PHOTO-ADDITIONS OF INDENES AND NAPHTHALENE WITH ACRYLONITRILE

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by

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TITLE : Photo-additions of Indenes and Naphthalene with Acrylonitrile

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SCOPE AND CONTENTS:

The products and mechanisms of some photo-reactions of indenes and naphthalene with acrylonitrile have been studied. Indene reacts with acrylonitrile when the hydrocarbon absorbs light, or when a triplet sensitizer is absorbing. Photolysis under the former condition yields 2-(1-indenyl)- and 2-(3-indenyl)propionitrile, and 6-cyano-2,3-benzobicyclo[3,2,0]hep-2-ene. Base-catalyzed isomerizations of the substituted indenes are reported. On sensitization, cis- and trans- isomers of 7-cyano-2,3-benzobicyclo [3,2,0] hep-2-ene are formed; the known indene dimer is a minor product. Adducts 1,1-dimethyl- and 1,1-diphenylindene with acrylonitrile are also described. Naphthalene adds to acrylonitrile on photolysis to afford trans-8-cyano-2,3-benzobicyclo [4.2.0] octa-2,4-diene and 1- and 2-naphthyl-2-propionitriles. Sensitization gives no detectable products. Studies on fluorescence quenching, solvent effect and deuterium-labelling indicates that exciplexes are formed between acrylonitrile and the excited hydrocarbons. Inter- or intra-molecular protonation of the exciplexes with subsequent reaction of the carbonium ion formed, is suggested to produce indenes or naphthalenes. Possible mechanisms for the formation of other products are proposed.

ACKNOWLEDGEMENT

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GENERAL INTRODUCTION

Chemical changes may be caused by heat, acid or base or treatment with many other reagents, or by the action of light. The study of changes in the molecular structure of substances induced by light constitutes the subject of photochemistry.

Photochemical transformations are occurring continually in our environment; such processes include photosynthesis, vision, vitamin formation, chemical processes in the upper atmosphere, and photo reactions of pollutants in the air, water and soil.

In technology, photochemistry is important in duplicating processes, and recently the utility of photo reactions in synthesizing various organic compounds has been fully recognized. It is clear, therefore, that photochemistry is a subject which deserves systematic study. In order to make use of photo reactions in synthetic chemistry, it is important to be able to predict the course of these reactions, and to do this one must understand their mechanisms.

Many of the photo reactions of organic compounds belong to one of two (large) groups[*]. First, there are changes of the type where a single molecule absorbs light and rearranges to a new molecule. This – the subject of rearrangements –

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[*] Other types of photochemical reactions are also known, which will not be discussed in this thesis. Examples are photo-oxidations and photo-reductions.

is very interesting, and a great deal has been discovered in this area in the past decade. Some examples are given in the introduction. The second important type of photo reaction occurs when one molecule absorbs light in the ultra-violet or visible region of the spectrum, forming a state called an excited state; it then combines with a second, unexcited molecule to form an addition product. This is called a photo-addition reaction, and this is the type of process with which the investigations reported in this thesis are concerned. Photo-addition reactions result in the formation of a more complicated molecule from simpler units, and are therefore of potential value in synthetic chemistry.

This thesis is concerned specifically with the photo-addition behavior of some aromatic systems. New, useful reactions are described, and experiments which partially elucidate the mechanism of some of these are reported.

Before dealing with this matter, a brief review of historical aspects of photochemistry will be given, followed by a survey of reactions relevant to the new chemistry to be described in the results.

HISTORY AND DEVELOPMENT OF ORGANIC PHOTOCHEMISTRY

A very considerable body of empirical information had been accumulated in the early days of organic chemistry regarding the photochemical behavior of a wide range of organic compounds, in large part due to the pioneering observations of Ciamician and Silber on the effects of prolonged exposures to sunlight and of Berthelot and Gaudechon on the effects of ultra-violet light(1).

Ciamician and Silber(2) showed that when an alcoholic solution of benzophenone was exposed to sunlight for eight days, the ketone was reduced to benzopinacol, and the alcohol was oxidized to formaldehyde:

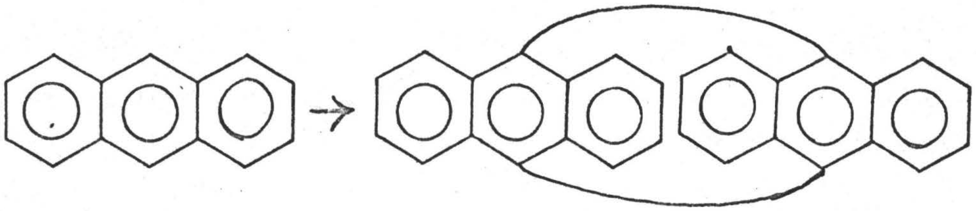
$$2\,C_6H_5COC_6H_5 + 2\,CH_3OH \rightarrow (C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$$

$$+ \quad 2 \quad H\,CHO$$

The same pattern of reaction also occurred for other simple ketones and aldehydes. Thus, acetophenone when exposed to sunlight for 26 days during winter, formed the corresponding pinacol(2).

Photo-reactions of non-ketonic compounds were also studies at an early stage. Vecchiotti and Zanetti(3), and Ciamician and Silber(4), observed that when a mixture of nitrobenzene (100 g) and toluene (20 g) were exposed to sunlight for six months, 20 g of benzoic acid were obtained, together with some p-aminophenol.

The formation of an insoluble white precipitate when anthracene is irradiated in benzene solution and the recognition that it is dianthracene (Eq.-1) were subjects of early observations by Fritsche(5), Elbs(6), and Orndorff and Cameron(7):



(1)

Ciamician and Silber(8), Mascarelli(9) and De Fazi(10) studied the photochemical reaction of a benzene solution of benzaldehyde and acenaphthylene by exposing to sunlight for two years, and found various products including two polymers, a trimer of benzaldehyde, together with some stilbene, "isostilbene", and resinous material. These examples seem to show the way in which photochemistry was followed in the early days.

Although numerous photochemical reactions were discovered at the turn of the century, useful application of these results was lacking. This was largely because techniques adequate to the task of resolving the complex mixtures which are often encountered had not yet been developed. Furthermore, due to the unavailability of artificial light sources of suitable intensity and spectral characteristics, the progress in this field was heavily dependent on the weather.

It is only in recent years that photochemistry has received great attention. Recent theoretical advances as well as the progress in spectroscopy and the arrival of new analytical methods, such as infrared, n.m.r. and chromatography, all have permitted the photochemists to approach the true fundamental problem of photochemistry - the detailed history of a molecule which absorbs radiation.

Among the latest developments, and perhaps the most significant one, is the discovery and specific utilization in chemical reactions of radiationless transfer of energy from triplet state* in solution and in the solid phase in which a donor molecule (sentizer D) in its lowest triplet state (T_1) transfers energy to an acceptor molecule (quencher, A) in its singlet ground state (S_o), which raises the acceptor to an excited triplet level and quenches the donor to its ground singlet state:

$$D(T_1) + A(S_o) \longrightarrow D(S_o) + A(T_1)$$

The first spectroscopic evidence for such triplet transfer in the condensed phase was observed by Terenin and Ermolaev in frozen binary solutions of aromatic compounds at 77°K. These investigators(11) elucidated the general aspects of intermolecular energy transfer between triplet states in

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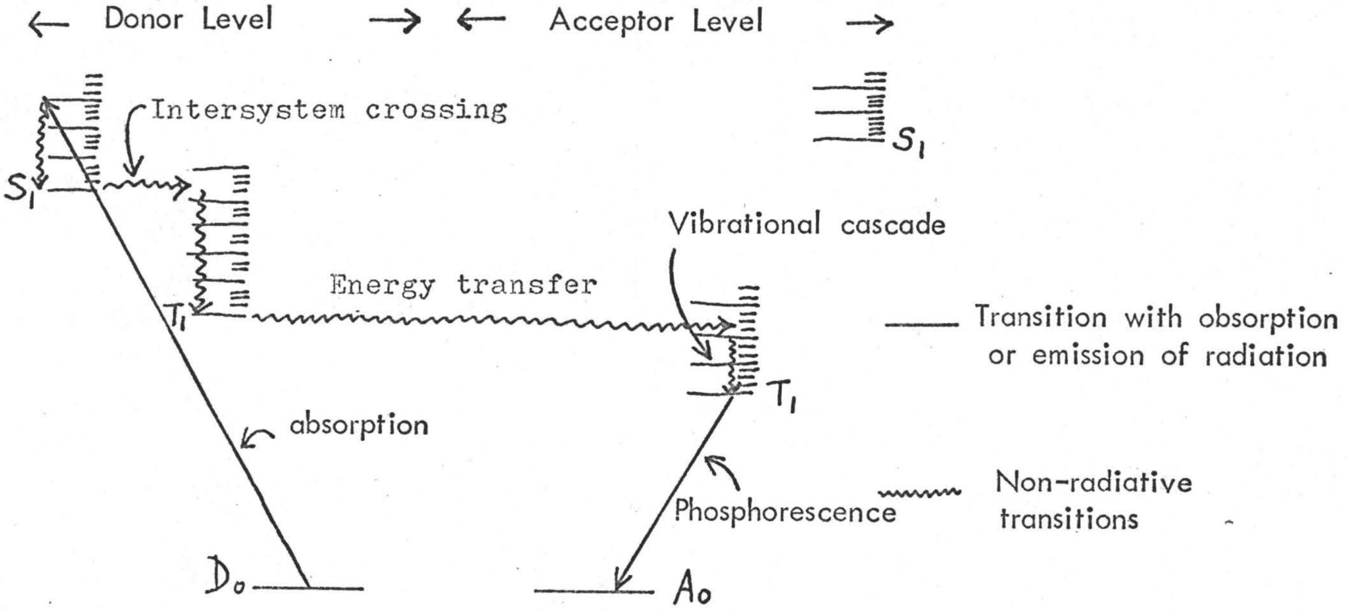
* In most photochemical reactions (excluding those involving ions or radical-ions), only two half-vacant orbitals are associated with a molecule in the excited state (the orbital from which the transition takes place and the antibonding orbital to which the electron is promoted), and consequently only two values for the multiplicity are obtained: 1 and 3. The former, in which the spin has been preserved, is called the "singlet state", and the latter, in which the spins are parallel, is the "triplet state". Photochemical reactions may occur from singlet and triplet states, and determining which state is involved in a given photochemical reaction is an important part of photochemistry.

solids. Thus phosphorescence* spectra of certain energy acceptors, such as naphthalene, 1-methyl- and 1-chloro-naphthalenes, and biphenyl were observed when light was absorbed by various donors, such as benzophenone, benzaldehyde, acetophenone and carbazole in donor-acceptor mixtures.

Scheme I : Triplet Energy Transfer Between Excited Donor (D*) and Acceptor (A)



Triplet energy transfer in liquid systems was first demonstrated by Bäckström and Sandros in 1958. These investigators irradiated a benzene solution of biacetyl and anthracene in a region where only biacetyl absorbed radiation, and obtained a yield of dianthracene(12). On further work, the same workers

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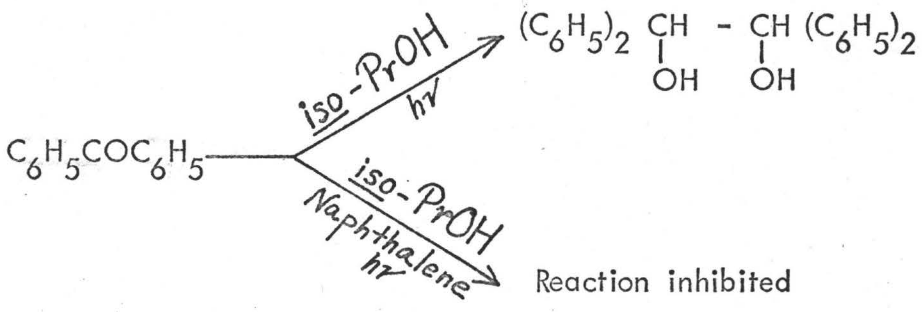
* Two types of emission from radiative deactivations of excited states are recognized. The type associated with excited singlet → ground state singlet emission is fluorescence, a short-lived (10^{-5} to 10^{-9} sec) emission of light; and the second type, the much longer lived (10^{-3} to 10^{-5} sec) emission associated with excited triplet → ground-state singlet deactivation, is phosphorescence. More generally, fluorescence is defined as the emission between states of the same multiplicity and phosphorescence as the emission between states of different multiplicity.

used benzophenone, whose triplet level lies 4000 cm^{-1} above that of biacetyl, to sensitize the biacetyl phosphorescence(13).

The importance of triplet states in solution photochemistry was conclusively demonstrated by Hammond, Turro and Leermakers(14), and Moore and Ketchum(15). In the experiment, two de-oxygenated solutions of benzophenone in isopropyl alcohol, one also containing naphthalene, were irradiated with 3660 A radiation, a good yield of benzopinacol was obtained in the first solution, but no product was formed in the solution to which naphthalene was added:



The inhibition of benzophenone photoreduction was interpreted in terms of triplet energy transfer from benzophenone to naphthalene, and is good evidence that a triplet state is involved in the photoreduction. The above two mentioned research groups have also carried out triplet energy transfer from benzophenone in solutions under a variety of conditions in a more quantitative study, and have derived rate constants for the reaction(15)(16).

In summary, utilization of triplet transfer in solution, is of great importance chemically for the following reasons:

(i) It can provide a means of sensitization initiating photochemical reactions in molecules which do not absorb directly at a suitable wavelength.

(ii) It provides a convenient means of producing and/or populating triplet species of molecules whose triplet state are not appreciably populated by direct absorption.

(iii) It provides a simple method of estimating the triplet energy levels of both donors and acceptors and of elucidating the mechanisms of photochemical reactions and the process of excitation transfer.

Pioneering workers in organic photochemistry were only concerned with the isolation and identification of the products of a reaction. Nowadays, investigators are still interested in product identification; however, modern work also makes use of quantitative measurements, energy transfer studies, and spectroscopic and theoretical concepts to probe the mechanism of a photochemical reaction. It is the elucidation of the mechanism of reactions which differentiates modern from classical photochemistry.

From the viewpoint of the organic chemist, the two types of photoreaction which seem the most important are photo-rearrangements and photoadditions; in both of these types of reaction, the products have a different carbon framework from the reactant(s), and the organic chemists, particularly those involved in synthesis, must be aware of the transformations which can occur.

Since the results reported in this thesis are concerned with the photochemistry of aromatic systems, a brief review of some of the known photochemistry of these compounds will be given.

PHOTO-REARRANGEMENT REACTIONS

Although the thermal chemistry of benzene and its derivatives has been extensively studied for well over a century, the photochemistry of benzene has received only scant attention until the last two decades.

In 1957, it was reported that on irradiation at 2537 A in a rigid glass at 77°K, benzene, and presumably its alkyl-substituted derivatives, undergoes ring rupture with the formation of non-aromatic product. In ethanol-containing matrices, a substituted triene appears to be the product(17):

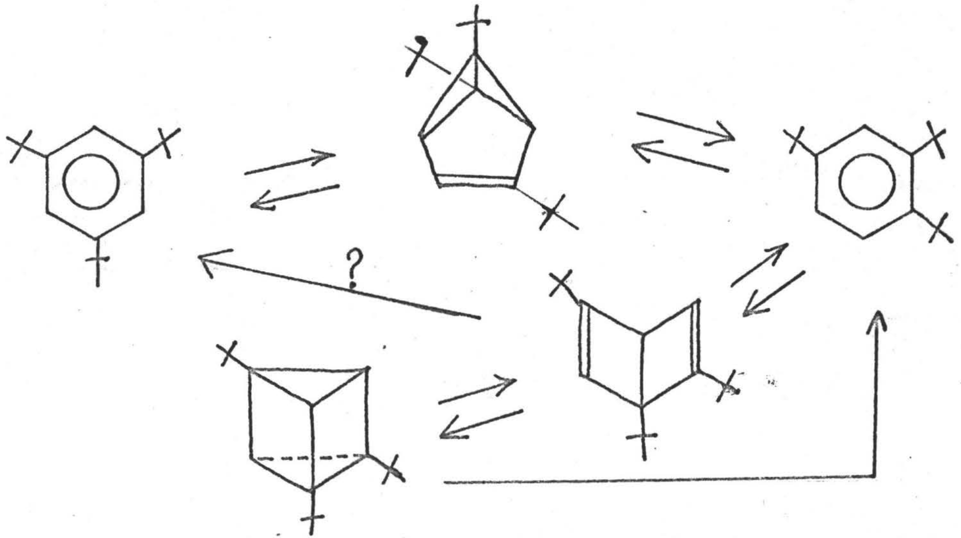
$$C_6H_6 + C_2H_5OH \xrightarrow[77^{\circ}K]{} CH_3CHOH(CH{=}CH)_2\text{-}H$$

Upon photolysis of benzene at 2537 A in the liquid phase, at 50°, fulvene formation has been observed(17). Recently, benzvalene has also been shown to be formed under similar conditions, especially when the benzene is diluted by a paraffinic solvent(18).

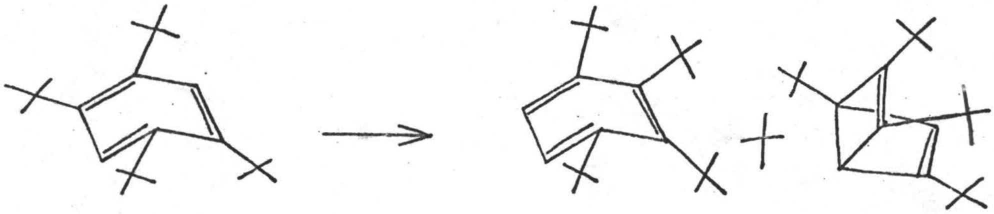
The 2537 A irradiation of alkyl-substituted benzenes induces an interesting 1,2-shift of an alkyl-group. Thus, o-di-t-butylbenzene undergoes photo-isomerization to form a photo-stationary equilibrium mixture of m- and p-di-t-butylbenzenes(19). Likewise, starting from m- or p-di-t-butylbenzene, the same photo-stationary composition was reached(19). The same type of photo-isomerization also occurs with o-t-butyltoluene(19) and o-xylene(20). Upon irradiation (2537 A) at 30°, mesitylene isomerizes to 1,2,4-trimethylbenzene. ^{14}C-labelling experiment shows a clear demonstration that the 1,2-shift of the methyl-group is a consequence of ring carbon atom interchange(21).

In contrast to the isomerization pathways of mesitylene and 1,2-disubstituted benzenes, 1,2,4-tri-t-butylbenzene and 1,2,5-tri-t-butylbenzene undergo a different kind of isomerization(22) to form a photo-stationary mixture of Dewar and Ladenburg benzenes, and benzvalene. Scheme II shows the observed interconversions of this photoreaction.

Scheme II : Photo-interconversions of tri-t-butylbenzenes



It is interesting to observe that upon photolysis, 1,2,4,5-tetra-t-butylbenzene rearranges to a more strained isomer, 1,2,3,5-tetra-t-butylbenzene, and the related Dewar benzene (Eq.-2) (23):

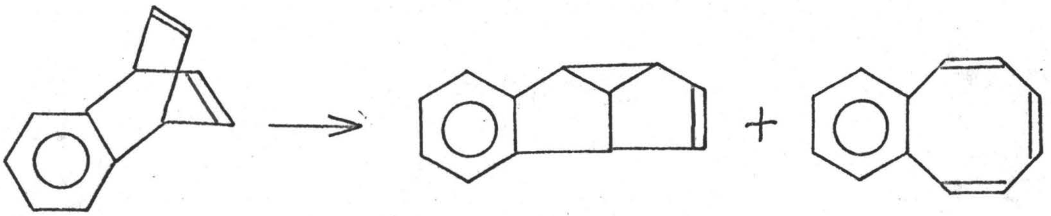


(2)

Almost all photo-isomerization reactions involving the benzene ring lead to non-aromatic products. In marked contrast, phenyl-substituted compounds undergo photo-rearrangements involving phenyl-migration. Thus, on irradiation, both 1,3,3- and 3,3,3-triphenylpropene cyclizes with concomitant phenyl-migration to form 1,1,2-triphenylcyclopropane(24). Another case of cyclization with phenyl-shift is the formation of 1,1,2,3-tetraphenylcyclopropane on photolysis of either 1,3,3,3- or 1,1,3,3-tetraphenylpropene(24).

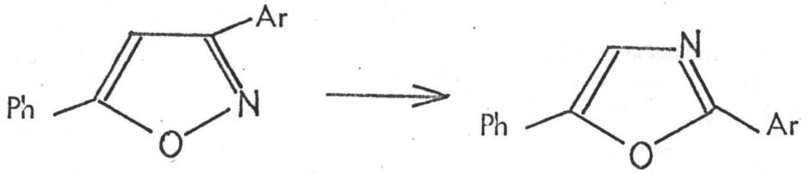
Photo-induced 1,2-phenyl migrations have also been demonstrated unequivocally in the phenyl-substituted aromatic and heterocyclic hydrocarbons. 1,1,3-triphenylindene undergoes photo-rearrangements to yield 1,2,3-triphenylindene(24). Similarly, 1,1-diphenylindene(25) gives 1,2- and 2,3-diphenylindenes on photolysis.

Recently, benzobarrelene has been converted into benzosemibullvalene and benzocyclooctatetraene (Eq.-3)(26), an analogous to the previous reported transformation of ballelene to semibullvalene(27).



(3)

Examples of rearrangement of phenyl-substituted five-membered heretocyclic compounds have recently been reported. Irradiation of 3,5-diphenyl- or 3-aryl-5-phenyl-isoxazoles result in the formation of the corresponding 2,5-diphenyl- and 2-aryl-5-phenyl-isoxazoles (Eq.4)(28):



(4)

Irradiation of a series of 2-substituted thiophenes (e.g. phenyl, p-tolyl, mesityl, α-naphthyl, and β-naphthyl-thiophenes), affords the corresponding 3-substituted thiophenes(29). ^{14}C-labelling experiments have shown that the rearrangement is confined to the thiophene ring and does not occur in the phenyl ring. The primary process of rearrangement involves an interchange of the C_2-C_3 carbon atoms without concomitant inversion of the C_4-C_5 carbon atoms. 3,4- and 2,4-diphenylthiophenes on photolysis also rearrange to 2,3- (isolated as phenanthro[9,10-b]thiophene) and 3,4-diphenylthiophenes, respectively. While 2,5-diphenylthiophene is virtually unreactive photochemically(29).

