Tetrahedron. Vol. 28, pp. 4635 to 4651. Pergamon Press 1972. Printed in Great Britain

# EXCITED STATE THEORY AND THE PHOTOCHEMISTRY OF BENZENE COMPOUNDS

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(*Received in the UK* 5 *May* 1972: *Accepted for publication* 12 *May* 1972)

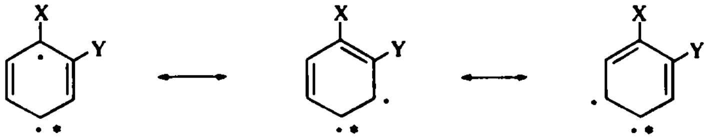
**Abstract**– The $S_{1\pi\pi^*}$ and $T_{1\pi\pi^*}$ excited states of substituted benzene compounds is described in terms of a set of resonant, valence bond structures. The derivation is principally based on the alpha and beta cleavages of substituents on the aromatic ring, the isomerizations of benzene, the p$K_a$'s of excited state molecules and nucleophilic aromatic substitution reactions.

The consequence of the explosion of knowledge in photochemistry has been the refinement of certain aspects of the subject. These have not been related to one another with a corresponding degree of understanding. There is also a vast quantity of photochemical reaction data existing with tentative mechanistic conclusions and some with none at all.

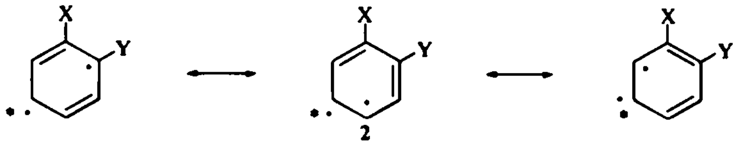
The purpose of this work is to formulate tentative mechanistic concepts which underlie existing photochemical reactions on benzene compounds with the hope that these will serve as a guide for further prediction, experimentation and calculation. The subject herein is restricted to pi orbital excitations of benzene compounds and the reactions resulting from $S_1$ and $T_1$. Obvious risks are incurred in that a reaction now thought to result from either of these two states may later be proven otherwise. In the formulation of these concepts, the excited state is envisioned as one entity which, analogous to ground state benzene, may be described in terms of a set of resonant, valence bond structures. Further the excited state molecule is regarded essentially as that of its ground state deficient of one electron with the dislocated electron ($\cdot^*$) in a high energy orbital not ordinarily used in ground state reactions, i.e. an "antibonding" orbital.

On reviewing the known reactions of photochemistry, it was evident that two major concepts evolve, 1 and 2, together with two secondary ones, 3 and 4.

1. The $S_{1\pi\pi^*}$ and $T_{1\pi\pi^*}$ excited states of benzene can be represented as a set of diene-diradical resonance structures such as **1** and **2**.



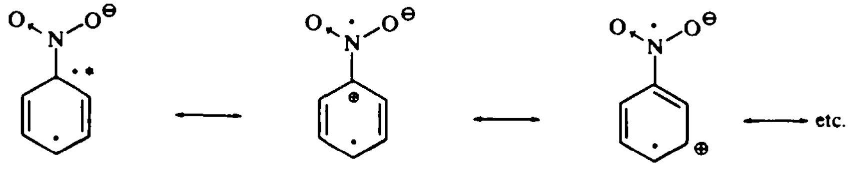
**1**



**2**

At the present time, it is not possible to determine whether there are several close-lying excited states of benzene when $X \neq Y$ or both sets are contributors to the same state.

2. With appropriate solvents, conditions and substituents, intramolecular or intermolecular charge-transfer (CT) processes occur (a) with electron-withdrawing substituents such as $NO_2$ (3), $CO_2H$ and COR,



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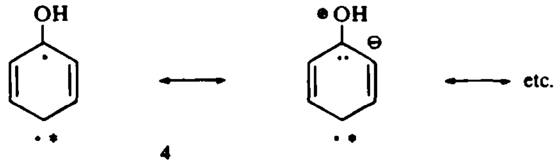
(b) with electron-donating substituents such as OH (4), $NH_2$, $NHCH_3$ and $N(CH_3)_2$,



