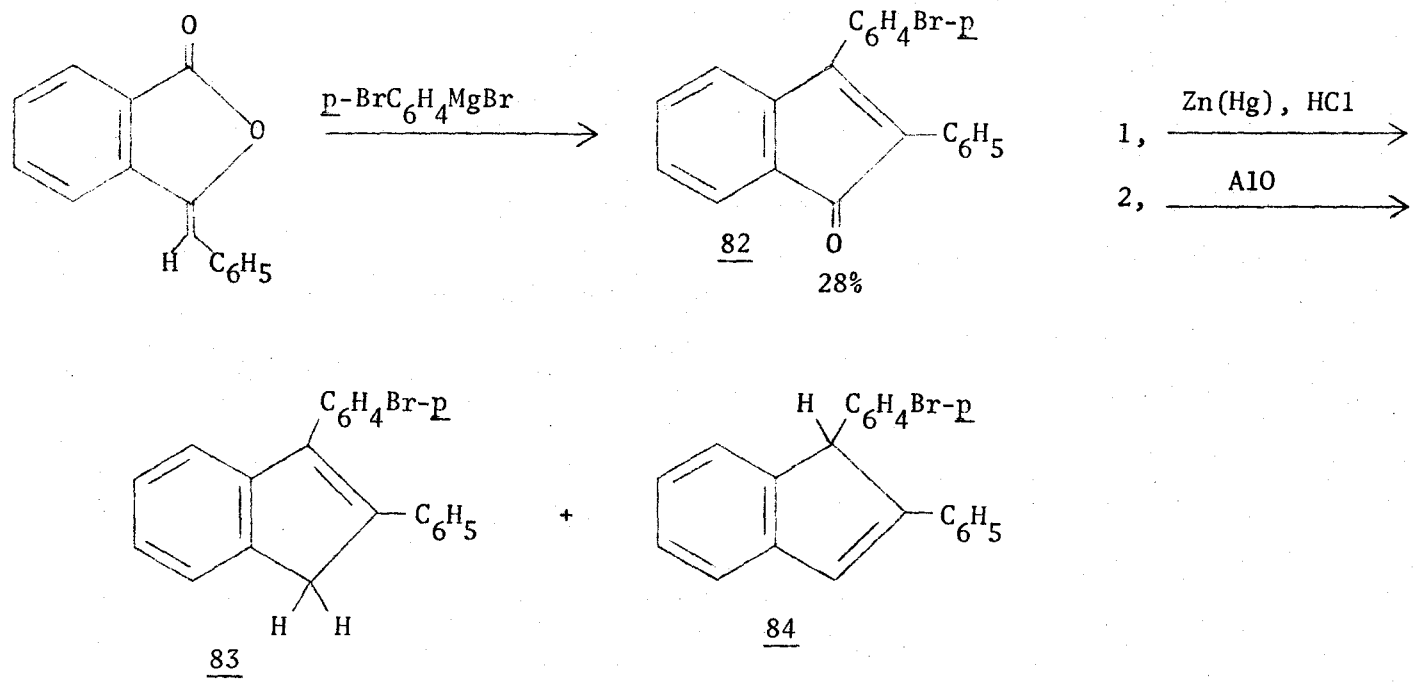
Scheme 4. Alternate synthesis of indene 79.

assigned to the methylene protons of 2-(p-cyanophenyl)-3-phenylindene (79) while the singlet at 4.95 was attributed to the methine proton of the corresponding 1,2-disubstituted isomer, 1-phenyl-2-(p-cyanophenyl)-indene (81). The n.m.r. integration of peak areas indicated that the 1,2-isomer predominated over 79 by the relative ratio of 7:1. Column chromatography on alumina of a portion of the oil resulted in isomerization of the 1,2-isomer to the more thermodynamically stable indene 79.

Reaction of benzylidene phthalide with an excess of p-bromophenylmagnesium bromide gave a 28% yield of 2-phenyl-3-(p-bromophenyl)-1-indenone (82), m.p. 177-179°C. The following i.r. stretching bands were observed: C—Br at 1065, C=C at 1605 and C=O at 1710 cm^{-1}. The n.m.r. spectrum showed only complex aromatic proton resonance at 6.95-7.45.

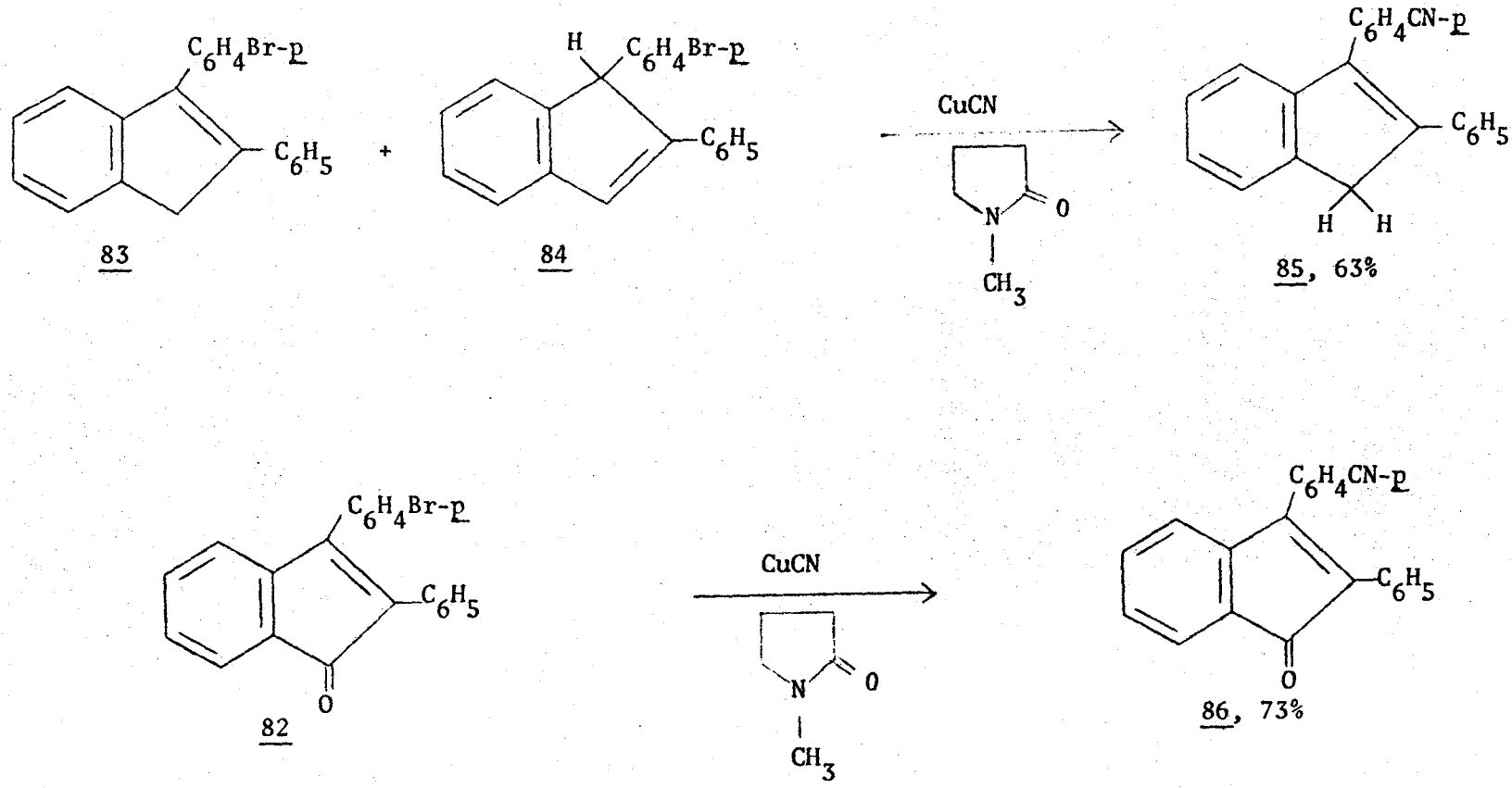
Reduction of 82 with an excess of zinc amalgam gave crude crystalline material which showed a high field n.m.r. singlet at 3.86 attributable to the methylene protons of the more thermodynamically stable reduction product, 2-phenyl-3-(p-bromophenyl)-indene (83). A singlet at 4.90 was attributed to the methine proton of the corresponding 1,2-isomer, 1-(p-bromophenyl)-2-phenylindene (84) and n.m.r. integration suggested the latter isomer constituted 80% of the reaction material. Column chromatography of the crystals and elution with hexane gave crystalline 2-phenyl-3-(p-bromophenyl)-indene (83), m.p. 163-165°C, as well as a mixture of the indenes 83 and 84 (combined yields of 18%). Scheme 5 outlines the synthesis of indene 83.

Aryl bromide C—Br stretching at 1068 cm^{-1} was apparent in the i.r. of 83 as was olefinic C=C stretching at 1600 cm^{-1}. A two proton singlet at 3.86 was assigned to the methylene protons and the remaining thirteen aromatic hydrogens appeared at 7.10-7.56.



Yield 18%; Ratio $\frac{83}{84} = \frac{20}{80}$

Scheme 5. Synthesis of 2-phenyl-3-(p-bromophenyl)-indene (83).



Scheme 6. Synthesis of indenes 85 and 86.

Conversion of the bromoindenes 83 and 84 to the cyanoindene 85 was accomplished in 63% yield by the method described previously[38]. Thus 2-phenyl-3-(p-cyanophenyl)-indene (85), m.p. 137-138°C, showed olefinic double bond stretching at 1610 cm^{-1} and nitrile stretching at 2230 cm^{-1}. The methylene protons resonated at 3.90 and the four protons on the cyanophenyl ring appeared as an A_2B_2 quartet centered at 7.54. The nine remaining aromatic protons had resonance from 7.09 to 7.55. The synthesis of indene 85 is shown in Scheme 6.

Conversion of the bromoindenone 82 into 2-phenyl-3-(p-cyanophenyl)-1-indenone (86) was accomplished in 73% yield by the method of Newman[38] described above. The indenone 86, m.p. 190.5-192.5°C, exhibited the following i.r. stretching frequencies: C=C at 1605, C=O at 1715 and C≡N at 2225 cm^{-1}. The aromatic protons of 86 showed a complex multiplet from 6.95 to 7.78. Scheme 6 illustrates the synthesis of indenone 86.

Phthalic anhydride was reacted with an excess of p-methoxyphenylacetic acid to give a 52% yield of p-methoxy-3-benzylidenephthalide (87), m.p. 147-148.5 °C. The infrared showed characteristic phthalide absorption at 1760 and 1775 cm^{-1} while the n.m.r. displayed a three proton methoxy singlet at 3.81, a one proton singlet at 6.29 assigned to the vinylic proton and an eight proton multiplet at 6.74-7.98 assigned to the eight aromatic hydrogens.

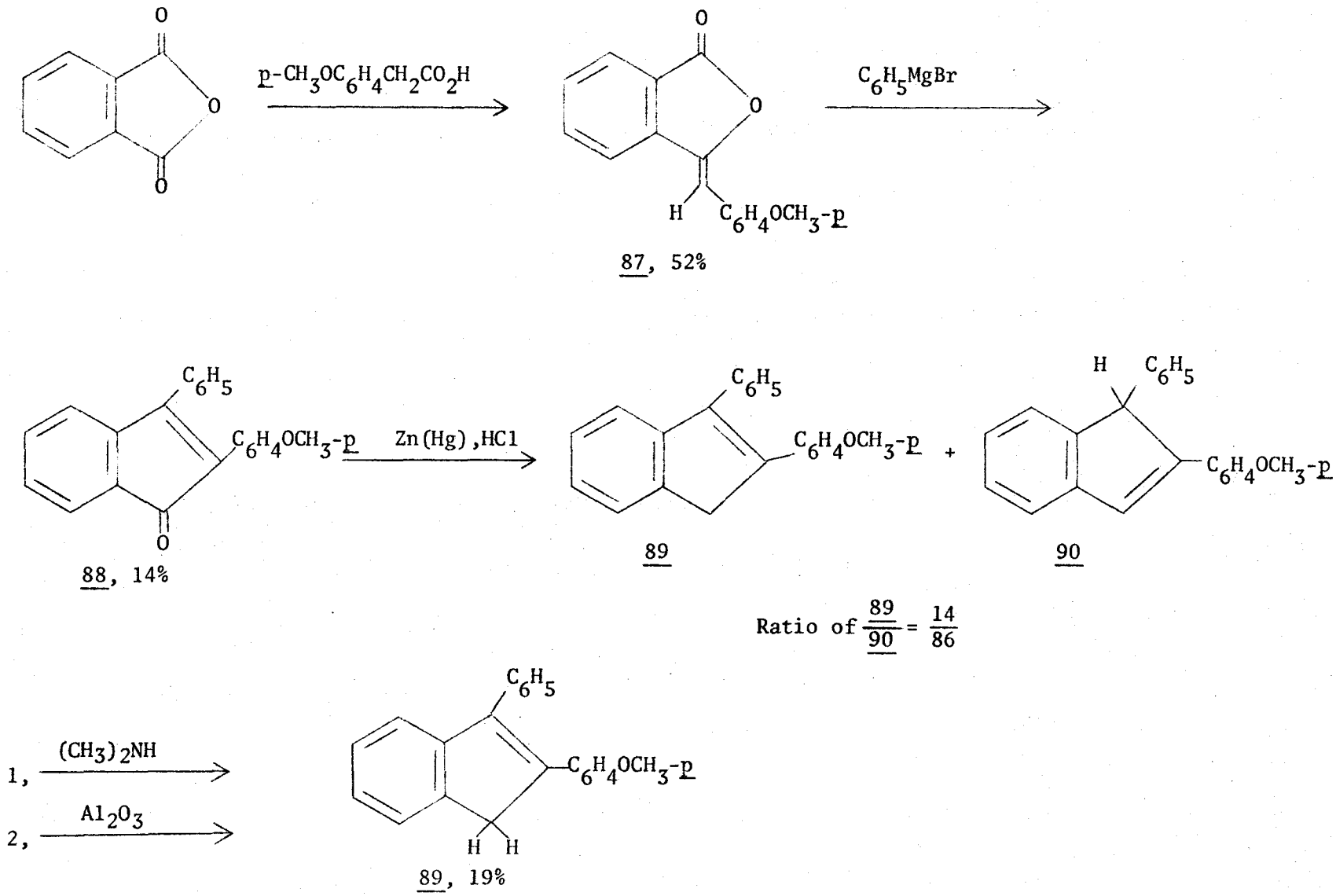
Reaction of an excess of phenylmagnesium bromide with 87 gave a 14% yield of 2-(p-methoxyphenyl)-3-phenyl-1-indenone (88), m.p. 118-119.5°C. The presence of C=C and C=O functions was verified by stretching frequencies at 1605 and 1710 cm^{-1} in the i.r. In addition, the presence of the methoxy substituent was confirmed by the symmetric and asymmetric aliphatic C—H stretching at 2845 and 2960 cm^{-1} respectively. The three methoxy protons resonated at

3.73 while the thirteen aromatic protons appeared as a complex multiplet from 6.60 to 7.60.

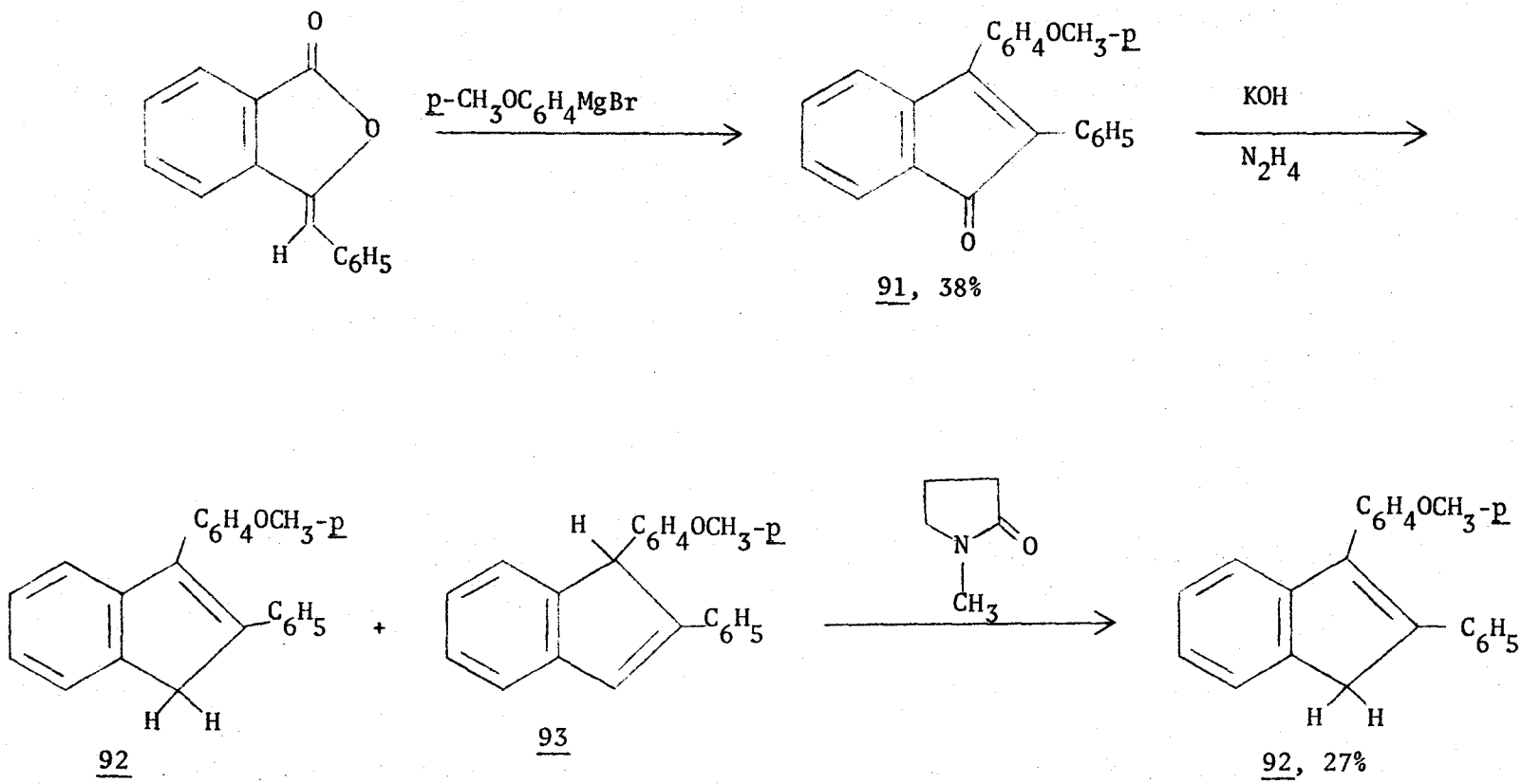
Reduction of the indenone 88 with zinc amalgam gave crude crystals showing two major spots on t.l.c. with approximately the same R_f value of 0.3 as well as two minor spots (R_f = 0.1 and 0.7). The sharp singlet observed in the n.m.r. at 3.69 was assigned to the methoxy protons, and singlets at 3.81 and 4.80 were assigned respectively to the methylene protons of the 2,3-disubstituted product 89 and the methine proton of the 1,2-isomeric product 90. There also was observed a complex aromatic multiplet at 6.65-7.40. Base equilibration with dimethylamine at room temperature followed by column chromatography gave a 19% yield of 2-(p-methoxyphenyl)-3-phenylindene (89), m.p. 124-126°C. Symmetric and asymmetric aliphatic C—H stretching bands were observed at 2840 and 2940 cm^{-1} respectively, while olefinic C=C stretching was present at 1605 cm^{-1}. The n.m.r. showed: a three proton singlet at 3.69 which was attributed to the methoxy protons, a two proton singlet at 3.81 due to the methylene protons, an A_2B_2 quartet centered at 6.92 due to the four protons on the methoxyphenyl ring and a nine proton aromatic multiplet at 7.16-7.45. Scheme 7 shows the various steps involved in the synthesis of 89.

Reaction of benzylidenephthalide with an excess of p-methoxyphenylmagnesium bromide gave a 38% yield of 2-phenyl-3-(p-methoxyphenyl)-1-indenone (91), m.p. 121.5-123°C. Characteristic i.r. bands for olefinic double bond and carbonyl stretching frequencies were observed at 1605 and 1710 cm^{-1} respectively. The n.m.r. of 91 had the three proton methoxy singlet present at 3.81 and an accompanying complex multiplet at 6.83-7.58 integrating for the thirteen aromatic protons.

Reaction of the indenone 91 with potassium hydroxide and hydrazine



Scheme 7. Synthesis of 2-(p-methoxyphenyl)-3-phenylindene (89).



Scheme 8. Synthesis of 2-phenyl-3-(p-methoxyphenyl)-indene (92).

hydrate in ethylene glycol (Huang-Minlon treatment) gave an oil which by n.m.r. analysis of the broad singlet at 4.65 and the remaining singlets at 3.78 and 3.83 was deemed to possess both the 1,2- and the 2,3-disubstituted indene products (indenes 93 and 92 respectively). Treatment in refluxing 1-methyl -2-pyrolidone followed by column chromatography on alumina gave a 27% yield of 2-phenyl-3-(p-methoxyphenyl)-indene (92), m.p. 115-116°C. Infrared analysis of 92 showed double bond stretching at 1610 cm^{-1} due to the presence of the indenyl double bond and bands at 2830 and 2930 cm^{-1} due to symmetric and asymmetric C—H stretching respectively found in the methoxyl substituent. A singlet in the n.m.r. at 3.78 was assigned to the three methoxy protons, while a two proton singlet at 3.83 was attributed to the methylene hydrogens. A complex multiplet at 6.85-7.49 integrated for the thirteen aromatic protons. The synthesis of indene 92 is outlined in Scheme 8.

PART II. PHOTOCHEMICAL REACTIONS

Irradiation of 1-p-bromophenyl)-1-phenylindene (67)

Direct irradiation of indene 67 gave rise to products of both phenyl and bromophenyl migration as witnessed by the n.m.r. spectra of the aliquots (see Figure 3). Sharp singlets at 3.84 and 3.86, with a respective peak height ratio of 6.0:1.0, were assigned to the methylene protons of 2-(p-bromophenyl)-3-phenylindene (77) and 2-phenyl-3-(p-bromophenyl)-indene (83) respectively on the basis of comparison with a series of standard mixtures of 77 and 83. The broad singlet at 4.87 was assigned to the methine protons of the corresponding 1,2-disubstituted compounds and n.m.r. integration showed that the 2,3-disubstituted isomers constituted 79% of the products formed and the 1,2-disubstituted compounds the remaining 21% products. After removal of 47% of crystalline 2-(p-

bromophenyl)-3-phenylindene (77), m.p. 181-183°C, the mother liquor was treated with base to isomerize the 1,2-disubstituted indenes to the corresponding 2,3-isomers. Integration by n.m.r. of the AB quartet at 6.67 and comparison with the integration area of the methylene singlets (Figure 4) indicated the presence of 12% of residual starting material 67. Peak area analysis (Figure 4) of the methylene absorptions showed the presence of additional 77 (28.5%) and the presence of a small amount (12%) of the product 83 of phenyl migration. The various products and their yields are outlined in Scheme 9. Also, the two main products of photolysis, indenes 77 and 83, were found to be unreactive under the conditions of irradiation.

Irradiation of 1-(p-cyanophenyl)-1-phenylindene (68)

The direct photolysis of 1-(p-cyanophenyl)-1-phenylindene (68) when monitored by n.m.r. (Figure 5) showed the starting material AB quartet centered at 6.76 to decrease with time while singlets appeared at 3.88 and 4.95. Comparison with signals observed for the expected migration products 79 and 85 enabled tentative assignment of the 3.88 singlet to the methylene group of 2-(p-cyanophenyl)-3-phenylindene 79 and the 4.95 singlet to the methine proton of 1-phenyl-2-(p-cyanophenyl)-indene (81). The n.m.r. integration of these two peaks at various times during photolysis showed a constant ratio of 7.1:1.0 in favor of the methylene singlet, i.e., 78% of the 2,3-isomer and 22% of the 1,2-isomer had been formed. Also, on v.p.c., the starting material peak at 10.0 min was seen to decrease in size as the photolysis proceeded while the product peak at 18.0 min increased in size with time.

After about 75% reaction, a 59% yield of crystalline material identical in physical and spectroscopic properties with 2-(p-cyanophenyl)-3-phenylindene (79) was obtained. Upon removal of these crystals, the mother liquor was

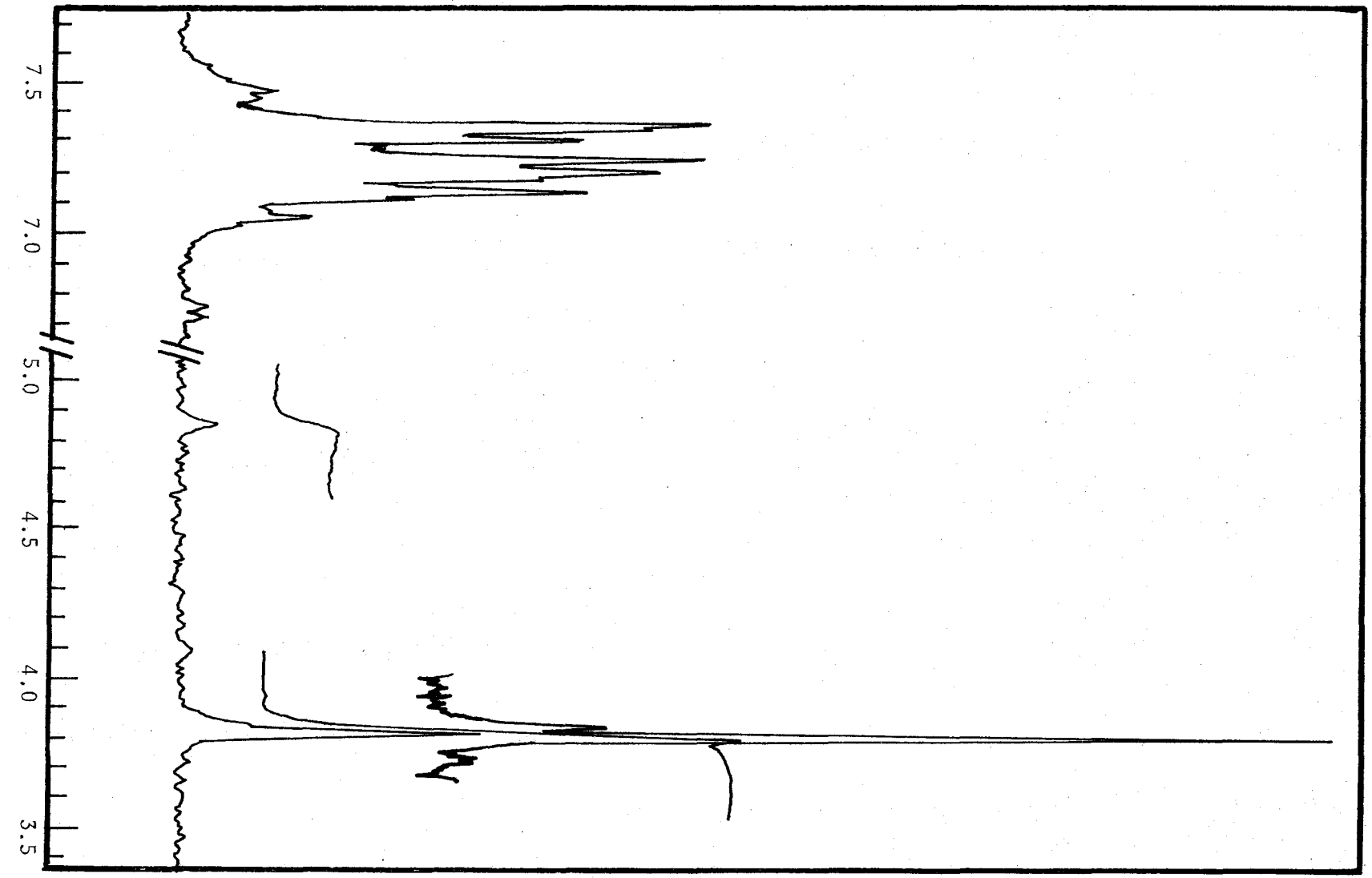


Figure 3. N.m.r. spectrum of aliquot from irradiation of 1-(p-bromopheny1)-1-phenylindene (67).