PHOTO-ADDITION REACTIONS

Photo-addition reactions are assuming a place of substantial importance in synthetic organic chemistry. Three types of photo-addition are generally recognized:

(i) A combination of two double bonds to form a cyclobutane derivative;

(ii) A Diels-Alder type of combination;

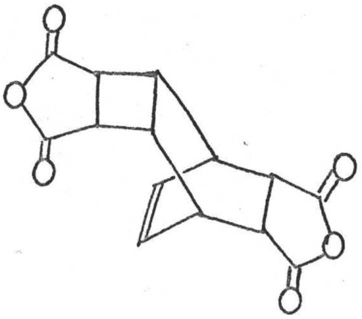
(iii) A 1,4-1,4 addition of dienes.

Class (i) is by far the most common.

A large number of aromatic compounds which undergo photo-additions have been extensively studied(30)(31). Dimerization of anthracene,(5)(6)(7)(32) acenaphthylene(33), indene(34) and a series of 2-substituted naphthalenes(35)(36) may be cited as examples.

Several different types of photo-addition reactions involving the benzene ring have now become known, and nearly all of these are transformed into non-aromatic compounds.

Benzene was shown to form an adduct with maleic anhydride on photolysis(37). The adduct (I) contains one molecule of benzene for every two molecules of the anhydride.



I

Similar 2:1 adducts* were also formed between maleic anhydride and substituted benzene derivatives (toluene, t-butylbenzene, chlorobenzene, and o- and p-xylenes). However, highly substituted benzenes, such as durene, essentially undergo no addition at all(38).

Maleic anhydride, maleimide, and cyclopentene-2,4-dione form an isoelectronic triad, but of these only maleic anhydride and maleimide have been shown to undergo either sensitized or unsensitized photo-addition to benzene(39)(40). The 2:1 adducts of maleimide or various N-substituted maleimides with benzene have structures analogous to that of the maleic anhydride adduct(39)(40).

Benzene also combines photochemically with acetylene derivatives. The initially formed cyclobutane adducts (1,2-cyclo-addition) are prone to undergo isomerization to ultimately produce cyclo-octatetraene derivatives. Thus, methyl propiolate in benzene solution gives methyl cyclo-octatetraenecarboxylate(43).

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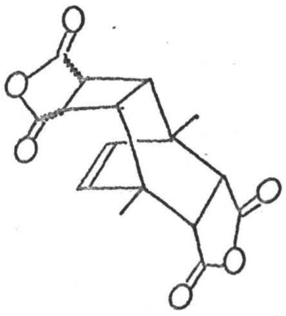
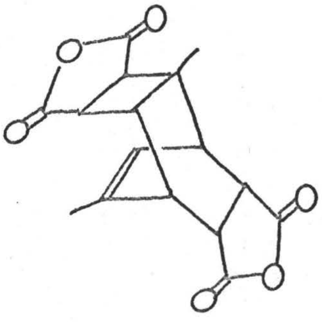
[*] Recent work of Bryce-Smith and Gilbert(41) has shown that two isomeric 2:1 adducts are formed by benzophenone-sensitized photo-addition of maleic anhydride to toluene, o- and p-xylene. In the case of p-xylene, spectroscopic data are consistent with provisional formulation of these adducts as the dianhydride (II) and (III). Their relative ratio is temperature dependent. At 20°, adduct (II) is formed almost exclusively, whereas at 110°, adduct (III) is the major product(42). The pairs of isomeric adducts formed by o-xylene and toluene are structurally analogous to adduct (III)(41).

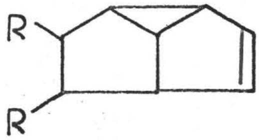


II



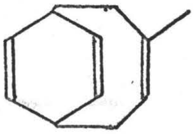
III

While acetylenes add to benzene in a 1,2-cyclo-addition fashion, alkenes often add in a 1,3-fashion. Hence, the adducts from cis-2-butene, 2,3-dimethyl-2-butene, cyclopentene and cyclooctene* with benzene are substituted tricyclo $[5.1.0.0^{4,8}]$oct-2-enes (IV)(42, 44)

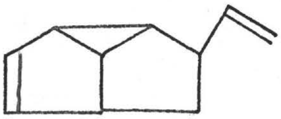


IV

A complex reaction pathway has been observed on photo-addition of benzene and its methyl-substituted derivatives (toluene, o-, m-, and p-xylenes, as well as durene) to conjugated dienes, in which both 1,3- and 1,4-cyclo-additions are operating(45). For example, isoprene adds to benzene to give two 1:1 adducts (VI) (1,4-cyclo-addition) and (VII) (1,3-cyclo-addition), together with some 2:2 adduct and substituted benzene(45).



VI



VII

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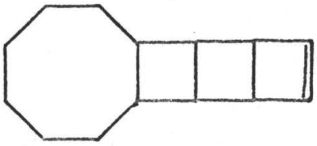
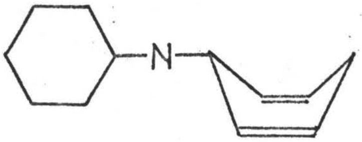
* A minor labile 1:1 adduct is also isolated, and its structure is assumed to be (V)(42).



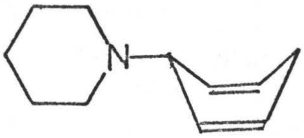
V

Similar adducts were also obtained from butadiene and benzene(45). However, acrylonitrile, which can be regarded as an analog of a conjugated diene having two more π-electrons, adds to benzene in a 1,2-addition fashion to give a cyanocyclobutane(46).

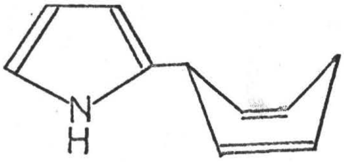
A very interesting reaction recently reported by Bryce-Smith and co-workers is that amine derivatives, such as cyclohexylamine, piperidine and pyrrole, all add to benzene in a 1,4-fashion, leading to adducts (VIII), (IX), and (X), respectively(42, 47).



VIII



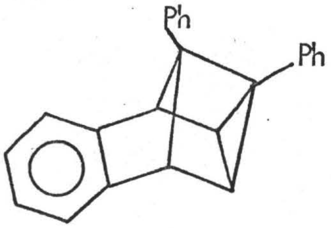
IX



X

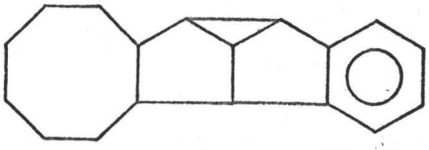
Benzonitrile, a photochemically very reactive substituted benzene, has been shown to undergo photo-addition with acetylenic compounds, such as 3-hexyne and 5-decyne, to form cyclooctatetraene derivatives (1,2-addition)(48). However, in contrast to benzene (*vide supra*), benzonitrile undergoes 1,2-addition with various olefins (for example, 1,1,2-trimethylethylene and *cis*-1,2-dichloroethylene) to give cyclobutane derivatives(48) (49).

The photochemical behavior of naphthalene is remarkably different from benzene. It reportedly does not react with maleic anhydride(50) but does undergo a 1,4-addition reaction with dienes (e.g., isoprene and butadiene) to form 1,4-dihydro-naphthalene derivatives(45). A double 1,2-cyclo-addition reaction between diphenylacetylene and naphthalene as well as its methyl-substituted derivatives was reported to give tetrahydronaphthalenes(51), having the interesting ring system shown (XI)



XI

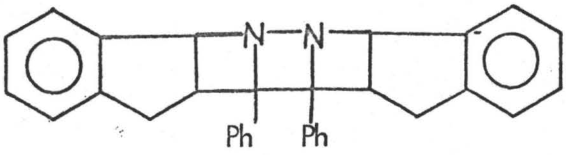
It has also been shown that naphthalene forms two 1:1 photo adducts with cyclooctene. Spectroscopic evidence is consistent with structure (XII) for the major product(42).



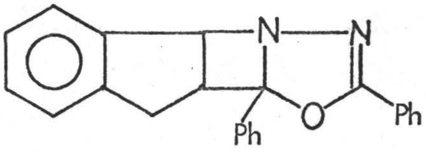
XII

Although 2:1 adducts are formed on photolysis of maleic anhydride and benzene derivatives, only 1:1 adducts are obtained on irradiation of condensed aromatic compounds with this anhydride. Thus, when the site of addition has appreciable olefinic character, cyclobutane derivatives are formed(52). Hence, phenanthrene(53) and indene(54) yield the corresponding cyclobutanes, while anthracene(55) forms a Diels-Alder adduct on photolysis with this anhydride.

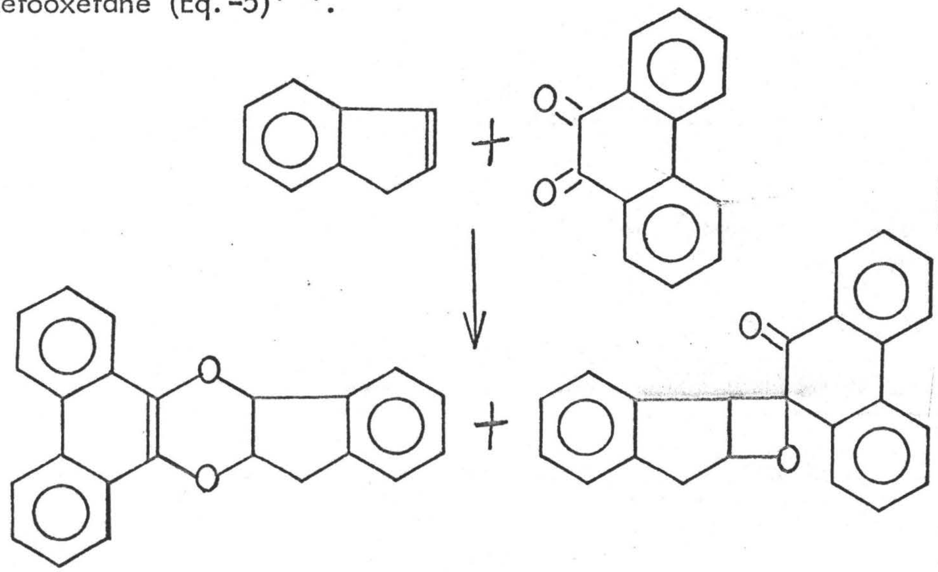
Other cross-addition reactions of indene and naphthalene which have been reported are few in number. Indene has been shown to form cyclobutanes with coumarin(34) and maleic anhydride(54). Upon irradiation, indene and 1,3,4-oxadiazole affords an adduct (XIII); however, in the presence of iodine, another adduct (XIV) is also obtained(56). When indene is irradiated with phenanthrenequinone, dihydro-1,4-dioxin is formed, together with the α-ketooxetane (Eq. -5)(57).



XIII



XIV



(5)

This thesis is mainly concerned with the photo-additions of aromatic compounds (indene and naphthalene) with acrylonitrile. The photo-adducts obtained have not been reported previously, and these will be described in

Part II (Results Section). A mechanism accounting for the formation of these new photo-adducts will be discussed in Part IV (Discussion Section).

PART II : RESULTS - PHOTO-ADDITION REACTIONS OF INDENES AND NAPHTHALENES WITH ACRYLONITRILE

This section describes the results of exploratory experiments with indenes, naphthalene and acrylonitrile. It is important, before proceeding with an account of the results, to outline some of the reasons for choosing these compounds for study. It is known that while indene undergoes efficient dimerization on (triplet) sensitized (acetophenone, benzophenone, Michler's ketone) photolysis,(34) the compounds polymerizes on direct irradiation,(34) i.e., when the light is absorbed by the hydrocarbon. This indicates a difference in excited state behavior of indene.

Since very few cross-addition of indene had been reported,(34,54,56) it was decided to investigate the sensitized and direct photo-additions of indene and acrylonitrile.

Acrylonitrile is a suitable ethylene derivative to use in trapping other excited molecules in a bimolecular reaction for the following reasons:

(i) It is transparent over much of the ultraviolet spectrum, having λ_{max} (EtOH) 215.5 mμ, logϵ 1.69,(58) and therefore may be present in high concentration without restricting the choice of light absorbing partner.

(ii) In solutions containing acrylonitrile and benzene,(46) indene or naphthalene (see experimental), no charge-transfer absorption is observed. This should simplify the mechanistric work in this system.

The studies were extended to indene derivatives and naphthalenes.

On sensitized photolysis, indenes add to acrylonitrile with the formation of cyclobutanes; however, no photo-adduct was detected in the corresponding photolysis of naphthalene and acrylonitrile.

On direct irradiation, indene and naphthalene revealed similar reactions with acrylonitrile; two kinds of adducts are formed. These are

(i) cyanoethyl derivatives,

(ii) cyclobutane derivatives of the hydrocarbons

The behavior of these hydrocarbons and the structural determinations of the photo-adducts will be described separately.

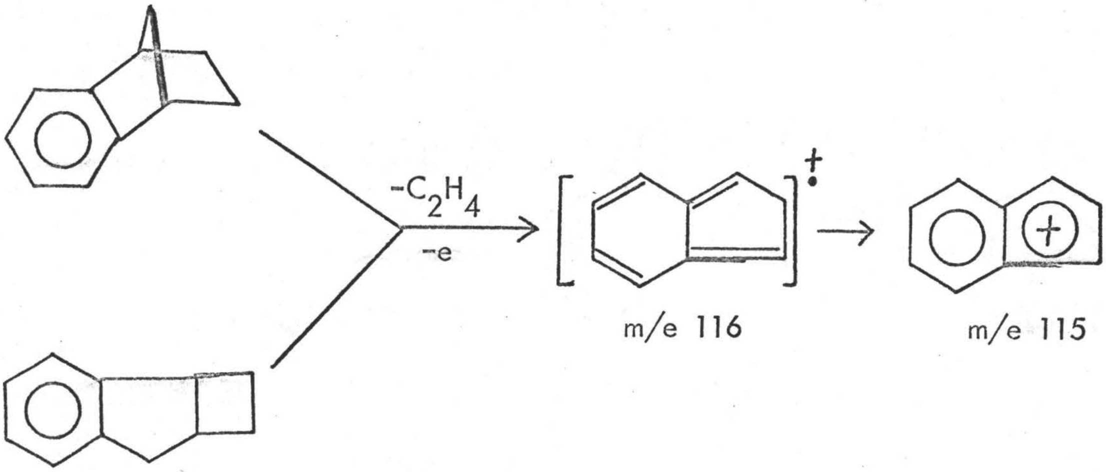
ACETOPHENONE-SENSITIZED PHOTOLYSIS OF INDENE AND ACRYLONITRILE

On acetophenone sensitized photo-addition of indene and acrylonitrile, three products were detected and the ratio analyzed by gas-liquid chromatography (see experimental). Analysis of aliquots revealed that three major products with retention times of 1.7, 2.0 and 8.0 min were formed. These were readily separated by chromatography on alumina; the 8.0 min product which was eluted first was identified as the product of sensitized dimerization of indene, m.p. 109-110°, lit. 109.5-111°(34).

The two nitrilic adducts (XV) (m.p. 70°) and (XVI) (m.p. 50°) both showed a sharp peak at 2240 cm^{-1} in the infrared (saturated nitrile). They were interconverted by treatment with potassium _tert_-butoxide in _tert_-butyl alcohol showing that they were epimers.

The mass spectra of both (XV) and (XVI) showed a very weak molecular ion peak with m/e 169 (M), and a base peak at m/e 116, which corrresponded to M-53 (Appendices I and II). This is consistent with either a cyclobutane(59) or a benzonorbonene(60) type of structure.

Bak and Conrow(59) observed that for cyclobutane derivatives, the most abundant fragment always corresponded to the one which arises from splitting of the cyclobutane ring. On the other hand, Goto and co-workers(60) showed that for bicyclo [2.2.1] heptane and bicyclo [2.2.2] octane derivatives, the elimination of CH_2-CH_2 by a retro-Diels-Alder (RDA) type fragmentation is a very favorable process, and consequently, produces a residual fragment ion which appears as a base peak (Scheme III). Hence the mass spectrum did not distinguish between the two possible structures.

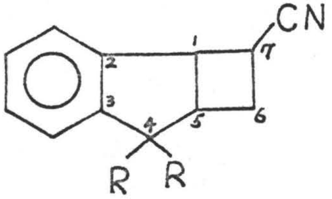


SCHEME III

However, the nuclear magnetic resonsnace spectra (Table I) were consistent with cyclobutane structures, since they did not show any

TABLE I

Nuclear magnetic resonance spectral data* for cyclobutane adducts of acrylonitrile and indene derivatives

Cyclobutane Derivative 	Chemical shifts #				
	H-1	H-5	H-6	H-7	Other
R = -H; m.p. 50°. (XVI)	3.98 b[++]	2.76 m	2.16,2.51 m	3.36 m	2.98,3.08 benzylic CH_2
R = -H; m.p. 70°, (XV)	3.94 b	—‡	1.95, 2.50 m	3.35 q	—‡
R = - CH_3, m.p. 72°, (XXII)	3.92 d	2.64 q	2.20 m	3.14 q	1.04, 1.26 (methyls)
R = - CH_3, m.p. 59°, (XXIII)	3.82 quin	2.69 q	1.99,2.19 m	3.24 q	1.00, 1.24 (methyls)
R = - C_6H_5, m.p. 224°, (XXI)	4.18 quin	3.24 q	1.3-2.0 m	3.74 q	

* All spectra recorded in $CDCl_3$ at 100 M c.p.s. on a Varian HA-100 instrument

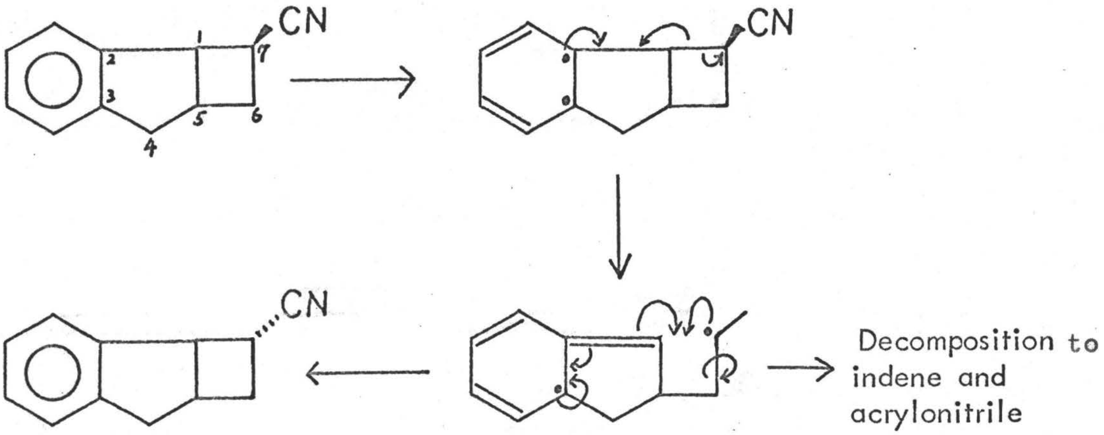
\# Chemical shifts given in p.p.m. downfield from tetramethylsilane

[++] m = multiplet; q = quartet; d = doublet; quin = quintent; s = singlet; b = broad peak

‡ · benzylic methylene and H-5 signals overlap.

resonance at high field (< 2.0 p.p.m.) which would be expected from the isomeric benzonorbornenes.

Their photochemical behavior also supports the cyclobutane structure for these adducts, and in addition, allows an assignment of the location of the nitrile group. Irradiation of either of the nitriles through Vycor resulted in formation of a mixture of two. This reaction is interpreted by the mechanism shown in Scheme IV

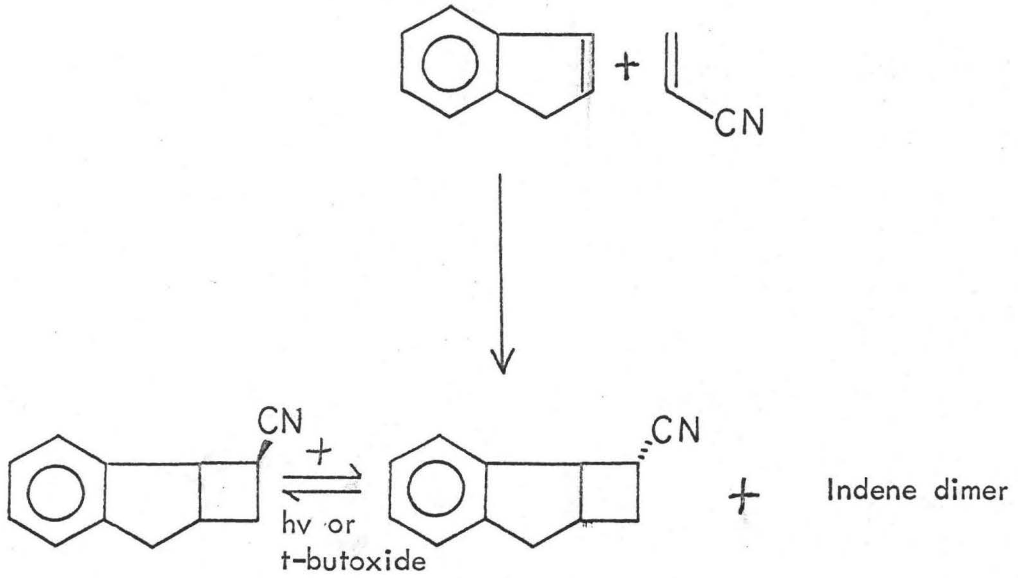


Decomposition to indene and acrylonitrile

SCHEME IV

Excitation followed by uncoupling of the C_1-C_7 bond (numbering as shown), rotation about the C_6-C_7 bond, and closure to regenerate the four-membered ring seems to be a reasonable sequence. The photolyic isomerization would not occur by this mechanism if the nitrile group were at C_6, and the reaction therefore allows us to place the substituent at C_7. Hence these products are the cis- and trans-isomers at 7-cyano-2,3-benzobicyclo $[3.2.0]$ hept-2-ene (XV) and (XVI) (Scheme V). Prolonged irradiation caused other products to form, probably via decomposition of the cyclobutanes to indene and acrylonitrile.