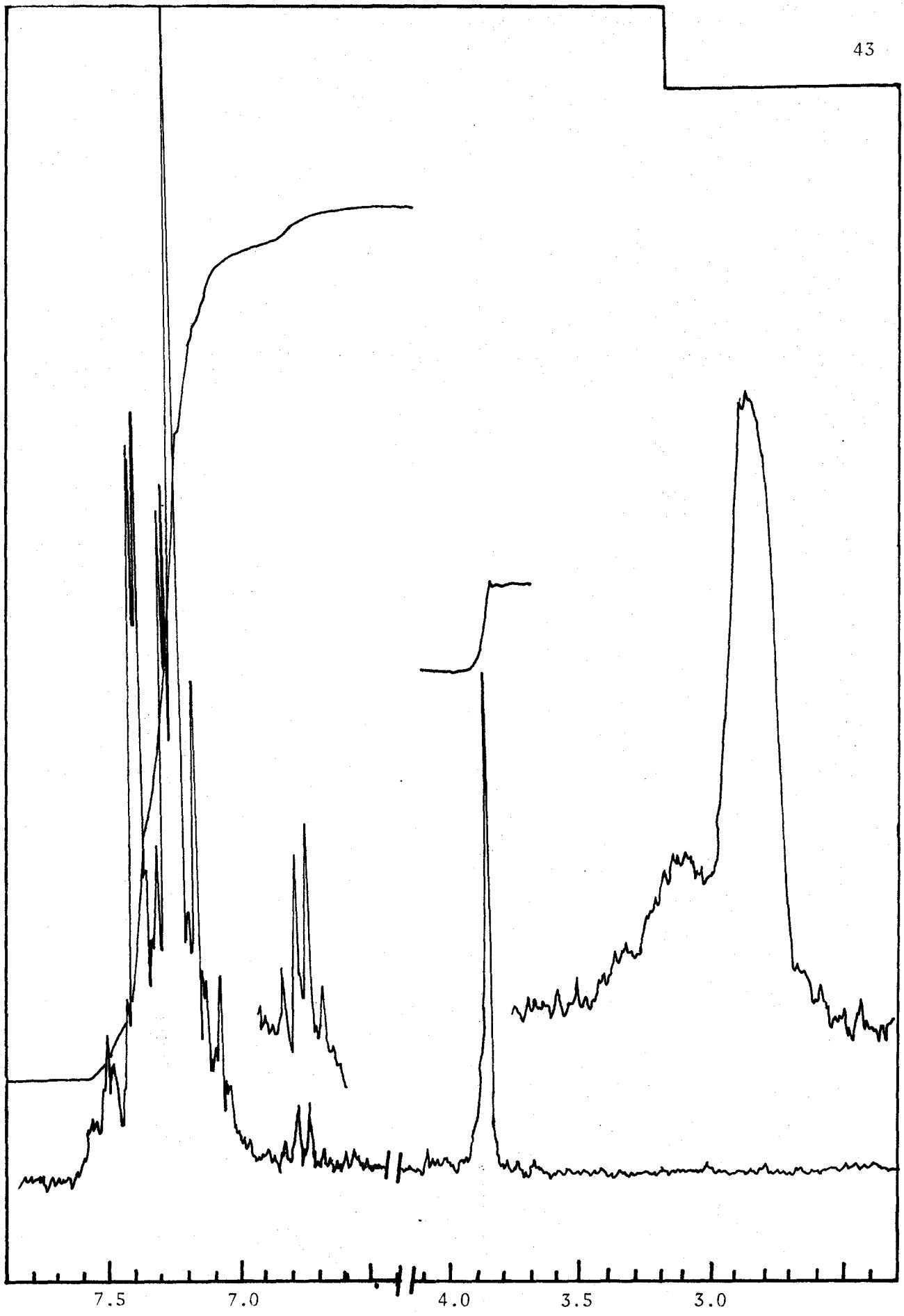
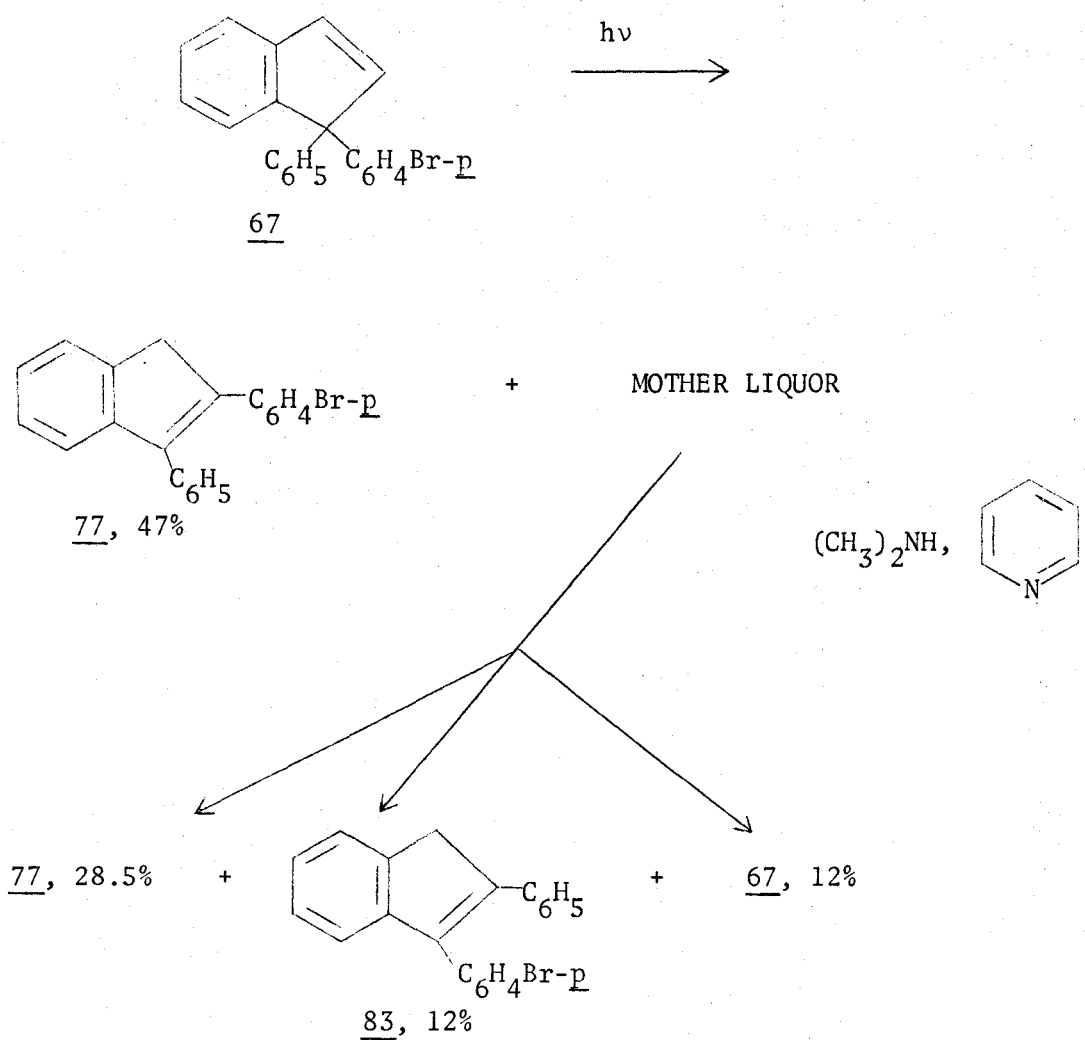


Figure 4. N.m.r. spectrum of mother liquor obtained in irradiation of 1-(p-bromophenyl)-1-phenylindene (67).



Yield of 77, 75.5%; Ratio $\frac{77}{83} = \frac{86}{14}$

Yield of 83, 12%;

Scheme 9. Irradiation of 1-(p-bromophenyl)-1-phenylindene (67).

treated with base to give an additional set of crystals. This new material showed n.m.r. absorption at 3.88 (CH_2 of indene 79), 6.76 (AB quartet of starting material 68) and 6.95-7.60 (multiplet). Integration of peak areas showed the presence of starting material 68 (28%) and the presence of an additional 7% of indene 79. Addition to the crystals of some synthetic 79 enhanced the methylene singlet at 3.88.

The v.p.c. analysis of this additional crystalline material showed, in addition to the 10.0 min starting material peak and the 18.0 min product peak, a small shoulder peak at 17.0 min retention time. Addition of a synthetic sample of 2-phenyl-3-(p-cyanophenyl)-indene (85) caused an increase in the size of the shoulder peak, while addition of a synthetic sample of 79 increased the main product peak at 18.0 min. The amount of product arising due to phenyl migration was estimated to be 1% by v.p.c. The possibility of photo-interconversion of products 79 and 85 was dismissed when each substance was found to be totally stable towards direct irratiation. Scheme 10 shows the reaction products and the yields obtained.

Irradiation of 1-(p-methoxyphenyl)-1-phenylindene (69)

The n.m.r. analysis of the total crude from direct irradiation of indene 69 indicated that at least two products were formed. Singlets at 3.69 and 3.81 were assigned to the methoxy and methylene singlets respectively of 2-(p-methoxyphenyl)-3-phenylindene (89) while the smaller singlet at 3.78 was assigned to the methoxy singlet of the residual starting material. The broad singlet at 4.80 was attributed to the methine proton of 1-phenyl-2-(p-methoxyphenyl)-indene (90), since if the indene 89 was formed to a large extent, then its less thermodynamically stable isomer (the 1,2-disubstituted species) should also be formed. Following the removal of 28% of 89, the mother liquor

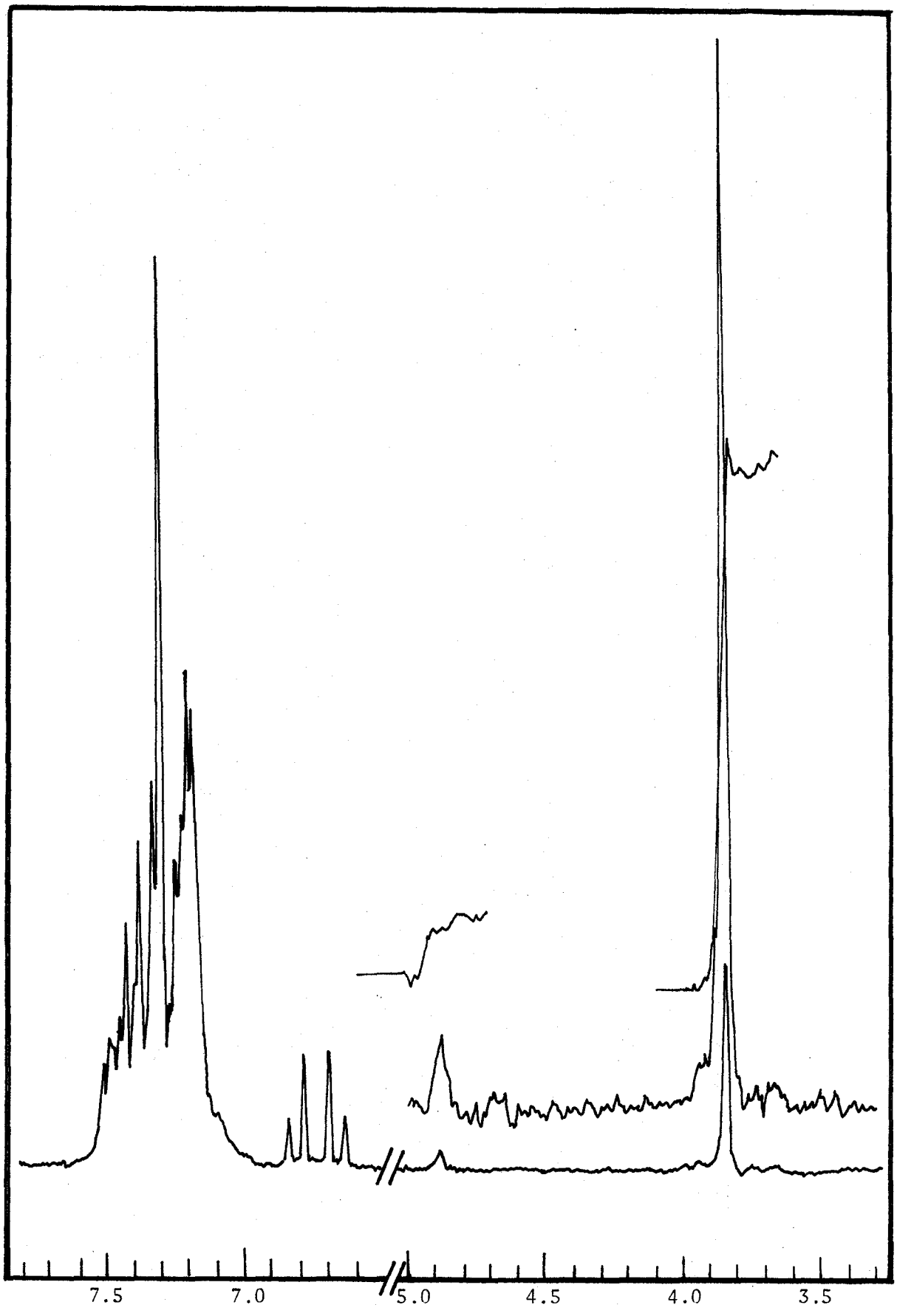
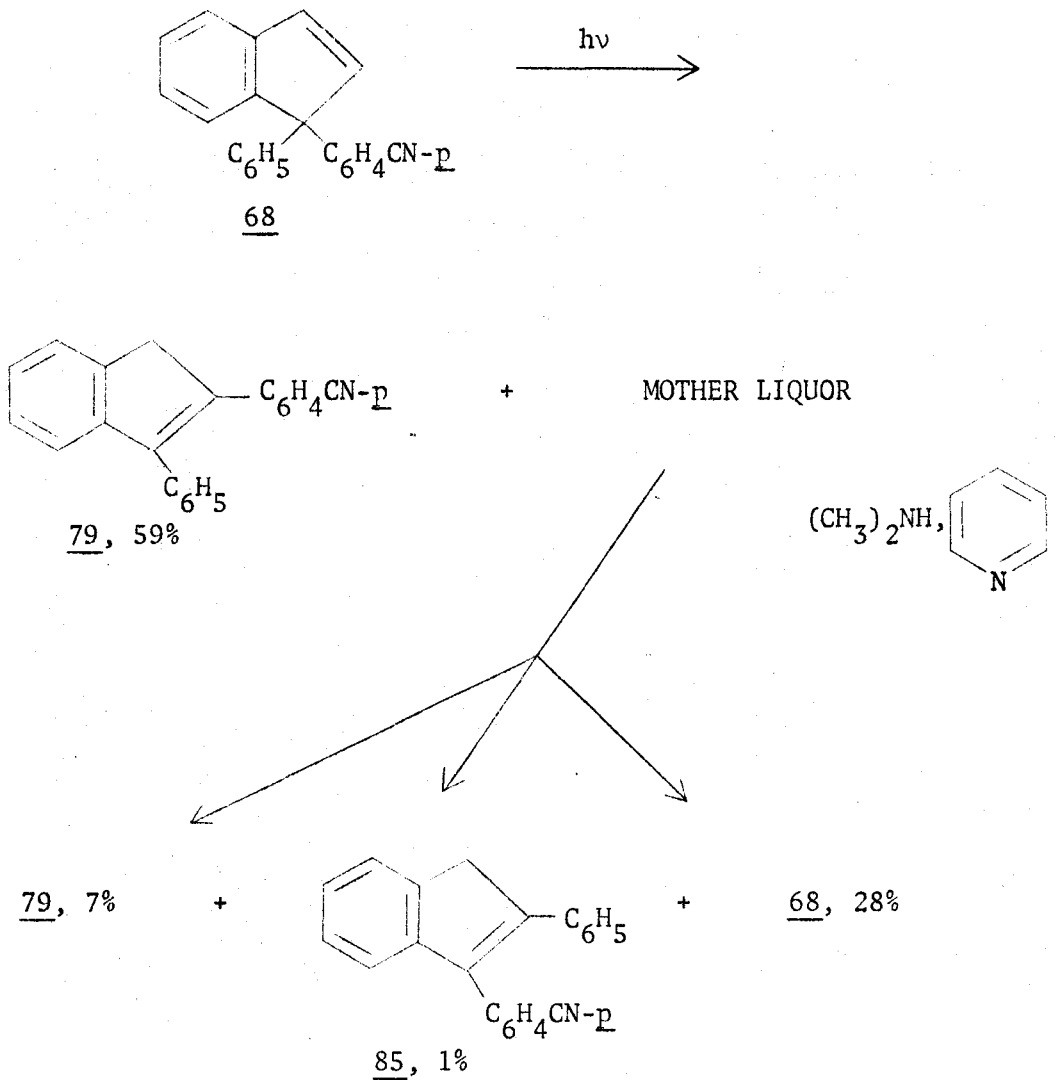


Figure 5. N.m.r. spectrum of aliquot from photolysis of 1-(p-cyanophenyl)-1-phenylindene (68).



Yield of 79, 66%;

Yield of 85, 1%;

Ratio $\frac{79}{85} > \frac{98}{2}$

Scheme 10. Irradiation of 1-(p-cyanophenyl)-1-phenylindene (68).

was treated with base to isomerize the 1,2-disubstituted isomer 90 to the isomer 89. Additional crystalline 89 (13%) was removed and the residual oil was analyzed by n.m.r. (see Figure 6) and v.p.c. The v.p.c. analysis showed the presence of starting material 69 (9% of the total material; retention time 5.0 min) and a broad product peak at 11.0 min. The n.m.r. showed,in the region 6.5 to 7.0,the characteristic absorption patterns associated with the presence of starting material 69 as well as the main products of methoxyphenyl and phenyl migration (indenes 89 and 92 respectively). (See the Appendices Section for n.m.r. spectra of these pure species). After assigning the peaks in that region to their respective compounds (see Figure 6), a peak height comparison of the signals for the protons ortho to the methoxy group in both 89 and 92 was made in the region 6.5 to 7.0. The ratios of the same peaks for a series of standard mixtures, containing known amounts of indenes 89 and 92, were noted. It was determined that indene 89 predominated in a 10:1 ratio over indene 92. Thus the oil contained a 45.5% yield of 2-(p-methoxyphenyl)-3-phenylindene (89), for a total yield of 86.5% for 89, and a 4.5% yield of 2-phenyl-3-(p-methoxyphenyl)-indene (92). The indenes 89 and 92 were shown to be unreactive under the photolysis conditions. Scheme 11 illustrates the reaction products and yields obtained.

Acetophenone sensitized photolysis of 1-(p-bromophenyl)-1-phenylindene (67)

On acetophenone sensitization in the irradiation of 1-(p-bromophenyl)-1-phenylindene (67), products of phenyl and bromophenyl migration were detected by n.m.r. analysis of aliquots. Singlets at 3.84 and 3.86 were assigned respectively to the methylene protons of the indenes 77 and 83. The integration ratio of 7.5:1.0 observed for the ratio of the latter two singlets to the methine singlet indicated that 79% of the reaction products consisted of the

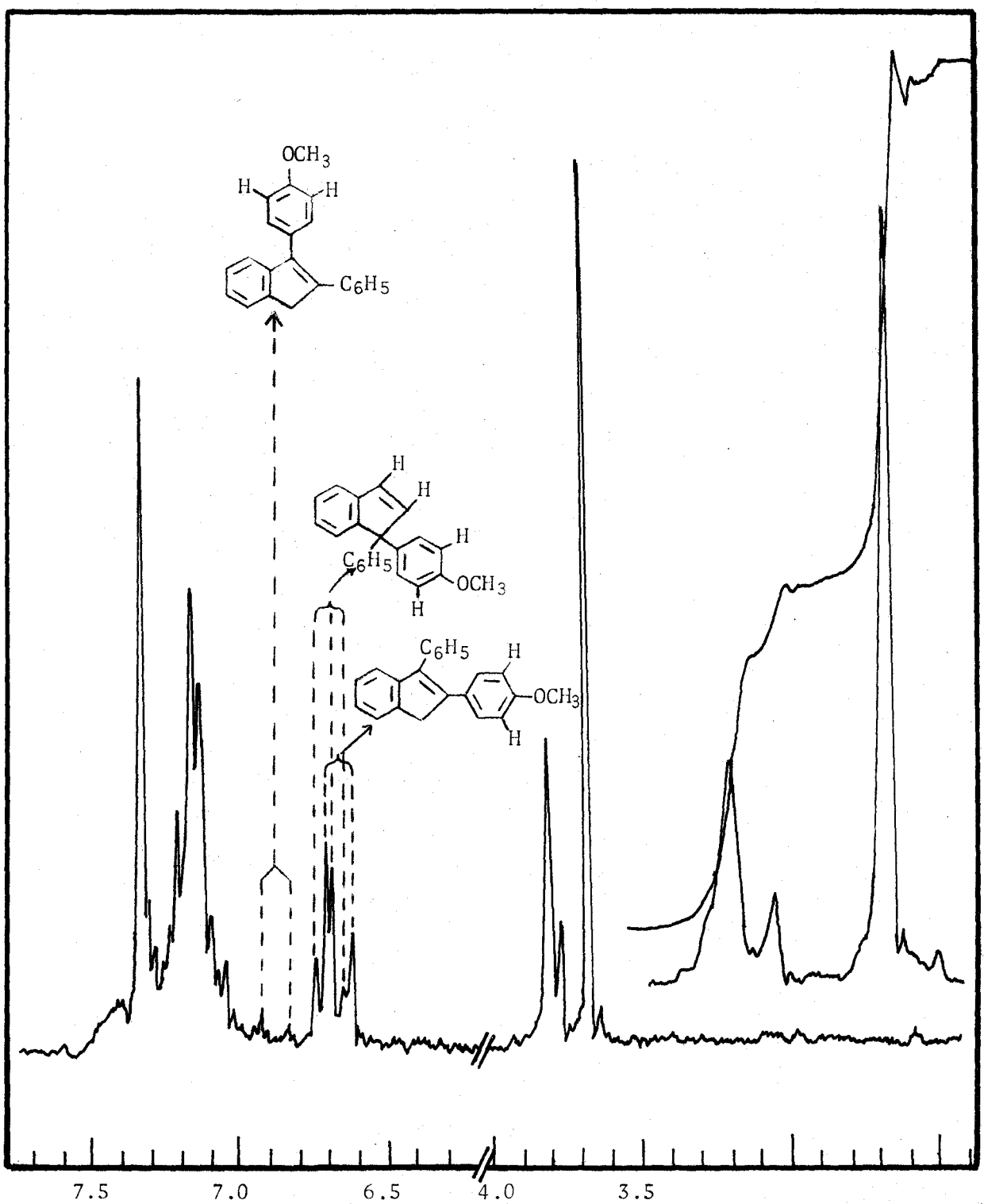
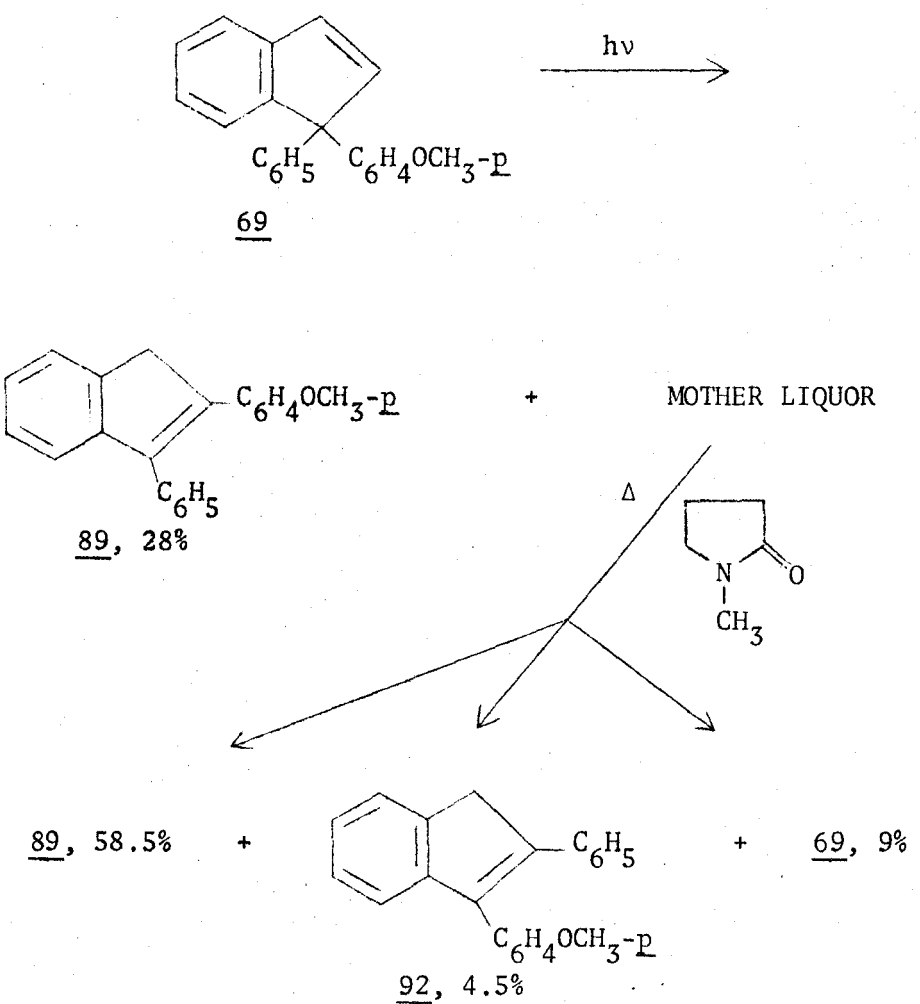


Figure 6. N.m.r. spectrum of residual oil from irradiation of 1-(p-methoxyphenyl)-1-phenylindene (69).



Yield of 89, 86.5%;

Yield of 92, 4.5%;

Ratio $\frac{89}{92} = \frac{95}{5}$

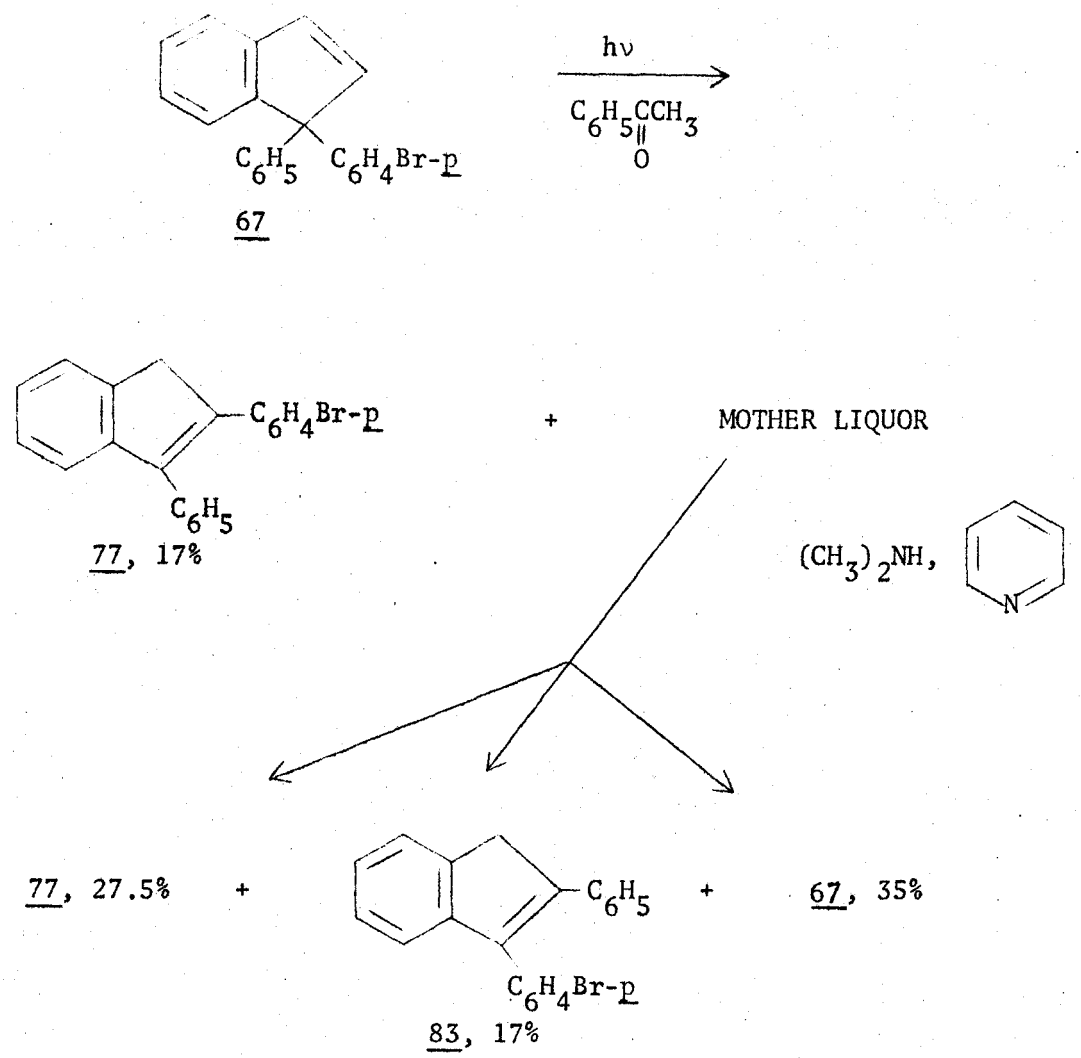
Scheme 11. Irradiation of 1-(p-methoxyphenyl)-1-phenylindene (69).

2,3-disubstituted isomers 77 and 83 and the remaining 21% was composed of the less thermodynamically stable 1,2-disubstituted indenes. After removal of 17% of crystalline 2-(p-bromophenyl)-3-phenylindene (77), the mother liquor was treated with base and analyzed by n.m.r. Integration of the area of the starting material AB quartet at 6.67 and comparison with the integration area of the methylene singlets gave a respective ratio of 0.78:1.0 indicating the presence of 35% of residual starting material 67. Peak area analysis of the methylene singlets at 3.84 and 3.86 indicated a respective ratio of 1.6:1.0 for the areas. This confirmed the presence of an additional 27.5% of 77 and the presence of 17% of 2-phenyl-3-(p-bromophenyl)-indene (83). The yields of the products are shown in Scheme 12.

Acetophenone sensitized photolysis of 1-(p-cyanophenyl)-1-phenylindene (68)

As in the direct irradiation of 68, it appeared from an analysis of the aliquots that only cyanophenyl migration was occurring due to the presence of the sole methylene singlet at 3.88. Again, the 2,3-isomer constituted 78% of the reaction product as indicated by the integration ratio of 7.1:1.0 for the area of the methylene singlet compared to the area of the methine singlet at 4.95. Crystallization rendered 2-(p-cyanophenyl)-3-phenylindene (79) in 59% yield. The filtrate, following base treatment, had an integration ratio of 2.8:1.0 for the area of the starting material quartet at 6.76 relative to the area of the methylene singlet at 3.88. This showed the presence of 29.5% of residual 68 and an additional 10% (total yield of 69%) of 79.

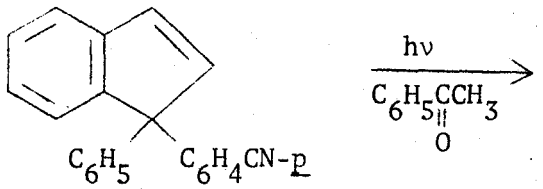
The v.p.c. analysis of the mother liquor, as in the case of the direct irradiation of 68, showed the shoulder peak at 17.0 min and the main product peak at 18.0 min retention time. Addition of an authentic sample of 2-phenyl-3-(p- cyanophenyl)-indene (85) enhanced the shoulder peak. The indene 85 was



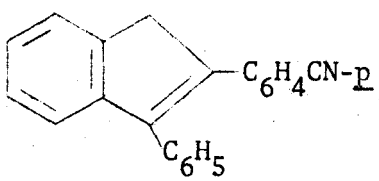
Yield of 77, 44.5%;
Yield of 83, 17%;

Ratio $\frac{77}{83} = \frac{72}{28}$

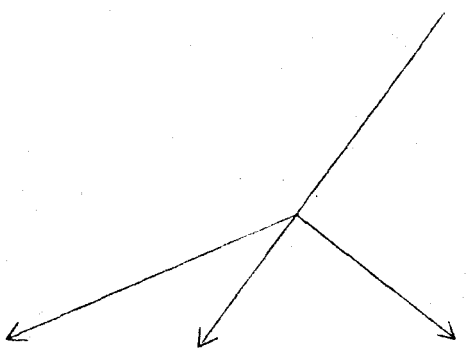
Scheme 12. Sensitized irradiation of 1-(p-bromophenyl)-1-phenylindene (67).

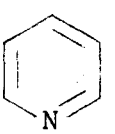


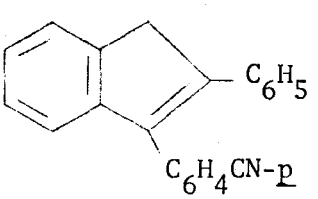
68



79, 59% + MOTHER LIQUOR



$(CH_3)_2NH$, 

79, 10% + 

+ 69, 29.5%

85, 1%

Yield of 79, 69%;

Yield of 85, 1%;

$$\text{Ratio } \frac{79}{85} > \frac{98}{2}$$

Scheme 13. Sensitized irradiation of 1-(p-cyanophenyl)-1-phenylindene (68).

estimated by v.p.c. peak heights to constitute 1% of the reaction mixture. Scheme 13 illustrates the reaction sequence and products.

The photochemical results are summarized in Table 4.

PART III: THERMAL REACTIONS

Thermolysis of 1-(p-bromophenyl)-1-phenylindene (67)

Thermolysis of the bromoindene 67 gave products of phenyl and bromophenyl migration as indicated by the presence in the n.m.r. (see Figure 7) of the methylene proton singlets at 3.84 and 3.86 due respectively to 2-(p-bromophenyl)-3-phenylindene (77) and 2-phenyl-3-(p-bromophenyl)-indene (83). Utilizing the same signals for a series of known weight:weight mixtures of indenes 77 and 83 indicated the presence of 55% of 77 and 45% of 83. Crystallization gave a 40% yield of 2-(p-bromophenyl)-3-phenylindene (77). Peak area analysis of the methylene singlets in the n.m.r. of the mother liquor showed an additional 12% of 77 and the presence of 48% of isomer 83.

Thermolysis of 1-(p-cyanophenyl)-1-phenylindene (68)

The n.m.r. analysis (see Figure 8) of the total crude after thermolysis of 1-(p-cyanophenyl)-1-phenylindene showed that two products were present because of the sharp singlets at 3.88 and 3.90. A comparison with the n.m.r.'s of a known series of mixtures of the indenes 79 and 85 enabled assignment of the 3.88 singlet to the methylene group of 2-(p-cyanophenyl)-3-phenylindene (79) and the 3.90 singlet to the methylene protons of 2-phenyl-3-(p-cyanophenyl)-indene (85). The comparison also suggested that the reaction mixture contained 82% of indene 79. This was verified when crystallization gave a 69% yield of 79, and peak height analysis of the methylene singlets in the n.m.r. (Figure 9) of the mother liquor showed an additional 12% of 79 and 19% of the product of

Figure 7. N.m.r. spectrum of total crude from thermolysis of 1-(p-bromophenyl)-1-phenylindene (67).

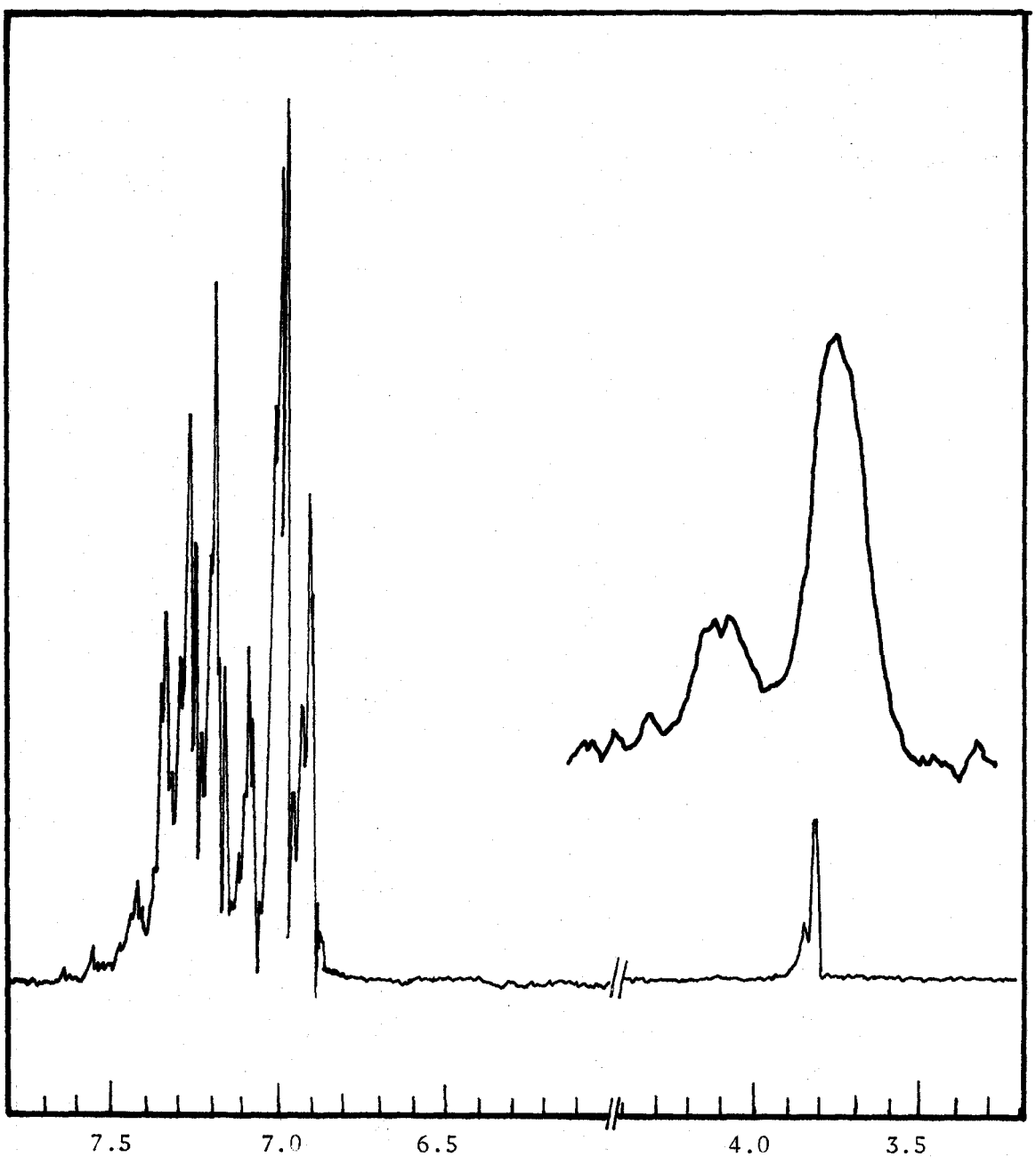


Figure 8. N.m.r. spectrum of total crude from thermolysis of 1-(p-cyanophenyl)-1-phenylindene (68).

Figure 9. N.m.r. spectrum of mother liquor from thermolysis of 1-(p-cyanophenyl)-1-phenylindene (68).

phenyl migration, 2-phenyl-3-(p-cyanophenyl)-indene (85).

Thermolysis of 1-(p-methoxyphenyl)-1-phenylindene (69)

The n.m.r. analysis (Figure 10) of the total crude following thermolysis of 1-(p-methoxyphenyl)-1-phenylindene (69) showed sharp singlets at 3.69 and 3.78. These were assigned respectively to the methoxy protons of 2-(p-methoxyphenyl)-3-phenylindene (89) and 2-phenyl-3-(p-methoxyphenyl)-indene (92). The peak height ratio of the signals assigned to the protons ortho to methoxy in 89 and 92 were compared to the ratios observed for the same signals of known weight to weight mixtures of 89 and 92. This indicated that indene 92 made up 53% of the two component reaction mixture. Crystallization gave 33% of 2-(p-methoxyphenyl)-3-phenylindene (89). The mother liquor, by similar peak height analysis of the methylene singlets, was shown to contain an additional 15% of 89 as well as 48% of 92.

The thermal results are summarized in Table 4 and the various products arising due to irradiation and thermolysis are shown in Scheme 14.

Table 4. Migratory Aptitudes in Rearrangements of 1-(p-Xphenyl)-1-phenylindenes

Energy Input	Substituent (-X)	Solvent	% Reaction	Product Ratio[a]
Ultraviolet (direct)	-CN	hexane	59	
		tert-butanol	72	79:85 > 98:2
		95% ethanol	95	
	-Br	hexane	88	77:83 = 86:14
	-OCH_3	hexane	91	89:92 = 95:5
(acetophenone sensitized)	-CN	tert-butanol	62	79:85 > 98:2
	-Br	hexane	78	77:83 = 72:28
Heat	-CN	diphenyl ether	100	79:85 = 82:18
	-Br	diphenyl ether	100	77:83 = 53:47[b]
	-OCH_3	diphenyl ether	100	89:92 = 48:52[b]

[a] An error of ±5% is implied for these ratios.

[b] These product ratios represent the mean of the estimates obtained by n.m.r. and by isolation technique.

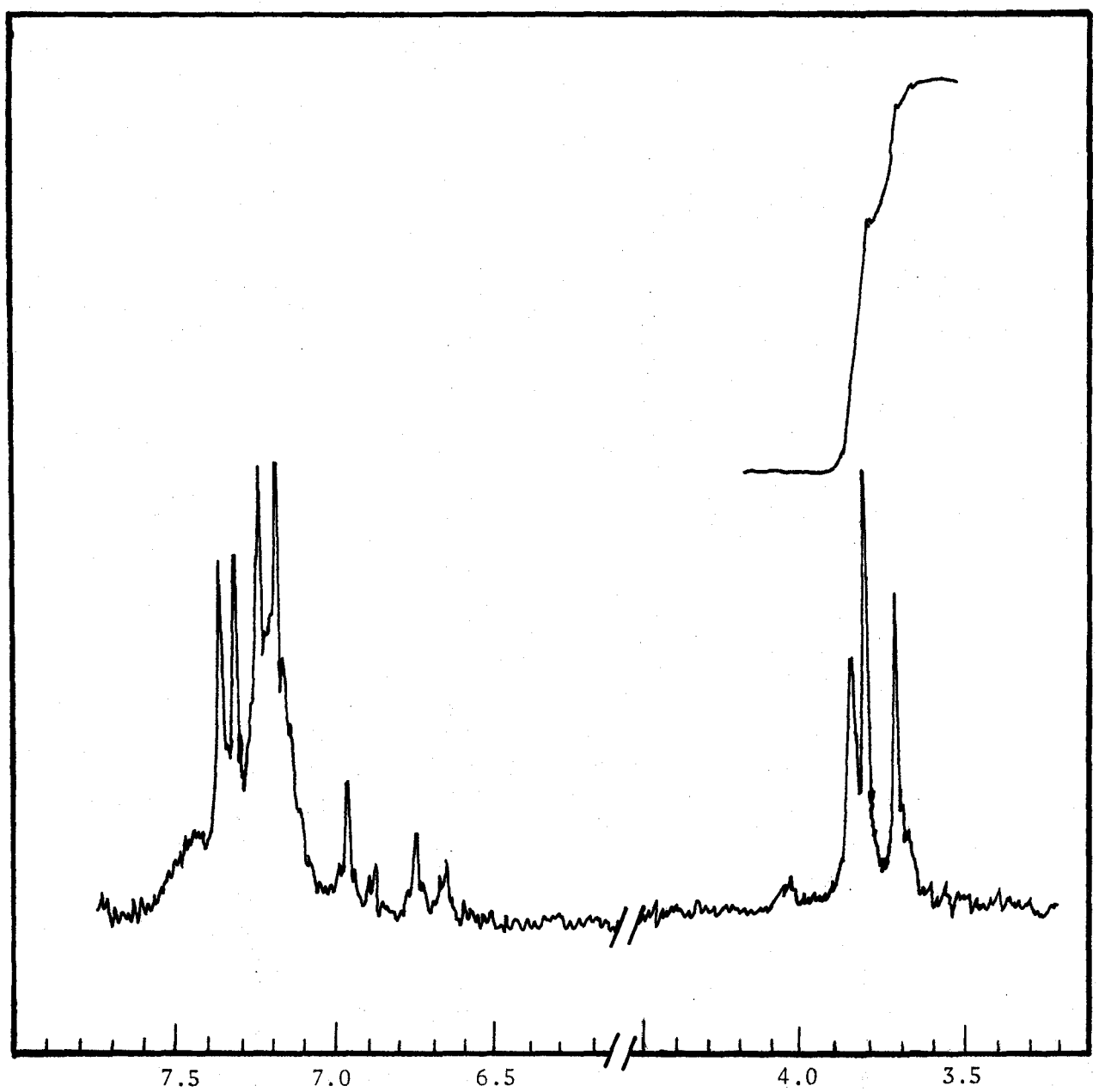
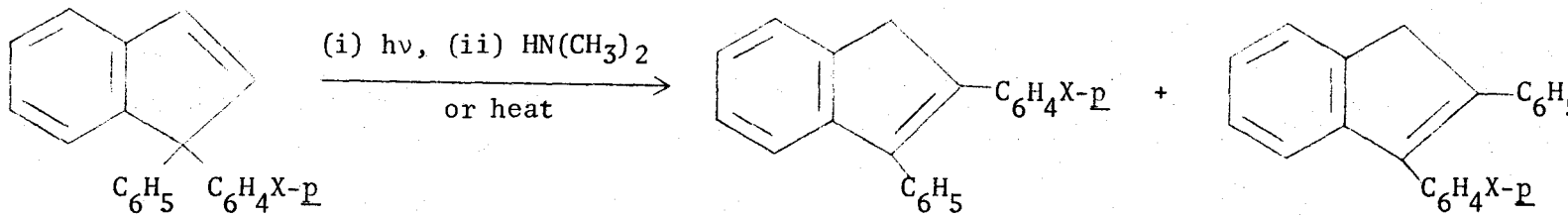


Figure 10. N.m.r. spectrum of total crude from thermolysis of 1-(p-methoxyphenyl)-1-phenylindene (69).



X = Br,	67	77	83
X = CN,	68	79	85
X = OCH_3,	69	89	92

Scheme 14. Reactants and products in rearrangement experiments.

PART IV: MECHANISTIC ASPECTS

In order to understand the nature of the phenyl migration step in the photolysis of the 1,1-diphenylindene system and to identify the excited state(s) involved, a quantitative study, utilizing quantum yield* techniques, was performed on both the direct and sensitized photolysis of 1,1-diphenylindene. Also, lifetime and rate studies were carried out on the excited state(s) to more fully understand the rearrangement process and to contrast the observations with ground state findings. The results are described in the following pages of the Results Section.

Quantum yield of formation of 2,3-diphenyl indene

The details of these measurements are given in the Experimental Section, Part II. The method of analysis used for these measurements was as follows: the total amount of 2,3-diphenylindene formed was measured by v.p.c. by comparing the area of the product peak with the area of an added known amount of internal standard (p-terphenyl) using an electronic integrator. The ratio of the areas of the two peaks was then juxtaposed to a calibration graph, a plot prepared by v.p.c. analysis of known mixtures of both the internal standard and product, where the exact weight of product formed was determined. The results for the direct photolysis are shown in Table 5 and the sensitized values in Table 6.

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*The quantum yield (ϕ) of a photochemical process describes the efficiency of that process. It is defined as:

$$\phi = \frac{\text{number of moles undergoing the process}}{\text{number of einsteins absorbed}}$$

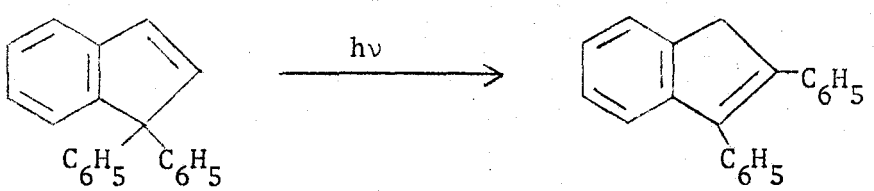
or

$$\phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$

1 Einstein = 6.02×10^{23} quanta.

TABLE 5

Quantum Yield of Formation of 2,3-Diphenylindene



Light absorbed by starting material (Einsteins × 10^4)	Amount of product formed (moles × 10^4)	Quantum yield
1.68	1.42	0.84
1.10	0.88	0.80

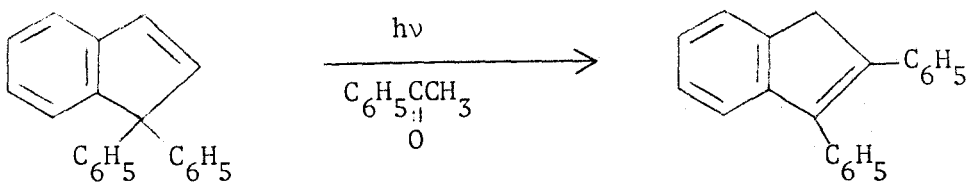
Solvent: 95% ethanol.

Concentration of 1,1-diphenylindene: 100 mg, 6.49×10^{-4} M.

Temperature: 9 ± 1°C

TABLE 6

Quantum Yield of Sensitized Formation of 2,3-Diphenylindene



Light absorbed by acetophenone (Einsteins × 10^3)	Amount of product formed (moles × 10^4)	Quantum Yield
7.95	4.83	0.061
8.42	5.20	0.062

Solvent: 530 ml of tert-butanol + 45 ml of methanol.

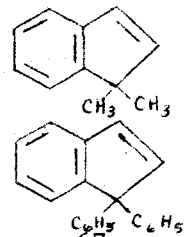
Concentration of 1,1-diphenylindene: 780 mg, 5.06×10^{-3} M.

Concentration of acetophenone: 3.0 g, 0.044 M.

Temperature: 9 ± 1°C

Acetophenone absorbed more than 99% of light.

TABLE 7. Spectroscopic Data

	U.V. Secondary Band		Fluorescence (0-0)		Phosphorescence (0-0)	
	λ (mμ)	ε	S_1 (mμ)[a]	E_{S_1}[b] ($\frac{kcal}{mole}$)	T_1 (mμ)	E_{T_1}[b] ($\frac{kcal}{mole}$)
 67	258	9,200	293[c]	97.5	454	63.0
	260	6,250	297[d]	96.2	454	63.0
	262	7,100	297	96.2	465	61.5
68	255	10,800	298	96.0	465	61.5
69	262	7,100	297	96.2	465	61.5

[a]Values obtained directly from the common point of intersection of the u.v. and fluorescence spectrum (77°K) of a solution of the compound in a cyclohexane matrix. All values obtained were agreeable with the long wavelength peak observed in the u.v. for each indene.

[b]Values obtained from formula: $E = \frac{hc}{\lambda} = \frac{2.86 \times 10^4}{\lambda}$.

Cf.[c,d]Values of 292.6 mμ and 297.7 mμ respectively obtained by J. D. Laposa and V. Morrison in a methylcyclohexane polycrystalline matrix (77°K). The instrument used was a Hanovia 150 Watt Xenon lamp, powered by a Bausch and Lomb power supply, together with a Jarrel-Ash Ebert monochromator.

When the calibration curve was plotted, a least squares fit showed that the resultant straight line had a 5% deviation in the slope. This is the assumed error in the quantum yield determinations.

Absorption and Emission Spectra

The ultraviolet spectra of 1,1-dimethylindene,1,1-diphenylindene and the three substituted phenylindenes 67, 68 and 69 showed virtually identical $\pi - \pi^*$ secondary band absorption at approximately 260 mμ. The u.v. spectrum of 1,1-dimethylindene indicated the zero-zero band (S_1) to be at 293 mμ, and a value of 292.6 mμ was obtained by Dr. J.D. Laposa of this department from the fluorescence spectrum of a solution of the indene in a methylcyclohexane polycrystalline matrix (77°K) obtained with the aid of a high resolution spectrometer (see Table 7). Likewise the zero-zero band (S_1) for 1,1-diphenylindene was estimated (from absorption) to be at 297 mμ and a high resolution fluorescence spectrum in methylcyclohexane (77°K) confirmed this by showing the $S_1 \rightarrow S_0$ transition to be 297.7 mμ.

The zero-zero bands for the remaining 1,1-diarylindenes (67, 68 and 69) were obtained by comparing the value of the first long wavelength u.v. peak with the common point of intersection of the u.v. and fluorescence spectra for that particular indene. These latter fluorescence spectra were recorded at 77°K in a cyclohexane matrix, with the aid of the Aminco-Bowman Spectrophotofluorometer. The singlet-state energies (E_{S_1}) calculated for the four diaryl compounds were the same (96 kcal per mole) within experimental error. These values are shown in Table 7.

The phosphorescence spectra were measured at 77°K in a 1:1 ethanol-ether matrix. The zero-zero bands (T_1) for triplet-singlet transition ($T_1 \rightarrow S_0$) were readily obtained by observing the first low wavelength peak in the phos-

phorescence spectra. These values are listed in Table 7 along with the corresponding triplet-state energies (E_{T_1}).

Biacetyl quenching of 1,1-dimethylindene fluorescence

Biacetyl is known as a quencher of both singlet and triplet excited states. Various concentrations of biacetyl were used to quench the fluorescence of 1,1-dimethylindene. The indene was irradiated at 279 mμ so that 98% of the incident light was going to the indene. The changes in fluorescence of the indene singlet with changes in biacetyl concentration were monitored at 330 mμ, a wavelength where there was no interference from biacetyl emission. Since 1,1-dimethylindene does not rearrange upon photolysis[34], the lifetime of the 1,1-dimethylindene singlet could be calculated. The results are given in Table 8. The Stern-Volmer plot (I_o/I) versus quencher (biacetyl) concentration was linear, and is shown in Figure 11.

Table 8. Quenching of 1,1-dimethylindene[a] Fluorescence[b] by Biacetyl

Biacetyl M × 10^3	I_o/I
-	1.00
1.00	1.06
2.00	1.14
3.00	1.16
4.00	1.30
5.00	1.41
6.00	1.46
7.00	1.60
8.00	1.71

[a]The 1,1-dimethylindene concentration was 1.00 × 10^{-3} M.

[b]The excitation wavelength was 279 mμ and the emission wavelength was 330 mμ; 98% of incident light was absorbed by indene.

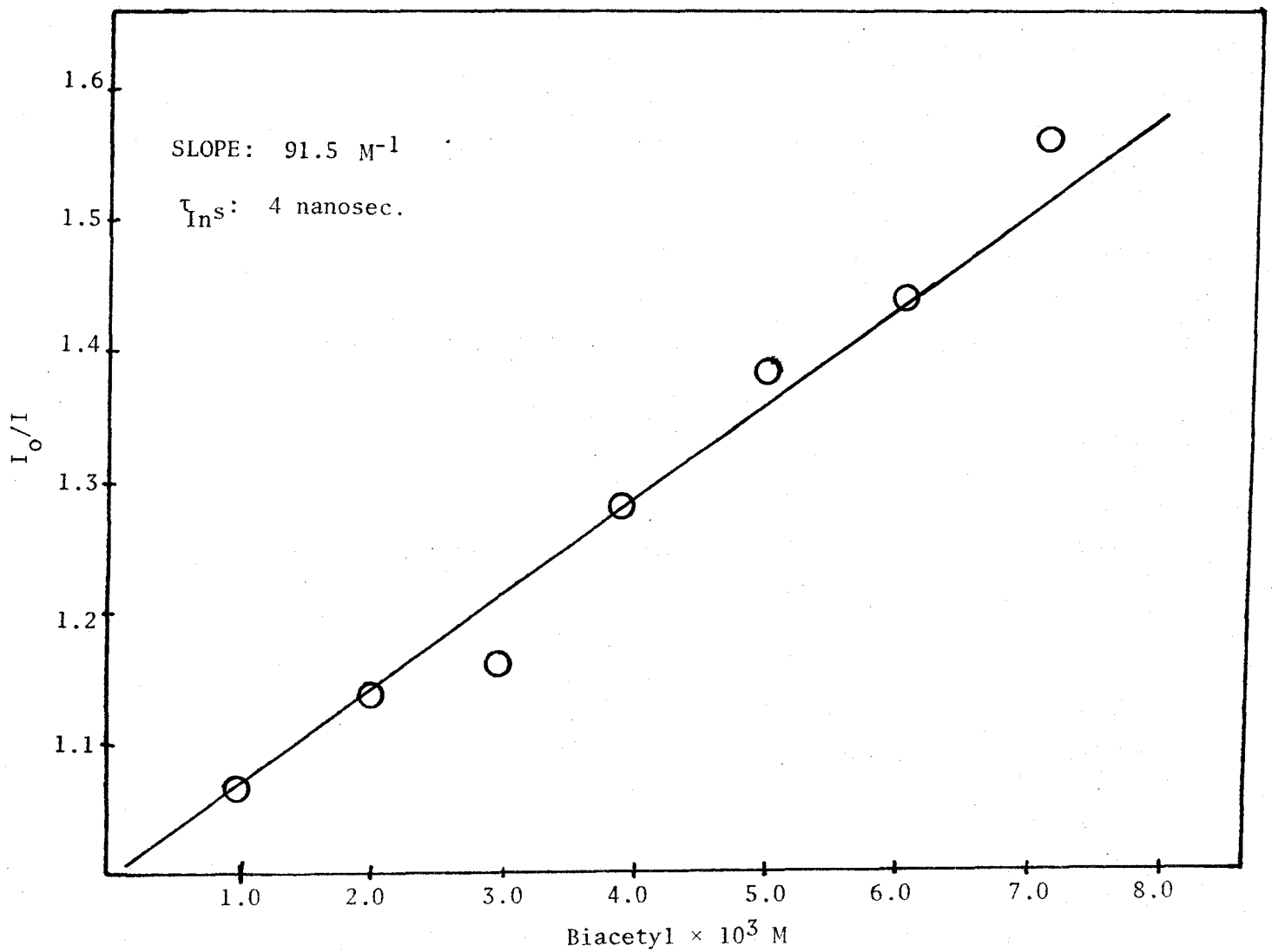


Figure 11. Quenching of 1,1-dimethylindene fluorescence by biacetyl.

Sensitization of biacetyl phosphorescence by 1,1-dimethylindene

It has been possible to study energy transfer to the singlet and triplet state of biacetyl by making use of the fact that it is one of the few substances that displays both fluorescence and phosphorescence in de-aerated solutions[43]. There is, however, no overlap of the fluorescence and phosphorescence bands. In this particular situation, biacetyl was used as an acceptor of triplet state energy to give its lowest triplet state.

The sensitization of phosphorescence of a series of biacetyl solutions by 1,1-dimethylindene was studied by exciting the indene at 279 mμ and reading the biacetyl phosphorescence (524 mμ) intensities directly off the microphotometer. The biacetyl concentrations and phosphorescence readings are shown in Table 9. The straight line plot of the reciprocal of the phosphorescence intensities versus the reciprocal of the biacetyl concentrations is shown in Figure 12 along with the value obtained for the triplet lifetime.

Table 9. Sensitization of Biacetyl Phosphorescence[a] by 1,1-dimethylindene[b]

Biacetyl M × 10^3	Biacetyl^{-1} M^{-1} × 10^{-2}	P[c]	1/P
1.05	9.53	17.0	0.0588
1.25	8.00	18.9	0.0530
1.66	6.02	22.0	0.0455
2.00	5.00	25.0	0.0400
3.00	3.33	29.5	0.0338
5.00	2.00	40.0	0.0250

[a]The excitation wavelength was 279 mμ and the emission wavelength was 524 mμ.

[b]The 1,1-dimethylindene concentration was 1.09×10^{-3} M.

[c]The values for P represent readings taken directly from the microphotometer.