SCHEME V



XV 45% XVI 50% 5%

It was noted that one resonance (assigned to H_1) in the nuclear magnetic resonance spectra of these isomers was at lower field in one of the isomers. This allowed a tentative assignment of stereochemistry, a point to which we will return later.

It was considered that equilibration studies might help in assigning the stereochemistry, and (XV) and (XVI) were equilibrated with t-butoxide: The ratio of (XV): (XVI) was 30:70 at 25°, corresponding to a small free energy difference at 0.5 Kcal/mole, and was of no help in settling the stereochemical problem.

PHOTO-CONDENSATION OF INDENE AND ACRYLONITRILE

Irradiation of indene and acrylonitrile in the absence of acetophenone, and with a Vycor filter so that indene was the sole absorbing species, led to the formation of three quite different adducts from the sensitized reaction, with retention times at 2.5, 3.3 and 3.8 min (see experimental). The major 2.5 min component was labile and was obtained by careful chromatography on silica gel. It had infrared absorption at 2240 cm^{-1} (saturated nitrile), and in the nuclear magnetic resonance spectrum, resonances* appeated at : 1.10, 3H (methyl), doublet (J=7.0); 3.0 and 3.6, 1H each (methines), mutliplets; 4.35 and 6.88, 1H each (vinylic), multiplets; 7.25 and 7.59, 4H (aromatic), multiplet, and was assigned the

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* The chemical shifts of all nuclear magnetic resonance spectral data will be given in parts per million (p.p.m.) downfield from tetramethylsilane. Coupling constants (J) are given in cycles per second (c.p.s.).

structure (XVII). This was a liquid, which gradually but cleanly isomerized to the 3.8 min component on standing at room temperature. The rate of isomerization was accelerated on heating or on adding triethylamine. Above data suggests that the compound is 2-(1-indenyl)propionitrile (XVII).

The 3.8 min component was assigned the structure (XVIII), also on the basis of the nuclear magnetic resonance spectrum, which showed resonances at: 1.56, 3H (methyl), doublet (J=7.0); 3.26, 2H (methylene), multiplet; 3.52, 1H (methine), quartet (J=7.0); 6.44, 1H (vinylic), triplet; 7.20, 4H (aromatic), multiplet. The location of the cyanoethyl substituent in the indene nucleus was assigned on C_3 rather than C_2, since it is known that 1-alkylindenes undergo base-catalyzed rearrangement to the corresponding 3-alkylindenes(62). Furthermore, it is known that protons at C_1 and C_3 of indene can be exchanged by treatment with deuterium oxide and triethylamine, while the C_2 proton is unaffected(63), this product was treated with triethylamine and deuterium oxide in dioxan at 20°. The doublet at 3.26 had disappeared in 27 hr, but there was no change in the vinylic peak, which further confirmed structure (XVIII) for the 3.8 min product.

On alumina, (XVIII) isomerized to a conjugated unsaturated nitrile, m.p. 114-115°, which had infrared absorption at 2201 cm^{-1} (conjugated nitrile), and the ultraviolet spectrum* had λmax (EtOH) 274 mμ, log ϵ 4.20. The nuclear magnetic resonance spectrum of this product is consistent

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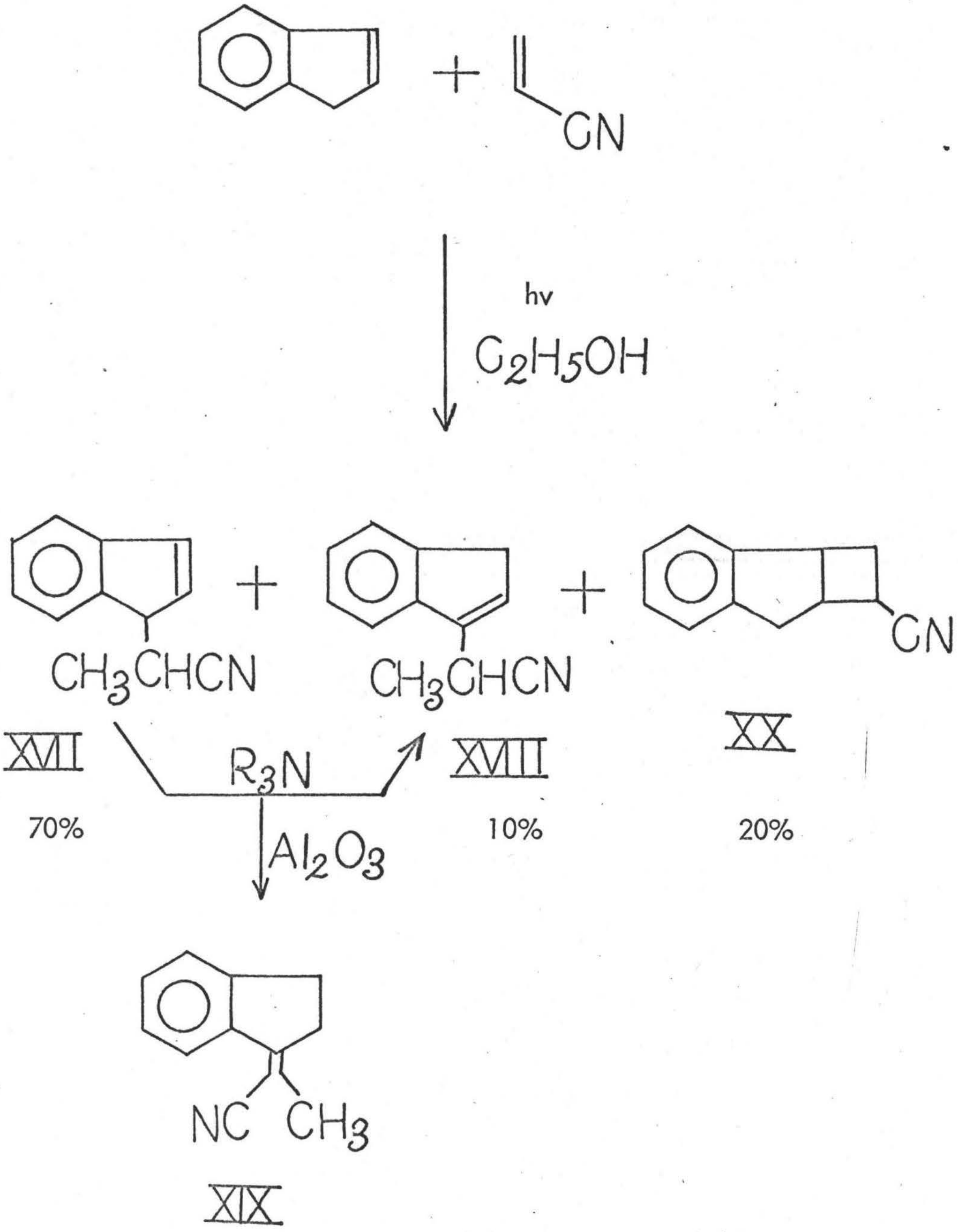
* Compare cis-cinnamonitrile which has λmax 273 mμ, log ϵ 4.22(64).

SCHEME VI


CN
hv
C_2H_5OH
CH_3CHCN
CH_3CHCN
CN
XVII
70%
R_3N
XVIII
10%
XX
20%
Al_2O_3
NC
CH_3
XIX

with structure (XIX), having resonances at 1.99, 3H (methyl), singlet; 2.89 4H (methylenes), multiplet; 7.27, 3H (aromatic), multiplet; and 8.28, 1H (aromatic), doublet of doublets (J=6.5 and 3.0). It is interesting to observe that one proton of the aromatic system was shifted well downfield from the remaining three aromatic protons. The similar downfield shift of one proton has been reported(65) in compounds related to (XIX), and its observation here assures us of the cis-relationship of the nitrile and phenyl groups.

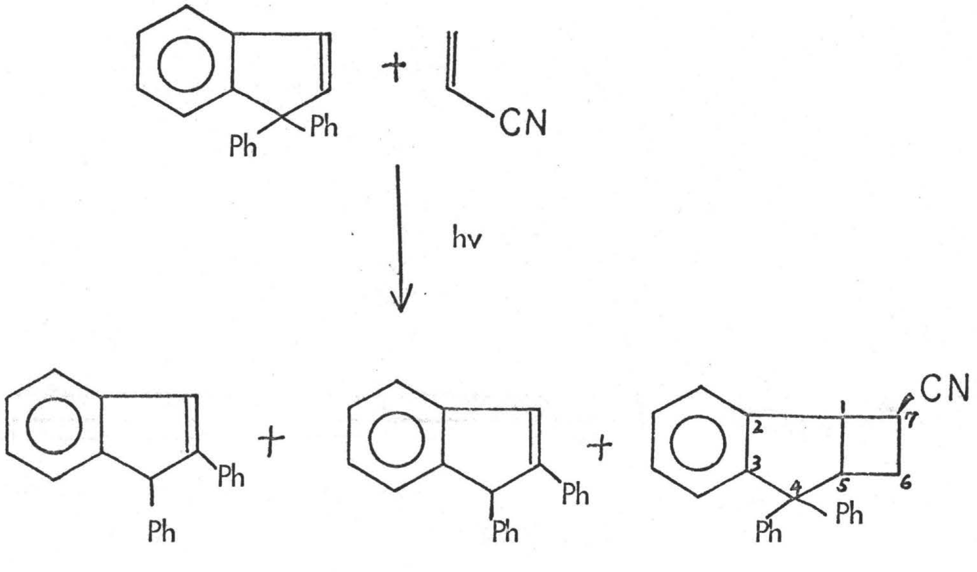
The component of retention time 3.3 min was difficult to obtain pure, and the nuclear magnetic resonance spectrum alone was not of great value in assigning the structure. It was possible to exclude the benzonorbornene system, as no resonance at high field (<2.0)(61) were observed. The nuclear magnetic resonance spectrum did resemble the spectra of the two adducts of the sensitized addition although it was not identical with either of them; since the latter were subsequently shown to be cyclobutane derivatives we assign structure (XX) to the 3.3 min adduct, but do not specify the stereochemistry of the cyano-group.

PHOTOLYSIS OF 1.1-DIPHENYLINDENE AND ACRYLONITRILE

Direct irradiation of 1,1-diphenylindene and acrylonitrile gave a cyano-cylobutane adduct (XXI), in addition to the products of phenyl migration, 1,2- and 2,3-diphenylindenes(25).

The nuclear magnetic resonance spectrum of the adduct (XXI) is given in Table I. The same adduct obtained from photolysis of 3-deuterio-

1,1-diphenylindene and acrylonitrile showed no signal at 4.18, this indicates that the 4.18 peak is due to H_1 in this adduct. The stereochemistry of this adduct is assigned as 4,4-diphenyl-7-cyano-2,3-bicyclo [3.2.0] hept-2-ene as shown in Scheme VII, applying the same argument used in the case of the cyclobutanes (XV), (XVI), (XXII) and (XXIII) as discussed in the next section.



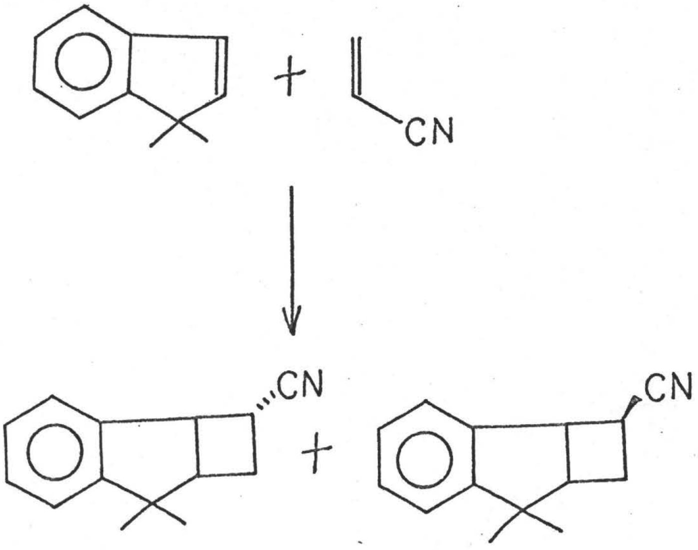
XXI

SCHEME VII

PHOTO-ADDITION OF 1,1-DIMETHYLINDENE AND ACRYLONITRILE

Direct irradiation and acetophenone sensitized photolysis of 1,1-dimethylindene with acrylonitrile gave the same two adducts which were identified as cis- (XXII) and trans- (XXIII), 4,4-dimethyl-7-cyano-2,3-benzobicyclo [3.2.0] hept-2-ene (Scheme VIII).

The mass spectra (Appendices I and III) of these adducts were in agreement with either cyclobutane or benzonorbornene derived structures(59,60) having very weak molecular ion peaks of m/e 197, and a base peak at m/e 144, which corresponded to M-53 (derived from a retro-Diels-Alder type fragmentation, see Scheme III). However, consideration of the nuclear magnetic resonance spectral data (Table I) eliminates the benzonorbonene structure and allows a tentative assignment of nitrile group stereochemistry in these adducts.



XXII XXIII

SCHEME VIII

First, the cyano-group is assigned to the C_7 rather than the C_6 position, since the chemical shift of the H_5 proton was similar to that of the cyclobutanes (XV) and (XVI), but not (XX). The methine proton resonance at lowest field (close to 4.0) was shown to be that of H_1, the benzylic methine, from the adduct (XXI) obtained from 3-deuterio-1,1-diphenylindene and acrylonitrile (see above). Since the deshielding effect of the cyano-group should be stronger for a vicinal proton on the same side of the four-numbered ring, and the H_1 resonance of the adduct (XXII) was seen at somewhat lower field than the corresponding epimer (XXIII), hence suggested that H_1 is cis to the cyano-group is (XXII), and trans- in (XXIII). Consistent with this argument is the fact that the H_1 signal in (XXII) is essentially a doublet (J = 6.5), while (XXIII) has the signal as a broad quintet. In the case where H_1 is cis to the cyano-group, it will strongly couple to one other proton H_5, and J will be a vicinal cis-coupling constant*. Examination of a model** shows that in this isomer the dihedral angle between the bonds to H_1 and H_7 is close to 90° and should cause negligible coupling of these protons(67).

On the other hand, the structure in which H_1 and the cyano-group are trans will have H_1 cis-coupled to two vicinal protons H_5 and H_7, and the signal from H_1 should be more complex than a doublet. Hence on the basis of these features in the nuclear magnetic resonance spectra, adduct (XXIII) is assigned the cis-configuration of the five-membered ring and the cyano-group. This is further confirmed by a spin-decoupling experiment. The H_1 proton (broad quintet) was simplified to a sharp triplet, when the H_7 proton was irradiated, indicating that they have a strong coupling to each other.

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* Steinmetz, Hartmann, and Schenck(66) give cis-vicinal coupling constants ranging from 6.7 to 11.5 for a series of cyclobutane derivatives.

** Courtauld Atomic Models, available from Griffin and George Limited, Wembley, Middlesex, England.

PHOTO-CONDENSATION OF NAPHTHALENE AND ACRYLONITRILE

The photo-additions of naphthalene and indene to acrylonitrile in which the hydrocarbon absorbs radiation are interesting in that analogous products are formed in the two reactions.

Photolysis (Pyrex filter) of naphthalene and acrylonitrile in alcohol gave a product, which showed two peaks of retention times 2.4 and 2.8 min. when subjected to gas-liquid chromatography (Column A, 175°). The ratio of the peak areas varied with conditions, but was approximately 1:9 for short photolysis times with _t_-butyl alcohol as solvent. The two components were separated by chromatography on silica gel. The component giving the 2.4 min peak appeared to be a mixture of 1-naphthyl- and 2-naphthyl-2-propionitrile, as the nuclear magnetic resonance spectra had two methyl signals (doublets, J = 7.0), two methine resonances (quartet, J = 7.0), and complicated signals in the aromatic region. 2-(1-naphthyl)-propionitrile prepared by methylation of 2-(1-naphthyl)-acetonitrile with sodium amide(67a) and methyl iodide had methyl, methine, and aromatic proton resonances corresponding to one set of peaks in the nuclear magnetic resonance spectra of the 2.4 min component. From the latter mixture a crystalline compound, m.p. 64-66° from ethanol was isolated which gave rise to the second set of nuclear magnetic resonance peaks, and clearly is 2-(2-naphthyl)-propionitrile.

The component of retention time 2.8 min was obtained as a single compound, m.p. 98 - 99°, and had infrared absorption at 2235 cm^{-1} (saturated nitrile). The mass spectrum (Appendices I and V) of this product is consistent with either a cyclobutane or a benzobicyclo [2.2.2] octadiene type structure, having a very weak molecular ion of m/e 181, and a base peak at m/e 128 (corresponding to M-53), derived from a retro-Diels-Alder type fragmentation or cyclobutane ring fission (Scheme III),$^{(59,60)}$ which eliminated the $CH_2=CHCN$ fragment. However, the ultraviolet spectrum had λmax (EtOH) 269 mμ, logϵ 3.91, with some absorption to longer wave length than 300 mμ, suggesting that the aromatic ring was conjugated with a double bond*.

The nuclear magnetic resonance spectrum showed a multiplet at 7.14, 4H (aromatic), a multiplet at 3.54, 3H (methines), and a multiplet at 2.65, 2H (methylenes).

In the vinyl region, two doublets (J = 10) appeared at 6.63 (1H) and at 5.93 (1H). The doublet at higher field showed some further splitting, and spin-decoupling demonstrated that this was due to coupling with the protons of the methylene group. Thus, irradiation of the 2-proton muiltiplet at 2.65 caused the higher-field doublet to become sharper. Structure (XXIV) is consistent with the spectral data. The vinyl protons would be coupled with $J_{\underline{cis}}$ for ethylene, which is in the 6-14 range$^{(67)}$. The higher field doublet, assigned to the vinyl proton at C_5 might reasonably be expected to be coupled to a proton at C_7, but not to protons at C_8**. The spin-decoupling experiment therefore demonstrates that the methylene group is at C_7. This adduct (XXIV)

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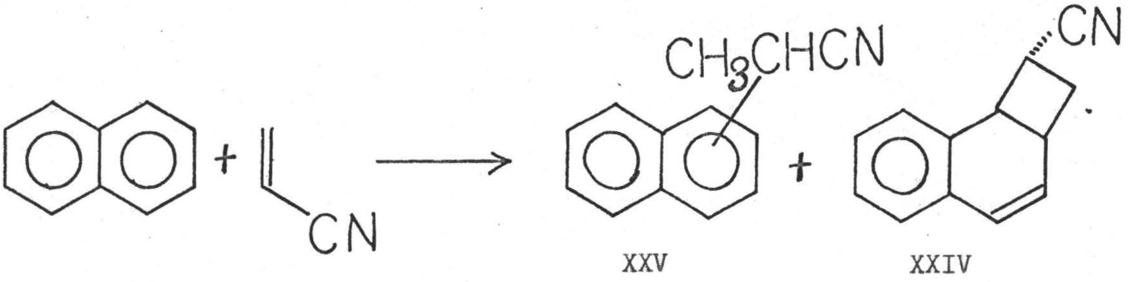
* The spectrum of 1,2-dihydronaphthalene has λmax (EtOH) 259 mμ, logϵ 3.98$^{(68)}$.

** Snyder and Franzus$^{(70)}$ report 4-bond coupling in 7-substituted norbornenes between the olefinic and anti-7 protons (J $\sim$0.8).

is 8-cyano-2,3-benzobicyclo [4.2.0] octa-2.4-diene (shown in Scheme IX) and one stereoisomer is formed, which has the trans-configuration, deduced from steric considerations of the unit cell packing(69).



SCHEME IX

Consistent with this conclusion is the observation that adduct (XXIV) could not be equilibrated with t-butoxide, in contrast to the cyanocyclobutanes from indene. This suggests the more stable, trans-structure for (XXIV). Comparison of space-filling models of cis-(XXIV) and the cis-adduct of indene (XV), shows that cis-(XXIV) is the more strained due to steric interaction of the aromatic ring with the cyano-group, and this could account for the difference in equilibrium position in the two systems.

Finally, it should be mentioned why the nuclear magnetic resonance spectral data point to the cyclobutane structure for (XXIV) rather than an isomeric benzobicyclo [2.2.2] octadiene derivative. First, as stated above, the ultraviolet spectrum of (XXIV) is very similar to 1,2-dihydronaphthalene(68). Second, it is difficult to see why a cyano-compound derived from benzobicyclo-[2.2.2] octane would not isomerize on equilibration with strong base. Third the nuclear mangetic resonance spectrum is not consistent with the latter structure*.

No reaction was observed on attempted (acetophenone, fluorene, and Michler's ketone) sensitization of the naphthalene-acrylonitrile addition.

The adduct (XXIV) when irradiated at 2537 A or with a Corex filter transmitting above 2500 A, decomposed to naphthalene (and presumably acrylonitrile). Several examples of aromatization by photo-elimination are known. Bicyclo [2.2.2] octadienones and benzobicyclo [2.2.2] octadienones undergo photolysis to give benzenes and naphthalenes, respectively, with the elimination of ketene(72). Likewise, elimination of carbene by irradiation of benzonorcaradiene derivatives(73) and dibenzonorcaradiene(74) gives the corresponding naphthalenes and phenanthrene. Of course, phenol and naphthol formation by photo-rearrangement of the substituent groups from cross-conjugated 4,4-disubstituted cyclohexadienenones and naphthalenones is a well known reaction(75). Reductive hydrogenolysis of 6-acetoxy-2,4-cyclohexadiene-1-one under ultraviolet irradiation with the formation of phenols has also been reported(76).

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* For example, the bridgehead protons of benzobicyclo[2.2.2] octadiene are further downfield (3.91) than any methine resonance in this adduct. Also the splitting of the vinyl resonances is inconsistent with the bicyclo-[2.2.2] octane system(71).

Indene and naphthalene revealed similar photochemical behavior when photo-condensed with acrylonitrile under directed irradiation, as described in Parts (2) and (5) in the results. In order to determine the nature of the excited state (or states) which undergo these photo-reactions, several experiments were carried out. These included on studies of the aromatic solvent induced chemical shifts, fluorescence quenching, the effect of solvent, as well as deuterium labelling experiments. The experimental results on this mechanistic work will be described in the following section.

PART III : MECHANISTIC RESULTS

INVESTIGATION OF POSSIBLE GROUND-STATE INTERACTION BETWEEN THE REACTANTS

Two methods were employed to study this interaction.

(I) Use of nuclear magnetic resonance techniques - observation of the aromatic solvent induced chemical shift.

The aromatic solvent induced chemical shifts* in nuclear magnetic resonance spectra is a common phenomenon in systems containing a polar solute and an aromatic solvent(77,78). Its origin is attributed to the formation of a very weak coordinated complex between the polar solute and aromatic solvent.

In order to establish the mechanism of the photo-addition reactions of aromatic hydrocarbons and acrylonitrile, it is very important to consider whether light is absorbed by the aromatic hydrocarbons, or by a complex formed from the aromatic hydrocarbons and acrylonitrile.

In a dilute solution of acrylonitrile in various aromatic hydrocarbons, a profound solvent shift was observed. Table II summarizes the corresponding $\Delta\delta$ values* for the three non-equivalent protons (labelled Ha, Hb, and Hc) of acrylonitrile, which is in the order : Hb > Hc > Ha

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* The changes in proton chemical shift, $\Delta\delta$, which occur when a polar molecule is transferred from an "inert" solvent such as carbon tetrachloride to an aromatic solvent (for example, benzene) is called the aromatic solvent induced chemical shift. These changes are usually geometrically specific; that is only protons bearing a definite relationship to the polar function suffer a shift(77,78).

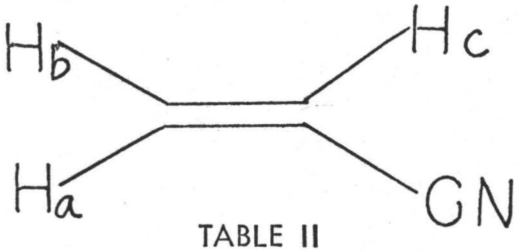


TABLE II

The proton chemical shift* of acrylonitrile (5 mole %) in aromatic hydrocarbon solutions

Solvent	Ha	$\Delta\delta$	Hb	$\Delta\delta$	Hc	$\Delta\delta$
Cyclohexane	369.8	0.0	358.2	0.0	334.0	0.0
Benzene#	311.5	+58.3	290.5	+67.7	269.5	+64.5
Indene	322.5	+47.3	300.0	+58.2	279.5	+54.5
1,1-dimethylindene	336.5	+33.3	317.5	+40.7	295.0	+39.0

* In c.p.s. measured at 60 Mc/s. relative to tetramethylsilane internal reference. "+" sign means an upfield shift, and "-" sign, a down field shift.

\# Schneider(80) reported the shifts of +42.0, +50.6, and +47.9 c.p.s. for the Ha, Hb, and Hc protons on changing the solvent from neopentane to benzene.

These relative shifts have been attributed as a greater tendency for Hb proton to be located nearer the center of the solvent aromatic ring. The assumption here is that the polar group tends to lie off the aromatic ring and the solute (acrylonitrile) and the aromatic solvent molecule prefer to have their molecular planes parallel as illustrated in Fig.-1(80).

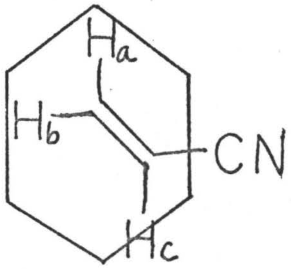


FIG.-1

TABLE III

The acrylonitrile proton shifts in different solvents containing indene*

Solvents	Ha	$\Delta\delta$	Hb	$\Delta\delta$	Hc	$\Delta\delta$
Cyclohexane#	369.8	+ 0.0	358.2	0.0	334.0	0.0
Cyclohexane	352.2	+17.6	337.0	+21.2	313.5	+20.5
Ethanol	368.5	+ 1.3	359.0	- 0.8	334.5	- 0.5
tert-butyl alcohol	366.5	+ 3.3	356.5	+ 1.7	324.5	+ 9.5

* Mole ratio (acrylonitrile/indene) = 1:9

\# No indene added

TABLE IV

The acrylonitrile proton shifts in different solvents containing 1,1-dimethylindene*

Solvent	Ha	$\Delta\delta$	Hb	$\Delta\delta$	Hc	$\Delta\delta$
Cyclohexane#	369.8	0.0	358.2	0.0	334.0	0.0
Cyclohexane	344.0	+25.8	327.0	+31.2	304.0	+30.0
Ethanol	366.5	+ 3.3	357.0	+ 1.2	332.5	+ 1.5
tert-butyl alcohol	356.0	+13.8	342.5	+15.7	320.0	+14.0

* Mole ratio (acrylonitrile/dimethylindene) = 1 : 9

\# No dimethylindene added

TABLE V

The acrylonitrile proton shifts in different solvents containing naphthalene*

Solvent	Ha	$\Delta\delta$	Hb	$\Delta\delta$	Hc	$\Delta\delta$
Cyclohexane#	369.8	0.0	358.2	0.0	334.0	0.0
Cyclohexane	356.8	+13.0	341.0	+17.2	318.5	+15.5
Ethanol	377.0	- 6.2	368.0	- 9.8	344.5	- 9.5
tert-butyl alcohol	369.5	+ 0.3	359.0	- 0.8	337.5	- 3.5

* Mole ratio (acrylonitrile/naphthalene) = 1:1

\# No naphthalene added

Furthermore, the magnitude of the solvent shifts also decreased in order: benzene > indene > dimethylindene, which is consistent with the known fact that introduction of substituents tends to decrease the solvent shifts(79).

Table III to V summarize the solvent shifts of acrylonitrile in dilute solutions of acrylonitrile-aromatic compound mixtures in different solvents. It turned out that the shifts for the different acrylonitrile protons is in a different order in alcohol solution. In addition, drastic reductions of the magnitude of the solvent shifts were also observed.

From this nuclear magnetic resonance data we can conclude therefore that some kind of interaction does exist between acrylonitrile and the aromatic hydrocarbons in solution. This interaction is presumably similar to that in the benzene-acrylonitrile system(80) and should be weak. Since the shifts are reduced in polar solvents, this probably means that the interaction is even weaker in these solvents, e.g., ethanol. Since most of the photochemistry was performed using ethanol as the solvent, we will assume that these ground state interactions are insignificant from the viewpoint of the photo-reaction mechanism.

(2) Ultra-violet spectra of acrylonitrile-aromatic hydrocarbon mixtures.

It has been shown that the photo-addition of maleic anhydride to benzene involves photo-activation of an intermediate charge-transfer complex rather than individually photo-activated benzene or maleic anhydride molecules(81). On the other hand, the photo-additions between benzene and N-substituted maleimide involves $n \rightarrow \pi^*$ transitions in the largely complexed N-substituted maleimides rather than charge transfer(42).

In order to establish the mechanism of the acrylonitrile aromatic hydrocarbon photo-addition, it is important to make a distinction between the two possible primary activation processes, namely, photo-activation of

(i) aromatic hydrocarbons

or

(ii) an acrylonitrile-aromatic hydrocarbon charge-transfer complex.

The extinction coefficients of naphthalene and indene, respectively, remain unchanged in solutions of varying acrylonitrile concentration, and furthermore, no new absorption bands were observed. These results indicated that no ground state charge-transfer complex was formed.

FLUORESCENCE QUENCHING OF AROMATIC COMPOUNDS BY ACRYLONITRILE

In the investigation of the excited state interactions of acrylonitrile and naphthalene, the effect of added acrylonitrile on the naphthalene fluorescence was studied. It was found that in solution naphthalene fluorescence was quenched by acrylonitrile very efficiently (Table VI) and the quenching obeys Stern-Volmer kinetics (see discussion).

In the case of indene and dimethylindene, the quenching is even more efficient (Tables VII and VIII), and the rates of quenching approach

TABLE VI

The quenching of naphthalene fluorescence by acrylonitrile

C_q (mole litre^{-1})*	I≠	I_o/I
0.0	88.0	1.00
0.2	68.5	1.28
0.4	56.0	1.57
0.6	43.5	2.02
0.8	36.5	2.41
1.0	33.2	2.65
1.2	28.5	3.09
1.4	26.8	3.28
1.6	23.2	3.79
1.8	21.5	4.09
2.0	19.5	4.51
2.2	19.2	4.58
2.4	18.0	4.89
2.6	16.8	4.24
2.8	15.6	5.64
3.0	14.66	6.03

* Quencher concentration

≠ I = fluorescence intensity with added acrylonitrile (quencher)

I_o = fluorescence intensity in the absence of quencher.

TABLE VII

The quenching of dimethylindene fluorescence by acrylonitrile

C_q (mole litre^{-1})	I	I_o/I
0.00	49.7	1.00
0.05	27.5	1.81
0.10	20.5	2.43
0.20	11.1	4.48
0.25	10.3	4.83
0.30	7.7	6.46
0.40	5.8	8.58
0.45	5.7	8.73
0.60	4.0	12.44
0.70	3.5	14.21
0.80	3.3	16.56
1.00	2.5	19.90

TABLE VIII

The quenching of indene fluorescence by acrylonitrile

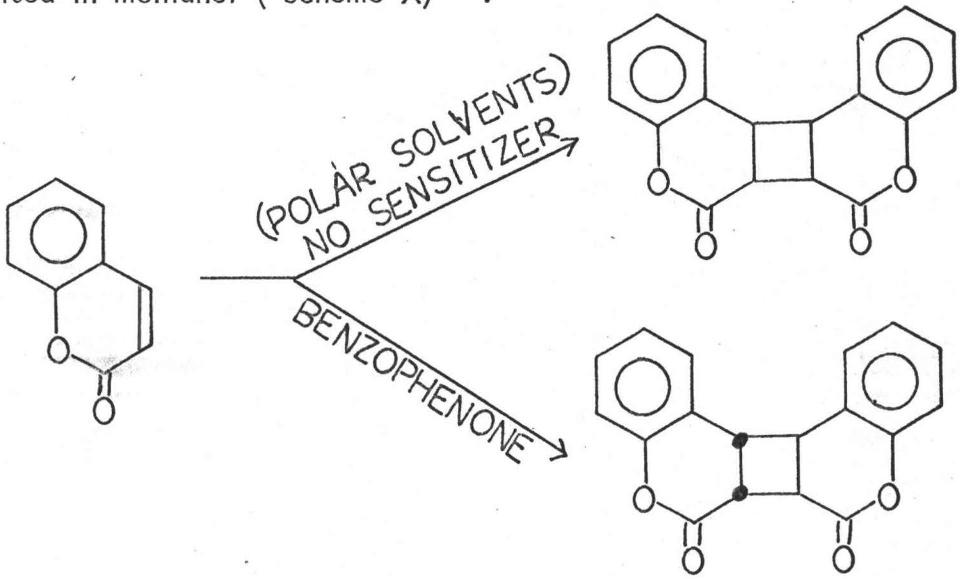
C_q (Mole litre^{-1})	I	I_o/I
0.00	54.35	1.00
0.10	16.0	3.4
0.20	9.4	5.75
0.30	5.9	9.15
0.40	4.2	12.8
0.50	3.3	16.5
0.60	2.5	21.8
0.70	2.2	23.7
0.80	1.95	27.9
0.90	1.55	35.1
1.00	1.44	39.0

The impact of these results will be considered in the Discussion Section the diffusion controlled rate (see discussion).

Fluorescence quenching has been studied extensively during the last two decades, and an excited state quenchee-ground state quencher complex has been shown to be responsible for this phenomenon in many cases. This complex has been termed an "exciplex state" (see discussion).

SOLVENT EFFECT

Photochemical reactions are often found to be solvent dependent. For example, in the direct photo-dimerization of coumarin, the head-to-head anti-dimer is formed in non-polar solvents to the virtual exclusion of the syn dimer. The ratio of anti to syn dimer decreases in polar solvents, and is reversed in methanol (Scheme X)(82).



SCHEME X

The photo-addition reaction of naphthalene and acrylonitrile was found to be solvent-dependent. The product distribution was highly dependent

TABLE IX

Solvent effect on the naphthalene-acrylonitrile photo-addition

Solvent	$\epsilon^{\#}$	pKa	Relative %≠ (XXV)	relative rate*
cyclohexane	2.02	-	0	0.00
dioxan	2.21	-	0	0.02
acetonitrile	37	-	0	0.05
tert-butyl alcohol	10.9	20.0	7.3 (±0.4)	1.39
iso-propyl alcohol	18.3	-	8.8 (±0.7)	1.41
dioxan-water (1:1)	-	-	13.5 (±1.6)	0.16
ethanol	24.3	19.1	21.9 (±0.2)	1.35
2-chloroethanol	25.8	14.31	-	7.49
2,2,2-trichloroethanol	-	12.24	53.1 (±0.6)	1.86
2,2,2-trifluoroethanol	-	12.37	67.8 (±0.4)	7.89
methanol	32.63	16.0	39.6 (±0.2)	1.00
acetic acid	6.15	4.76	19.3 (±1.1)	0.56
formic acid	58.5	3.77	74.2 (±0.1)	0.58

* Measured by vpc using p-bromobenzophenone as an internal standard

\# ϵ = dieletric constants of solvents

≠ The balance of the product is cyclobutane adduct (XXIV)

TABLE X

Solvent effect on indene-acrylonitrile photo-addition

Solvent	Relative %# (XVII + XVIII)	Relative rate*
Cyclohexane	83.1 (± 0.5)	0.70
dioxan	80.6 (± 0.8)	1.03
acetonitrile	75.8 (± 0.4)	1.15
methanol	77.7 (± 1.0)	1.00
ethanol	79.1 (± 0.7)	1.15
iso-propanol	81.7 (± 1.4)	1.22
tert-butyl alcohol	78.4 (± 0.3)	1.06
acetic acid	80.4 (± 0.4)	1.00

* Measured by vpc using benzophenone as an internal standard

\# The balance of the product is cyclobutane adduct XX.

on the nature of solvent and its dielectric constant and acid strength (Table IX).

Three effects can be noticed:

1. No substituted naphthalenes (XXV) were formed in aprotic solvents, such as cyclohexane, hexane, or acetonitrile.
2. In protic solvents, the yield of the substituted naphthalenes (XXV) increased almost invariably with increasing dielectric constant and acidity of the solvent.
3. The relative rates of reaction were also solvent-dependent. The rate was much higher in the protic solvents relative to the aprotic ones.

In the case of indene, no profound solvent effect could be observed (Table X). The relative rates of reaction varied slightly with various solvents; however, the product ratio was virtually identical in all the solvents studied.

DEUTERIUM-LABELLING EXPERIMENTS

Since the solvent demonstrated a very specific influence on the naphthalene-acrylonitrile photo-addition, it was logical to study the role the solvent plays in the reaction.

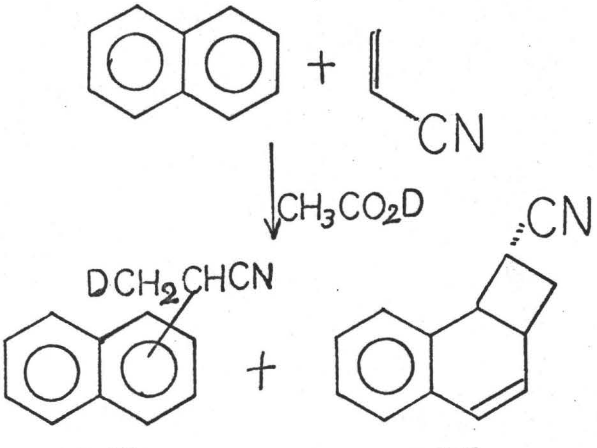
The reaction was carried out using deuterium acetate as solvent and gave products, in which deuterium was incorporated in the substituted naphthalenes (XXV) (Scheme XI).

TABLE XI

m/e	relative intensity
182 (M^+, molecular ion)	100.0
183 $(M + 1)^+$	15.7*

* The relative intensity of the $(M+1)^+$ peak, calculated from natural abundances of isotopes, is 14.56.

SCHEME XI



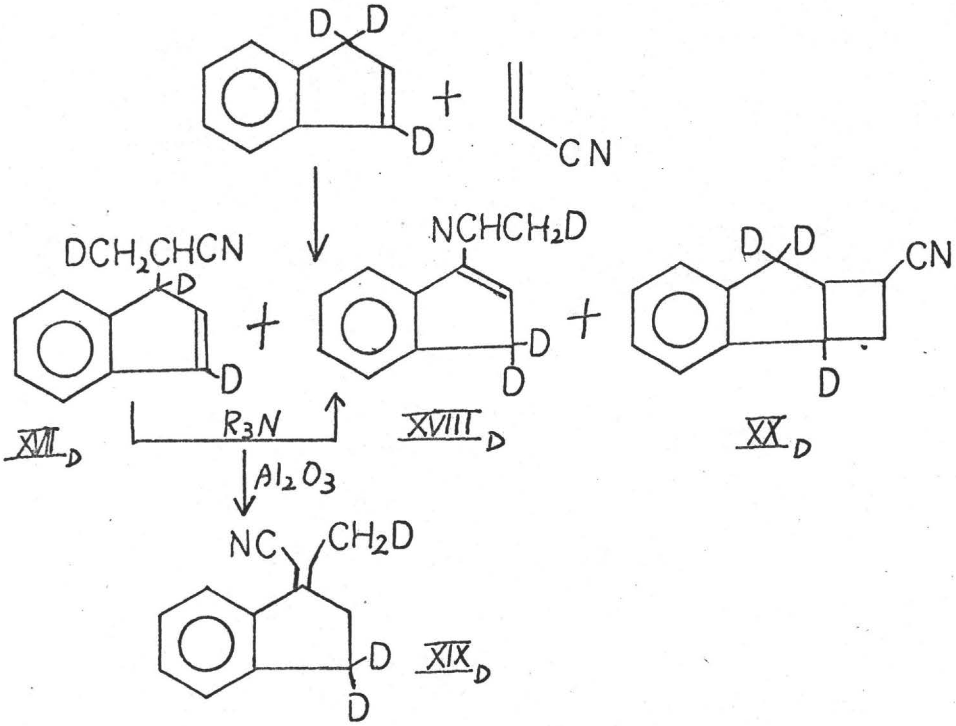
XXV$_D$ XXIV

The nuclear magnetic resonance spectral of the substituted naphthalenes isolated had two methyl signals at 1.64 and 1.71 (broad doublet); two methine resonances at 3.91 and 4.49 (triplet); and complicated signals in the aromatic region. This is consistent with the assigned structure that the deuterium was incorporated in the methyl-protons. The areas ratio of the methyl- and methine-proton peaks was 2:1, hence only one deuterium was incorporated. This was further confirmed from mass spectral data (Table XI and Appendix VI).

This experiment therefore showed that one proton of the methyl-group in the substituted naphthalenes had come from the solvent, and furthermore was the most acidic proton in the solvent.

In the case of the indene-acrylonitrile photo-addition, in which solvents apparently did not have any great effect, the reaction was carried out using indene-1,1,3-d_3 and the result is shown in Scheme XII

SCHEME XII



The nuclear magnetic resonance spectra of the products isolated (that is, XVIIId and XIXd) were all consistent with the assigned structures (Table XII). This clearly demonstrated that in the indene-acrylonitrile photo-addition, one proton of the methyl-group in the substituted indenes is derived from the methylene protons of indene itself, and does not originate in the solvent used.

TABLE XII

Nuclear magnetic resonance spectra of adducts XVIIId and XIXd

Proton signal	XVIIId	XIXd
methyl-	1.65,2H (broad doublet)	2.05,2H(broad singlet)
methylene	3.85,2H (broad triplet)	2.90,2H(broad doublet)
methine-	3.85,1H(broad triplet)	-
olefinic	6.56,1H (broad singlet)	-
aromatic	7.30,4H (multiplet)	7.26 & 8.35, 4H (multiplet)

PART IV. DISCUSSION

In the results section, two kinds of work were described; the first part was concerned with the separation and identification of the products of photo-additions of indene derivatives or naphthalene and acrylonitrile, while the latter section dealt with mechanistic work. This discussion will deal mainly with mechanistic problems. However, it is worthwhile to briefly consider the synthetic utility of the reactions which were discovered.

SYNTHETIC UTILITY OF ACRYLONITRILE-AROMATIC HYDROCARBON PHOTO-ADDITIONS

Scheme VI shows two indene derivatives which are readily obtained by this photochemical route; they are (XVIII) and (XIX). If the 3-substituted indene (XVIII) is the desired product, the photolysis mixture is evaporated, then heated with an amine to convert XVII to XVIII, and distilled. If the unsaturated nitrile XIX is required, the mixture after being heated is chromatographed slowly on alumina. The less stable indene derivative (XVII) and the cyclobutane (XX) can also be obtained, but their isolation requires careful work or recovery is poor.

The products of triplet sensitization (XV) and (XVI) are efficiently produced by the reaction in Scheme V, and their separation is not troublesome. These comments also apply to the products of the addition of 1,1-dimethylindene and acrylonitrile, which are the same in the direct and sensitized reactions.

From the naphthalene-acrylonitrile reaction, the cyclobutane derivative (XXIV) may be obtained by using a Pyrex filter and a hydroxylic solvent of low dielectric constant in the photolysis. If excitation is by shorter wavelength light, e.g. using a Corex filter, or a hydroxylic solvent of high dielectric constant is used, or both, the mixture of l- and 2-substituted naphthalenes (XXV) can be prepared.

THE MECHANISTIC ASPECTS OF ACRYLONITRILE - AROMATIC HYDROCARBON ADDITIONS

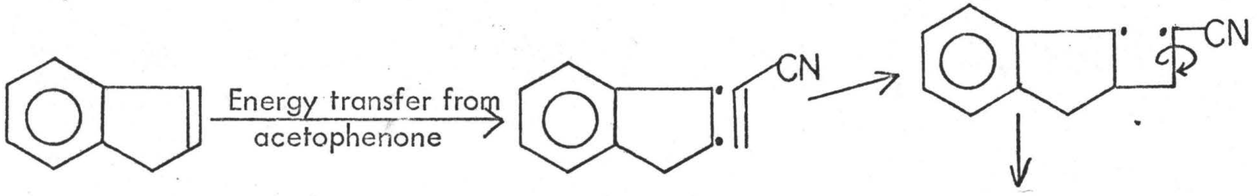
(a) The excitation process

As pointed out in the results section, it is reasonable that although weak "complexes" of the aromatic hydrocarbons are formed, as evidenced by nuclear magnetic resonance data, the species which is excited in these reactions is the unperturbed hydrocarbon. Participation in "collision" or "van der Waals" complexes should not alter the electronic structure of the hydrocarbon significantly. Also, ultraviolet absorption spectra showed no charge-transfer absorption. Therefore, in direct irradiations, the primary photo-activation process was the excitation of the ground state singlet ⟶ excited singlet of the hydrocarbons In the sensitized reactions, high energy triplet sensitizers with efficient intersystem crossing rate were used, so that excitation was to the excited triplet states of the hydrocarbons.