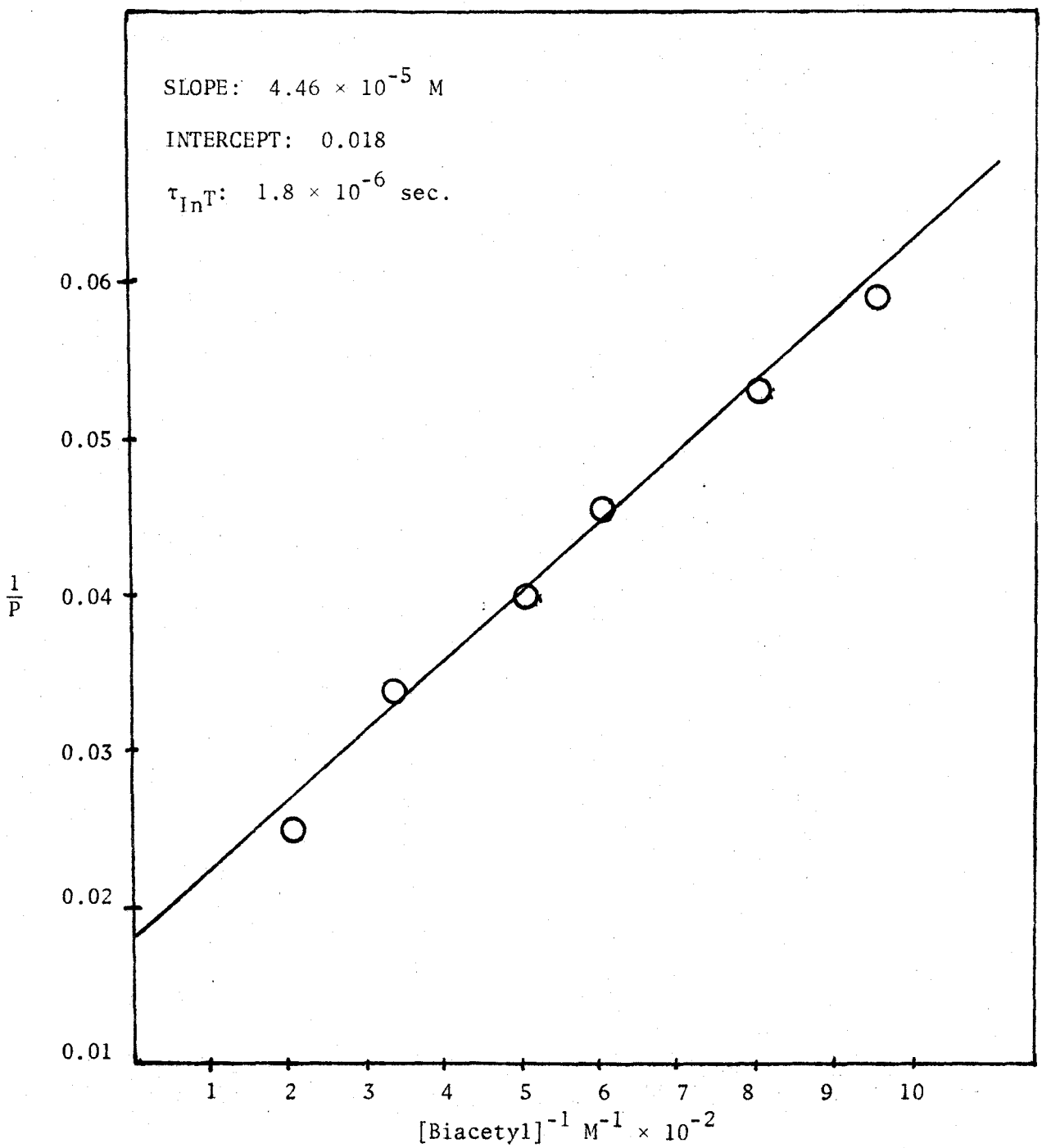


Figure 12. Sensitization of biacetyl phosphorescence by 1,1-dimethylindene (1.09×10^{-3} M).

Quenching of the formation of 2,3-diphenylindene by acrylonitrile

The rate of rearrangement of 1,1-diphenylindene to 2,3-diphenylindene was obtained by a series of quenching experiments utilizing different acrylonitrile concentrations. The per cent completion of the reactions was kept low so as to minimize light absorption by product and to prevent reaction of product with acrylonitrile. Since the tube with no quencher had a quantum yield for product formation of 0.82 (see Table 4), the quantum yields of the other tubes could be calculated by comparing the per cent product present in each tube to the per cent product formed in the tube with no quencher. The per cent product formed in each case, along with the relative quantum yields are shown in Table 10. A plot was made of the reciprocal quantum yields for 2,3-diphenylindene formation versus acrylonitrile concentration in each tube (see Figure 13). A straight line correlation was observed enabling calculation of the rate constant k_r for the reaction.

Table 10. Quenching of 2,3-diphenylindene formation by acrylonitrile.

Acrylonitrile, M	% Product[a]	Φ	$1/\Phi$
0	25.2	0.82[b]	1.22
0.15	22.9	0.735	1.36
0.25	21.0	0.680	1.47
0.35	20.0	0.650	1.54
0.50	18.2	0.592	1.69
0.65	16.9	0.549	1.82

Excitation source: two (2537 Å) monochromatic lamps.

Solvent: hexane.

[a]Numbers represent the per cent 2,3-diphenylindene formed if 100% of light had been going to starting material (1,1-diphenylindene), i.e., corrections have been made for the light absorbed by product at 2537 Å. Example: with no quencher present, v.p.c. analysis by internal standard method shows 20.5% product, but accounting for light absorption at 2537 Å by product gives a yield of 25.2% product.

[b]The value, taken from Table 5, for the direct photolysis.

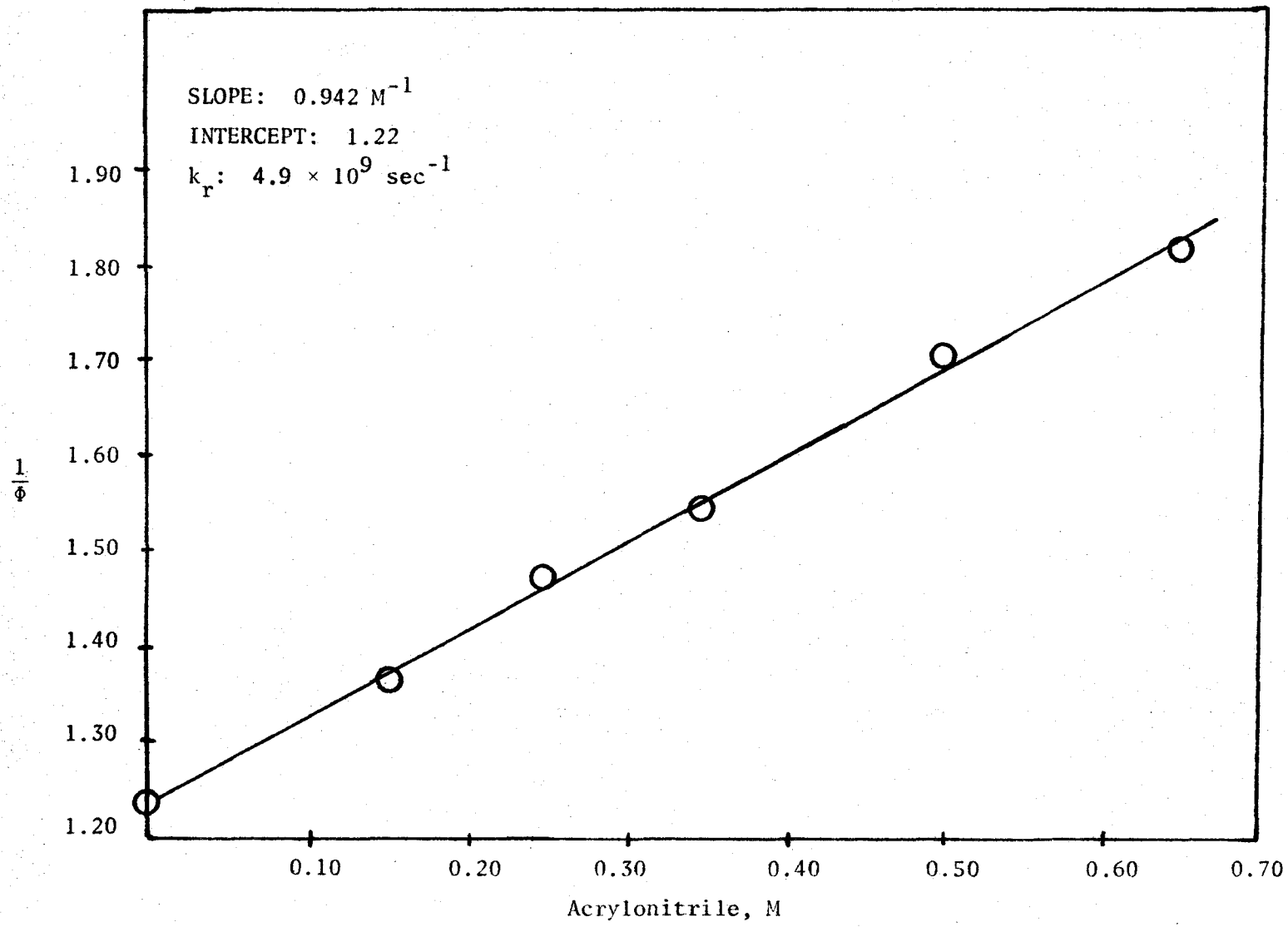


Figure 13. Quenching of 2,3-diphenylindene formation by acrylonitrile.

EXPERIMENTAL

Materials

All solvents and reagents were distilled before use. Hexane (B & A reagent) was purified by a 24 hr treatment with fuming sulfuric acid followed by washings with water, 10% sodium bicarbonate solution and water. After drying over sodium sulfate, the fraction boiling at 66-67°C was collected. This purified solvent had no absorption above 250 mμ. The light petroleum used was Mallinckrodt Analytical reagent and had boiling range 30-60°C.

Other reagents and solvents distilled prior to usage were: 1-methyl-2-pyrrolidone (Eastman practical), b.p. 30-32°C/1 mm; 2,4,6-collidine (Aldrich Analyzed reagent), b.p. 163-165°C; tert-butyl alcohol (Baker Analyzed reagent), b.p. 81-82°C; acetophenone (Fisher Certified reagent), b.p. 196-198°C; bromobenzene (Eastern reagent), b.p. 153-155°C; diphenyl ether (Eastern reagent), b.p. 54-56°C/0.5 mm; biacetyl (Matheson Coleman and Bell Chromatoquality reagent), distilled under nitrogen, b.p. 88-89°C; acrylonitrile (Fisher Certified reagent), purified by the method of Bevington* and distilled, b.p. 76-77°C.

Aldrich reagent 4-bromobenzophenone was recrystallized from benzene, m.p. 81-82°C. The p-dibromobenzene (Aldrich reagent) was recrystallized from ether-light petroleum, m.p. 87-89°C. Other solid reagents used were: 4-bromophenylacetic acid (Aldrich reagent), m.p. 115-116°C; 4-methoxyphenylacetic acid, 99% (Aldrich Analyzed reagent), m.p. 86-88.5°C; p-bromoanisole (Fisher highest purity), b.p. 210-212°C (m.p. 13-14°C).

Photochemical reaction conditions and analytical methods

The lamp used in the photochemical irradiations, with the exceptions of the quantum yield and acrylonitrile (as quencher) experiments, was a Hanovia

*J. C. Bevington and D. E. Eaves, Trans. Farad. Soc., 55, 1777 (1957).

Type L 450 W in a water-cooled immersion apparatus. A magnetic stirrer was provided along with a capillary inlet and outlet for nitrogen. Nitrogen was passed through the solution during and for 30 min prior to the photolyses. The quantum yield studies employed a Philips SP 500 W high pressure mercury arc lamp equipped with a lampholder cooling jacket. The quenching experiment, using acrylonitrile, utilized two lamps (2537 Å) in a Srinivasan-Griffin Photochemical Reactor (Rayonet) manufactured by the Southern New England Ultraviolet Company.

Aliquots were analyzed by vapour phase chromatography (v.p.c.) and by nuclear magnetic resonance (n.m.r.) spectrometry. A Varian-Aerograph Model 204-B dual column gas chromatograph with flame ionization detectors was used. A flow rate of 50-70 ml/min of helium was used with a 5' x 1/8" column of 5% QF-1 on Diataport 60/80. All n.m.r. spectra were run on a HA-100 spectrometer and all spectra were taken in deuteriochloroform solution. Chemical shifts are reported as p.p.m. downfield from internal tetramethylsilane. Where n.m.r. was used to determine the abundance of one or more materials, either peak area integration or triangulation was employed. The average of several integrations or triangulations was used. The estimated maximum analytical error was ±5%.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer with n-hexane (purified as above) as solvent. Infrared spectra were obtained on a Perkin-Elmer Model 337 or on a Beckman IR-5 instrument using spectral grade carbon tetrachloride or chloroform as solvent. Fluorescence and phosphorescence studies were performed with the use of an Aminco Bowman Spectrophotofluorometer utilizing a Xenon lamp for excitation. Nitrogen was Canadian Liquid Air certified grade. Melting points were taken on a Kofler hot stage and are uncorrected. The alumina used for column chromatography was Fisher Alumina Absorp-

tion while MN-Silica Gel G/UV_{254} (Machery, Nagel and Co.) was utilized for thin-layer chromatography (t.l.c.).

Elemental analyses were performed by: Dr. A. B. Gygli, Toronto, Ontario and by Galbraith Laboratories, Knoxville, Tennessee.

Syntheses

1-(p-Bromophenyl)-1,1-diphenylcarbinol (70)

A solution of 0.30 mole of phenylmagnesium bromide in ether (120 ml) was added under nitrogen to a rapidly stirred solution of 51 g (0.19 mole) of p-bromobenzophenone in 300 ml benzene. A red solution formed instantly but the color disappeared upon stirring overnight, leaving a white flocculent precipitate. The entire reaction mixture was then added to 200 ml of 3N H_2SO_4 and the aqueous phase was extracted with 3 x 50 ml portions of benzene. Subsequent washing of the combined benzene solutions with 200 ml of 5% $NaHCO_3$, then with 200 ml of water followed by drying ($MgSO_4$) and evaporation of solvent yielded an orange oil. Upon dissolving the oil in ether-hexane and cooling to 0°C, there was obtained 40 g of crude brown crystals, m.p. 92-97°C. The mixture was then chromatographed on a 80 x 4.0 cm column of alumina, slurry-packed in hexane, and elution was with 10% ether-hexane. Fractions 10-50 (400 ml fractions) yielded a total of 36 g (0.106 mole, 56%) of 70 as colorless needles, m.p. 99-100°C. The n.m.r. spectrum had peaks at 2.80 (s, 1 H) and 7.30-7.70 (m, 14 H). The i.r. spectrum had a strong band at 3400-3500 and a sharp peak at 3600 cm^{-1}.

3-(p-Bromophenyl)-3,3-diphenylpropionic acid (71)

A mixture of 3.60 g (0.106 mole) of 70 and 14.3 g (0.138 mole) of malonic acid was heated for 3 hr, under nitrogen at 150°C. An additional 14.3 g of malonic acid was added after the first and second hours of heating. The

temperature was raised to 160°C for 30 min, and the resultant melt was cooled, dissolved in 300 ml ether and extracted with 2 x 400 ml portions of 2.5% KOH. The aqueous phase was acidified with concentrated HCl. Cooling to 0°C produced brown colored crystals which were filtered and decolorized with carbon in refluxing 95% ethanol. Recrystallization from 95% ethanol gave 26.0 g (0.068 mole, 64%) of 71 as colorless needles, m.p. 190-192°C. The n.m.r. had peaks at 3.60 (s, 2H), 6.90-7.35 (m, 14 H) and 10.50 (broad singlet, 1 H). The i.r. showed a sharp band at 1725 and a broad band at 2800-3200 cm^{-1}.

3-(p-Bromophenyl)-3-phenyl-1-indanone (72)

Compound 72 was synthesized according to the method of Johnson[35].

A solution of 25.9 (0.068 mole) of the acid 71 in 50 ml of benzene was stirred and cooled in an ice bath, and 15.6 g (0.075 mole) of PCl_5 was added during 5 min. Upon removal of the ice bath, the contents of the flask were heated during 20 min (HCl evolution) to the boiling point and refluxing was continued for 10 min. Then, with continued stirring, the flask was cooled in an ice-salt bath until the internal temperature fell to about -10°C. With continued efficient cooling, there was added over a 15 min period a solution of 38.6 ml (0.34 mole) of stannic chloride in 40 ml benzene. During this addition, the temperature was maintained below 15°C. Stirring was continued for 1 hr at 0-10°C after which the solution was let warm to room temperature overnight. The complex was then decomposed by careful addition of 35 g of ice plus 30 ml of concentrated HCl. This two-phase mixture was refluxed for 2-3 hr (a few ml of ether were added). The aqueous phase was separated and extracted with 3 x 40 ml portions of benzene. These extracts were combined but kept separate from the original organic phase. Each wash solution was used first with the original organic phase and then with the extracts. The

washes were 100 ml of water, 100 ml of 10% Na_2CO_3, 100 ml of water and 50 ml of saturated NaCl solution. The benzene was evaporated after drying (Na_2SO_4) to give an oily residue. Addition of ether-light petroleum, followed by scratching of the inner walls of the flask, gave 18.6 g (0.051 mole, 75%) of crystalline material, m.p. 87-90°C. Recrystallization from ether-light petroleum gave colorless granules of the ketone 72, m.p. 91-92°C. The i.r. spectrum had strong absorption at 1710 cm^{-1} while the n.m.r. peaks appeared at 3.45 (s, 2 H) and 6.65-7.50 (m, 13 H).

Anal. Calc'd. for $C_{21}H_{15}BrO$: C, 69.43; H, 4.16; Br, 21.99. Found: C, 69.37; H, 4.22; Br, 21.97.

3-(p-Bromophenyl)-3-phenyl-1-indanol (73)

The indanol 73 was prepared according to the procedure of Brown and Jackman[36].

A solution of 34 g (0.094 mole) of the ketone 72 and 0.88 g (0.024 mole) of sodium borohydride in 500 ml of 95% ethanol was stirred for 48 hr at room temperature. A further 3.5 g (0.095 mole) of sodium borohydride was added and the solution was stirred for an additional 6 hr. The solution was then slowly poured into 250 ml of chilled $6NH_2SO_4$. A white flocculent precipitate was filtered and washed with water. A methylene chloride solution of the crystals was dried (Na_2SO_4) and the solvent evaporated to give 28.4 g (0.078 mole, 83%) of 73 as a white powder with melting range 120-170°C. The i.r. spectrum showed bands at 3300-3500 and 3600 cm^{-1}. The n.m.r. exhibited peaks at 1.90 (broad singlet, 1 H), 2.70 (q, J = 7.0 c.p.s., 1 H), 3.25 (q, J = 7.0 c.p.s., 1 H), 5.05 (broad triplet, J = 7.0 c.p.s., 1 H) and 6.70-7.40 (m, 13 H). The mass spectrum had a parent peak at m/e = 365.

1-(p-Bromophenyl)-1-phenylindene (67)

The procedure of Brown and Jackman[36] was employed to synthesize the indene 67.

A solution of 25.0 (0.068 mole) of the indanol 73 in 400 ml of glacial acetic acid with 1.8 g (0.01 mole) of p-toluenesulfonic acid was refluxed for 40 min. The mixture was cooled and poured into 500 ml of water. It was then extracted with 3 x 150 ml fractions of methylene chloride and the combined extracts were successively washed with 3 x 100 ml portions of 10% Na_2CO_3 and with 300 ml of water. The organic extracts were dried (Na_2SO_4) and concentrated to yield 20.1 g of crude crystalline material, m.p. 115-117°C. Recrystallization from ether-light petroleum gave 19.0 g (0.055 mole, 81%) of 67 as colorless rods, m.p. 118-119°C. The i.r. had bands at 820, 1010, 1480, 1600 and 3065 cm^{-1}. The n.m.r. spectrum showed resonance at 6.67 (AB quartet, δ_A 6.63, δ_B 6.71, J_{AB} = 5.0 c.p.s., 2 H) and 6.95-7.40 (m, 13 H).

Anal. Calc'd. for $C_{21}H_{15}Br$: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.93; H, 4.31; Br, 22.86.

1-(p-Cyanophenyl)-1-phenylindene (68)

Conversion of 67 to the cyanoindene 68 was achieved by following the method of Newman and Boden[38].

The bromoindene 67 (11.3 g, 0.033 mole) and 5.3 g (0.059 mole) of cuprous cyanide in 30 ml of 1-methyl-2-pyrrolidone were refluxed under nitrogen for 2 hr. The reaction mixture was cooled and poured into 8.6 g (0.176 mole) of sodium cyanide in 200 ml of water. The mixture was shaken thoroughly and 500 ml of benzene were added. The entire mixture was filtered through a sintered glass funnel containing celite. The organic layer was separated, washed with 200 ml of 10% sodium cyanide solution and then with 300 ml of water.

The benzene layer was separated, dried (Na_2SO_4) and evaporated to give a black oil. Dissolution of the oil in refluxing 95% ethanol with subsequent cooling to room temperature gave 7.9 g of brown granules, m.p. 147-151°C. Recrystallization from 95% ethanol yielded 7.0 g (0.024 mole, 73%) of 68 as colorless granules, m.p. 152-154°C. The i.r. showed peaks at 840, 1500, 1600, 2230 and 3060 cm^{-1}. The n.m.r. absorption was at 6.76 (AB quartet, δ_A 6.69, δ_B 6.83, J_{AB} = 5.0 c.p.s., 2 H) and 7.06-7.51 (m, 13 H).

Anal. Calc'd. for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N. 4.78. Found: C, 90.08; H, 5.02; N, 4.87.

1-(p-Methoxyphenyl)-1-phenylindene (69)

The procedure used was that of Bacon and Rennison[39].

Freshly cut sodium (0.69 g, 0.03 mole) was added, under nitrogen, to 12 ml of anhydrous methanol in the reaction flask. When dissolution was complete, the warm solution was diluted with 10 ml of dried and redistilled 2,4,6-collidine, followed by 0.95 (0.005 mole) of vacuum-dried cuprous iodide, the bromoindene 67 (3.47 g, 0.01 mole) and collidine (30 ml). The mixture was stirred and refluxed under nitrogen. After 7 hr an aliquot (2 ml) was taken and analyzed in the following manner: the aliquot was added to 10 ml of 6N HCl and extracted with 2 x 10 ml fractions of ether, after which the ethereal solutions were dried (Na_2SO_4) and concentrated. The n.m.r. of the residual material had peaks at 3.77 (s), 6.70-6.90 (complex multiplet) and 6.95-7.45 (complex multiplet). After 20 hr the entire reaction mixture was added to 100 ml of 6N HCl. Extraction with 2 x 100 ml fractions of ether, drying (Na_2SO_4) and evaporation of ether gave a brown oil that showed 3 spots (R_f = 0.5, 0.6, 0.7) on t.l.c. (5% ether-light petroleum). Chromatography of the oil on a 37 x 4 cm column of alumina and elution with hexane gave 200 ml fractions

as follows: fractions 6-18 contained 1.0 g of 1,1-diphenylindene, m.p. 89-90°C; fractions 20-25 gave 0.20 g of 67. Elution was continued with 2% ether-light petroleum and fractions 29-40 gave 0.60 g of crystals, m.p. 74-76°C. Recrystallization from light petroleum gave 0.53 g (0.0018 mole, 19%) of 69 as fluffy needles, m.p. 77-78°C. The i.r. had absorption at 828, 1040, 1188, 1245, 1510, 1605, 2840, 2910, 2935, 2960 and 3065 cm^{-1}. The n.m.r. peaks occurred at 3.77 (s, 3 H), 6.75-6.84 (m, 4 H) and 7.10-7.45 (m, 11 H).

Anal. Calc'd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.61; H, 6.02.

p-Bromo-3-benzylidenephthalide (74)

The procedure of Weiss[40] was employed.

A mixture of 54.2 g (0.366 mole) of phthallic anhydride, 94.6 g (0.440 mole) of p-bromophenylacetic acid and 1.4 g (0.017 mole) of anhydrous sodium acetate were heated at 230-240°C for 2 hr under a stream of nitrogen. The reaction mixture was then cooled and dissolved in refluxing 95% ethanol. Upon cooling, there was obtained 90 g of crystalline material, m.p. 170-173°C. Recrystallization from 95% ethanol gave 88.6 (0.293 mole, 80%) of 74 as slender yellow needles, m.p. 174-176°C. The i.r. absorption occurred at 981, 1073, 1267, 1660, 1765 and 1780 cm^{-1}. The n.m.r. peaks were at 6.20 (s, 1 H) and 7.20-8.00 (m, 8 H).

Anal. Calc'd. for $C_{15}H_9BrO_2$: C, 59.82; H, 3.01; Br, 26.53. Found: C, 59.69; H, 2.96; Br, 26.43.

2-(p-Bromophenyl)-3-phenyl-1-indenone (75)

The procedure followed was essentially that of Allen et al[41].

A solution of 75 g (0.476 mole) of bromobenzene in 150 ml of ether and

and 11.6 g (0.476 g atom) magnesium were used to prepare phenylmagnesium bromide. The magnesium dissolved during 30 min, and the solution was refluxed 15 min. To the vigorously stirred warm solution was added 28.7 g (0.095 mole) of the phthalide 74 in 800 ml of benzene at a rate which maintained refluxing. At the end of the addition, a brown precipitate appeared. After distillation of excess solvent, the reaction mixture turned bright red in color. On cooling in ice, the complex was destroyed by the addition of 15 ml of concentrated H_2SO_4 in 300 ml water. The benzene layer was separated and the aqueous layer was extracted with 200 ml of benzene. The combined benzene fractions were dried ($MgSO_4$) and the solvent removed to afford a dark red oil. On cooling an ethereal solution of the oil, at 0°C for 1 week, 14.6 g of crystals were obtained. Recrystallization from ether-methylene chloride gave 13.5 g (0.037 mole, 39%) of 75 as red rods, m.p. 151-152°C. The i.r. bands occurred at 1015, 1080, 1185, 1610 and 1720 cm^{-1}. The n.m.r. showed a multiplet at 7.06-7.60.

Anal. Calc'd. for $C_{21}H_{13}BrO$: C, 69.82; H, 3.62; Br, 22.12. Found: C, 69.77; H, 3.72; Br, 22.17.

2-(p-Bromophenyl)-3-phenylindene (77)

The method of Martin[42] was modified to obtain 77.

A mixture of 150 g (2.3 g.atom) of zinc, 26 g (0.096 mole) of mercuric chloride, 10 ml of concentrated HCl and 250 ml of water was stirred for 15 min. The aqueous solution was decanted and the amalgamated zinc covered with 150 ml of 95% ethanol and 60 ml of concentrated HCl. Then 10.0 g (0.028 mole) of the indenone 75 was added and the mixture was refluxed for 4 hr. The reaction was quenched by the addition of 150 ml of water. The liquid phase was decanted and extracted with 2 x 100 ml portions of methylene chloride. The combined organic extracts were washed with 100 ml of water and dried (Na_2SO_4). Evapora-

tion gave an orange oil which crystallized on addition of ether and light petroleum, giving 4.8 g (50%) of crystalline material 76, m.p. 142-153°C. However, t.l.c. (35% ether-light petroleum) showed two close running spots (R_f = 0.4, 0.6). The n.m.r. had peaks at 3.84 (s) and 4.90 (s) in relative ratio of 4:3 respectively, as well as at 7.07-7.54 (m). A portion (250 mg) of the crude product was applied to a 30 x 4.0 cm column of alumina, slurry-packed in hexane. Elution was with hexane and 50 ml fractions were collected. Fractions 36-40 gave 50 mg of crystals with melting range 163-180°C. The v.p.c. (5' x 1/8" of 5% QF-1 on Diatoport 60/80, 210°C) showed two equal-size peaks at 6.0 and 7.0 min retention time. Fractions 41-48 yielded 58 mg of 77 as colorless needles, m.p. 182-185°C. The i.r. showed absorption at 705, 828, 1014, 1080 and 1600 cm^{-1}. The n.m.r. absorption was at 3.84 (s, 2 H) and 7.00-7.60 (m, 13 H).

Anal. Calc'd. for $C_{21}H_{15}Br$: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.44; H, 4.29; Br, 22.91.

2-(p-Cyanophenyl)-3-phenylindene (79)

Using the procedure employed in the preparation of the cyanoindene 68, 4.1 g (0.012 mole) of the bromoindenes 76 was reacted with 1.9 g (0.021 mole) of cuprous cyanide for 2 hr in 10 ml of refluxing 1-methyl-2-pyrrolidone. The work up, as described in the synthesis of 68, gave a brown oil. Addition of light petroleum to the oil afforded 2.2 g of brown crystals. Recrystallization from ether gave 1.4 g (0.005 mole, 42%) of 79 as colorless needles, m.p. 214-216°C. The i.r. bands were at 698, 835, 1600 and 2225 cm^{-1}. The n.m.r. resonance occurred at 3.88 (s, 2 H) and 7.02-7.60 (m, 13 H).

Anal. Calc'd. for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.78. Found: C, 89.96; H, 5.22; N, 4.79.