(b) Bond formation process

It is clear that in these photoadditions different mechanisms are operating, depending on whether the hydrocarbon absorbs light or triplet sensitizers are used. This difference is most striking in the case of indene and acrylonitrile (see Schemes V and VI).

Turro and Bartlett found that on photocycloaddition of dienes and halogenated ethylenes, a more stable biradical intermediate is produced, which then cyclizes to give cyclobutane derivatives.(83) The triplet sensitized reaction of indene and acrylonitrile can be depicted in terms of similar biradical mechanism (Scheme XIII).



SCHEME XIII

(XV) + (XVI)

Energy transfer from the triplet state of the sensitizer to the indene, followed by attack of indene triplet on acrylonitrile to produce the more stable biradical, which can close to a four-membered ring forming both epimers, as observed.

Since both acetophenone (E_T = 74 Kcal/mole)(84) and Michler's ketone (E_T = 61 Kcal/mole)(84) sensitized indene-acrylonitrile photo-addition gave the same products, this clearly demonstrates that the triplet excited species of indene (E_T = 59 Kcal/mole)(85) rather than acrylonitrile (E_T = 62 Kcal/mole)(86) is the reacting species.

The similar biradical mechanism can also be applied to explain the sensitized dimethylindene-acrylonitrile photo-addition. In the direct irradition of dimethylindene and acrylonitrile, the same adducts were obtained as in the sensitized reaction. This could be due to intersystem crossing of excited dimethylindene singlet to the triplet, followed by the same biradical mechanism. Naphthalene appears to be unreactive from the triplet. This may be because the reaction would involve loss of aromaticity (no such losses occur in the indene and dimethylindene cases).

The triplet-derived adducts were therefore not unexpected products; their formation is consistent with the "biradical rule" (83) for many triplet addition reactions.

The reactions observed on direct irradiation of indene and naphthalene, in particular the formation of the substituted indene and naphthalene derivatives, e.g., XVII, XVIII, and XXV, posed a more intriguing problem. It was suspected, in view of the relatively slow intersystem crossing of aromatic hydrocarbons (87) that these products might arise from reaction of singlet states. The first direct evidence to support this came from fluorescence quenching studies.

FLUORESCENCE QUENCHING STUDIES

It was found that the quenching in solutions of aromatic hydrocarbon fluorescence by acrylonitrile was very efficient (Table VI to VIII), and the quenching obeys Stern-Volmer kinetics (Figs II and III) . This shows that a bimolecular quenching process is operative, (88) and the following relationship applies, (88)

$$I_o/I = \phi_o/\phi = 1 + k_q \tau [A] \qquad (6)$$

where I_o/I and ϕ_o/ϕ are the relative fluorescence intensities and relative fluorescence quantum yields in the absence and presence of acrylonitrile $[A]$. K_q is the rate constant of bimolecular quenching $(1\ \text{mole}^{-1}\ \text{sec}^{-1})$ or aromatic hydrocarbon fluorescence by acrylonitrile, and τ is the measured fluorescence lifetime (sec) in the absence of A.

The apparent rate constant of quenching (K_q) derived from Eq.-6 using the

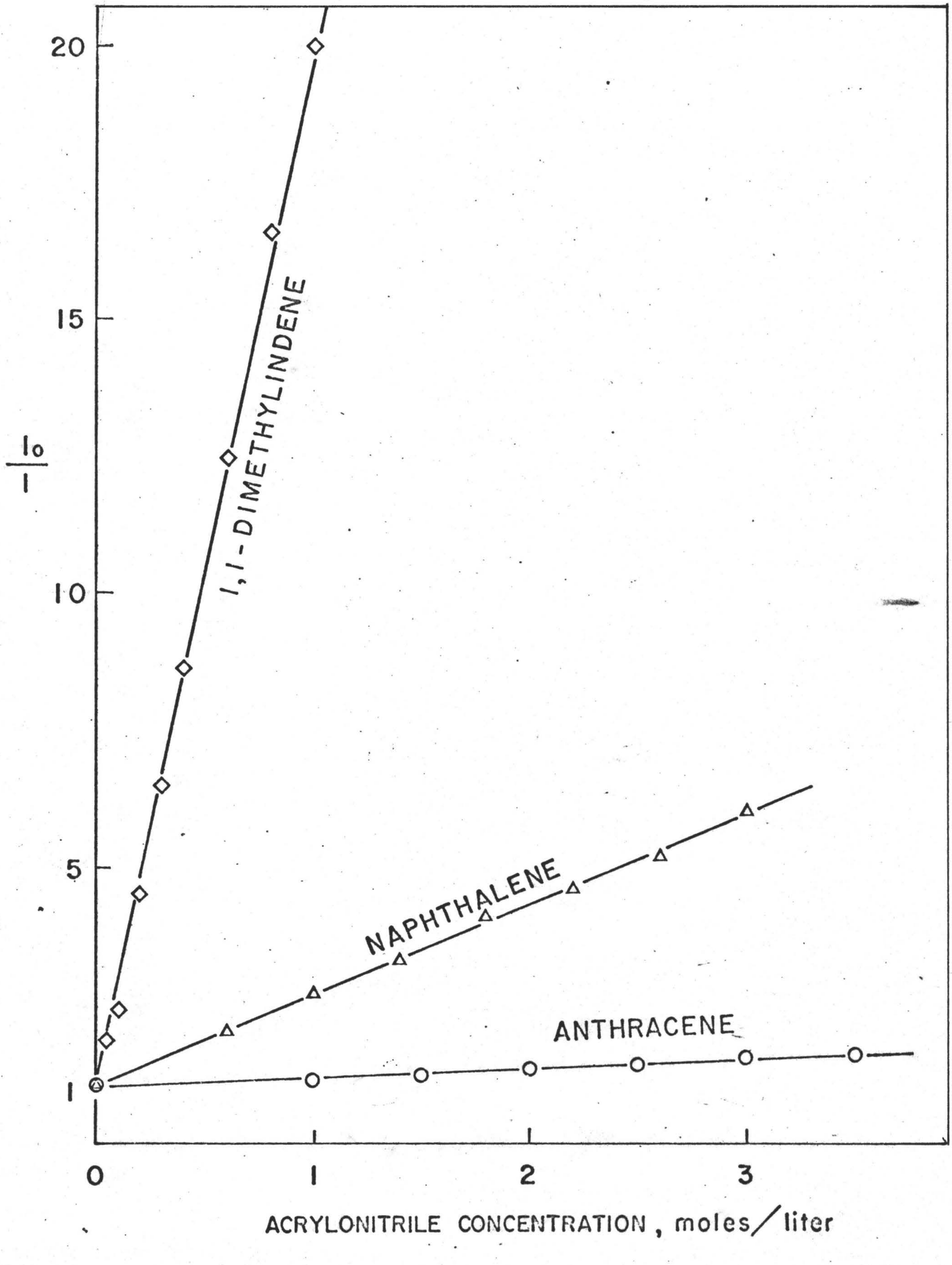


FIG-11: Plot of relative fluorescence intensity versus acrylonitrile concentration slope of the plot of I_o/I vs [A] (Fig. II) and a value of 10^{-7} sec.† for the lifetime of the naphthalene lowest excited singlet state gives a value of 1.72×10^7 litre mole^{-1} sec^{-1} in 95% ethanol at room temperature, which is between the reported K_q's in the quenching of naphthalene fluorescence by various dienes ($10^7 \sim 10^9$ Sec^{-1})$^{(89, 90)}$ and olefins (10^6 sec^{-1})$^{(91)}$. Comparison of this figure with the rate constant of intersystem crossing for naphthalene singlet excited state to triplet excited state (10^6 sec^{-1})$^{(87)}$, is very interesting, since it means that the acrylonitrile can intercept the naphthalene singlet at a rate competitive with intersystem crossing.

In the case of dimethylindene, the quenching is more efficient, and a slope of 18,9 is obtained (from Table VII and Fig. II). Assuming that the lifetime of singlet excited state of dimethylindene is on the order of 10^{-8} sec*, this gives a Kq of 18.9×10^8 litre mole^{-1} sec^{-1}, a value which approaches the diffusion controlled rate (5.4×10^9 litre mole^{-1} sec^{-1} at 25°)$^{(93)}$.

It is interesting to note that in the indene case, a non-linear curve is obtained when I_o/I is plotted against [A]. However, if the plot of I_o/I vs $[A]^2$ is made a straight line is obtained.

This result can be explained by a 1:2 stoichiometry between quenchee and quencher as was reported previously by Waker, Bednar, and Lumry for the indole-alcohol system$^{(94)}$. A Stern-Volmer expression derived from this 1:2

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* This is approximately the mean lifetime of the lowest singlet excited states for most of the organic aromatic compounds.

† A value measured by Mataga, Tamura and Nishimura$^{(92)}$ in various solvents, and is in agreement with several other reported values$^{(92)}$.

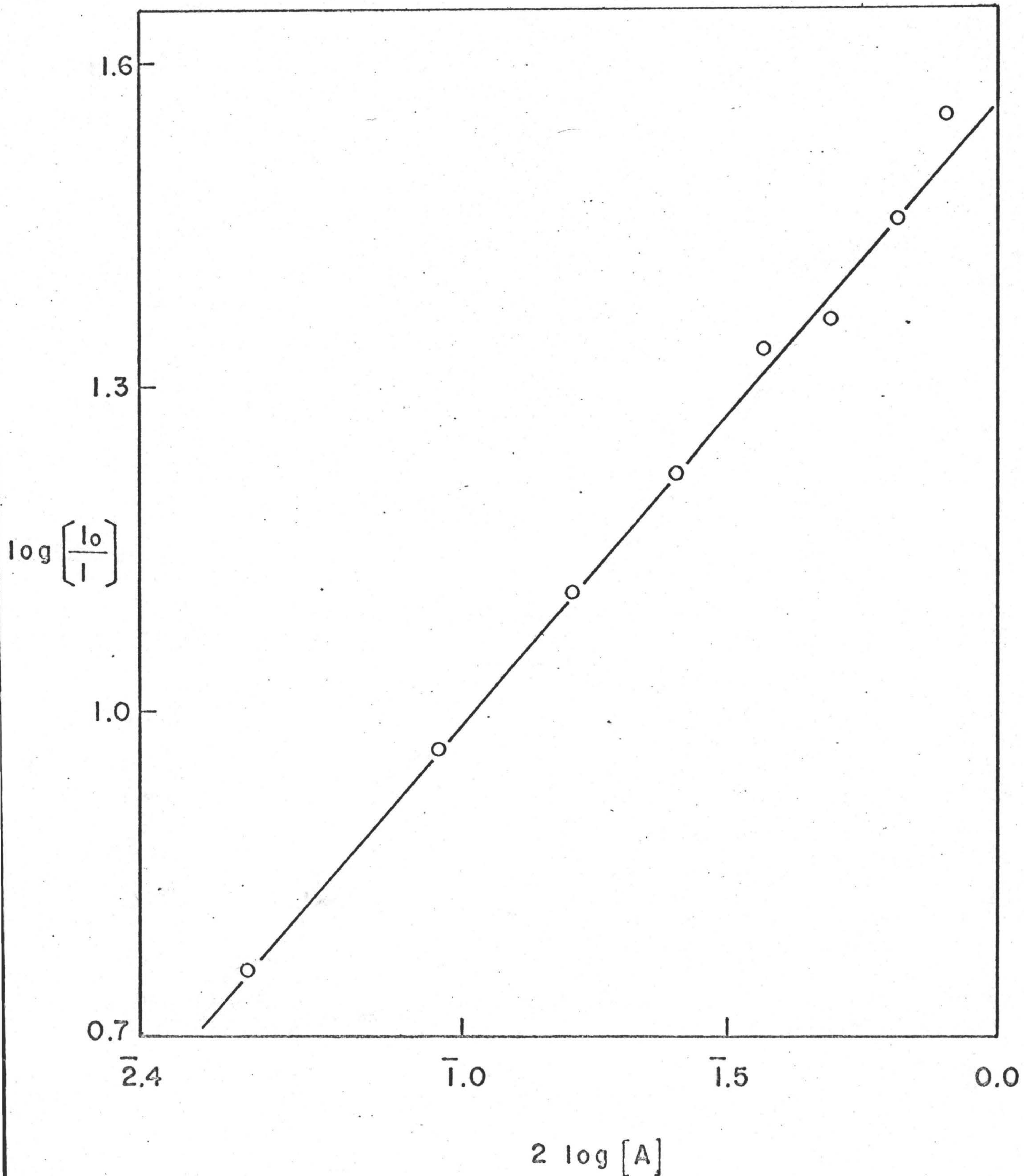

FIG-III : Log-Log plot of relative fluorescence intensity against $[\text{acrylonitrile}]^2$ (mole litre^{-1}) for indene stoichiometry is:

$$I_o/I = \phi_o/\phi = 1 + kq\,\tau\,[A]^2 \qquad (7)$$

therefore a plot of I_o/I vs $[A]^2$ produces a straight line. From this, the Kq of indene is calculated to be approximately 35×10^8 litre mole^{-1} sec^{-1}, a value which again approaches the diffusion controlled rate.

An examination of the ultraviolet absorption spectra of the two compounds shows that the 0-0 transition to the lowest excited singlet electronic level of acrylonitrile requires about 40 Kcal/mole more energy than that of naphthalene, and 20 Kcal/mole more than indene, thus straight energy transfer according to process (8) (where N represents a molecule of naphthalene, A is acrylonitrile, and an asterisk denotes excitation) would be a very unfavourable endothermic process, hence the quenching behavior of the aromatic hydrocarbon-acrylonitrile

$$N^* + A \longrightarrow N + A^* \qquad (8)$$

system is most readily rationalised on the basis of the mechanism used for exciplex[#](94) formation.

Possible schemes for decay of the exciplex include the following

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[#] The term "exciplex" is suggested to include all complexes formed between one molecule in an excited state and one or more unexcited molecules(94) and is intended to be non-specific as to the kind of binding forces involved(91).

$$(NA)^* \longrightarrow N + A + h\nu \qquad (9)$$

$$(NA)^* \longrightarrow N + A + \text{heat} \qquad (10)$$

$$(NA)^* \longrightarrow N + {}^3A \qquad (11)$$

$$(NA)^* \longrightarrow \text{products} \qquad (12)$$

$$(NA)^* \longrightarrow {}^1N + A \qquad (13)$$

where $(NA)^*$ = exciplex state between the aromatic hyrdocarbon (quenchee) and acrylonitrile (quencher),

^3A = triplet excited state of acrylonitrile

and ^1N = singlet excited state of the aromatic hydrocarbon.

In all experiments studied, no shifted fluorescence, such as would be expected from reaction (9) has been observed. If process (11) is important, photo-adducts characteristic of acrylonitrile triplets should be produced even under conditions where the intersystem crossing is unimportant. However, the triplet sensitized reactions presented previously rule out the possibility that the substituted indenes and naphthalenes arise from a triplet of acrylonitrile.

The significance of process (10) is not clear. However, if it is the major pathway for the decay of the exciplex, then acrylonitrile would facilitate non-radiative excited singlet → ground state singlet decay of the aromatic hydrocarbons, as is observed with dienes and fluorescence quenching of naphthalene(89).

Since the fluorescence quenching by acrylonitrile described above requires that exciplexes are formed in the systems studied, it is appropriate at this point to consider what is known about these species. This will introduce ideas needed in the postulation of a reaction mechanism, and the following discussion will lead to a description of the hydrocarbon-acrylonitrile complexes.

THE NATURE OF THE EXCIPLEX STATE

Recently, Hammond and co-workers (89,90) reported that the fluorescence of many aromatic compounds, and notably that of anthracene and naphthalene derivatives, is strongly quenched by conjugated dienes. The quenching is efficient, strong, and in some cases approaches the diffusion controlled rate.

From the results obtained from naphthalene-quenched dimerization of cyclohexadiene,(90) the same authors are able to show that quenching of the excited singlet states of aromatic hydrocarbons by conjugated dienes does not lead to production of major amounts of electronically excited states of the quenchers. These results are also compatible with the conclusion that no electronic excitation is transferred, but are not sufficiently precise to exclude the formation of small amounts of diene triplets. In some cases, the formation of new products having the composition of adducts from the quenchee and the quencher are observed(89,90) These new products are formed with a very low quantum yields, and their appearance parallels fluorescence quenching closely, so presumably the chemical combination is an occasional consequence of the destruction of singlet excited states of aromatic compounds by dienes.(90)

To explain this photochemical phenomenon,(95) Weiss first suggested that fluorescence quenching involves formation of a charge-transfer complex between quencher and quenchee. This notion has been further developed by Ferguson(96) and by Hochstrasser.(97)

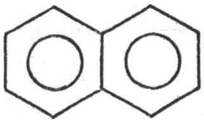
Although the generality of this mechanism is not certain, there is a great deal of evidence supporting it in special cases. For example, in the quenching of the fluorescence of a number of dyes (by certain anions) including uranin, quinin sulfate, and uranyl sulfate, it is found that the common anions may be placed in a series of decreasing quenching power.(98)

$$I^- > CNS^- > Br^- > Cl^- > C_2O_4^{=} > SO_4^{=} > NO_3^- > F^-$$

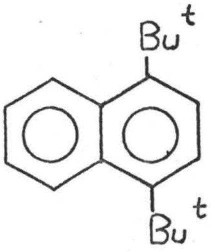
This series follows closely the trend of other charge-transfer phenomena, suggesting very strongly that the quenching is connected with the donor power of the anions.(98)

However, Orgel(98) points out that charge-transfer is not necessarily the only, or even the most usual, mechanism of fluorescence quenching in solution. Murrel and Tanaka (99) affirm the probable importance of other configurations in delocalizing excitation between partners in excited states, on the basis of their calculations of changes in electronic transition energies which occur on dimerization of various aromatic compounds.

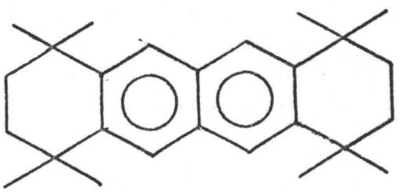
On studying the fluorescence quenching of aromatic compounds by dienes, Hammond and co-workers (89, 90) reported that addition of alkyl substituents to naphthalene reduces sensitivity to quenching. In the series XXVI - XXVIII, the rate constants for fluorescence quenching(by trans-piperylene) were 140x, 13x and 8.7×10^6 litre $mole^{-1}$ sec^{-1} respectively. While naphthalene and



XXVI



XXVII



XXVIII

1-methylnaphthalene had rate constants of 250x and 110 x 10^6 litre mole^{-1} sec^{-1} respectively, when 1,3-cyclohexadiene was used as quencher.

On the other hand, the addition of methyl groups as substituents on the diene in general increases the rate of quenching (Table XIII)(90)

Table XIII

Quenching of naphthalene fluorescence by dienes

diene	Kqx10^{-9} litre mole^{-1} sec^{-1}
2,5-dimethyl-2,4-hexadiene	3.96
1,3-cyclohexadiene	2.50
4-methyl-1,3-pentadiene	1.20
trans-2-trans-4-hexadiene	0.62
trans-2-cis-4-hexadiene	0.51
cis-2-cis-4-hexadiene	0.23
3-methylene cycolhexene	0.17
trans-2-methyl-1,3-pentadiene	0.11
trans-piperylene	0.11
cis-piperylene	0.092
2,3-dimethyl-1,3-butadiene	0.015

If we consider the aromatic compounds as acceptors, and dienes as donors, then the effect of methyl substituents follows closely the stability of charge-transfer complexes.(100)

However, since no sign of new emission due to complexes has been detected in these studies, Hammond constructs a model (instead of using the charge-transfer model), designed to account for some of the reactivity relationships observed.(90) The results turn out to be closely related to a model used by Salem(90) to calculate interaction energies in excited complexes.

$$\Phi \approx a\,\Psi(A^{*}\,.\,Q) + b\Psi(A.\;Q^{*})$$

where A is the aromatic compound; Q, the diene and asterisk denotes excitation; Φ is the total wave function for the complex. The $S \rightarrow {}^{1}S$ excitation energies of conjugated dienes are considerably greater than those of the quenchee, the contribution from the second configuration (A.Q*) will be expected to be rather small. However, at least a small amount of the electronic excitation is transferred to the quencher within the complex‡, presumably giving rise to the rapid internal conversion.(90)

A recent study of the influence of solvents on the fluorescence of complexes by Weller (101) adds considerably to the understanding of the mechanism of electron transfer reactions in the excited states.

Experiments carried out on the system of anthracene (acceptor) and diethylaniline (donor) in different solvents with increasing dielectric constant revealed two effects on the charge-transfer emission: that is, a red shift and a considerable decrease in intensity.(101)

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‡ This figure is arrived at by estimating that fluorescence with intensity as high as a few per cent of the emission from the parent hydrocarbons could be detected(90).

The strong decrease in intensity of the complex emission has been discussed in connection with the results of lifetime measurements on the same complexes in different solvents. It has been found that the mean lifetime of the excited complex, which is the order of100 nsec, is shortened by a factor of about three, when the solvent dielectric constant increases from 2 to 12, whereas, the relative intensity of the complex emission simultaneously decreases by about a factor of 40, so that ultimately, in highly polar solvents like acetonitrile ($\epsilon = 37$), no complex emission at all can be observed, although there is a strong quenching of anthracene fluorescence by the diethylaniline.(102)

Flash experiments in systems of polyaromatic hydrocarbons (anthracene, naphthacene, perylene, and coronene) and diethylaniline in solutions gives transient absorption spectra in which the species: A^- (acceptor anion), D^+ (donor cation), and ^3A (triplet excited state of acceptor) can be identified.(101) This suggests the electron transfer reaction to be:

$$^1A.....D \xrightarrow{K_q} (A_s^- ......D_s^+) \qquad (14)$$

where Kq is the rate constant, in which a partially solvated ion-pair is formed, as the prime cause of fluorescence quenching.