2-(p-Cyanophenyl)-3-phenyl-1-indenone (80)

The procedure and work up used in the synthesis of 68 was repeated on 5.0 g (0.014 mole) of the bromoindenone 75 and 2.3 g (0.025 mole) of cuprous cyanide in 10 ml of pyrrolidone. The work up gave brown crystals and recrystallization from ether gave 2.3 g (0.076 mole, 54%) of 2-(p-cyanophenyl)-3-phenyl-1-indenone (80) as colorless crystals, m.p. 147-148°C. The i.r. had absorption at 1065, 1080, 1182, 1610, 1715 and 2230 cm^{-1}. The n.m.r. resonance was at 7.10-7.62 (m).

Anal. Calc'd. for $C_{22}H_{13}NO$: C, 85.97; H, 4.26; N, 4.56. Found: C, 86.02; H, 4.56; N, 4.79.

2-(p-Cyanophenyl)-3-phenylindene (79)

A mixture of zinc (37.5 g, 0.6 g.atom), mercuric chloride (6.5 g, 0.024 mole) and 60 ml of water was stirred for 10 min and the aqueous solution decanted. The zinc was covered with 40 ml of 95% ethanol and 15 ml of concentrated HCl. The indenone 80 (2.0 g, 0.0065 mole) was reacted as described in the preparation of 77 and gave upon work up 0.82 g (0.0028 mole, 43%) of a brown oil. The n.m.r. had peaks at 3.88 (s) and 4.95 (s) in the relative ratio of 1:3.5 respectively, as well as at 7.01-7.63 (m). Chromatography, on a 25 x 4.0 cm column of alumina, of a part (200 mg) of the oil and elution with hexane gave 180 mg of crystalline 2-(p-cyanophenyl)-3-phenylindene (79), m.p. 213-215°C.

2-Phenyl-3-(p-bromophenyl)-1-indenone (82)

The procedure of Allen et al.[41], as used in the synthesis of 75, was employed on a mixture of 23.4 g (0.105 mole) of benzylidene phthalide and 0.525 mole of p-bromophenylmagnesium bromide (the latter was made by the addition of

123 g (0.525 mole) of p-dibromobenzene in 300 ml of ether to 12.8 g (0.525 g.atom) of magnesium. The work up, identical to that described in the preparation of 75, gave a red oil. Addition of 25 ml each of ether and light petroleum to the oil rendered 12.1 g of crude red crystals, m.p. 167-174°C. Recrystallization from ether gave 82 as bright orange rods, m.p. 177-179°C, yield 10.7 g (0.030 mole), 28.5%. The i.r. peaks were at 1010, 1070, 1180, 1605 and 1710 cm^{-1}. The n.m.r. resonance was at 6.95-7.45 (m).

Anal. Calc'd. for $C_{21}H_{13}BrO$: C, 69.82; H, 3.62; Br, 22.12. Found: C, 69.85; H, 3.67; Br, 22.33.

2-Phenyl-3-(p-bromophenyl)-indene (83)

The procedure used in the preparation of 77 was again used in the synthesis of 83.

Zinc (31.7 g, 0.485 g.atom), mercuric chloride (5.26 g, 19.4 mmole), HCl (3 ml) and water (35 ml) were stirred for 15 min and the aqueous phase was decanted. Addition to the amalgam of 40 ml of 95% ethanol, 15 ml of HCl, and 2.0 g (5.55 mmole) of 82 was followed by a 3 hr reflux. Water (100 ml) was added and the liquid phase was extracted with 2 x 75 ml portions of methylene chloride. Drying of the organic extracts ($MgSO_4$) and evaporation of solvent left a yellow oil. Addition of light petroleum gave 440 mg of crystals, m.p. 170-177°C. The t.l.c. (hexane) showed two close moving spots (R_f = 0.5, 0.7). The n.m.r. had peaks at 3.88 (s) and 4.90 (s) in relative ratio of 1.0:2.0 respectively, and at 6.91-7.60 (m). The crystals were applied to a 30 x 4.0 cm column of alumina, slurry-packed in hexane. The elution was with hexane and 50 ml fractions were collected. Fractions 20-28 gave 285 mg of yellow crystals, m.p. 168-180°C. The n.m.r. had peaks at 3.86 (s), 4.90 (s) in relative ratio of 1:10 respectively, as well as a multiplet at 6.90-7.60.

Fractions 30-34 yielded 78 mg of 83 as colorless needles, m.p. 163-165°C (combined yield of crystalline material was 363 mg (1.05 mmole, 18%)). The i.r. of 83 showed absorption at 690, 833, 1012, 1070 and 1600 cm^{-1}. The n.m.r. peaks occurred at 3.86 (s, 2 H) and 7.10-7.56 (m, 13 H).

Anal. Calc'd. for $C_{21}H_{15}BrO$: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.75; H, 4.32; Br, 23.12.

2-Phenyl-3-(p-cyanophenyl)-indene (85)

Again, using the procedure employed in the preparation of 68, 283 mg (0.81 mmole) of indenes 83 and 84 were reacted for 2 hr with 132 mg (1.47 mmole) of cuprous cyanide in 3 ml of refluxing 1-methyl-2-pyrrolidone. Upon work up, as described in the synthesis of 68, a brown oil was obtained. Addition of light petroleum and ether gave, upon cooling to 0°C, 180 mg of yellow crystals. Recrystallization from 95% ethanol produced 155 mg (0.51 mmole, 63%) of 85 as colorless plates, m.p. 137-138°C. The i.r. peaks were at 693, 845, 1610 and 2230 cm^{-1}. The n.m.r. peaks came at 3.90 (s, 2 H), 7.09-7.55 (m, 9 H) and 7.54 (A_2B_2 quartet, δ_A 7.44, δ_B 7.64, J_{AB} = 8.0 c.p.s., 4 H).

Anal. Calc'd. for $C_{22}H_{15}N$: C, 90.17; H, 5.15; N, 4.78. Found: C, 90.47; H, 4.94; N, 4.88.

2-Phenyl-3-(p-cyanophenyl)-1-indenone (86)

1.39 g (3.85 mmole) of the bromo-indenone 82 was converted to the cyanoindenone 86 as described for the preparation of 1-(p-cyanophenyl)-1-phenylindene (68) by treatment with cuprous cyanide (0.62 g, 6.93 mmole) in 7 ml of 1-methyl-2-pyrrolidone. Upon work up, as described for 68, a brown oil was obtained which on addition of ether gave 0.92 g of red crystals, m.p.

170-180°C. Recrystallization from ether yielded 0.86 g (2.80 mmole, 73%) of 86 as red rods, m.p. 190.5-192.5°C. The i.r. had bands at 1065, 1078, 1180, 1605, 1715 and 2225 cm^{-1}. The n.m.r. resonance was at 6.95-7.78 (m).

Anal. Calc'd. for $C_{22}H_{13}NO$: C, 85.97; H, 4.26; N, 4.56. Found: C, 86.15; H, 4.37; N, 4.52.

p-Methoxy-3-benzylidenephthalide (87)

As described previously for the preparation of 74, a mixture of 18.6 g (0.125 mole) of phthallic anhydride, 25.0 g (0.150 mole) of p-methoxyphenylacetic acid and 0.50 g (0.006 mole) of anhydrous sodium acetate was heated to give a yellow oil upon work up. Dissolution of the oil in hot 95% ethanol gave, upon cooling, 18.1 g of crystals. Recrystallization from 95% ethanol gave 16.5 g (0.066 mole, 52%) of 87 as bright yellow needles, m.p. 147-148.5°C. The i.r. had absorption at 985, 1177, 1266, 1600, 1760 and 1775 cm^{-1}. The n.m.r. peaks were at 3.81 (s, 3 H), 6.29 (s, 1 H) and 6.74-7.98 (m, 8 H).

Anal. Calc'd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.87; H, 4.68.

2-(p-Methoxyphenyl)-3-phenyl-1-indenone (88)

The method of Allen et al.[41], as used to synthesize 75, was employed.

Phenylmagnesium bromide was prepared from 42.4 g (0.270 mole) of bromobenzene in 60 ml of ether by adding the solution to 6.56 g (0.270 g.atom) of magnesium so that a refluxing temperature was maintained. The mixture was then refluxed for 20 min and a solution of 12.5 g (0.050 mole) of the phthalide 87 in 400 ml benzene was slowly added so as to maintain refluxing. The work up as described in the synthesis of 75 gave a red oil. Trituration with ether-light petroleum gave 5.9 g of red crystals, m.p. 100-115°C. Recrystallization

from ether-methylene chloride yielded 2.2 g (0.007 mole, 14%) of 88 as red needles, m.p. 118-119.5°C. The i.r. absorption occurred at 1028, 1175, 1245, 1605, 1710, 2845, 2940 and 2960 cm^{-1}. The n.m.r. peaks were at 3.73 (s, 3 H) and 6.60-7.60 (m, 13 H).

Anal. Calc'd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.54; H, 4.98.

2-(p-Methoxyphenyl)-3-phenylindene (89)

The method of Martin[42] described previously in the preparation of 77 was employed on 5.0 g (16.0 mmole) of the indenone 88. A mixture of 88 g (1.35 g.atom) of zinc, 15.2 g (0.056 mole) of mercuric chloride, 6 ml of concentrated HCl and 140 ml of water was utilized to form the amalgam. Upon work up, 1.1 g (3.7 mmole) of crude crystalline material was obtained, m.p. 160-170°C. The t.l.c. (hexane) showed two major spots with approximately the same R_f value of 0.3 and two minor spots (R_f = 0.1, 0.7). The n.m.r. had a sharp singlet at 3.69, two singlets at 3.81 and 4.80 (relative ratio of 1:3.2 respectively) and a complex multiplet from 6.55 to 7.40. This crude material was treated with 30 ml of pyridine and 5 ml of dimethylamine for 12 hr at room temperature, water (25 ml) and benzene (25 ml) were added, the organic layer separated and washed with 25 ml of 3N H_2SO_4 and with 15 ml of water. After drying (Na_2SO_4) evaporation of solvent yielded 0.93 g of slightly red crystals. Chromatography on a 25 x 2.5 cm column of alumina, slurry-packed in hexane and elution with hexane gave 0.90 g (3.0 mmole, 19%) of 89 as colorless needles, m.p. 124-126°C. The i.r. had peaks at 698, 830, 1032, 1182, 1255, 1605, 2840, 2920, 2940 and 2960 cm^{-1}. The n.m.r. absorption was at 3.69 (s, 3 H), 3.81 (s, 2 H), 6.92 (A_2B_2 quartet, δ_A 6.67, δ_B 7.17, J_{AB} = 9.0 c.p.s., 4 H) and 7.16-7.45 (m, 9 H).

Anal Calc'd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.42; H, 5.93.

2-Phenyl-3-(p-methoxyphenyl)-1-indenone (91)

The procedure of Allen et al.[41] as described previously in the synthesis of the indenone 75 was used.

The p-methoxyphenylmagnesium bromide was from 100 g (0.535 mole) of p-methoxybromobenzene in 200 ml of ether, and 13.0 g (0.535 g.atom) of magnesium. A solution of 26.5 g (0.120 mole) of benzylidenephthalide in 800 ml of benzene was slowly added with stirring to the warm grignard reagent so as to maintain refluxing. Upon work up there resulted a red oil. Trituration with ether-light petroleum yielded 16.0 g of red crystals, m.p. 80-120°C. Recrystallization from ether-hexane gave 14.4 g (0.046 mole, 38%) of 91 as clusters of red needles, m.p. 121.5-123.0°C. The i.r. showed bands at 1030, 1175, 1250, 1605, 1710, 2845, 2940 and 2965 cm^{-1}. The n.m.r. absorption occurred at 3.81 (s, 3 H) and 6.83-7.58 (m, 13 H).

Anal. Calc'd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.58, H, 4.96.

2-Phenyl-3-(p-methoxyphenyl)-indene (92)

The Huang-Minlon modification of the Wolff-Kishner reduction was utilized in the preparation of 92.

The indenone 91 (8.0 g, 0.026 mole) and 125 ml of ethylene glycol, 2.7 ml (0.052 mole) of 99% hydrazine hydrate and 4.3 g (0.078 mole) KOH were refluxed for 4 hr. The mixture was cooled to 10° and extracted with 3 x 150 ml portions of ether. The ethereal extracts were washed with 50 ml of water, dried (Na_2SO_4) and the ether evaporated to give a dark oil. The n.m.r. of the oil displayed peaks at 3.78 (s), 3.83 (s), 4.65 (broad singlet) and 6.86-7.40 (m). The oil was dissolved in 10 ml 1-methyl-2-pyrrolidone and the solution refluxed under nitrogen for 3 hr. Upon cooling, the solution was extracted

with 2 x 100 ml fractions of benzene and the combined benzene layers were washed with 50 ml of water, and dried (Na_2SO_4). Evaporation of solvent gave 2.4 g of yellow crystals, m.p. 108-110°C. Chromatography on a 35 x 2.5 cm column of alumina, slurry-packed in and elution with hexane yielded 2.1 g (0.007 mole, 27%) of the indene 92 as colorless needles, m.p. 115-116°C. The i.r. absorption occurred at 700, 838, 1040, 1175, 1246, 1610, 2830, 2900, 2930 and 2950 cm^{-1}. The n.m.r. showed peaks at 3.78 (s, 3 H), 3.83 (s, 2 H) and 6.85-7.49 (m, 13 H).

Anal. Calc'd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.38; H, 6.16.

Photochemical Reactions

Irradiation of 1-(p-bromophenyl)-1-phenylindene (67)

A solution of 49 mg (0.143 mmole) of 1-(p-bromophenyl)-1-phenylindene (67) in 300 ml of hexane was irradiated through quartz with the type L 450 W lamp. The reaction was stopped at 1 min intervals; aliquots were withdrawn, analyzed by n.m.r., and returned to the reaction solution and the photolysis continued. Each aliquot displayed n.m.r. peaks at 3.84 (s), 3.86 (s), 4.87 (broad singlet), (relative integration ratio of singlets at 3.84 and 3.86 to singlet at 4.87 was 7.5:1.0; relative integration ratio of singlet at 3.84 to singlet at 3.86 was 6.0:1.0), 6.67 (AB quartet) and 6.95-7.60 (m). The reaction was stopped (photolysis time, 3 min) and the solvent was removed under vacuum. Addition of light petroleum to the residue gave 23 mg (0.067 mmole, 47%) of colourless crystals, m.p. 181-183°C, identical with an authentic sample of 2-(p-bromophenyl)-3-phenylindene (77). The mother liquor was treated with pyridine (2 ml) and dimethylamine (0.5 ml) as described in the preparation of 89 to give 26 mg (0.076 mmole) of crystalline material. The n.m.r. of these

crystals had peaks at 3.84 (s), 3.86 (s), 6.67 (AB quartet), and 6.95-7.60 (m). The n.m.r. integration showed the respective ratio of the singlets to the quartet to be 3.3:1.0 (therefore the crystals contained 0.018 mmole of starting material 67). The relative ratio of the area of the singlet at 3.84 to that at 3.86 was 2.4:1.0 (therefore an additional 0.041 mmole of 77 were present, combined total yield of 77, 0.108 mmole, 75.5%; the amount of 2-phenyl-3-(p-bromophenyl)-indene (83) was 0.017 mmole, 12%).

Irradiation of 2-(p-bromophenyl)-3-phenylindene (77)

A solution of 25 mg of 77 in 150 ml of hexane was irradiated for 10 min with the Hanovia Type L 450 W lamp. A 5 min aliquot showed, upon removal of solvent, an identical n.m.r. spectrum with that obtained for an authentic sample of 77.

Irradiation of 2-phenyl-3-(p-bromophenyl)-indene (83)

The procedure used above for indene 77 was repeated on 25 mg of 83. The n.m.r. spectrum was found to be unchanged upon photolysis.

Irradiation of 1-(p-cyanophenyl)-1-phenylindene (68)

A solution of 200 mg (0.68 mmole) of 1-(p-cyanophenyl)-1-phenylindene (68) in 400 ml of tert butanol was irradiated through quartz with the type L 450 W lamp setup described previously. Aliquots (12 mg, 0.04 mmole) were taken at various stages and analyzed by v.p.c. and n.m.r. All aliquots showed the following n.m.r. absorption: singlets at 3.88 and 4.95 (relative ratio 7.1:1.0 respectively), 6.76 (AB quartet, δ_A 6.69, δ_B 6.83, J_{AB} = 5.0 c.p.s.) and 7.00-7.60 (m). The v.p.c. (220°C) showed the starting material peak (retention time, 10.0 min) to decrease with time while the product peak (retention time, 18.0 min) increased. The 11 min aliquot indicated 75% reaction.

Upon evaporation of solvent (photolysis time, 11 min), 10 ml of 1:1 ether-light petroleum were added to the residual oil. This gave 116 mg (0.40 mmole, 59%) of crystalline material, m.p. 208-212°C. Recrystallization from ether gave 110 mg of material, m.p. 214-216°C, identical with synthetic 2-(p-cyanophenyl)-3-phenylindene (79). Treatment of the mother liquor with dimethylamine (0.5 ml) and pyridine (3.0 ml), as described in the procedure for the preparation of 89, gave 72 mg (0.24 mmole) of crystalline material whose n.m.r. displayed signals at 3.88 (s) and 6.76 (AB quartet) in the relative integration ratio of 1.0:3.5 (therefore the amount of 79 was 0.05 mmole, total combined yield of 79 was 0.45 mmole, 66%; the amount of 1-(p-cyanophenyl)-1-phenylindene (68) was 0.19 mmole). The v.p.c. (220°C) of this crystalline material showed the starting material peak (10.0 min), a small shoulder peak (17.0 min) and the product peak (18.0 min). The peak height ratio of shoulder to product peak was 1.0:7.0. Addition of authentic 2-phenyl-3-(p-cyanophenyl)-indene (85) to the crystalline material enhanced the size of the shoulder peak, while addition of 79 enlarged the product peak. The estimated (v.p.c.) amount of 85 present was 2 mg (1% of total reaction product).

Irradiation of 2-(p-cyanophenyl)-3-phenylindene (79)

A solution of 100 mg of 79 in 300 ml of tert butanol was irradiated for 1 hr and aliquots were taken at 20 min intervals. Upon evaporation of solvent, the n.m.r. of each aliquot was found to be identical with that obtained for a pure sample of 79. No singlet absorption in the 4.9-5.0 region was observed.

Irradiation of 2-phenyl-3-(p-cyanophenyl)-indene (85)

The procedure used above for compound 79 was repeated on 50 mg of 85

and n.m.r. indicated the presence of solely the indene 85.

Irradiation of 1-(p-methoxyphenyl)-1-phenylindene (69)

A solution of 99 mg (0.332 mmole) of 1-(p-methoxyphenyl)-1-phenylindene (69) in 200 ml of hexane was irradiated through quartz with a 150 W Hanovia lamp. The reaction was stopped at 10 min intervals; aliquots were withdrawn, analyzed by n.m.r., then returned to the reaction vessel and the photolysis continued. Each aliquot had n.m.r. signals at 3.69 (s), 3.78 (s), 3.81 (s), 4.80 (broad singlet) and 6.60-7.55 (complex multiplet). The integration ratio of the singlet at 3.81 to the singlet at 4.80 was a constant 6.9:1.0. The reaction was stopped (photolysis time, 37 min) and the solvent evaporated leaving crystalline material (99 mg). Addition of light petroleum gave 27 mg (0.091 mmole, 28%) of colorless crystals, m.p. 123-125°C, identical with an authentic sample of 2-(p-methoxyphenyl)-3-phenylindene (89). The filtrate was treated with pyridine (6 ml) and dimethylamine (1 ml), as outlined in the procedure for the synthesis of 89, and gave upon addition of light petroleum an additional 13 mg (0.044 mmole, 13%) of 89. The v.p.c. (200°C) of the residual oil (58 mg, 0.195 mmole) showed peaks at 5.0 min (due to 69, estimated 9% (0.030 mmole) of reaction mixture) and 11.0 min (a broad product peak). The n.m.r. of the residual oil showed peaks at 3.69 (s), 3.78 (s), 3.81 (s) and 6.63-7.55 (m). Analysis by n.m.r. and comparison with the n.m.r. calibration spectra for indenes 89 and 92 indicated the presence in the oil of a 10:1 ratio of 2-(p-methoxyphenyl)-3-phenylindene (89) to 2-phenyl-3-(p-methoxyphenyl)-indene (92), i.e., 0.150 mmole (45%) of 89 and 0.015 mmole (4.5%) of 92.

N.m.r. calibration of indenes 89 and 92

The n.m.r. spectra were recorded for a series of mixtures of 2-(p-

methoxyphenyl)-3-phenylindene (89) and 2-phenyl-3-(p-methoxyphenyl)-indene (92) in $CDCl_3$. The amounts of each substance in each tube was as follows:

Tube 1, 10 mg of 89, 20 mg of 92;

Tube 2, 10 mg of 89, 10 mg of 92;

Tube 3, 15 mg of 89, 5 mg of 92;

Tube 4, 20 mg of 89, 4 mg of 92.

Irradiation of 2-(p-methoxyphenyl)-3-phenylindene (89)

A solution of 100 mg of 89 in 200 ml of hexane was irradiated for 45 min and aliquots were withdrawn and analyzed by n.m.r. at 15 min intervals. The n.m.r. spectra were identical with that of a pure sample of 89.

Irradiation of 2-phenyl-3-(p-methoxyphenyl)-indene (92)

The procedure used above for indene 89 was repeated on 100 mg of 92 and n.m.r. spectra showed no change as the photolysis proceeded.

Sensitized Irradiations

The sensitized photolyses were performed using the same Hanovia type L 450 W lamp setup except that a pyrex sleeve was placed around the lamp.

Acetophenone sensitized irradiation of 1-(p-bromophenyl)-1-phenylindene (67)

A solution of 200 mg (0.575 mmole) of 1-(p-bromophenyl)-1-phenylindene (67) and 2.0 g (0.0147 mole) of acetophenone in 400 ml hexane was photolyzed for 18 min. Aliquots were withdrawn at 10 min. and at 18 min. The acetophenone and solvent were distilled and the aliquots were analyzed by n.m.r. Each aliquot showed peaks at 3.84 (s) and 3.86 (s) (constant ratio of 2.6:1.0 respectively), 4.87 (broad singlet), 6.67 (AB quartet) and 6.95-7.62 (m). The n.m.r. integration ratio for the two sharp singlets (at 3.84 and 3.86) to the

singlet at 4.87 was a constant 7.5:1.0. The reaction was stopped after 18 min and the solvent and acetophenone were removed by distillation under vacuum. Addition of light petroleum to the residue gave 33 mg (0.096 mmole, 17%) of crystals, m.p. 180-182°C, identical with authentic 2-(p-bromophenyl)-3-phenylindene (77). The filtrate was treated with pyridine (6.0 ml) and dimethylamine (1.0 ml) as described previously to give a light brown oil. Chromatography on a 11 x 2.5 cm column of alumina, slurry-packed in hexane and elution with hexane gave 160 mg (0.461 mmole) of crystalline material. The n.m.r. displayed peaks at 3.84 (s), 3.86 (s), 6.67 (AB quartet) and 6.95-7.60 (m). The following n.m.r. integration ratios were observed:

6.67 (AB quartet): 3.84 (s) and 3.86 (s) = 0.78:1.0;

3.84 (s):3.86 (s) = 1.6:1.0.

Analyses of these peak area integration ratios showed the presence of:

1-(p-bromophenyl)-1-phenylindene (67), 0.203 mmole, 35%;

2-(p-bromophenyl)-3-phenylindene (77), 0.159 mmole, total yield for 77 of 0.255 mmole, 44.5%; and

2-phenyl-3-(p-bromophenyl)-indene (83), 0.099 mmole, 17%.

Acetophenone sensitized irradiation of 1-(p-cyanophenyl)-1-phenylindene (68)

A solution of 200 mg (0.68 mmole) of 1-(p-cyanophenyl)-1-phenylindene (68) and 2.0 g (0.0147 mole) of acetophenone in 400 ml of tert butanol was photolyzed through pyrex for 30 min. Aliquots were withdrawn at 10 min intervals. Each aliquot showed the following n.m.r. data: 3.88 (s) and 4.95 (s), (relative ratio of 7.1:1.0 respectively), 6.76 (AB quartet, J_{AB} = 5.0 c.p.s.) and 7.05-7.62 (m). After distillation of solvent and acetophenone under vacuum, crystallization from light petroleum gave 116 mg of crystals, m.p. 213-215°C. This material (0.40 mmole, 59%) was identical to authentic 2-(p-cyanophenyl)-

3-phenylindene (79). The mother liquor was treated with dimethylamine (0.5 ml) and pyridine (3.0 ml) as described in the synthesis of 89. The mother liquor (82 mg, 0.28 mmole) showed the following n.m.r. data: 3.88 (s), 6.76 (AB quartet) and 6.95-7.62 (m). The following n.m.r. integration ratio was observed:

6.76 (AB quartet): 3.88 (s) = 2.8:1.0.

Analysis of this ratio indicated the presence of:

1-(p-cyanophenyl)-1-phenylindene (68), 0.20 mmole, 29%;

2-(p-cyanophenyl)-3-phenylindene (79), 0.07 mmole, total yield for 79 of 0.47 mmole, 69%.

The v.p.c. (220°C) of the mother liquor showed the following peaks at retention times of:

9.5 min, 68;

17.0 min, shoulder peak, assigned to 85;

18.0 min, 89.

The ratio of shoulder to main peak (18.0 min) was 1:8. Addition of 2-phenyl-3-(p-cyanophenyl)-indene (85) to the mother liquor enhanced the shoulder peak. The amount of 85 present was estimated to be 1% (v.p.c.).

Thermal Reactions

Thermolysis of 1-(p-bromophenyl)-1-phenylindene (67)

A solution of 42 mg of 67 in 2.5 ml of diphenyl ether was refluxed under nitrogen for 24 hr. The diphenyl ether was removed by vacuum distillation leaving a crystalline residue (42 mg) which showed the following n.m.r. absorption: singlets at 3.84 and 3.86 (relative ratio of 1.08:1.00) and a multiplet at 7.00-7.60. An n.m.r. calibration plot (see below), using the singlet signals

of the methylene protons at 3.84 and 3.86, indicated the presence in the reaction mixture of 55% of 2-(p-bromophenyl)-3-phenylindene (77) and 45% of 2-phenyl-3-(p-bromophenyl)-indene (83). The v.p.c. (200°C) showed a broad peak (retention time, 11 min) and t.l.c. hexane showed only one spot. Addition of light petroleum-ether to the crystals yielded 17 mg (40%) of 2-(p-bromophenyl)-3-phenylindene (77), m.p. 181-183°C. The mother liquor (25 mg) contained, by comparison with the calibration plot, an additional 5 mg of 77 (total yield of 77, 22 mg (52%)) and 20 mg (48%) of indene 83.

N.m.r. calibration of indenes 77 and 83

Known amounts (10, 15 and 20 mg) of the bromoindene 77 were added consecutively to n.m.r. tubes containing 20, 8 and 10 mg respectively of the bromoindene 83 in $CDCl_3$. A calibration plot was made of the known weight ratios of the substituents versus the actual peak area ratios observed for the methylene singlets at 3.84 and 3.86.

Thermolysis of 1-(p-cyanophenyl)-1-phenylindene (68)

A solution of 68 (75 mg) in 2.5 ml of diphenyl ether was refluxed under nitrogen for 24 hr. Upon removal of the diphenyl ether by vacuum distillation, the n.m.r. of the crystalline residue (74 mg) displayed singlets at 3.88 and 3.90 (relative peak height ratio of 3:1 respectively) and a complex multiplet at 6.95-7.60. An n.m.r. calibration plot (see below) indicated the presence in the residue of 83% of 2-(p-cyanophenyl)-3-phenylindene (79) and 17% of 2-phenyl-3-(p-cyanophenyl)-indene (85). Addition of 10 ml of light petroleum gave 52 mg (69%) of 79, m.p. 212-215°C. The mother liquor (22 mg) showed n.m.r. absorption at 3.88 (s) and 3.90 (s) (relative ratio of 2.0:3.0 respectively) and at 6.90-7.60 (m). Comparison with the calibration plot

showed the presence of 14 mg (19%) of 2-phenyl-3-(p-cyanophenyl)-indene (85) and 9 mg (total 61 mg, 81%) of 2-(p-cyanophenyl)-3-phenylindene (79).

N.m.r. calibration of indenes 79 and 85

As described previously for compounds 77 and 83, a calibration plot was made of known weight ratios of 79 and 85, versus the observed peak height ratios of the methylene singlets at 3.88 and 3.90. The mixtures were: 20 mg 79, 20 mg 85; 14 mg 79, 20 mg 85.

Thermolysis of 1-(p-methoxyphenyl)-1-phenylindene (69)

A solution of 54 mg of 69 in 2.0 ml of diphenyl ether was refluxed for 10 hr under nitrogen. After distillation of solvent, the v.p.c. (210°C) showed a broad peak (retention time, 9.0 min). The n.m.r. of the residual crystals (54 mg) showed absorption at 3.69 (s), 3.78 (s), 3.81 (s) and 6.60-7.55 (complex multiplet). Comparison with the n.m.r. calibration plot (see below) of indenes 89 and 92 indicated the presence of 47% of 89 and 53% of 92. Addition of light petroleum gave 18 mg (33%) of 2-(p-methoxyphenyl)-3-phenylindene (89), m.p. 121-124°C. The mother liquor (34 mg), by comparison with the n.m.r. calibration data, was found to contain additional 89 (8 mg, combined yield 26 mg, 48%) as well as 2-phenyl-3-(p-methoxyphenyl)-indene (92) (26 mg, 48%).

N.m.r. calibration of indenes 89 and 92

The calibration plot used in the direct irradiation case was utilized here.

Thermolyses of indenes 77, 79, 83, 85, 89 and 92

A solution of 25 mg each of the indenes 77, 79, 83, 85, 89 and 92 was

refluxed in 2.0 ml of diphenyl ether under nitrogen for 24 hr. Upon vacuum distillation of the diphenyl ether, the n.m.r. spectrum of each residue was shown to be identical with that of the starting indene.

Quantum Yields

Quantum yield determination on the formation of 2,3-diphenylindene

The Philips SP 500 W mercury arc lamp was used at the focus (12 cm) of a convex lens 11 cm in diameter. The filter solutions for the direct photolysis were contained in a three compartment cell. Each compartment was 11.7 cm in diameter with a 5 cm path length and each had an internal cooling coil. Compartment partitions and ends were neoprene gasketed quartz disks.

The filter solutions used were: compartment one (nearest lamp), 276 g of nickelous sulfate hexahydrate per litre of distilled water; compartment two, 215 g of cobalt sulfate heptahydrate per litre of distilled water; cell three, 0.050 g of potassium iodide and 0.022 g of iodine dissolved in one litre of distilled water. A separate cell containing chlorine gas at 1 atm was used behind the third cell. This cell had a diameter of 11.5 cm and a path length of 1.0 cm. These filter solutions provided a small symmetrical transmission band from 245 to 270 mμ with 3% transmission at 258 mμ and 0% at 245 and 270 mμ.

A 4 hr pre-irradiation of the nickel sulfate and cobalt sulfate solutions raised the transmittance to a value which was constant with continued irradiation.

For quantum yield measurements, a cell with quartz windows 11.7 cm in diameter by 5.0 cm path length, sealed with "viton" gaskets, contained the solution of 1,1-diphenyl indene in ethanol. Behind this, an identical cell containing a 0.006 M potassium ferrioxalate (actinometer solution) was used to

measure the light not absorbed by the organic solution.

Each quantum yield determination required three irradiations: the first with solely the actinometer present, the second with both organic solution and actinometer, and the third was a repeat of the first. When only the actinometer was present, it was placed in the position occupied by the organic solution in the second irradiation. The light output during the second irradiation was calculated by using the values obtained from the first and third irradiations, values which differed by less than 5%, and by correcting for the change in the transmitted light during the second irradiation. The quantum efficiency of conversion of ferrioxalate was assumed to be 1.25 at the wavelengths used in the direct photolysis. All cells were cooled with water maintained at 9±1°C and a fresh actinometer solution was used for each irradiation.

Duplicate quantum yields were measured on 1,1-diphenylindene. A typical run involved the photolysis of 100 mg (3.73×10^{-4} mole) of indene in 575 ml of ethanol. The solution was purged with argon prior to and during the photolysis. Both actinometer and photolysis solutions were stirred mechanically. Irradiation for 9.0 hr led to the absorption by the indene of 1.28×10^{-4} Einsteins of light. Analysis by v.p.c., using stock p-terphenyl solutions as internal standard and correcting for light absorbed by product at one-half reaction, showed the formation of 23.6 mg (8.80×10^{-5} mole) of 2,3-diphenylindene giving a value of 0.80 for the quantum yield of product formation. A duplicate run gave a value of 0.84. Table 5 of the Results Section gives the pertinent data for the quantum yields.

Quantum yield determination on sensitized formation of 2,3-diphenylindene

The acetophenone sensitized photolysis was performed in an analogous

manner except that the filter system was as follows: compartment one (nearest lamp), 1.5 g of stannous chloride dihydrate per litre of 15% hydrochloric acid; compartment two, 150 g of cobalt sulfate heptahydrate and 12 g of nickelous sulfate hexahydrate per litre of 0.1 N H_2SO_4; compartment three, distilled water. This combination of filter solutions had maximum transmission of 77% at 340 mμ and 0% at 310 and 390 mμ. The stannous chloride solution was freshly prepared for each quantum yield determination. The solution cell contained 780 mg (2.91×10^{-3} mole) of indene and 3.0 g (0.025 mole) of acetophenone in a solution of 530 ml of tert-butanol and 45 ml of methanol. The quantum efficiency of conversion of ferrioxalate was taken as 1.23. Duplicate quantum yields were measured by the v.p.c. method (using p-terphenyl as internal standard) and the data obtained are listed in Table 6 of the Results Section.

Spectra and Quenching Experiments

Ultraviolet and fluorescence spectra

All ultraviolet spectra were taken in hexane as solvent and the relevant data are recorded in Table 7. Fluorescence spectra were also taken in hexane at room temperature and in a matrix of spectral cyclohexane at 77°K. The pertinent data from these spectra are shown in Table 7 of the Results Section.

Quenching of 1,1-dimethylindene fluorescence by biacetyl

The fluorescence of 1,1-dimethylindene, 1.00×10^{-3} M, in hexane, (excitation 279 mμ) was monitored at 330 mμ. Various concentrations of biacetyl were used to quench the fluorescence. These figures are listed in Table 8 and the resultant graph is shown in Figure 11 of the Results Section.

Quenching of the formation of 2,3-diphenylindene by acrylonitrile

Relative quantum yields of 2,3-diphenylindene formation were measured using the Rayonet Reactor and the accompanying Merry-Go-Round (turn-table) apparatus in which six 13 x 2.0 cm quartz tubes were rotated during photolysis. Solutions (20 ml) were contained in each tube, such that each solution was 0.0025 M in 1,1-diphenylindene, and different concentrations (0.15, 0.25, 0.35, 0.50 and 0.65 M) in acrylonitrile. One tube contained only the indene solution with no acrylonitrile. The solutions were deoxygenated by bubbling nitrogen through them for 10 min and the tubes were then capped. The time of irradiation was chosen so as to give a range of conversion between 5 and 20%. The amount of photoproduct (2,3-diphenylindene) in each tube was determined by v.p.c., using p-terphenyl as the internal standard. It was assumed that the light absorbed in each tube was the same since all tubes were of similar dimensions and contained the same volume of solution and also because the concentration of 1,1-diphenylindene was the same in each tube. Corrections were made in each case for the amount of light being absorbed by product at one-half reaction.

The absolute quantum yields could be determined using the known value of 0.82 obtained for the direct photolysis of 1,1-diphenylindene (see Table 5). The results obtained are shown in Table 10 and Figure 13 of the Results Section.

Phosphorescence spectra

All phosphorescence spectra were measured in ethanol-ether (1:1) at 77°K. The solvents were redistilled 95% ethanol and ether (analytical reagent). Critical data from these spectra are shown in Table 7.

Sensitization of biacetyl phosphorescence by 1,1-dimethylindene

1,1-Dimethylindene, 1.09 x 10^{-3} M in hexane, was used to sensitize the phosphorescence of a series of biacetyl solutions 1.05, 1.25, 1.66, 2.00, 3.00 and 5.00 x 10^{-3} M in hexane. Prior to each reading, 6-10 cycles of the freeze, pump and thaw method were administered to 1.0 ml of each solution contained in a small quartz tube of dimensions 6 x 1.0 cm. The excitation wavelength of the 1,1-dimethylindene was 279 mμ and the phosphorescence of the biacetyl was monitored at 524 mμ. The spectrophotofluorometer was standardized after each run with a solution of 50 mg of fluorescein in 100 ml of 0.1 N sodium hydroxide to ensure drift-free readings. All readings were recorded at room temperature and the results are listed in Table 9 and Figure 12 of the Results Section.

DISCUSSION

A unimolecular photochemical rearrangement may be represented by the following steps:

(a) the absorption of light by the molecule with resulting excitation to excited singlet state from the ground state;

(b) excited state reactions;

(c) possible ground state reactions, leading finally to products.

To fully understand the mechanism of the 1,1-diphenylindene rearrangement to 2,3-diphenylindene requires the understanding of these steps. The data present in this thesis enable the postulation of a mechanism for the photochemical rearrangement studied.

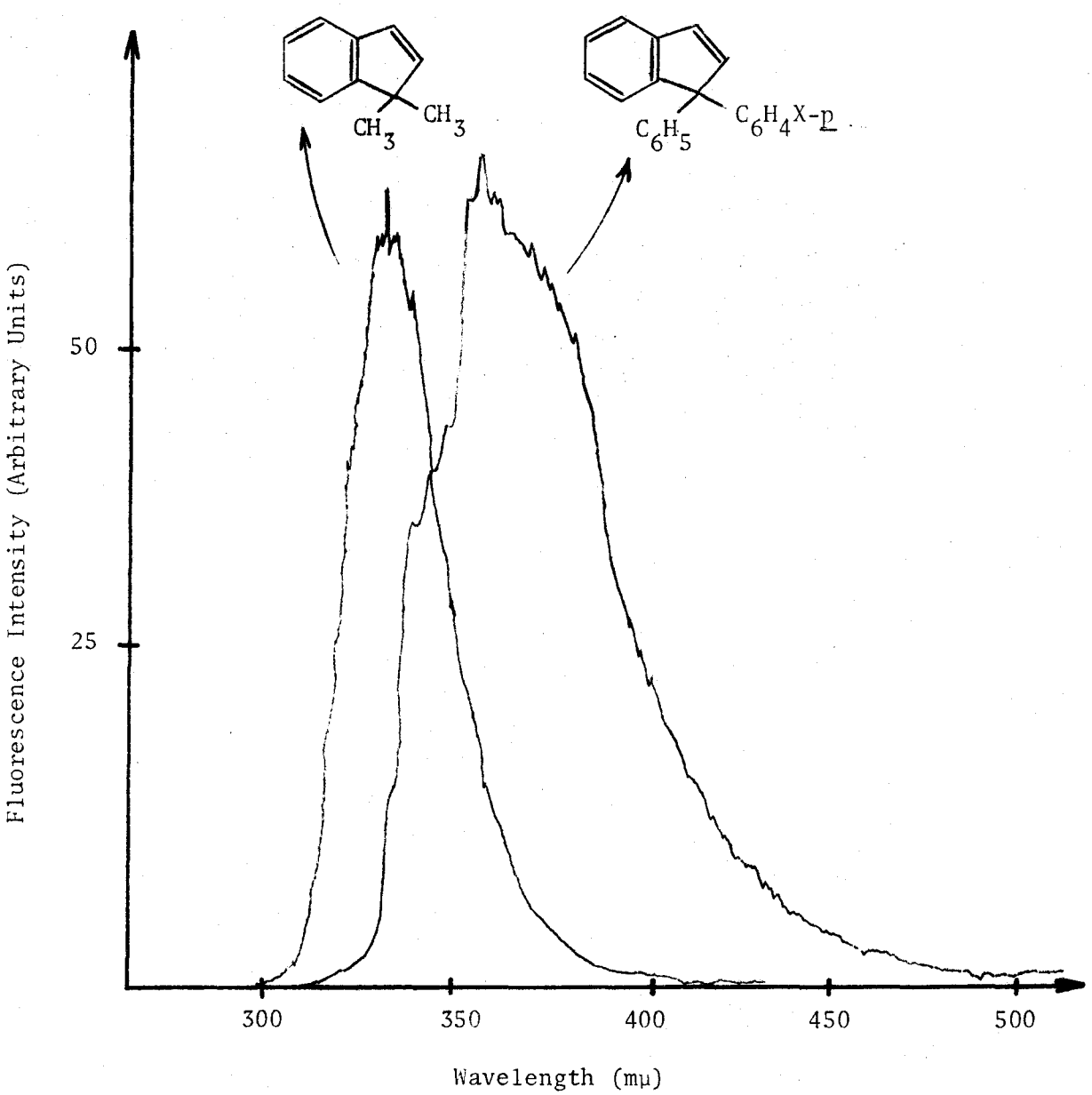
PART I: Excitation Processes

In Table 7 of the Results Section, it was seen that 1,1-dimethylindene (64), 1,1-diphenylindene (37), 1-(p-bromophenyl)-1-phenylindene (67), 1-(p-cyanophenyl)-1-phenylindene (68) and 1-(p-methoxyphenyl)-1-phenylindene (69) had π-π^*, long wavelength absorption bands, at approximately λ_{max} = 260 mμ. Each compound also showed a long wavelength shoulder peak at 293-298 mμ. Thus, in all cases where direct irradiation conditions were employed, the indenes were excited to their lowest π-π^* singlet states (S_1).

The fluorescence emissions of 1,1-dimethylindene and the four 1,1-diarylindenes were easily detectable at room temperature. However, the emission spectra were virtually structureless. The onset (short wavelength) of fluorescence was at 306 mμ for 1,1-dimethylindene and at 330-335 mμ for the four diarylindenes (see Figure 14). This slight difference may be accounted for when we consider that Robertson[44] detected a slight increase in wavelength for the 0 $\rightarrow$ 0 band with increasing molecular weight of substituent in a series of alkyl benzenes. Thus, in progressing from the 1,1-dimethyl- to the 1,1-

Figure 14. Fluorescence Spectrum of 1,1-dimethylindene and 1-(p-Xphenyl)-1-phenylindenes (X = H, Br, CN, OCH_3) in Hexane at 20°C.

$\lambda_{excitation}$, 285 mμ



diphenyl-system (a difference of 124 amu) a corresponding shift in the 0 → 0 band for emission might be expected. Recording each spectrum in a cyclohexane matrix at 77°K, however, shifted each fluorescence curve to lower wavelength such that the emission from each compound began at 290 mμ. Comparison of these latter fluorescence spectra with the ultraviolet absorption showed that the spectra overlapped.

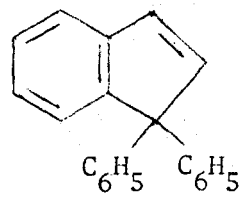
The point of intersection of the spectra for each indene occurred at or near the long wavelength shoulder peak found in the ultraviolet spectrum for each of the indenes. This point of intersection was designated as the 0 → 0 band, and was used in obtaining $\Delta E_{0,0}$ for the S_1 state. The absorption and fluorescence spectra for 1,1-diphenylindene are compared in Figure 15.

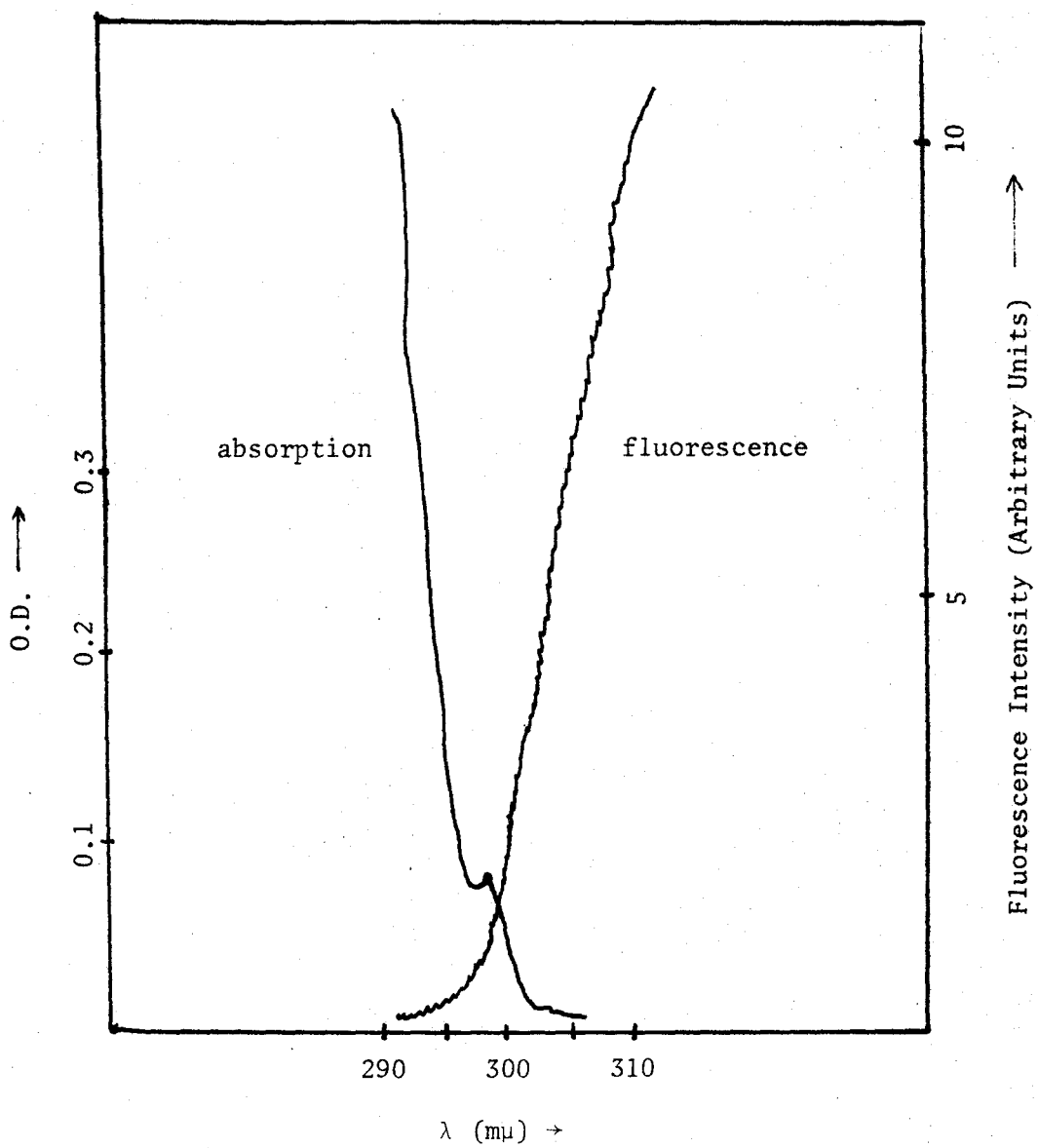
In gases the 0 → 0 transition in absorption and fluorescence spectra is the common band. In solution, however, relaxation effects are important. Lippert et al.[45] have shown that the separation between absorption and fluorescence band maxima is small at low temperatures because molecular movements are frozen; and the same is true at high temperatures because of violent motions. At intermediate temperatures, however, the 0 → 0 band separation may be significant because the excited molecule can relax into a new environment before radiating.

The fact that each of the four diarylindenes has virtually the same 0 → 0 band (297 mμ) and hence the same singlet energy (96.2 kcal/mole) (see Table 7 of the Results Section) means that in the irradiation, the excited state (S_1) of each indene has the excitation localized in the styrene group.

Likewise, in the phosphorescence spectra (77°K) of the three substituted diarylindenes (67, 68 and 69) the position of the 0 → 0 band, which establishes the $T_1 \rightarrow S_0$ energy difference, was at 465 mμ in all three cases

Figure 15. Fluorescence (77°K) and Absorption Spectra of 1,1-Diphenylindene





(Table 7, Results Section). This compared with a value of 454 mμ for the parent 1,1-diphenylindene molecule. The triplet state energies (E_T) were 61.5 kcal/mole for indenes 67, 68 and 69, and 63.0 kcal/mole for 1,1-diphenylindene. The introduction of substituents onto the phenyl ring therefore resulted in only a very minor change in the triplet state nature of each indene.

It therefore follows that, in the sensitized irradiations using acetophenone (E_T = 73.6 kcal/mole), the large difference (>10 kcal/mole) in triplet state energies of each indene and acetophenone guarantees that triplet energy transfer from the acetophenone to the indene is occurring at a diffusion-controlled rate. The reaction in this case must certainly involve the indene triplet state (T_1). Also, the excited triplet state electron distribution of the substituted 1,1-diphenylindenes (67, 68 and 69), should be similar to that of 1,1-diphenylindene (37) since the excitation should be heavily localized in the indene moiety, as in the singlet S_1 cases, whose triplet energy of 63.0 kcal/mole is low relative to benzonitrile, anisole or bromobenzene. In fact, Lewis and Kasha[46] reported that benzonitrile had a triplet energy of 77 kcal/mole and phenol, a reasonable model for anisole, had E_T equal to 82 kcal/mole. The triplet energy for bromobenzene is 82.6 kcal/mole[47].

PART II: Quantum Yields and Reaction Rates

Since both the direct and sensitized photolyses of 1,1-diphenylindene (37) gave the same ratio of 2,3-diphenylindene (36) to 1,2-diphenylindene (66),[34] it was decided to determine if the same excited state was involved in each case. It was found (Results Section, Tables 5 and 6) that the direct irradiation (ϕ = 0.82 mole/einstein) was much more efficient than the acetophenone sensitized reaction (ϕ = 0.06 mole/einstein). However, since triplet energy-transfer from

sensitizer should be occurring at a diffusion controlled rate in the sensitized rearrangement, the generation of the indene triplet state (T_1) should occur with unit quantum yield. Therefore, the triplet inefficiency must arise in the processes which the T_1 state undergoes. It also follows that the direct reaction must be proceeding via the excited singlet state (S_1) and not by T_1.

Quenching of 1,1-dimethylindene fluorescence by biacetyl was found to obey Stern-Volmer kinetics (Figure 11, Results Section) in accord with the following equation:

$$I_o/I = \phi_o/\phi = 1 + k_q \cdot \tau \cdot [BA] \quad (48)$$

where I_o/I and ϕ_o/ϕ are the relative fluorescence intensities and relative fluorescence quantum yields in the absence and presence respectively of biacetyl ([BA]). The term k_q is the rate constant (units of $\ell.mole^{-1}sec^{-1}$) for bimolecular quenching of the indene fluorescence by biacetyl, and τ is the fluorescence lifetime (sec) in the absence of biacetyl. Using the value of 91.5 M^{-1} obtained for the slope and assuming k_q, the diffusion-controlled rate constant (calculated from Debye's equation[49]), to be 2.2×10^{10} $\ell.mole^{-1}sec^{-1}$, a lifetime for the singlet excited state of 1,1-dimethylindene was derived ($\tau_{I_n S} = 4.1 \times 10^{-9}$ sec).

The assumption above that the biacetyl quenching of 1,1-dimethylindene fluorescence is diffusion-controlled has a parallel in that Dubois and Wilkinson[50] found diffusion-controlled quenching of naphthalene, benzene and toluene fluorescence by biacetyl.

It was also found that the quenching of 1,1-dimethylindene fluorescence by acrylonitrile obeyed Stern-Volmer kinetics[51]. A slope ($k_q \cdot \tau$) of 18.9 M^{-1} was obtained. Substituting for τ, the value of 4.1×10^{-9} sec, gave a value for k_q of 4.6×10^9 $\ell.mole^{-1}sec^{-1}$. It is assumed that k_q for 1,1-dimethylindene and 1,1-diphenylindene are the same, and this rate constant was used to determine

the rate of rearrangement of the S_1 state of 1,1-diphenylindene.

A Stern-Volmer plot of reciprocal quantum yield ($1/\phi$) for 2,3-diphenylindene formation versus acrylonitrile concentration ([Q]) was linear over the concentration range employed (Figure 13, Results Section). A rate constant (k_r) for rearrangement of S_1 was calculated to be 4.9×10^9 sec^{-1}, using the usual steady state assumptions (see Appendix 1) and the resulting equation (3),

$$1/\phi^{Product} = 1 + (k_d+k_f)/k_r + k_q/k_r([Q]) \qquad (3)$$

where k_d is the rate constant encompassing non-radiative processes, k_f is the rate constant for fluorescence and k_q is the quenching rate constant. The intercept ($1 + (k_d+k_f)/k_r$) was equal to 1.22, and k_d+k_f for S_1, as obtained from this plot, was 1.0×10^9 sec^{-1}.

An estimation of the triplet lifetime ($\tau_{I_n}T$) of 1,1-dimethylindene was obtained by the sensitization of biacetyl (BA) phosphorescence with 1,1-dimethylindene (Table 9 and Figure 12 of Results Section). The steady-state treatment, as employed by Dubois and Wilkinson[52], (see Appendix 2) gave the following equation (4).

$$1/P_{BA}T = x \times k_t \times \tau_{I_n}T + x \times [BA]^{-1} \qquad (4)$$

$P_{BA}T$ are the phosphorescence readings recorded for the biacetyl, x represents a series of terms containing lifetimes and rate constants, k_t is the rate constant for quenching of $I_n{}^T$ by BA. The plot of $P_{BA}T^{-1}$ vs $[BA]^{-1}$ was linear with slope equal to 4.46×10^{-5} M and intercept of 0.018.

A number of studies of triplet-energy transfer[53,54] have been made which show that when the triplet level of the donor is at least 1000 cm^{-1} above that of the acceptor, triplet-energy transfer occurs with a rate constant very close to that predicted from Debye's equation for a diffusion-controlled reaction.

Thus as the energy gap between the excited state triplet of 1,1-dimethylindene (E_T = 63.0 kcal/mole) and the triplet state of biacetyl (E_T = 54.9 kcal/mole) is 8.1 kcal/mole[55] or 2800 cm^{-1}, then the value for k_q may be taken as diffusion-controlled, or 2.2 x 10^{10} $\ell.mole^{-1}sec^{-1}$. This gives a value for $\tau_{I_n}T$ of 1.8 x 10^{-6} sec, for 1,1-dimethylindene.

A rate constant ($k_r^{T_1}$) for rearrangement of T_1 of 1,1-diphenylindene was calculated with the aid of equation (5),

$$\phi_{T_1} = \frac{k_r^{T_1}}{k_D + k_r^{T_1}} \qquad (5)$$

where ϕ_{T_1} represented the quantum yield (0.062) for rearrangement of T_1 of 1,1-diphenylindene and k_D represented the rate constants for the radiative and non-radiative processes of T_1 of 1,1-diphenylindene. The value used for k_D was 5.5 x 10^5 sec^{-1} ($1/\tau_{I_n}T$). The rate constant $k_r^{T_1}$ was calculated to be 3.6 x 10^4 sec^{-1}.

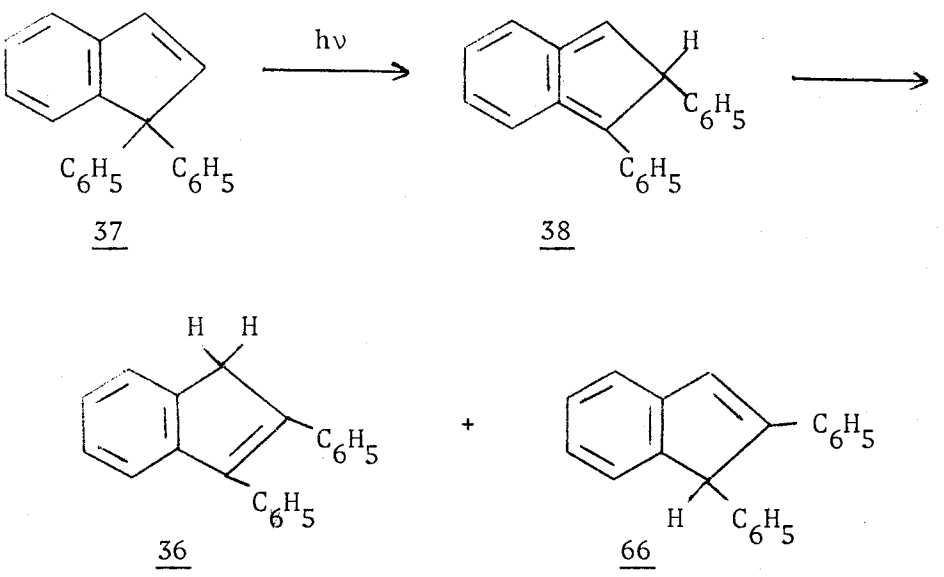
The value for $k_r^{T_1}$ was an approximation since k_D for T_1 of 1,1-diphenylindene was assumed to be the same as k_D (measured) for 1,1-dimethylindene triplet. Arriving at a more accurate value for $k_r^{T_1}$ would have necessitated doing simultaneous quenching and sensitization work, and would be a far more complicated process.

PART III: Migratory Aptitudes and the Transition State Polarities

A. Photo Migrations

In a study of the photochemical rearrangement of 1,1-diphenylindene (37)[34], a ground state isoindene intermediate was postulated, which underwent hydrogen migration to form either 36 or 66.

The initial step, that involving an excited state phenyl migration,



37 38 36 66

was probed in the present work, by irradiating 1-(p-cyanophenyl)-1-phenylindene (68). The fact that almost exclusive p-cyanophenyl migration was observed (Results Section, Table 4) suggested that the migrating phenyl carried a great deal of negative charge. Thus, the transition state for p-cyanophenyl migration was initially thought to involve the presence of a species wherein resonance stabilization of a net negative charge on the migrating phenyl was enhanced by the cyano-substituent. However, direct irradiation of 1-(p-methoxyphenyl)-1-phenylindene (69) (Results Section, Table 4), showed a 95% preference for the product arising from p-methoxyphenyl migration. Also, the irradiation of 1-(p-bromophenyl)-1-phenylindene (67) gave a predominance of the product of p-bromophenyl migration (86%). Thus it seemed that introduction of a substituent, regardless of whether the substituent had a positive or negative σ_p value*,

*This parameter (σ_p) is a characteristic of the para-substituent and represents the ability of the group to attract or repel electrons[56]. A positive δ_p value for a substituent indicates that the substituent is a stronger electron attractor than hydrogen. σ_p for the -CN group is +0.63, +0.23 for -Br and -0.27 for $-OCH_3$. Thus a p-methoxy group is a better donor of electrons than hydrogen which is better than either -Br or -CN substituents.

enhanced the rate of migration of the phenyl ring bearing that substituent.

Similar results were observed in the acetophenone sensitized irradiations (Table 4, Results Section) where a marked preference was observed for the products of p-bromo- and p-cyanophenyl migration.

B. Thermal Migrations

The results of the thermal reactions (Table 4, Results Section) were significantly different from the photochemical reactions. Heating the 1-(p-cyanophenyl)phenylindene (68) gave 18% of the product of phenyl migration 85, while heating the p-bromoindene 67 and the p-methoxyindene 69 gave virtually an equal distribution, in each case, of the possible migration products.