This ion-pair represents a geometrically quite arbitrary encounter complex of the solvated radical ions, both of them being in their characteristic doublet ground states. Its mean lifetime depends on the sum of the rate constants of all possible reactions by which it can disappear.

The calculated free energy changes, ΔG, of reaction $^{(14)}$ for almost all aromatic hydrocarbons are negative; therefore, reaction (14) indeed, will occur spontaneously at least in acetonitrile. In solvents of lower dielectric constants than acetonitrile, ΔG will eventually become positive, so that the rate of reaction (14) will decrease with decreasing dielectric constant of the solvent.$^{(101)}$

$$^{1}A \,.....\, D \xrightarrow{Kc} {}^{1}(A^{-}D^{+}) \qquad (15)$$

However, the rate of charge-transfer complex formation (new emission species) will be solvent independent*, and is in competition with reaction (14). The probability of charge-transfer complex formation (r_c),

$$r_c = Kc/Kc + Kq$$

where Kc is the rate constant for the formation of charge-transfer complex, will strongly decrease with increasing solvent dielectric constant. It is this solvent dependence of r_c which essentially determines the relative intensity of the charge-transfer complex emission.$^{(101)}$

The mean lifetime of the excited charge-transfer complex can depend on solvent polarity through reaction (16),

$$^{1}(A^{-}D^{+}) \longrightarrow (A_s^{-} \,.....\, D_s^{+}) \qquad (16)$$

which leads to quenching of the charge-transfer complex fluorescence.

---

*This is in accord with the ground state charge-transfer phenomena, that the positions of the absorption maxima for charge-transfer complexes of neutral donors and acceptors, are generally not much affected by changes in solvent.$^{(103)}$

From the above discussion, it seems reasonable to assume that the "exciplex" state itself actually consists of an ion-pair complex and a charge-transfer complex, which can interconvert, and the interconversion (either rate or equilibrium) is solvent dependent. The situation may be represented as follows:

$$D^* + A \rightarrow (A^-D^+) \overset{K}{\rightleftharpoons} (A_s^- \ldots\ldots D_s^+)$$

charge-transfer state $\qquad$ ion-pair state

The wave function for (A^-D^+) may be written

$$\Phi_{\text{charge-transfer}} \approx a\Psi_{(A^-D^+)} + b\Psi_{(A^+D^-)} + c\Psi_{(A.D^*)} + d\Psi_{(A^*.D)}$$

If A is a much better electron acceptor than D, then the coefficient a will be much greater than b. Hence it is easy to see why the charge-transfer state assumes the structure $(A_s^- \ldots\ldots D_s^+)$ as the partners in the complex begin to separate, as for example, in a polar medium.

If the acrylonitrile exciplexes can have the ion-pair structure, and K is larger in polar solvents, then this could explain the solvent effect on the protonation reaction.

Having considered some attempts to describe excited state interactions, it remains to define a species which may be useful in finding a mechanism for the indene- and naphthalene-acrylonitrile reactions.

While Hammond and co-workers (89,90) do not favour a charge-transfer component in the naphthalene-diene exciplexes, this type of species does explain their results, if the excited aromatic molecule is the acceptor. Also, Weller's work on solvent effects (101) does indicate that the charge-transfer interaction can be very important, at least in certain donor-acceptor pairs.

Acrylonitrile should be a good acceptor, and even if Hammonds' arguments for dienes are correct, there is no reason why acrylonitrile (having a strong electron-withdrawing group) should behave like a diene. Also, the lowest spectroscopic singlet level of acrylonitrile is of much higher energy than naphthalene (about 40 Kcal/mole) or indene (about 20 Kcal/mole), hence the A.Q* term in the exciplex wave function should be very small.

It is suggested therefore that the exciplexes of acrylonitrile are well described as follows:

$$\Phi_{\text{exciplex}} = a\Psi_{(A.N^*)} + b\Psi_{(A^-N^+)^*} + c\Psi_{(A^*.N)}$$

where A is acrylonitrile, and N, the aromatic hydrocarbons, a,b and c are constants, c being small.

A description of the ion-pair type suggested by Weller(101) to be important in polar solvents, is also reasonable, but the above description is satisfactory in that it explains the results at hand (*vide infra*).

THE INFLUENCE OF SOLVENT

In the naphthalene-acrylonitrile photo-addition reactions, initial experiments showed that substituted naphthalenes (XXV) only formed in protic solvents. Subsequent work revealed a remarkable dependence of the product ratio on the dielectric constant and the acid strength of the solvent (Table IX).

It was found that the ratio of substituted naphthalenes (XXV) to cyclobutane adduct (XXIV) decreased in the order

$HCOOH > MeOH > EtOH > CH_3COOH >$ iso-PrOH > tert-BuOH > aprotic solvents

which follows nicely the decreasing order of the acidity and the dielectric constant of the solvent (Table IX) (acetic acid appears to be anomolous).

In order to clarify the participation of protic solvents in the reaction, deuterium acetate was used as solvent. Products isolated showed that in the substituted naphthalenes, deuterium which is the most acidic hydrogen in the solvent, was incorporated in the methyl-group. Both the solvent effect and the labelling experiment are consistent with a protonation step by the solvent as leading to the substituted naphthalenes (XXV).

PROPOSED MECHANISM FOR FORMATION OF THE SUBSTITUTED NAPHTHALENES

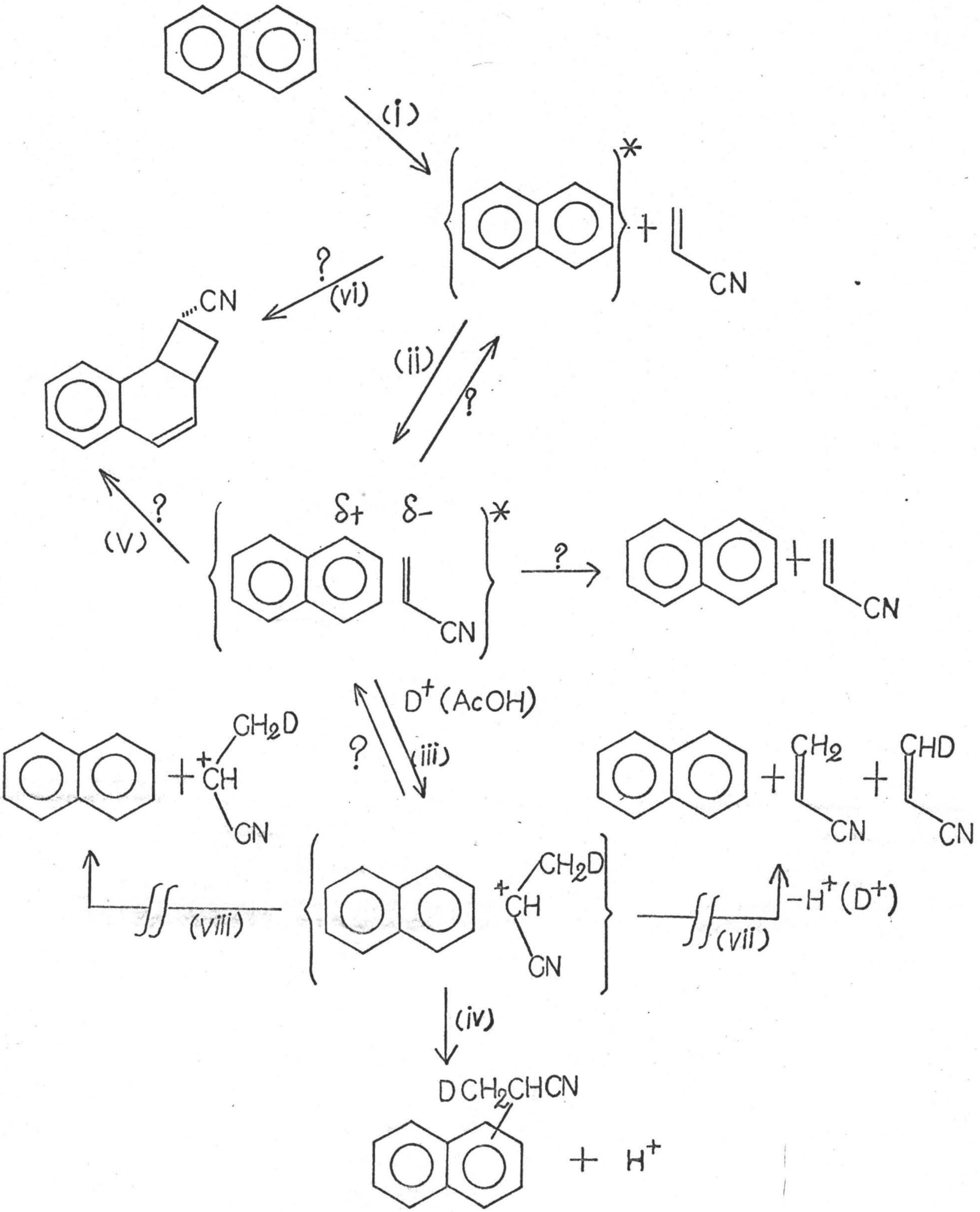
The following mechanism (Scheme XIV) seems to account economically for the formation of products (XXIV) and (XXV). The steps are:

(i) Excitation of the naphthalene to the excited singlet state.

(ii) Capture of this state by acrylonitrile, leading to a complex, and resulting in fluorescence quenching of the hydrocarbon.

(iii) Protonation of the exciplex, giving rise to a cation which can then undergo eletrophilic substitution with naphthalene to afford the products (XXV).

The exciplex may collapse to the cyclobutane adduct (XXIV), at a rate competitive with protonation, or of course it may simply decay to ground state reactants.

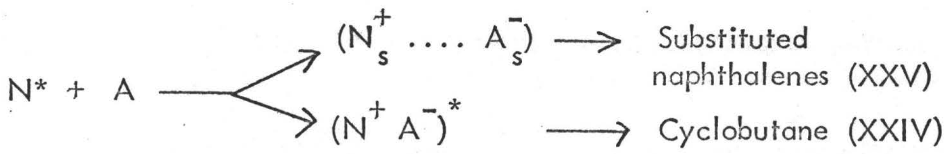

(i)
*
+
CN
?
(vi)
CN
(ii)
?
?
(v)
δ+
δ-
*
CN
?
+
CN
D⁺ (AcOH)
?
(iii)
+
CH₂D
CH
CN
+
CH₂
+
CHD
CN
CN
(viii)
CH₂D
CH
CN
(vii)
-H⁺(D⁺)
(iv)
DCH₂CHCN
+ H⁺

SCHEME XIV

We should now consider how this scheme explains the experimental observations. First of all, the deuterium labelling experiment shows that the solvent acts as a proton donor. Knowing this, it is possible to explain the change in product ratio with solvent acidity and polarity, since if protonation competes with cyclo-addition (reactions iv and v in the Scheme), then the amount of protonation should be greater in polar, acidic solvents (cf. Table IX).

An alternate explanation for the influence of solvent is suggested by the ideas of Weller(101). It has been suggested that in exciplex formation, two different types of complexes are in competition. One is an ion-pair type of complex (whose formation is solvent-dependent); the other is a charge-transfer type (which should not be so heavily dependent on solvent)(101). Thus, if the substituted naphthalene products arise from the former complex, and the cyclobutane adduct from the latter, then we can explain why the product ratio varies with the dielectric constant of the solvent. That is, increasing dielectric strength of the solvent favors formation of the ion-pair complex, thereby forming more substituted naphthalene products (Scheme XV)

SCHEME XV



N* = excited naphthalene molecules

A = acrylonitrile

The position of protonation of the acrylonitrile moiety is interesting; the protonated species is represented as an α-cyanoethyl carbonium ion - a high energy species. Such a species does not exist as such in solution, since no α-cyanoethyl methyl ether was obtained in the reaction in methanol*. Thus the protonated exciplex appears to collapse to the substituted naphthalenes, and does not dissociate to naphthalene and the cyano-carbonium ion. The latter statement is also supported by the observation that acrylonitrile recovered from the reaction in deuterium acetate showed very little ($<0.5\%$) deuterium incorporation.

It is suggested that the protonation occurs at the position of highest electron density in the acrylonitrile moiety of the exciplex; if the acrylonitrile is acting as an electron acceptor by having the lowest antibonding orbital partly filled, then C_β should have the higher electron density.**

It should be noted that the ratio of α/β substituted naphthalenes is 2:1, consistent with an electrophilic substitution mechanism.

Alternative mechanisms should be considered. One obvious possibility is that the solvent protonates acrylonitrile (ground state), and the carbonium ion formed reacts with naphthalene. This protonation by solvents such as ethanol is an unknown and very unlikely process. However, were the acrylonitrile to become excited, then protonation would be possible, and the reaction sequence

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* α-Cyanoethyl methyl ether(104) is stable under the photolysis conditions. Analysis of the photolysis mixture by g.l.c. (5ft. x 1/8 inch. 10% carbowax on chromosorb W at 70°) could not detect the presence of the ether.

** The calculated π-charge densities(105) at C_α and C_β are 0.7526 and 0.8683, respectively.

might be as follows

$$N^* + A \xrightarrow{\text{via process 8 or 11}} A^* \qquad (17)$$

$$A^* + ROH \longrightarrow (A^{+})^* \qquad (18)$$

$$(A^{+})^* + N \longrightarrow \text{cyanoethylnaphthalenes} \qquad (19)$$

The evidence against this is as follows. First, as noted above, the free ion ($CH_3\overset{+}{C}HCN$) does not appear to exist in these reactions, since it should either lose a proton (which could be detected in the deuterium labelling experiments) or be captured by solvent, and neither of these processes are observed. Also, there is the problem of excitation of the acrylonitrile. Naphthalene singlet does not have sufficient energy to excite acrylonitrile to its lowest spectroscopic singlet, thus precluding energy transfer. The lowest triplet of the nitrile would be formed in the acetophenone sensitization experiments, yet no reaction occurred.

The formation of the cyclobutane adduct (XXIV) can also be rationalized on the basis of an exciplex intermediate. First, it is the only other photo-product obtained. It would be difficult to explain why the product ratio of the substituted naphthalenes and cyclobutane adduct varies so smoothly with the magnitude of the dielectric constant and the acid strength of the solvent, if this cyclobutane adduct is arising from a different mechanism. Second, if the adduct (XXIV) does not arise from an exciplex intermediate, then in the 2-methoxy-naphthalene and acrylonitrile photo-addition, it would be expected that more substituted naphthalenes would be formed, because a methoxy-group should enhance the stability of the exciplex formed. In actual fact a cyclobutane adduct is the predominant product (106).

It was seen earlier that the naphthalene-acrylonitrile photo-addition, the formation of cyclobutane adduct is favored in solvents of weak acidic strength and low dielectric constant. The only exception to this rule was acetic acid. The anomalous effect of acetic acid is understandable since it has high acid strength (favoring substituted naphthalene formation), and low dielectric constant (favoring cyclobutane formation) (Table IX).

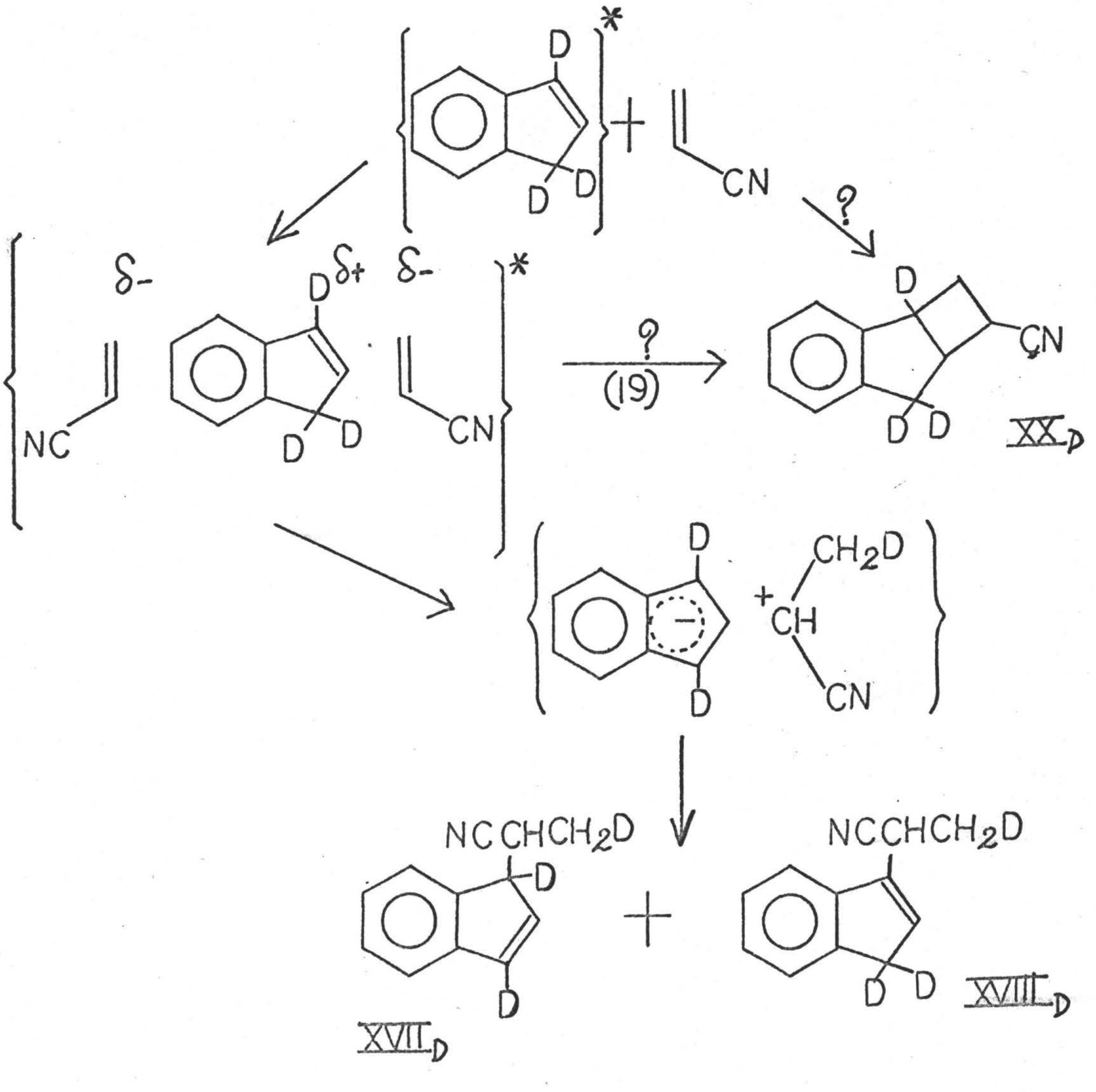
Hence it is maintained that the exciplex formation, followed solvent protonation as shown in Scheme XIV, is the most reasonable mechanism.

It is not known whether the formation of cyclobutane (XXIV) occurs via the exciplex, or in a parallel competing reaction (Scheme XIV). It is also not known with certainty whether the exciplex which is responsible for fluorescence quenching is the same as the species which reacts with solvent. The latter point could be determined by comparison of parameters from the fluorescence quenching with quantum yield measurements. It can be seen (Appendix VI) that it is possible that excited states of naphthalene other than the lowest singlet and triplet states could be complicated in the reaction. For example, T_2 could be formed by inter-system crossing from the initially formed lowest excited singlet state.

In the case of the indene-acrylonitrile photo-addition, both the cyclobutane (XX) and the substituted indene (XVII) and (XVIII) products are obtained. In this case, the product ratio does not change significantly with changes in the dielectric constant and the acid strength of the solvent (Table X).

This difference in indene and naphthalene photo-additions may be attributed to the presence of acidic methylene protons in the former hydrocarbon. Hence, the substituted indene products arise from a proton transfer mechanism as shown in Scheme XVI.

The origin of the cyclobutane product is uncertain. It may arise from the original exciplex (process 19) formed.



Scheme XVI

The reaction was carried out using indene-1,1,3-d_3 and one deuterium was found in the methyl-groups of the substituted indene products (XVII) and (XVIII). Hence proton transfer from the indene moiety in the complex is apparently more rapid than solvent protonation. This mechanistic picture also accounts for the absence of substituted indenes in the reaction of 1,1-dimethylindene.

It is interesting to note that this weakening of an acidic hydrogen in one partner of a pair bonded in an exciplex was proposed by Lowdin to account(104) for changes in nucleic acid structure.

This reaction with indene and acrylonitrile is almost certainly just one example of what is probably a very general class of proton shifts. Perhaps other as yet undiscovered examples of intermolecular protonation, resembling the naphthalene reactions, also exist.

PART V : EXPERIMENTAL

The nuclear magnetic resonance spectra were obtained with a Varian HA-100 or A-60 spectrometer. The chemical shifts are δ values (p.p.m.) measured downfield from tetramethylsilane ($\delta = 0$) as internal standard. Infrared spectra were run on a Beckman IR-5 or on a Perkin-Elmer 521 instrument and ultraviolet spectra were determined on a Cary model 14 spectrophotometer. Mass spectra were measured on a Hitachi Perkin-Elmer MRU 6 instrument. Gas-liquid chromatography was performed with a Varian 204B dual column instrument with 35 ml/min helium, using Column A (5 ft x $\frac{1}{8}$in. 5% SE-30 on Chromosorb W). Melting points were taken on a Kofler hot stage and are uncorrected.

Nitrogen was Canadian Liquid Air certified grade and was further purified by successive passage through vanadous sulfate solution (107), concentrated sulfuric acid, and potassium hydroxide pellets.

Alumina used was Absorption, Fisher Alumina and the silica gel was Grace, 923 (100-200 mesh).

Unless specifically stated, all column chromatography was performed with a 2.5 x 90 cm column, slurry-packed in 10% benzene-hexane. Elution was begun with this mixture, and the benzene concentration was increased 5% for every additional liter of eluant; 250 ml fractions were collected.

Yields in photolysis reactions are not absolute yields, but are based on unrecovered hydrocarbon starting material.