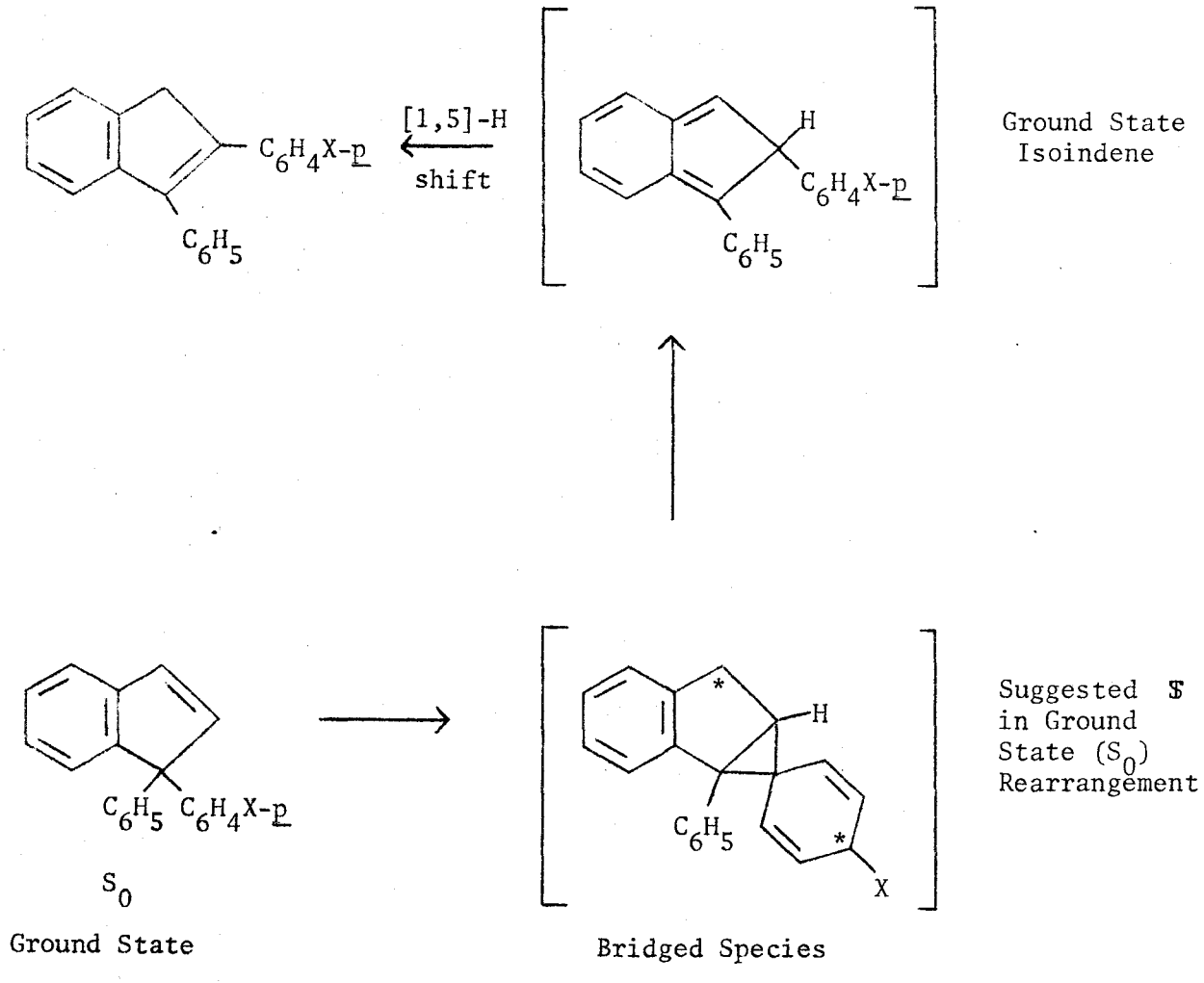
Since the ground state rearrangements of indenes are thought to involve an isoindene intermediate flanked by two [1,5] sigmatropic shifts[19-25], it was hoped by introduction of a substituted phenyl to gain some knowledge of the initial [1,5] sigmatropic shift, i.e., the phenyl migration step.

As mentioned previously, the rate constant for rearrangement of the excited state (S_1) of 1,1-diphenylindene was found to be 4.9×10^{9} sec^{-1} at 20°. The rate constant for rearrangement in the corresponding ground state process was measured by Miller[24,25] and the value was 2×10^{-4} sec^{-1} at 280°. Since the rate constants differ by such a large amount ($\sim 10^{13}$ sec^{-1}), it is assumed that the transition states for migration are quite different from each other. The suggested transition state for the thermal reaction is outlined in Scheme 15; both the isoindene intermediate and the ground state hydrogen shift were discussed in the Introduction.

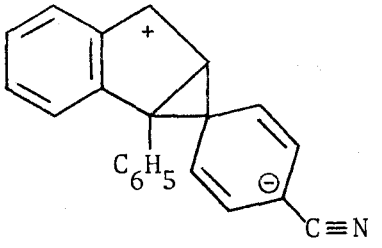
In the ground state case, the bridged species 94 is postulated as a possible transition state species. Each asterisk denotes either a positive or negative charge, or radical center on the bridging phenyl. For example:

SCHEME 15.

Suggested Transition State Involved in Ground State Rearrangements of 1-(p-Xphenyl)-1-phenylindene

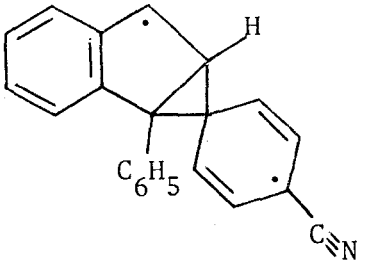


regarding the thermolysis of the p-cyanoindene 68 wherein 82% of the product resulted from p-cyanophenyl migration, the transition state could be envisaged as follows. A full negative charge resides on the p-cyanophenyl ring and such



$

charge can easily be accommodated by the cyano substituent. However, one would predict that if such were the case, substituting p-methoxy for p-cyano would necessitate the preferred migration of phenyl over p-methoxyphenyl. Instead, a 50:50 ratio of the products of phenyl and p-methoxyphenyl migration is observed upon thermolysis of the p-methoxyindene 69. In the case of the p-bromoindene 67, if the migrating group were to carry a negative charge, then p-bromophenyl would best be expected to accommodate this charge (since δ_p for -Br is equal to +0.23). However, again virtually equal amounts of products of p-bromophenyl and phenyl migration are observed. Thus, a more plausible explanation would be one where each asterisk represents an electron as in the proposed structure 94.



94

It was found for certain ground state free radical rearrangements[15] (Introduction, Part III, No. 3), that electron withdrawing substituents, such as -CN, were able to accommodate an additional electron and thus stabilize the transition state for migration. With p-Br as substituent, the stabilization was only slightly better than with -H, while p-CN stabilized the transition state such that the rate increased ten-fold over that for p-Br; p-methoxy as substituent was found to be slightly worse at stabilizing a radical center than hydrogen in this situation, but slightly better in another case[57].

Thus, the results observed for the 1,1-diphenylindene system would seem to fit in with such a scheme, wherein a diradical species (94) is generated following thermolysis of starting material (S_0). Any charge transfer that could occur in the ground state molecules (room temperature) is also ruled out by the fact that all the indenes had identical u.v. spectra and ought not to if the charge localization varies from indene to indene. There could, however, be some charge transfer occurring in the transition state.

PART IV: Charge Transfer in Excited State

The term charge transfer complex was first used by Mulliken[58] to describe a certain type of complex with distinctive features. For a long time it had been known that mixtures of certain molecules could form highly colored mixtures or solutions, although the colored mixture seemed not to be a new chemical substance, but possessed the chemical properties of the components.

According to Mulliken, this phenomenon arose from the formation of weak complexes between two molecules, if one was an electron acceptor and the other an electron donor. The interaction between the two states could be present in either the ground state or excited state. In the ground state a small amount of charge is transferred from the donor to the acceptor which contributes some

additional binding energy to the complex. In the excited state complex, the extent of charge transfer is very much greater than in the ground state.

Two broad classes of donors may be considered. In the first class, the donor has a π-electron system which donates electrons. The second class of donors is that in which the donated electrons are from a non-bonding, or lone pair. Acceptors may be classified as π-acceptors, in which the donated electrons go into a π-orbital of the acceptor, or as δ-acceptors. We will discuss the π-electron systems only. Thus, the 1-aryl groups in 1,1-diphenylindenes might, a priori, be considered as either electron donors or electron acceptors with respect to the indene system.

The donor and acceptor properties of molecules are, of course, modified by chemical substitution. Substituents fall into two classes: those which are electron donating and increase the donor properties, and those which do the reverse. Alkyl substitution increases the donor ability of a benzene ring due to a flow of charge from the alkyl group to the rest of the molecule. Another strong electron donating group is methoxy. A strong electron withdrawing group such as nitro or cyano renders a benzene derivative a good acceptor. A decrease in the ionization potential would be predicted for a series of monosubstituted benzenes wherein the donor ability of the molecule increases with each change in substituent. Similarly the ionization potential increases if the hydrogen of benzene is replaced by an electron withdrawing substituent. This trend was reported by Sykes (Table 11)[59]. Thus, the ease of ionizing a series of monosubstituted benzenes varies directly with the electron donating ability of the substituent.

Schulte-Frohlinde[60,61] postulated charge transfer processes in the intermolecular fluorescence quenching of substituted naphthalene derivatives

Table 11

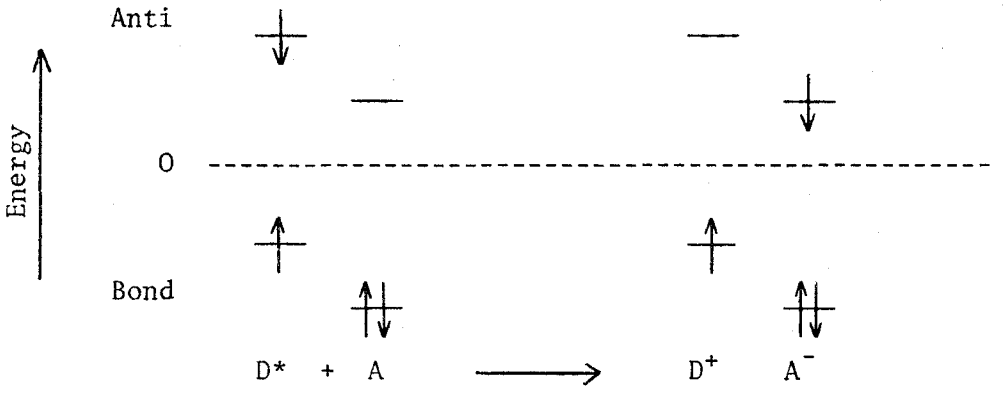
Ionization potentials of some substituted benzenes

Group R (C_6H_5-R)	Ionization Potential (eV)
OH	8.5
OCH_3	8.2
H	9.2
NO_2	9.9

by suitable quenchers. Weller[62] correlated quenching rates with singlet excitation energies, and oxidation and reduction potentials of donors (D) and acceptors (A) in the reaction

$$D^* + A \longrightarrow \text{quenching via exciplex.}$$

The following molecular orbital scheme was envisaged.



It was based on the concept that, in the complex an electron has been transferred from the donor to the acceptor. The energy of the highest bonding orbital in either molecule is associated with the ionization potential and the energy of the lowest antibonding orbital with the electron affinity. Thus, the molecule with the lower ionization potential always acts as donor and the one with the

higher electron affinity acts as acceptor. Table 12 gives some relevant electrochemical data. The oxidation and reduction potentials (in volts) are given respectively by $E(D/D^+)$ and $E(A^-/A)$.

The free energy (ΔG) released from the electron-transfer reaction can be calculated from the redox potentials of the A^-/A and D/D^+ couples (measured in acetonitrile)[67-70]. The pertinent equation [6] is

$$\Delta G = -E_{0,0} + [E(D/D^+) - E(A^-/A)] \qquad [6]$$

where $E_{0,0}$ is the energy of the excited species and it is assumed that ΔG is determined only by the enthalpy. For example, substituting the values from Table 12 for a complete electron transfer process that might occur from the excited indene portion to the benzonitrile group, gives the following.

$$\Delta G = -96.2 \text{ kcal/mole} + [(1.68)(23.06) - (-2.45)(23.06)] \text{ kcal/mole}$$
$$= -1.2 \text{ kcal/mole}$$

Since the sign of ΔG is negative, then the charge transfer process will occur spontaneously. A similar calculation can be done for the charge transfer process predicted to occur in the excited state of the 1-(p-methoxyphenyl)-1-phenylindene (69). The direction of these charge transfer processes are indicated below and the free energy values are listed in Table 13. Hence each charge transfer process should be spontaneous in the direction indicated.

Organic bromides are known to under[60] carbon-halogen bond fission under normal polarographic reduction conditions[64].

If phenyl were to migrate preferentially for the indenes 67, 68 and 69, and if charge transfer occurred from the phenyl group to the styrene portion, the free energy for such a process would be equal to

Table 12

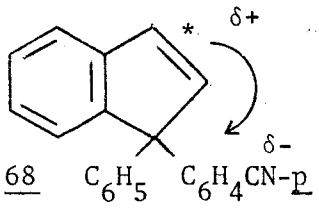
Oxidation and Reduction Potentials

Compound	$E(D/D^+)$ volts	$E(A^-/A)$ volts
1,1-dimethylindene	+1.68[63]	-2.45†[64]
p-methylanisole[ξ]	+1.61	-
p-tolunitrile	-	-2.75*[64,66]

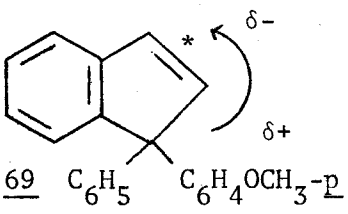
†Value for styrene.

ξEstimated value; average for substituent effect of methyl upon benzene, naphthalene and bromobenzene was added to value for anisole (1.76 volts)[64,65].

*Reference electrode is silver (all other values have a saturated calomel electrode as reference). Adding +0.30 volts to silver electrode data gives corresponding calomel data[64].



68 C_6H_5 C_6H_4CN-p



69 C_6H_5 $C_6H_4OCH_3$-p

Table 13

ΔG (Calculated) for Intramolecular Excited State Charge Transfer

Compound	ΔG (kcal/mole)
1-(p-bromophenyl)-1-phenylindene, 67	——*
1-(p-cyanophenyl)-1-phenylindene, 68	-1.2
1-(p-methoxyphenyl)-1-phenylindene, 69	-2.7

*No value was calculated for indene 67 as the reduction potential of p-bromotoluene is not known.

$$\Delta G = -E_{0,0} + [E(D/D^{+}) - E(A^{-}/A)]$$

$$= -96.2 \text{ kcal/mole} + [(2.2)^{a}(23.06) - (-2.54)(23.06)] \text{ kcal/mole}$$

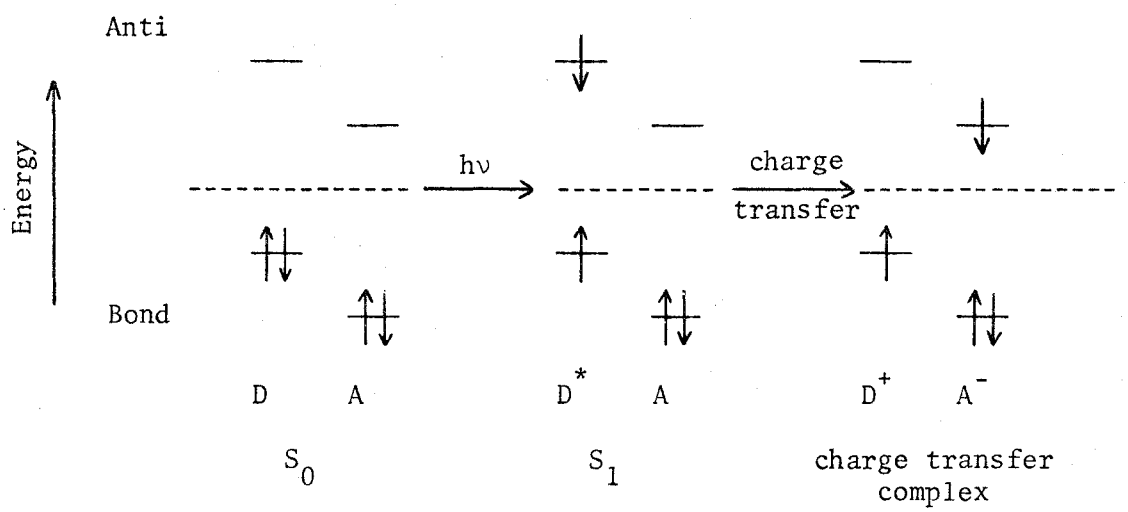
$$\sim +13 \text{ kcal/mole}$$

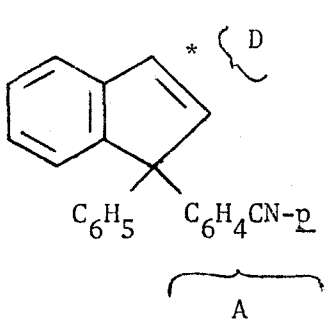
[a] oxidation potential for toluene[71]

Such a large value for ΔG means that the process is not spontaneous.

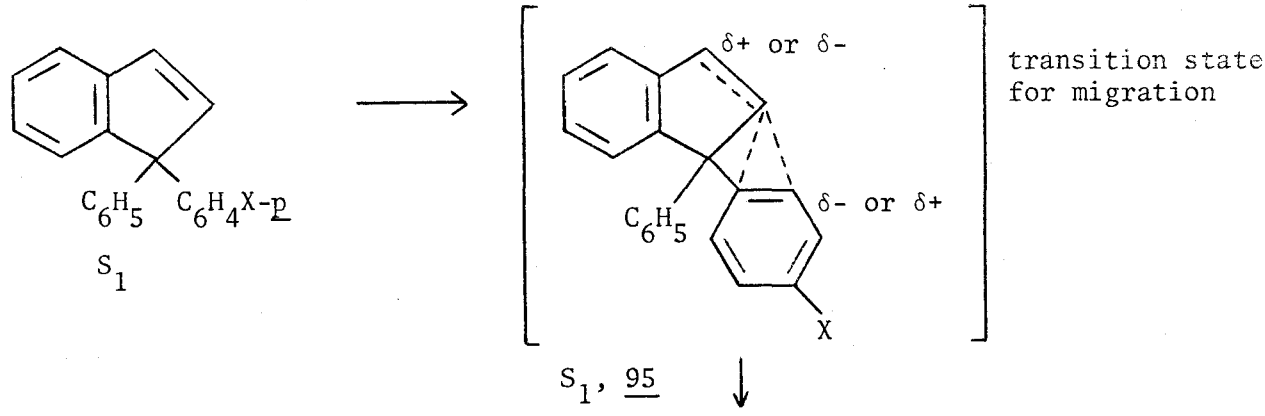
Also, if charge transfer were to occur from the styrene portion to the phenyl group, the free energy would likewise be a large positive number. This is because $E(A^{-}/A)$ for benzene or toluene have not yet been measured (too high a potential is required in the solvent system).

A simple molecular orbital picture to illustrate the charge transfer occurring in the case of the excited singlet (S_1) of 1-(p-cyanophenyl)-1-phenylindene (68) is as follows:





Thus, the suggested transition state 95 for the excited state rearrangement of 1-(p-Xphenyl)-1-phenylindene is shown below. It involves placing a net positive (δ+) or negative (δ-) charge on either the migrating phenyl or the indene double bond.



ground state isoindene intermediate

Irradiation of the p-cyanoindene 68 gave product (98%) of p-cyanophenyl migration. Thus p-cyanophenyl did essentially all the migrating. A mechanism where negative charge is on the bridging phenyl should show a migratory dependence on sigma minus (σ-) values*. Where X = -CN, the excess charge is readily accepted by the p-cyanophenyl ring since the cyano group can stabilize a negative charge rather well via inductive and resonance effects (σ_p^- = 0.88). Likewise, where X = -Br, we could expect a transfer of charge from the excited styrene chromophore to the p-bromophenyl ring. For it should be remembered that ΔG for the charge transfer-process from phenyl ring to styrene portion (or vice versa) was a large positive number; however, it was not possible to calculate ΔG for charge transfer involving the p-bromophenyl ring. Noting that p-bromo-

*Most carbanion-stabilizing groups act through a mixture of inductive and conjugative effects. Cohn and Jones[72] dealt with substituent constants σ_p^- based on the pKa's of m- and p- substituted phenols in water at 25°C. The σ_p^- (sigma minus) values contained both resonance and inductive components. As usual, the more positive the σ_p^- value, the more anion stabilizing the substituent.

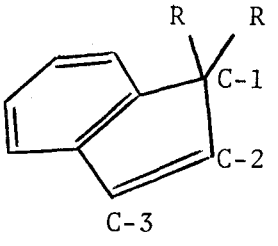
phenyl migrated preferentially (86%) over phenyl in the excited state rearrangement, one might expect a transfer of charge from the excited styrene chromophore of 67 to the p-bromophenyl ring. This excess charge on the bromophenyl ring can be stabilized by the bromine substituent (σ_p^- = 0.25).

Where X = $-OCH_3$, p-methoxyphenyl migration predominated (95%) in the photolysis mixture. This indicates a change in mechanism for the p-anisyl group (σ_p^- = -0.13), i.e., it accommodates positive charge, because the direction of charge transfer is reversed in this case.

Thus the structure 95, showing the suggested transition state for the charge transfer process, could explain the selectivity in results encountered in the irradiation of indenes 67, 68, and 69.

PART V: Orbital Symmetry Considerations

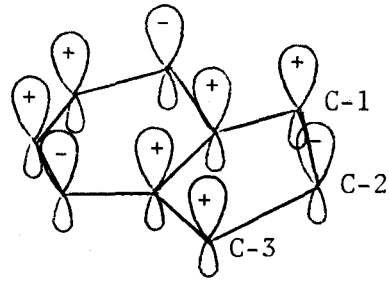
In view of the success of the Woodward-Hoffmann rules[73] in interpreting concerted reactions, including sigmatropic rearrangements[74,18], it is appropriate to give a brief account of the predictions of these rules with regard to the migrations of the indene system 96.



96, R = H, CH_3 or C_6H_5

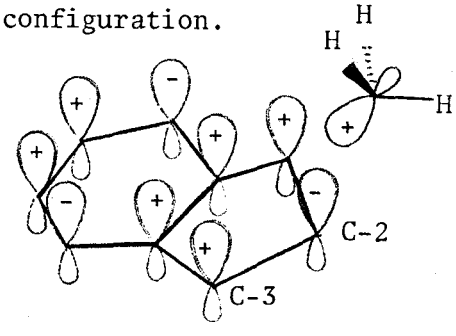
Concerning the excited state migrations of the indene system, a model for the transition state for migration of 96, following the ideas of Woodward and Hoffmann[73], would consist of an indenyl radical and a methyl radical,

hydrogen atom, or phenyl radical. The symmetry of the lowest unoccupied molecular orbital (LUMO) of the indenyl radical then determines whether or not migrations in the excited state are allowed. This indenyl radical has 9π electrons and the orbital is x_6[75].



LUMO (x_6) of indenyl radical

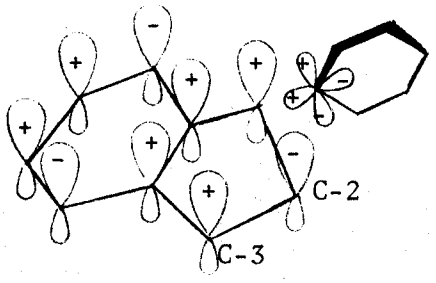
It is seen that the coefficients at the migration start (C-1) and terminus (C-2) are of opposite sign and thus suprafacial migrations from C-1 to C-2 of groups (such as hydrogen or methyl) which interact with the indene π system only through σ orbitals are forbidden. The model for the transition state for methyl migration shows the unfavourable overlap when migration occurs with retention of configuration.



Transition state for methyl migration (excited state)

However, a phenyl group has p orbitals available which have the correct symmetry for favourable overlap with x_6 at C-1 and C-2. This could explain why phenyl migrates and hydrogen[34] or methyl[34] apparently do not, in the excited

state.



Transition state for phenyl migration (excited state)

Turning next to the ground state processes, we note that the Woodward-Hoffmann rules cannot give an unambiguous answer, since the highest orbital of the ground state indenyl radical has a node at C-2, the migration terminus[75].

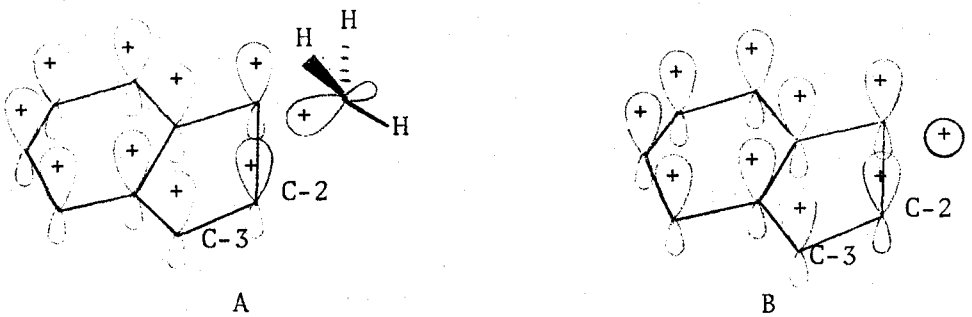
To examine these processes, the method developed by Zimmerman[76,77] may be used, which does not depend on properties of the molecular orbitals. He pointed out that, in a concerted reaction, if the number of sign inversions in the atomic orbital array is even (a Hückel array) the ground state reaction is allowed where 4n + 2 electrons are involved and disallowed for 4n electrons. Also, for an odd number of sign inversions (a Möbius array) the ground state reaction in a 4n + 2 electron system is forbidden but is allowed in a 4n electron system. These rules are summarized in Table 14.

Table 14

Summary of Huckel-Mobius rules for ground state. Excited state results are the reverse[76].

	Hückel (0,2,4... inversions)	Möbius (1,3,5... inversions)
(4n + 2)e	allowed	forbidden
(4n)e	forbidden	allowed

Considering the migration of a hydrogen atom or methyl group in the indene case, it is apparent that there are no sign inversions in the 10 electron (4n + 2) transition state. Thus, both hydrogen and methyl migrations are thermally allowed. Hydrogen, in fact, has been found to migrate readily whereas methyl migrates only very slowly in the indene system.



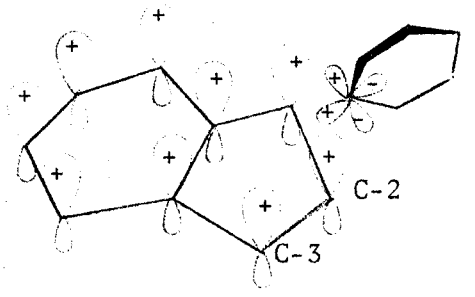
A B

Transition states for ground state migrations: A - for methyl shift; B - for hydrogen shift.

Considering the possible transition state model for the ground state migration of a phenyl group from C-1 to C-2, phenyl is seen to be opposed by its π system, to migration. The 14 electron (4n + 2) system is also seen to have one sign inversion and phenyl migration is thus forbidden. However, considering interaction only with the σ bond to the phenyl group, the system has 10 electrons and no sign inversions. Phenyl is thus allowed to migrate thermally by virtue of this σ interaction. In actual fact, phenyl has been found to migrate efficiently (but less readily than hydrogen) in the thermolysis of some indenes[24].

Zimmerman's rules predict that hydrogen and methyl migration are forbidden (10 electrons, no sign inversions) in the excited state and that phenyl migration is allowed (14 electrons, 1 sign inversion) in the excited state. These facts agree with the predictions of the Woodward-Hoffmann rules for the

photochemical processes.



Transition state for phenyl migration (ground state)

CONCLUSIONS

In the work described, a comparison of migratory aptitudes of substituted phenyl groups was used to probe the ground and excited state aryl shifts. The transition states for migration for these [1,5] sigmatropic shifts could thus be easily studied since migratory aptitudes were compared in the same molecule.

It could not be predicted, a priori, which substituted phenyl should migrate, or to what extent, upon thermolysis or photolysis. There were no rules which allowed a prediction to be made. In thermolysis, preferential p-cyanophenyl migration was observed while p-bromo- and p-methoxyphenyl groups had about the same migratory aptitude, relative to an unsubstituted phenyl substituent. In the irradiations, all three p-substituted phenyl groups migrated preferentially, the selectivity being highest for p-cyanophenyl and lowest for p-bromophenyl.

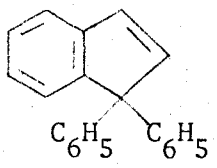
The ground state behaviour indicated a diradical transition state picture for the phenyl migration step. However, some polarity may also be ascribed to this transition state. The excited state results indicated a form of charge transfer was occurring between excited indene and phenyl substituent and that, depending upon the substituent, the migrating group bore either a positive or negative charge.

The photochemical and thermal results were at first viewed with some consternation because of the lack of a precedent in the literature and because of a lack of instantly available explanations. However, while the interpretations are certainly not the last word, they are reasonable and may be correct.