Indene was J.T. Baker, Practical Grade, twice distilled, b.p. 65°/

15 mm. Naphthalene (Fisher Reagent) was crystallized twice from benzene and had m.p. 79-80°. Acrylonitrile was Eastman Practical Grade, distilled four times, b.p. 75-76°. Acetophenone (Eastman Reagent) was distilled and had b.p. 87-90°/15 mm. Solvents were distilled before use.

Deuterium oxide was obtained from Columbia Organic Chemicals, Inc., and was specified at 99.7% D_2O. 1,1-Diphenylindene was prepared as described previously(25) and 3-deuterio-1,1-diphenylindene was obtained using sodium borodeuteride (Merck, Sharp and Dohme of Canada Limited) in the reduction of 3,3-diphenyl-1-indanone.

Microanalyses were by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Photo-condensation of Indene and Acrylonitrile

Indene (2.0g; 0.0172 mole) and acrylonitrile (20.0 g; 0.377 mole) in 95% ethanol (400 ml) were stirred and purged with nitrogen for 30 min prior to and during the 2 h photolysis. The latter was carried out using a Hanovia type L 450W lamp in a conventional quartz immersion apparatus, which had an outlet for withdrawing aliquots. A Vycor sleeve was used. Gas-liquid chromatography of aliquots showed that three products were formed, having retention times (Column A, 175°) 2,5, 3.3 and 3.8 min, labelled (XVII), (XVIII) and (XX) respectively in the ratio 70:10:20 as measured from peak areas. After the 2h photolysis, the mixture was filtered through silica gel to remove a small amount of polymer, and the solvent and residual indene were removed under vacuum at room temperature. The mixtures from nine such runs were combined and the three components were separated by chromatography on a 2.5 x 90 cm column of silica gel, slurry-packed in 10% benzene-hexance, using the gradient elution procedure described above. The fractions were monitored by gas-liquid chromatography. Fractions 1-6 contained indene (0.5 g); fractions 10-18 contained (XVII), 2.03 g; fractions 20-24 contained (XVII) and (XX), 1.297 g, and 30-37 contained (XVIII), 0.807 g, m.p. 80.5 - 81.5° from ethanol.

Fractions 25-29 were combined and chromatographed on a 4.0 x 90 cm column of silica gel, slurry-packed in 50% benzene-hexane, and eluted with this solvent, 250 ml fractions being collected. Fractions 9-22 contained (XX), 0.883 g, and 27-41 contained (XVIII), 0.313 g. By this procedure (XVII) was obtained as an oil, 2.03 g; 21.6%, identified as 2-(1-indenyl)-propionitrile. Component (XVIII) had m.p. 80.5 - 81.5°, 1.22 g; 13.0%, and was shown to be 2-(3-indenyl)-propionitrile as described in the Results section.

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.35; H, 6.38; N, 8.35.

Compound (XX) was also an oil, 1.08 g; 11.5% which had a nitrile band at 2240 cm^{-1}, and the nuclear magnetic resonance spectrum (100 M c.p.s.) which had at 7.23, mult. area 4 (aromatics); 3.83, broad peak area 1 (benzylic methine) and at 2.00, mult. area 1 (alicyclic methylene). The remaining proton signals were super-imposed in a complex multiplet from 2.50 - 3.50 p.p.m. This resembled the spectra of the sensitized reaction products. Also, the mass spectrum of (XX) was almost identical with the spectra of the latter products, having a weak molecular ion, m/e 169, a base peak, m/e 116 (100) and a second strong peak, m/e 115. (Appendices I and II). From these comparisons (XX), is identified as 6-cyano-2,3-benzobicyclo[3.2.0]hept-2-ene.

Isomerization of 2-(1-Indenyl)-propionitrile (XVII)

Treatment of (XVII) (0.1 g; 0.0006 mole) with triethylamine (1.0 g)(63) in water (1.0 ml) and dioxane (5.0 ml) for 12 h was followed by the addition of water and ether, and separation of the ether layer, which was washed with saturated salt (NaCl) solution, and dried ($MgSO_4$). Evaporation of the solvent afforded 2-(3-indenyl)-propionitrile (XVIII), 0.9 g (90%), m.p. 80.5 - 81.5° (from ethanol).

Deuteration of (XVIII)

The procedure of Bergson(63) was followed. To a solution of (XVIII) (50 mg) in dioxane (5.0 ml) was added 2 ml of a 1:1 mixture of deuterium oxide and triethylamine. The mixture was stirred at 25° for 27 h, when the reaction was poured into water, and immediately extracted with ether. The ether layer was washed with salt (NaCl) solution, and dried ($MgSO_4$). The n.m.r. of the residue on evaporating the ether showed a vinylic proton peak at 6.44 but the benzylic methylene peak 3.26 p.p.m. had disappeared, confirming the structure 2-(3-indenyl)-propionitrile for (XVIII).

Isolation of 2-(3-Indenyl)-propionitrile (XVIII) by Distillation

If (XVIII) is the desired product in the above photolysis, the ethanol is distilled at atmospheric pressure, and the residue is then distilled at 2.0 mm. From 11.0 g of photolysis mixture, distillation gave 5.27 g of 2-(3-indenyl)-

propionitrile, b.p. 100 - 115°/1 mm, m.p. 80-81°, from ethanol.

Isomerization of 2-(3-Indenyl)-propionitrile on Alumina

A solution of 2-(3-indenyl)-propionitrile (0.5 g) in benzene was left on a 2.5 x 30 cm column of alumina for one week. The column was eluted with 3 l of benezene to obtain 0.42 g (84%) of needles, m.p. 114.5-115° (from benzene-hexane). This was identified* as 2-(1-indanylidene)-propionitrile (XIX).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.97; H, 6.58; N, 8.22

Acetophenone Sensitized Photolysis of Indene and Acrylonitrile

Acetophenone (5.0 g; 0.0417 mole), indene (5.0 g; 0.0431 mole) and acrylonitrile (15 g; 0.283 mole) in ethanol (400 ml) were photolyzed as above, with a Corex filter. After the 3 h photolysis, the solvent and most of the residual starting materials were distilled. The residue was chromatographed on alumina for the above general procedure. Fractions 1-55 contained indene dimer (0.11 g), m.p. 109-110°, lit(34) m.p. 109.5-111°. Fractions 7-14 contained (XVI), 0.90 g, m.p. 48.5-50° from benzene-hexane, identified as trans-7-cyano-2,3-benzobicyclo[3,2,0]hept-2-ene (Table 1).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: 85.08;, H, 6.54; N, 8.22.

Fractions 19-26 contained (XV), 0.44 g, m.p. 70.5-72° from benzene-hexane, identified as cis-7-cyano-2,3-benzobicyclo[3,2,0] hept-2-ene (XV) (Table I).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.29; H, 6.60; N, 8.28.

Fractions 15-18 contained (XV) and (XVI) total 0.475 g, which were

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* C.K. Ingold and J.F. Thorpe(108) isolated a compound by elimination of the carbothoxyl group from ethyl 2-(3-indenyl)-2-cyanopropionate, for which they reported m.p. 118°, and assigned it the structure 2-(3-indenyl)-propionitrile (XVIII). We have repeated their experiments, and have found that their product is identical with the nitrile m.p. 114.5-115°, to which we assign structure (XIX).

separated by further chromatography on a 2.5 x 30 cm column of alumina, eluted with the usual benzene-hexane mixtures. Fractions 4-11 contained 0.115 g of (XVI), while 0.360 g of (XV) was found in fractions 14-21.

The ratios reported in Scheme V were measured by gas-liquid chromatography (Column A, 200°) on the photolysis solution before work-up. Retention times were (XVI), 1.7 min; (XV), 2.0 min and indene dimer 8.0 min.

Base-catalyzed Epimerization of the 7-Cyano-2,3-benzobicyclo[3,2,0]hept-2-enes (XV) and (XVI)

Under a blanket of nitrogen, (XV) (the *cis*-isomer) (0.8 g; 0.00473 mole) in tetrahydrofuran (10 ml) was added to potassium t-butoxide from *tert*-butyl alcohol (30 ml) and potassium (1.0 g). The mixture was stirred at room temperature, and aliquots were withdrawn at 15 min intervals. These were added to dilute hydrochloric acid, and ether extracted. The ether solution was washed with salt (NaCl) solution, and dried ($MgSO_4$). This solution was monitored by gas-liquid chromatography (Column A, 200°). The same peaks as are obtained in the photolysis of retention times 1.7 and 2.0 min were observed, and an equilibrium was reached in 1 h. No change in ratio occurred in 48 h, and after this time the reaction was quenched with dilute HCl, and ether extracted. The mixture obtained on ether evaporation was chromatographed on alumina (2.5 x 30 cm column). The usual benzene-hexane mixtures were used as eluant; fractions 3-8 contained the *trans*-isomer (XVI), 0.23 g, m.p. 48-50°. The *cis*-isomer (XV) was eluted in fractions 11-20, 0.56 g, m.p. 71-72°. The gas-liquid chromatographic *cis*:*trans* ratio at equilibrium was 70:30. An identical experiment was performed using pure (XVI), the trans-isomer, as starting material and the same equilibrium mixture was obtained.

Photo-epimerization of the 7-Cyano-2,3-benzobicyclo [3,2,0]hept-2-enes

A solution of the cis compound, (XV) (0.5 g, 0.003 mole) in ethanol (400 ml) was irradiated with the 450W Hanovia lamp, fitted with a Vycor sleeve. The progress of the reaction was followed by gas-liquid chromatography (g.l.c) (Column A, 200°). In 9 h a photostationary state of cis/trans ratio 45/55 appeared to be reached. This ratio did not change on 12 h photolysis, but the g.l.c. showed slow decomposition of (XV) and (XVI) resulting in the appearance of several other peaks.

An identical run, starting with 0.5 g, 0.003 mole of the trans-isomer (XVI) gave the same stationary state composition, measured by g.l.c., which was apparently reached more quickly (3 h) than with the cis-compound.

Photo-addition of 1,1-Dimethylindene and Acrylonitrile

1,1-Dimethylindene (2.0 g; 0.014 mole)(109) and acrylonitrile (3.7 g, 0.07 mole) in ethanol (400 ml) were irradiated (Vycor sleeve) in the usual apparatus for 6 h. The solvent was distilled and the products from five of these runs were combined and chromatographed on alumina. Fractions 7-18 contained (XXII) (Table I) 1.176 g, needles m.p. 70.5-72°, from benzene-hexane. This was assigned the structure trans-7-cyano-4,4-dimethyl-2,3-benzobicyclo-[3.2.0]hept-2-ene.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.37; H, 7.79; N, 6.99.

Fractions 24-37 contained 1.16 g of (XXIII), m.p. 58-59°, needles from benzene-hexane, identified as the cis-isomer, as described in the Results section.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.35; H, 7.76; N, 6.93.

Fractions 19-23 were mixtures of the two isomers, total 0.98 g which were further chromatographed on a 2.5 x 30 cm column of alumina to obtain 0.49 g of cis- and 0.49 g of trans-isomer.

The cis:trans ratio in the photolysis was measured by g.l.c. (Column A 200°) and was approximately 40:60.

Acetophenone Sensitized Photo-Addition of 1,1-Dimethylindene and Acrylonitrile

Acrylonitrile (3.7 g; 0.07 mole), 1,1-dimethylindene (2.0 g; 0.014 mole), and acetophenone (2.0 g; 0.0167 mole) in ethanol were photolyzed with the Hanovia lamp and a Corex filter for 5.5 h.

The solutions from five such reactions were combined, the solvent and residual starting materials distilled, and the mixture chromatographed on alumina as in the previous experiment to obtain 4.60 g of cis-adduct and 2.94 g of trans-compound, identical with the products of the direct photolysis by m.p. and n.m.r. and infrared spectra.

Photoaddition of 1,1-Diphenylindene and Acrylonitrile

Acrylonitrile (20.0 g; 0.377 mole) and 1,1-diphenylindene (1.349 g; 0.00503 mole)(25) in ethanol (400 ml) were photolyzed in the usual way (Vycor filter) for 2 h. After solvent evaporation, the mixture was chromatographed on a 4.0 x 90 cm column of alumina, slurry-packed in 10% benzene-hexane. The column was eluted with 2 l of 10%, 2 l of 20%, 2 l of 30% benzene-hexane and finally with 4 l of benzene, and 250 ml fractions were collected. Fractions 5-13 contained 1,1-diphenylindene 360 mg, m.p. 90-92° (from light petroleum, b.p. 80-110°).

Fractions 31-34 contained a nitrile adduct infrared band at 2420 cm^{-1} 300 mg, m.p. 219-222° (from ethyl acetate). This had a molecular ion of m/e 321, and is assigned the structure cis-7-cyano-4,4-diphenyl-2,3-benzobicyclo[3,2,0]hept-2-ene (XXI) from the n.m.r. spectrum (Table I).

Anal. Calcd. for $C_{24}H_{19}N$: C, 89.68; H, 5.96. Found: C, 89.33; H, 6.11.

Preparation of 1-deuterio-(XXI)

3-Deuterio-1,1-diphenylindene (1.45 g; 0.00542 mole) and acrylonitrile (20.0 g; 0.377 mole) in ethanol (400 ml) were photolyzed and chromatographed as above to afford 1-deuterio-(XXI) 137 mg, m.p. 220-222°. The quintet at 4.18 in the n.m.r. spectrum of (XXI) (Table I) was absent from the spectrum of 1-deuterio-(XXI), identifying the quintet as the resonance of H-1 in this adduct.

Photo-condensation of Naphthalene and Acrylonitrile

Acrylonitrile (2.0 g; 0.0377 mole) and naphthalene (0.1 g; 0.00078 mole) in tert-butyl alcohol (80 ml) (under nitrogen at 30°) were irradiated through Pyrex with the Hanovia 450W lamp for 40 min. Gas-liquid chromatography (Column A, 175°) showed two peaks at 2.4 and 2.8 min, in the ratio of 8:92 respectively. The mixtures from five such reactions were evaporated and combined, and the mixture was chromatographed on a 2.5 x 30 cm column of silica gel slurry packed in benzene. The column was eluted with benzene, and 250 ml fractions were collected. Fractions 1-3 contained naphthalene (0.286 g); fractions 4-20 contained 0.461 g of naphthalene and 3 mg of the 2.4 min product separated by sublimation. The latter was identical with the product from photolysis using a Corex filter or longer photolysis times and is described in the next experiment. Fractions 23-36 contained the 2.8 min product, 50 mg, m.p. 98-99° from ether. This is assigned the structure trans-8-cyano-2,3-benzobicyclo[4,2,0]octa-2,4-diene (XXIV), from the data described in the Results.

Anal. Calcd. for $C_{13}H_{11}N$; C, 86.15; H, 6.12; N, 7.73. Found: C, 86.19; H, 6.14; N, 7.82.

Identification of the 2.4 Min Component

Photolysis of naphthalene (0.5 g; 0.00391 mole) and acrylonitrile (10 g; 0.189 mole) in ethanol (400 ml) with a Pyrex sleeve for 2.5 h (use of a Corex sleeve for 2 h gave similar results) gave a solution containing much polymer. This appeared after 40 min and was not observed in the previous small scale reactions. The polymer was removed by filtration (7.6 g) and the mixtures from ten reactions were combined and chromatographed on a 2.5 x 90 cm column of silica gel, slurry-packed in and eluted with benzene, 250 ml fractions being collected. Fractions 1-4 contained naphthalene 0.599 g, m.p. 79°. Fractions 6-19 were the 2.4 min component 0.239 g; 20-28 were a mixture of the 2.4 min component and (XXIV), 0.616 g, while fractions

26-42 were pure (XXIV), 1.743 g, m.p. 98°. Fractions 6-19 were combined dissolved in the minimum volume of ethanol and kept in the refrigerator for several days. Crystals were deposited which were filtered and recrystallized from ethanol and had m.p. 64-66°. This compound had peaks at 7.58 p.p.m. mult., area 7 (aromatics); 3.92, quartet, area 1 (methine); 1.67, doublet, area 3 (methyl). This compound is assigned the structure 2-(2-naphthyl)-propionitrile from the n.m.r. spectrum and by its non-identity with authentic 2-(1-naphthyl)-propionitrile$^{(67a)}$.

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73, Found: C, 86.00; H, 6.18; N, 7.59.

The mother liquors from the above crystallization were mainly 2-(1-naphthyl)-propionitrile, having peaks at 7.55, mult., area 7 (aromatic); 4.49 quartet, area 1 (methine), and at 1.72 doublet, area 3 (methyl). This n.m.r. was identical with that of an authentic sample, prepared by methylation of (1-naphthyl)-acetonitrile$^{(67a)}$, which had b.p. 136-138/0.5 mm, lit. b.p. 125-127°/0.5 mm. The ratio of the 1- and 2-substituted naphthalenes formed in the photolysis was 2:1, estimated from the n.m.r. spectrum of the mixture.

Photolysis of trans-8-Cyano-2,3-benzobicyclo[4,2,0]-octa-2,4-diene (XXIV)

A solution of the cyano compound (XXIV), (80 mg, 4.42×10^{-4} mole) in ethanol (80 ml) was photolyzed for 10 min using a low-pressure Hanovia 87A-45 mercury lamp (Vycor envelope) giving 95% of the radiation at 253.7 mμ. On distillation of the solvent, and sublimation of the residue, 54 mg (95%)

of naphthalene were obtained, m.p. and mixed melting point 78.5-79.5°.

Attempted Base-catalyzed Epimerization of trans-8-Cyano-2,3-benzobicyclo[4,2,0]octa-2,4-diene ((XXIV)

The adduct (XXIV) (100 mg) in tert-butyl alcohol (10 ml) was added under nitrogen to potassium t-butoxide from potassium (1.0 g) and tert-butyl alcohol (20.0 ml). The mixture was stirred at 60° for 5 h, poured into cold acid (HCl), ether extracted, and the extracts dried ($MgSO_4$). Gas-liquid chromatography (Column A, 175°) did not show any peaks other than starting material. The solution was filtered through silica gel, and a quantitative recovery of starting material (XXIV), m.p.98-99° was obtained. A similar experiment was conducted as above, with a reflux time of 20 h. Gas-liquid chromatography with a reflux time of 20 h. Gas-liquid chromatography showed no new peaks, but it was observed that the starting material gradually disappeared and no identifiable material was isolated from the experiment.

Effects of Added Acrylonitrile on the Ultraviolet Absorptions of Indene and Naphthalene

The ultraviolet spectra of the following solutions were examined (1 mm path length) using the Cary 14 spectrometer.

(a) Naphthalene (0.125 g; 9.765 x 10^{-4} mole) in ethanol, to make 100 ml)

(b) Naphthalene (0.125 g; 9.765 x 10^{-4} mole), and acrylonitrile (2.5 g; 4.7 x 10^{-2} mole) in ethanol (to make 100 ml).

(c) Indene (0.05 g; 4.3 x 10^{-4} mole) in ethanol (to make 100 ml of solution).

(d) Indene (0.05 g; 4.3 x 10^{-4} mole) and acrylonitrile (0.5 g; 9.43 x 10^{-3} mole) in 100 ml ethanol solution.

The spectra of (a) and (b) were identical, as were those of (c) and (d), the absorption being measured from 200-800 mμ. No long wavelength band appeared on adding acrylonitrile to the hydrocarbon. Dilution of these solutions to allow measurement of the molar absorbance at the hydrocarbon λ_{max} showed that acrylonitrile had no effect on either of these properties.

Attempted Sensitization of the Naphthalene-Acrylonitrile Photo-Addition

(1) With acetophenone

Naphthalene (0.5 g; 0.00391 mole), acrylonitrile (10.0 g; 0.189 mole), and acetophenone (5.0 g; 0.0417 mole) in ethanol (400 ml) were photolyzed through Pyrex in the usual apparatus for 4 h.

(2) with Michler's ketone

Naphthalene (0.1 g; 0.00074 mole), acrylonitrile (2 g; 0.038 mole), and Michler's ketone (0.1 g; 0.00037 mole) in absolute methanol (75 ml) were photolyzed through Corning filter glass (5-60)* for 20 h.

(3) With fluorene

Naphthalene (0.1 g; 0.0074 mole), acrylonitrile (2 g; 0.038 mole), and fluorene (0.1 g; 0.0006 mole)

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* This filter glass transmits light between 345 and 520 mμ, and has a maximum transmittance of 65% at 430 mμ, thus ensuring that no light is absorbed by naphthalene molecules.

in absolute methanol (75 ml) were photolyzed through Corning filter glass (5-60)* for 8 h.

Much polymer was formed in all reactions, but no products were observed by g.l.c. (Column A, 175°)

Quenching of Aromatic Hydrocarbon Fluorescence by acrylonitrile

Aromatic hydrocarbon fluorescence was measured, without degassing the solution, on an Aminco-Bowman spectrophotofluorometer using quartz cells with 1 cm path length. The results are shown in part (2) of the mechanistic results section.

(1) Quenching of naphthalene fluorescence

The solution was prepared by mixing a naphthalene (3.69 g, 0.0576 mole) in ethanol solution (250 ml) with an equal volume of ethanol solution containing varying concentrations of acrylonitrile; the latter solutions were prepared from a standard concentrated solution by dilution. Excitation was at 320 mμ, the fluorescence was observed at 353 mμ. The results are shown in Table VI.

(2) Quenching of dimethylindene fluorescence

The solution was prepared by mixing a dimethylindene (1 g, 0.007 mole) in ethanol solution (100 ml) with an equal volume of ethanol solution containing the appropriate concentration of acrylonitrile. (Excitation was at 303 mμ, the

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* This filter glass transmits light between 345 and 520 mμ, and has a maximum transmittance of 65% at 430 mμ, thus ensuring that no light is absorbed by naphthalene molecules

fluorescence was observed at 349 mμ) The results are shown in Table VII.

(3) Quenching of indene fluorescence

The solution was prepared by mixing an indene (2 g, 0.0172 mole) in ethanol solution (100 ml) with an equal volume of ethanol solution containing the appropriate concentration of acrylonitrile. Excitation was at 300 mμ, the fluorescence was observed at 344 mμ. The results are shown in Table VIII.

Solvent Effect on the Naphthalene-Acrylonitrile Photo-Addition

Naphthalene (0.2 g; 0.00156 mole) and acrylonitrile (4 g; 0.0754 mole) in various solvents (70 ml) (under nitrogen at 30°) were irradiated through Pyrex with the Hanovia 450W lamp for 1 h. The reaction mixture was evaporated and the residue obtained was analyzed by g.l.c. (Column A, 200°) and the relative peak areas were measured using a Varian Aerograph Model 475 Digital Integrator, and the results are shown in Table IX.

Solvent Effect on the Indene-Acrylonitrile Photo-Addition

Indene (0.2 g; 0.0017 mole) and acrylonitrile (2 g; 0.0377 mole) in various solvents (70 ml) were irradiated through Vycor for 1 h, and the product ratio was determined by the same method described above. The results are shown in Table X.

Deuterium-Labelling Experiments

(1) Photolysis of naphthalene and acrylonitrile in deuterium acetate.

Acrylonitrile (2 g; 0.0377 mole) and naphthalene (0.1 g; 0.00078 mole) in deuterium acetate (70 ml) (under nitrogen at 30°) were irradiated through Corex with the Hanovia 450W lamp for 90 min. The mixtures from five such reactions were evaporated and combined, and the mixture was separated by column chromatography described previously, to obtain 3-deuterio-2-(1-naphthyl)- and (2-naphthyl)-propionitriles (XXVd) and trans-8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (XXIV). The products were subjected to nuclear magnetic resonance and mass spectral analysis.

To analyze the deuterium content in the recovered acrylonitrile, the distillate (which contained mainly deuterium acetate and unreacted acrylonitrile) was added with 5 ml of freshly distilled cyclopentadiene, and the mixture was allowed to stand for 3 h, and was evaporated. The residue which contained a mixture of 4-endo- and exo-cyanobicyclo[2.2.1]hep-2-ene was dissolved in ether, neutralized by aq. bicarbonate solution. The ether layer was dried and evaporated. The residue was then purified through g.l.c. (5 ft x $\frac{3}{8}$in. 10% SE-30 on chromosorb W, 170°). The mass spectrum of the mixed adduct showed a $(M + 1)^+$ peak with a relative intensity of 10.4% relative to the molecular ion peak (M^+).

A blank obtained from the same procedure (excluding the photolysis) showed a $(M + 1)^+$ peak with relative intensity of 9.9%. Thus, indicated that no more than 0.5% of the recovered acrylonitrile had deuterium incorporated.

Photolysis of Indene-1,1,3-d_3 and Acrylonitrile

Indene-1,1,3-d_3 (2 g; 0.017 mole) and acrylonitrile (10 g; 0.189 mole) in anhydrous methanol (400 ml) were photolyzed through Vycor for 2.5 h. The mixtures from six such reactions were evaporated under steam bath (during this time, most of the1-substituted indene rearranged into the corresponding 3-substituted isomer) and combined. This was added with ether and the polymers were filtered off. The solution was left on a 4.0 x 60 cm column of alumina for 4 h, and was then eluted with benzene. The residue after evaporating the solvent was chromatographed on silica gel by the above general procedure. Fractions 37-44 contained XIXd. Fractions 45-62 contained mainly XVIIId, which was further purified by recrystallization from benzene-hexane. Fractions 63-69 contained mostly the cyclobutane adduct XX, which was crystallized from ether-hexane at dry-ice temperature, and had m.p. 65.5-67° (from benzene-hexane).

APPENDIX

Photochemical terminology used, but not defined in this thesis may be found in reference 112.

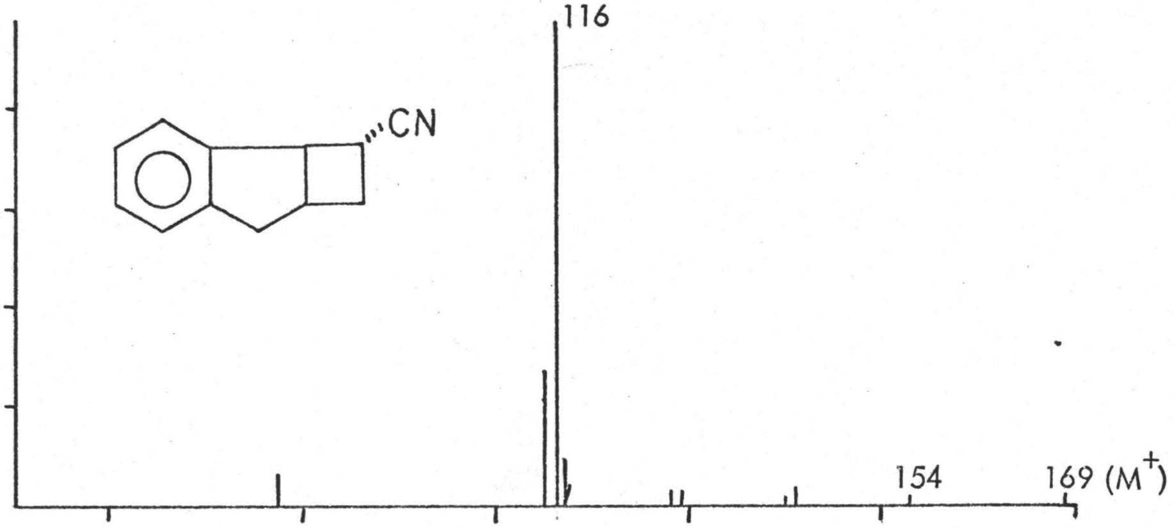
I Partial Mass Spectra of the Cyclobutanes

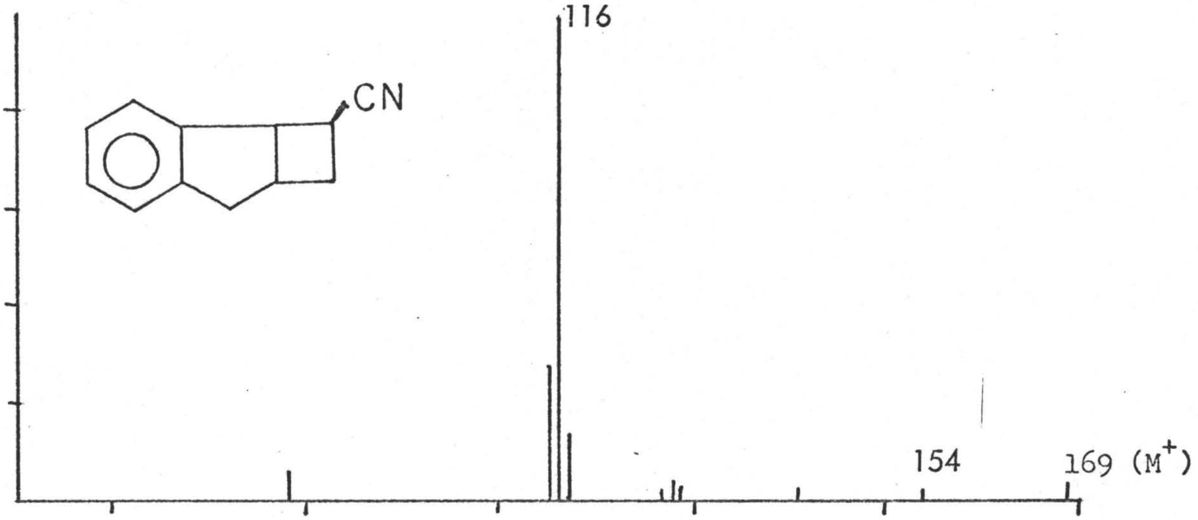
(intensity is in parentheses)

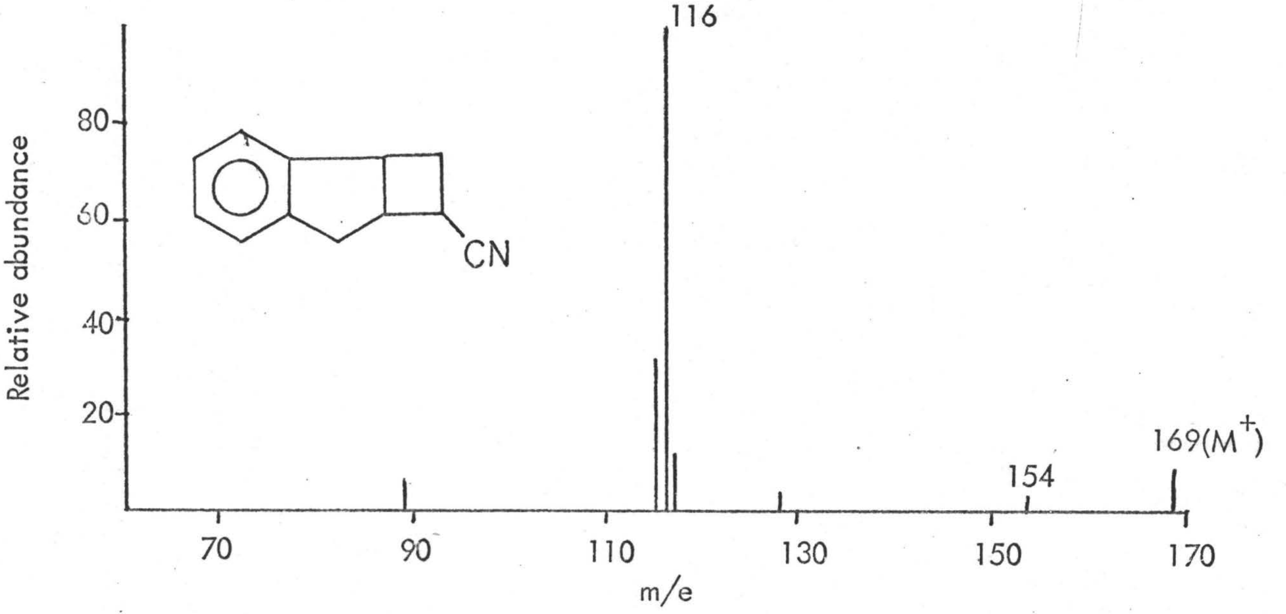
Compd.	M	M-15	RDA	RDA-1	RDA-15
XIV	169(1)	154(1)	116(100)	115(27)	-*
XV	169(3)	154(2)	116(100)	115(28)	-
XX	169(8)	154(3)	116(100)	115(32)	-
XXII	197(1)	182(3)	114(100)	143(6)	129(56)
XXIII	197(2)	182(2)	114(100)	143(7)	129(67)
XXIV	181(2)	-	128(100)	127(9)	-

* No indication means that the intensity of the corresponding peak is less than 1% of the base peak.

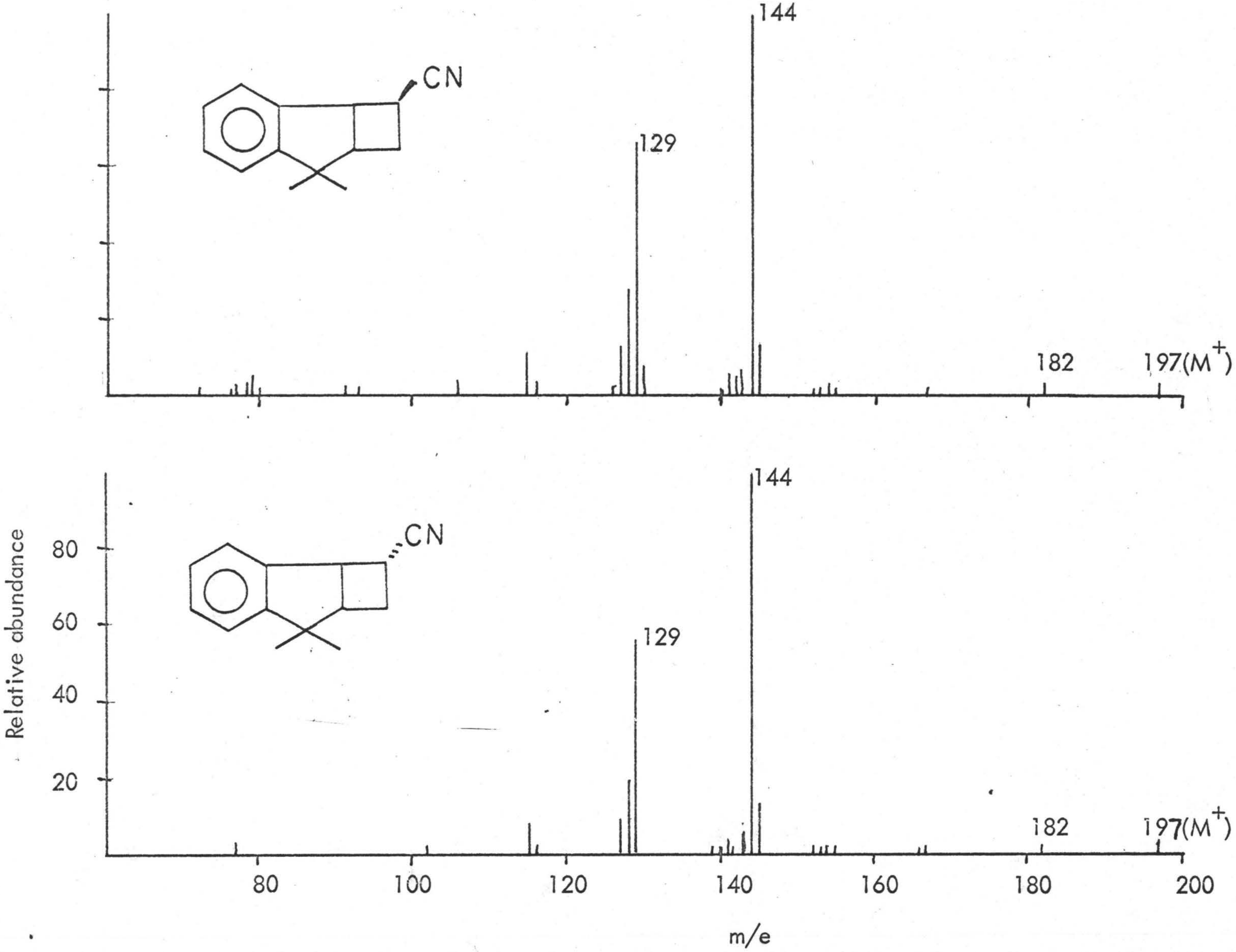
II Mass Spectra of the Indene Cyclobutanes



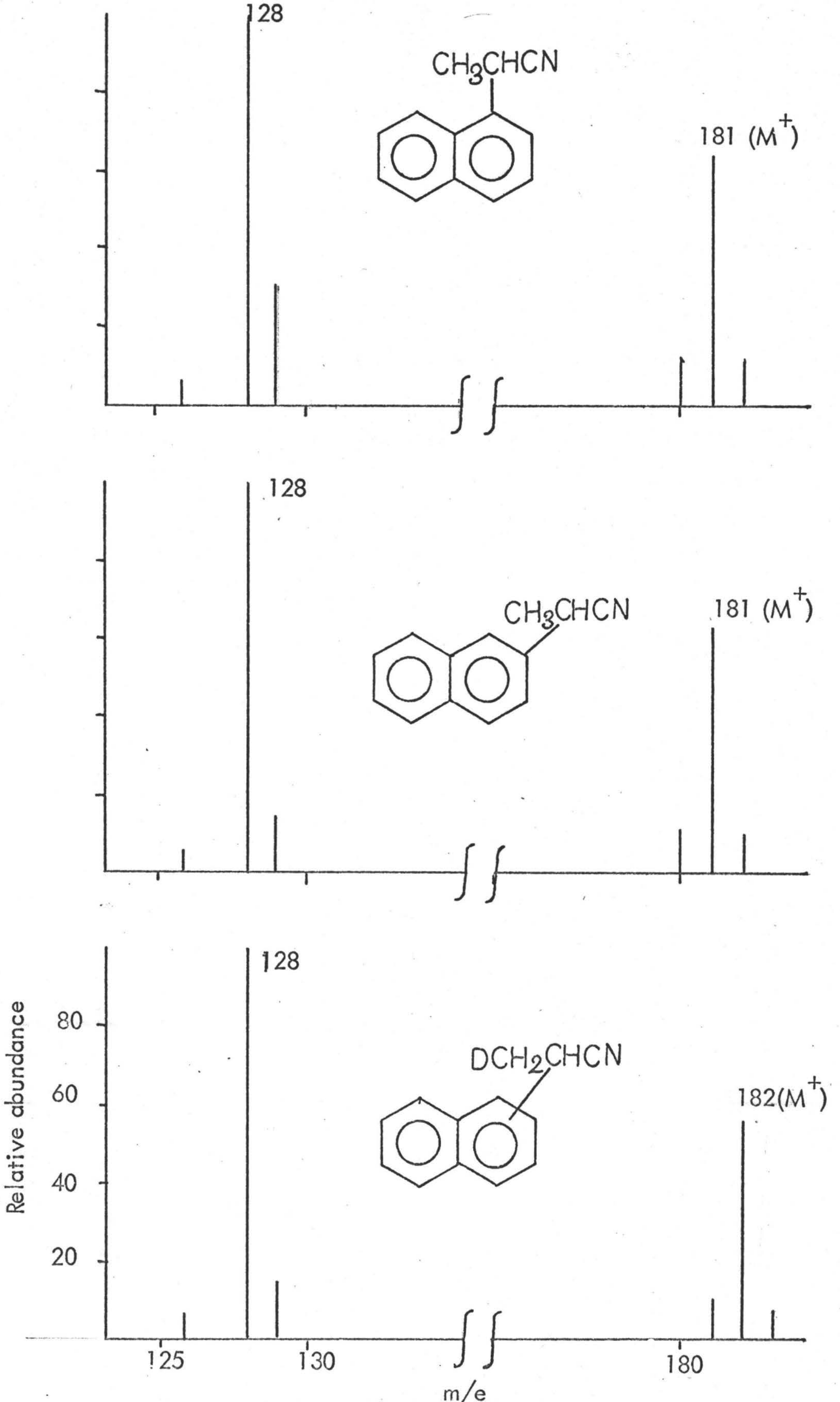




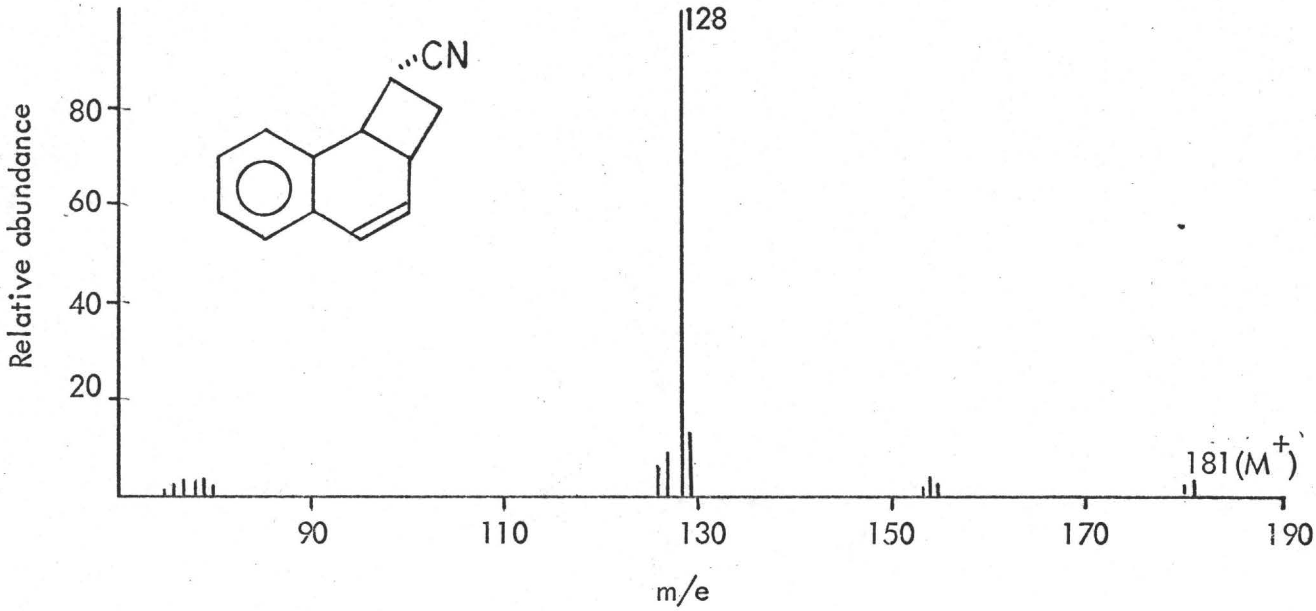
III Mass Spectra of the Dimethylindene Cyclobutanes



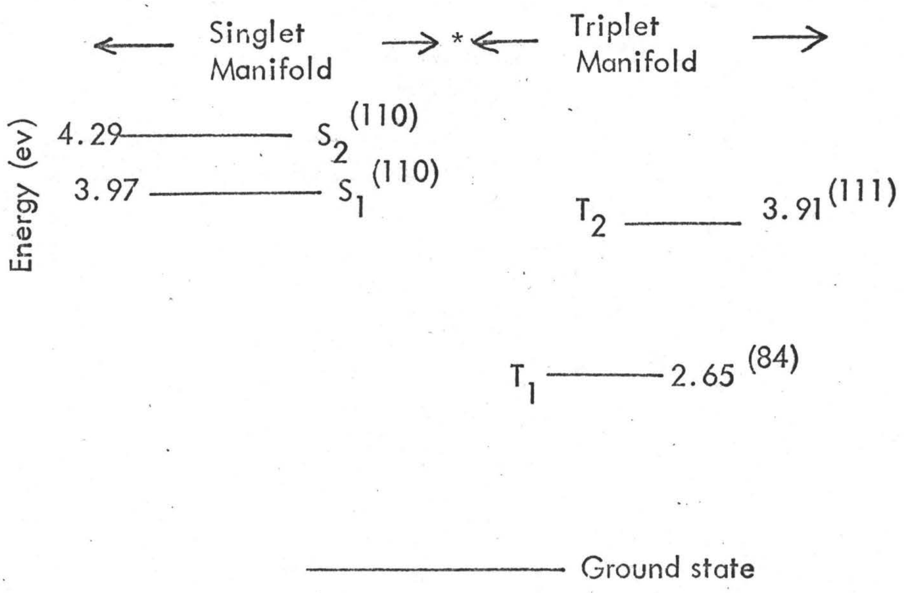
IV Partial Mass Spectra of the Naphthalenes



V Mass Spectrum of the Naphthalene Cyclobutane



VI Energy diagram of naphthalene



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