APPENDICES

APPENDIX 1

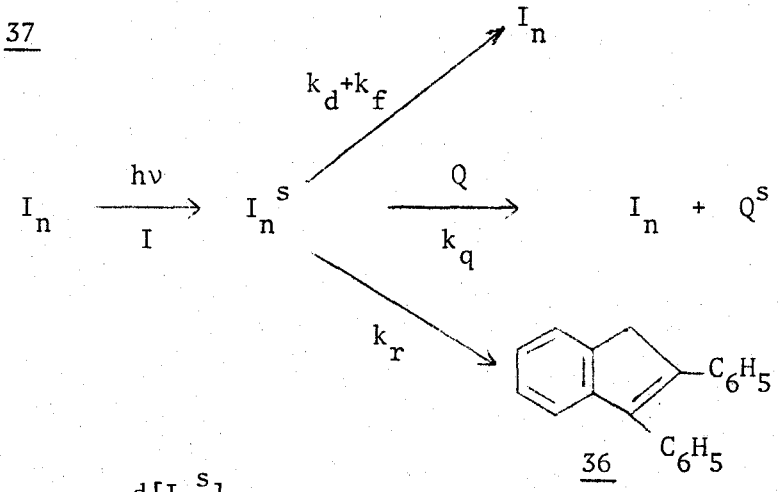
1,1-Diphenylindene Rearrangement—Steady-State Treatment



$\equiv I_n$

Q = quencher

37



36

Steady State: $$\frac{d[I_n^s]}{dt} = I - k_r[I_n^s] - k_q[Q][I_n^s] - k_d[I_n^s] - k_f[I_n^s] = 0 \qquad (1)$$

$$\phi^{Product} = \frac{k_r[I_n^s]}{I} \qquad (2),\ \text{substitute for I from (1) in (2)}$$

$$\phi^{Product} = \frac{k_r[I_n^s]}{k_r[I_n^s] + k_q[Q][I_n^s] + k_d[I_n^s] + k_f[I_n^s]}$$

$$\frac{1}{\phi^{Product}} = 1 + \frac{k_d}{k_r} + \frac{k_q[Q]}{k_r} + \frac{k_f}{k_n} \qquad (3)$$

APPENDIX 2

Sensitization of Biacetyl (BA) Phosphorescence by 1,1-Dimethylindene—Steady-State Treatment

Solving the steady-state equations gives:

$$1/P_{BAT} = x \times k_t \times \tau_{I_n T} + x \times [Ba]^{-1} \quad (4)$$

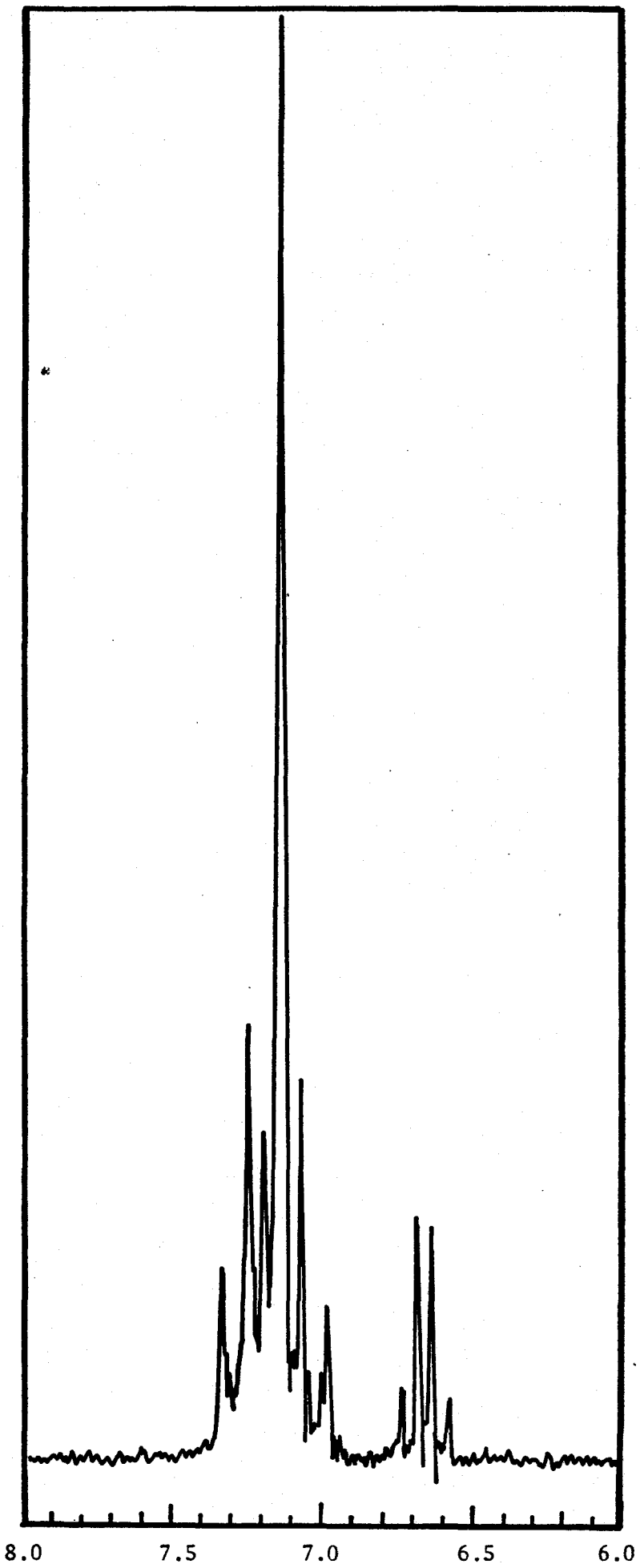
P_{BAT} = phosphorescence readings for BA as recorded by the microphotometer;

x = series of terms including rate constants and lifetimes;

k_t = rate constant for quenching of 1,1-dimethylindene triplet ($I_n{}^T$) by BA; assumed to be diffusion controlled (2.2×10^{10} $\ell.mole^{-1}sec^{-1}$);

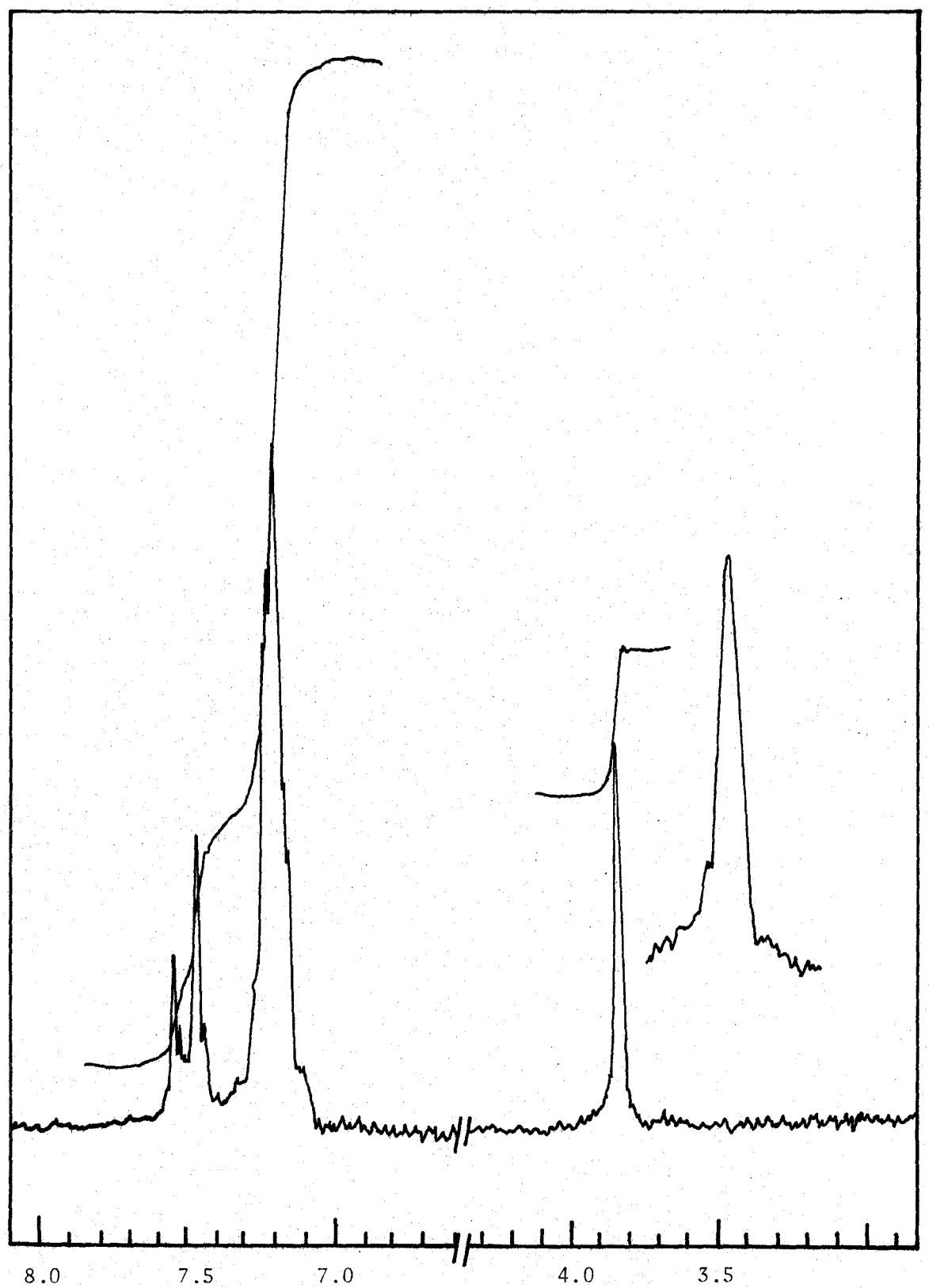
$\tau_{I_n T}$ = lifetime (sec) of $I_n{}^T$.

Thus a plot of $1/P_{BAT}$ vs $[BA]^{-1}$ should give a straight line with intercept:slope $= k_t \times \tau_{I_n T}$.

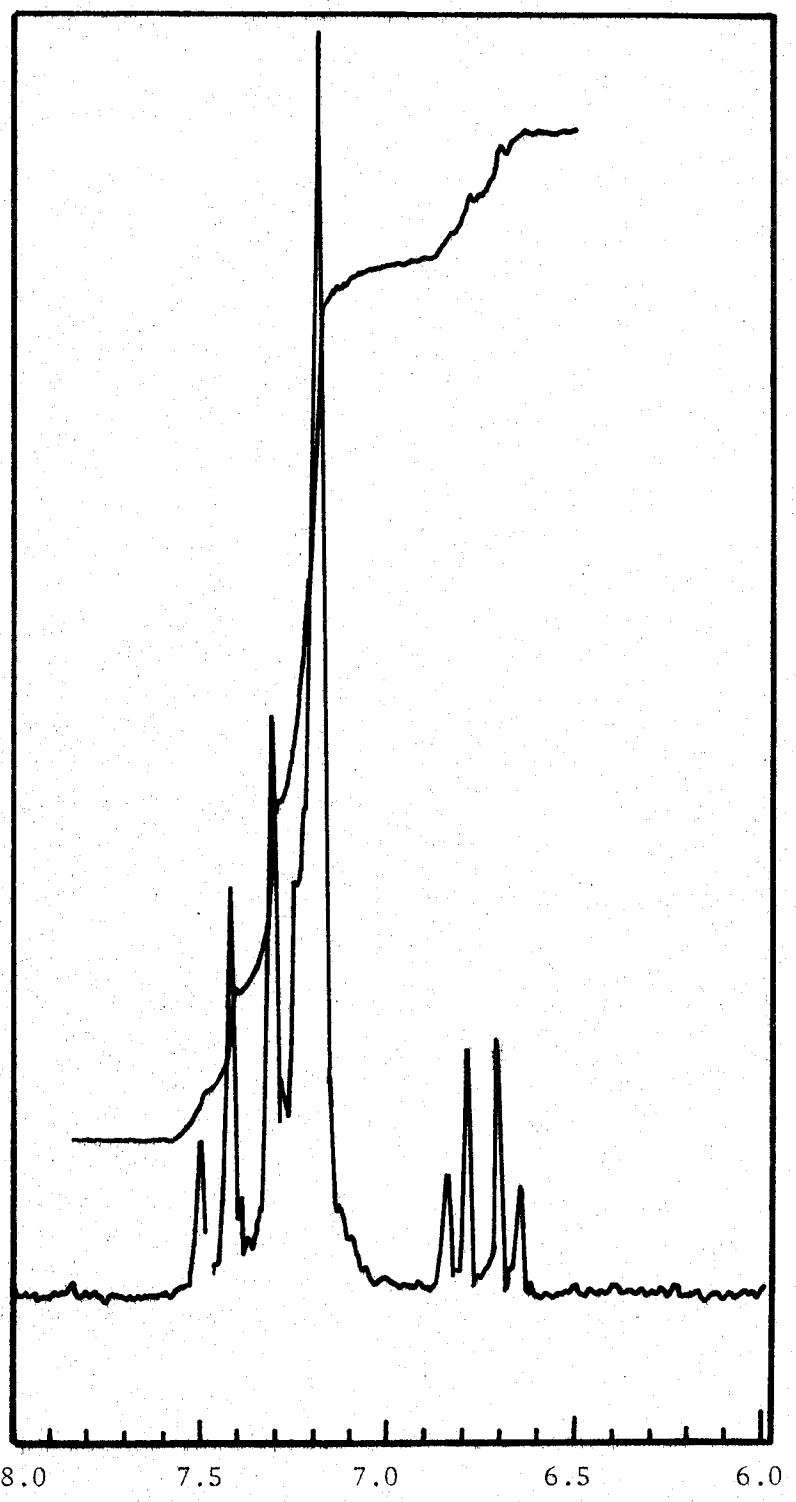


N.m.r. spectrum of 1-(p-bromophenyl)-1-phenylindene (67).

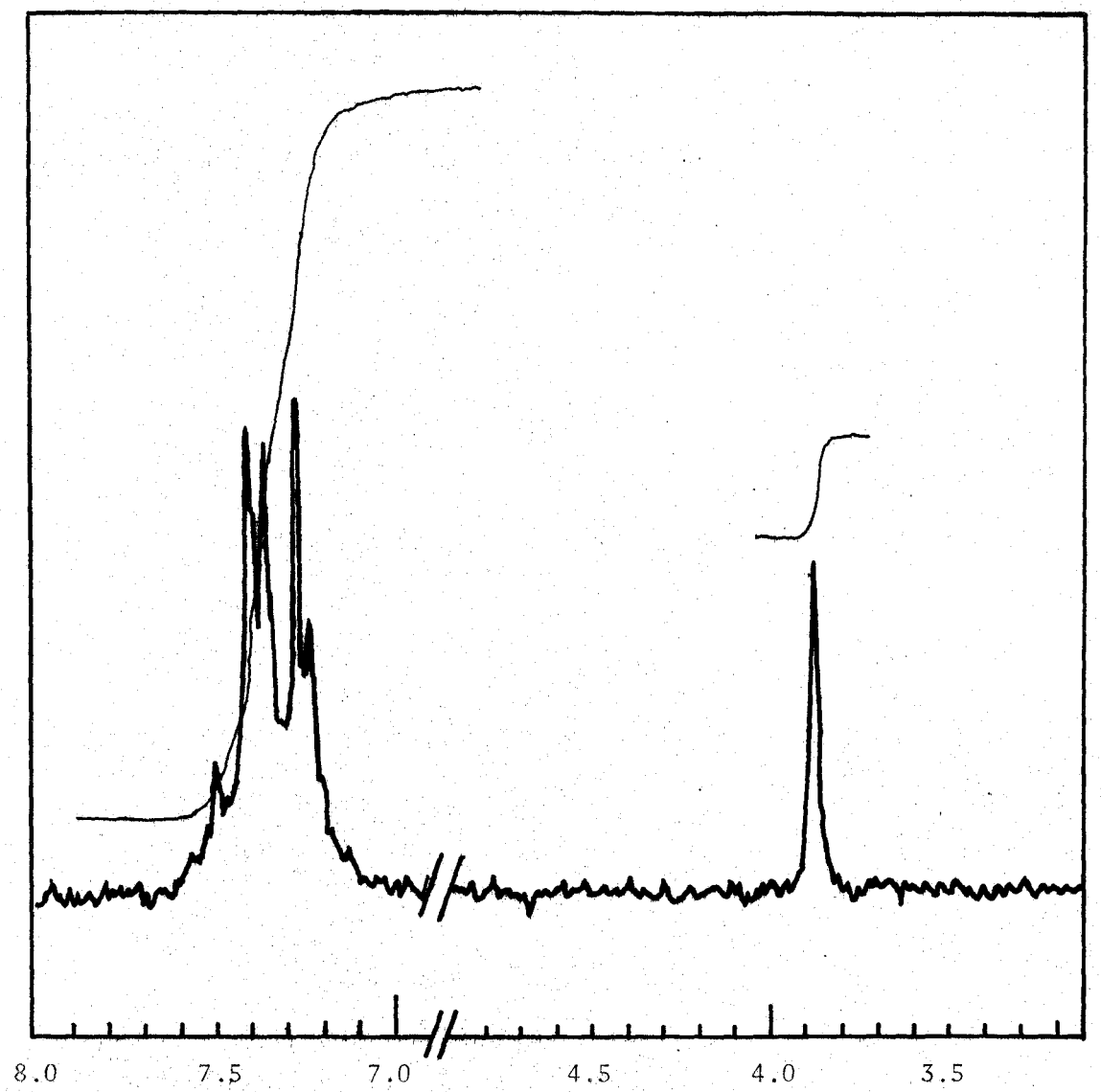
N.m.r. spectrum of 2-(p-bromophenyl)-3-phenylindene (77).



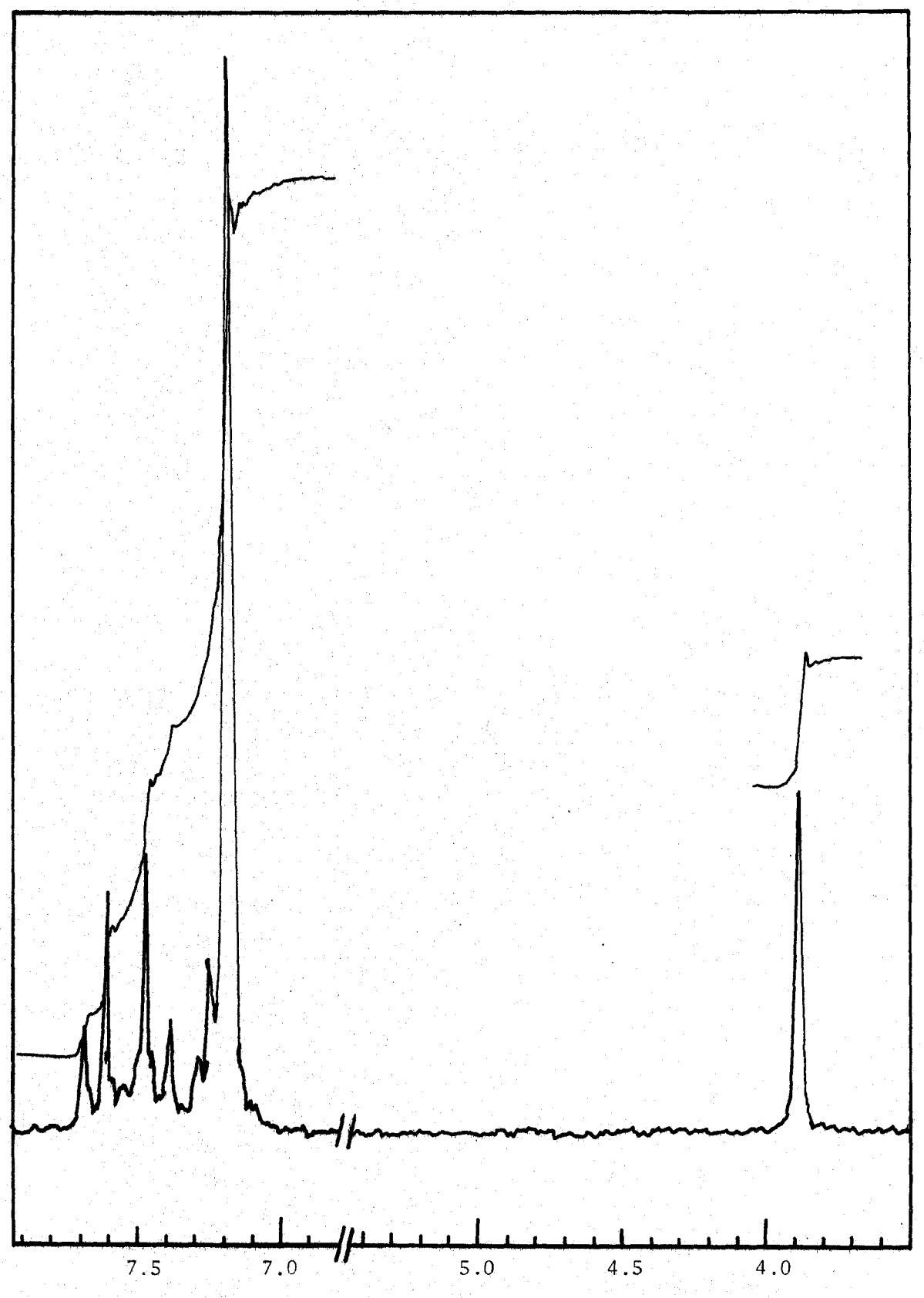
N.m.r. spectrum of 2-phenyl-3-(p-bromophenyl)-indene (83).



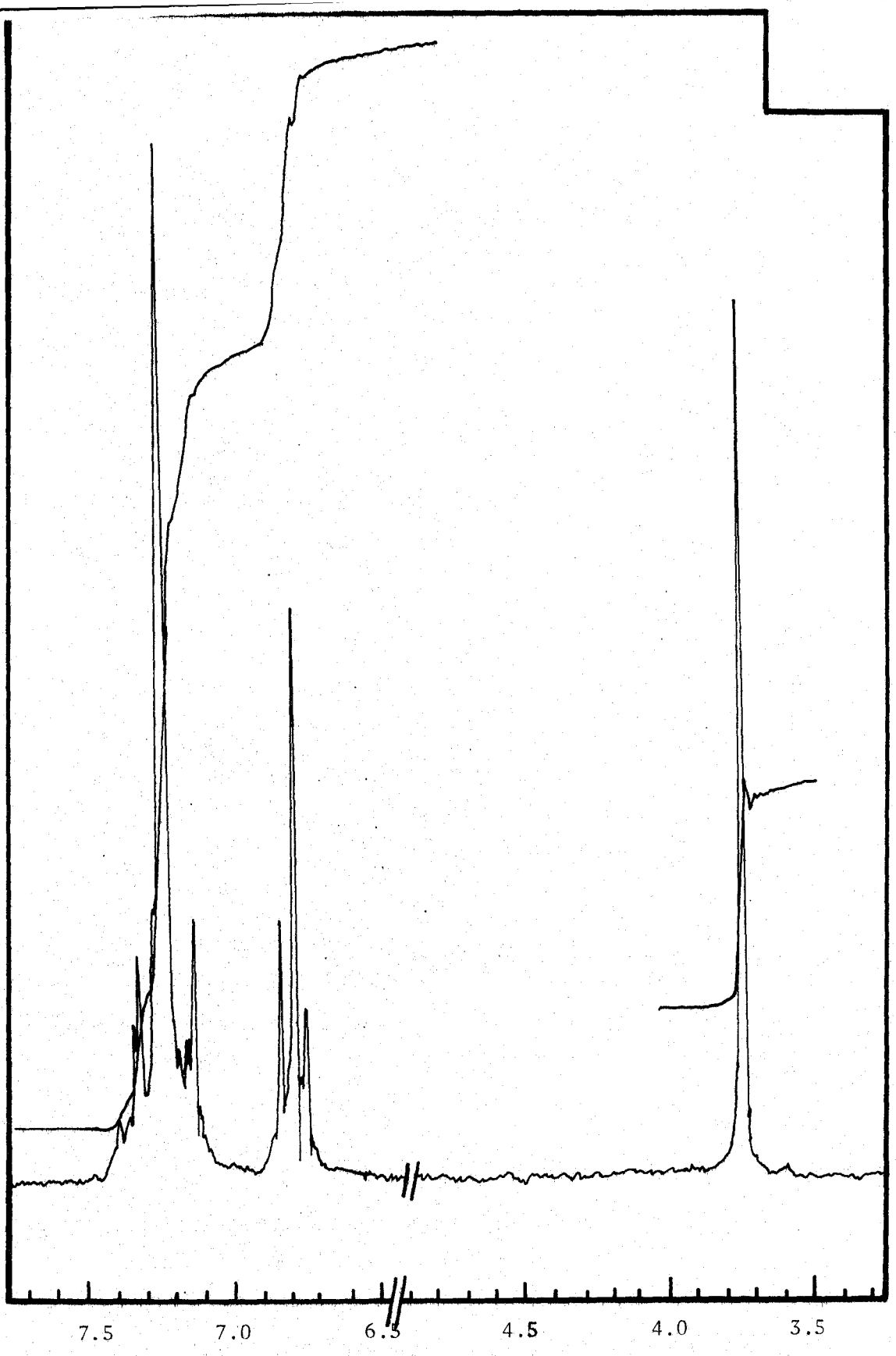
N.m.r. spectrum of 1-(*p*-cyanophenyl)-1-phenylindene (68).



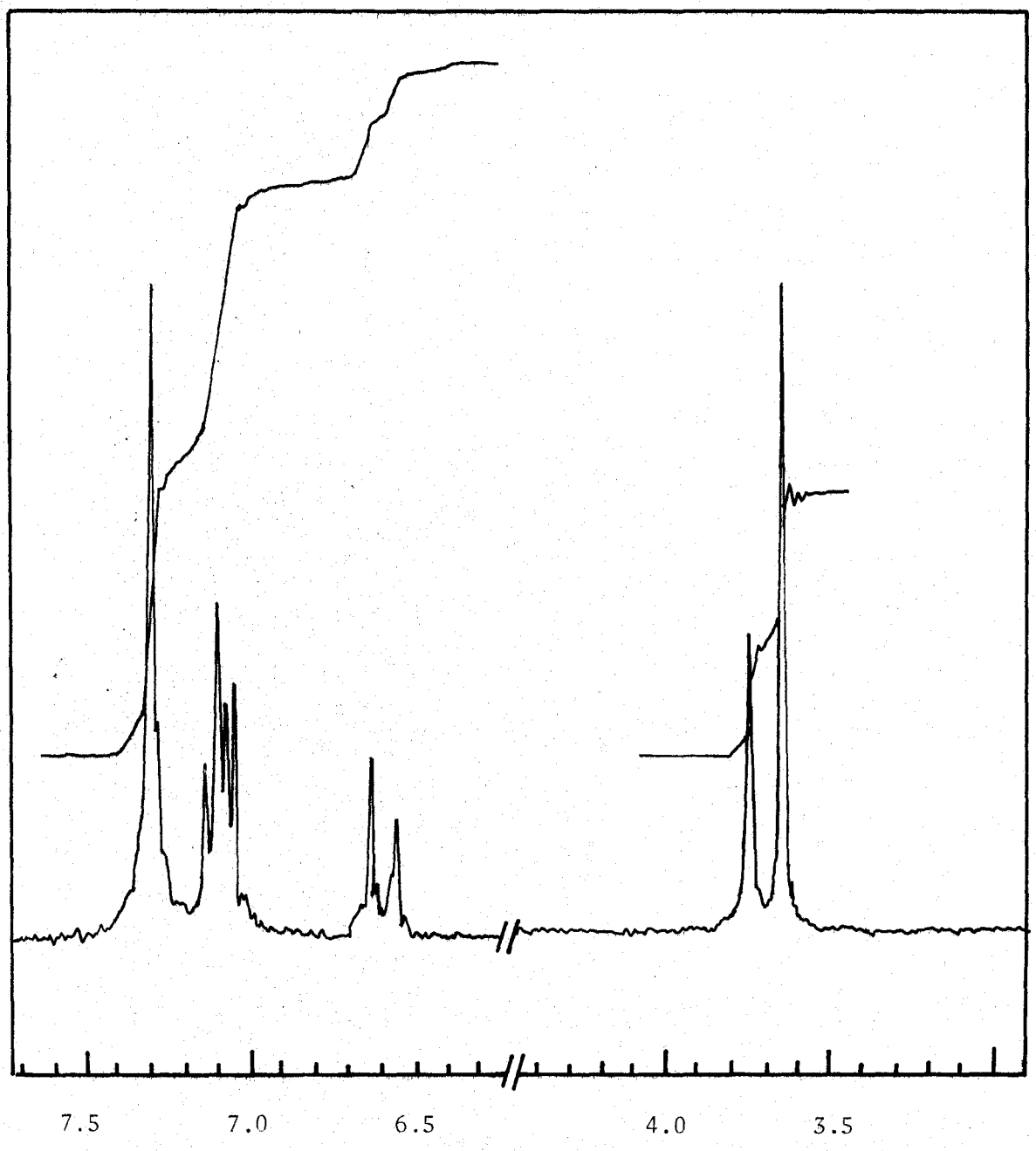
N.m.r. spectrum of 2-(p-cyanophenyl)-3-phenylindene (79).



N.m.r. spectrum of 2-phenyl-3-(p-cyanophenyl)-indene (85).



N.m.r. spectrum of 1-(p-methoxyphenyl)-1-phenylindene (69).



N.m.r. spectrum of 2-(p-methoxyphenyl)-3-phenylindene (89).

N.m.r. spectrum of 2-Phenyl-3-(p-methoxyphenyl)-indene (92).

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