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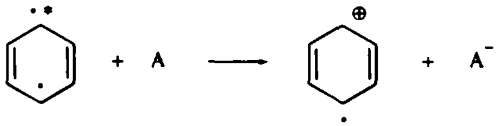
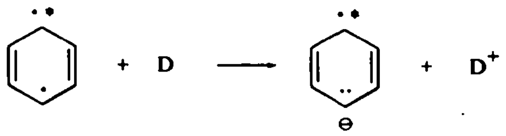
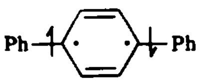
(c) with acceptor molecules (A) such as maleic anhydride, and

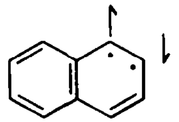


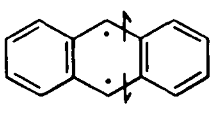
(d) with donor molecules (D) such as occurs with the aromatic molecular complexes.



3. The $T_1$ and $S_1$ states of benzene can be stabilized and the radicals localized to a degree by functional groups. For example, contributing structures giving enhanced stabilization to the $S_1$ states of *p*-terphenyl, naphthalene and anthracene are those of **5**, **6** and **7** respectively.



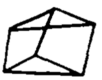




5 6 7

4. Photochemical reactions can occur from species such as **9**, **10**, **11**, **12** and **13** under appropriate conditions such as low temperatures and population of the proper excited state of benzene. These structures represent a change in the relative positions of atoms from that of benzene and those predicted for the excited states of benzene. As a consequence, these cannot be a representation of the benzene excited state as it is first formed.


**9**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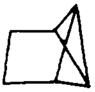
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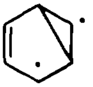
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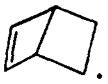
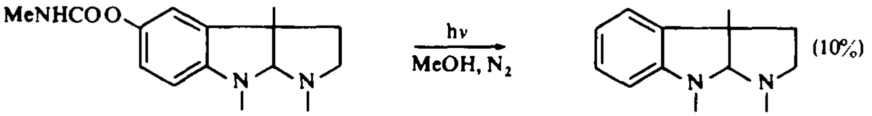

**13**

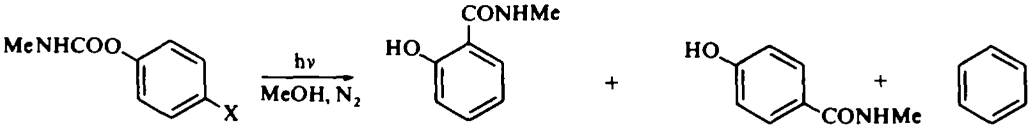
The four subject areas which were most prominent in the development of these concepts are (1) the alpha and beta cleavages of substituents on the aromatic ring, (2) the isomerizations of benzene, (3) $pK_a$'s of excited state molecules and (4) nucleophilic aromatic substitution reactions.

### *Alpha and beta cleavages*

The instigation to formulate this set of concepts was a certain set of data obtained in our Laboratory on the decarbamation reaction and related studies. Physostigmine (**14**) undergoes decarbamation to **15** during irradiation whereas N-methyl-O-phenyl-carbamate **16** is converted mainly to photo-Fries products with the formation of only a small quantity of benzene. Consequently we began investigating the effect of the *para* substituent on the photolysis of carbamates. The amount of aryl-oxygen cleavage with the various substituents are X=H, 1% (49% recovered starting material); X=Me, none detectable (60% recovered starting material); X=OMe, 0·4% (32% recovered starting material); X=F, 2% (56% recovered starting material); X=Ph, 11% (79% recovered starting material). "Zectran" (17) gave 5% 2,6-dimethyl-N, N-dimethylaniline, 7% 2,6-dimethyl-N-methylaniline, 1% 2,6-dimethylaniline, and 14% 18 (33% recovered starting material). Therefore the *para* substituent does indeed affect the course of the photochemical reaction.



**14** **15**



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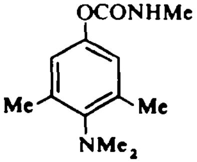
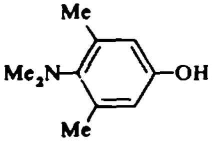
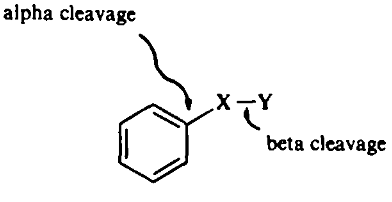


**17**



**18**

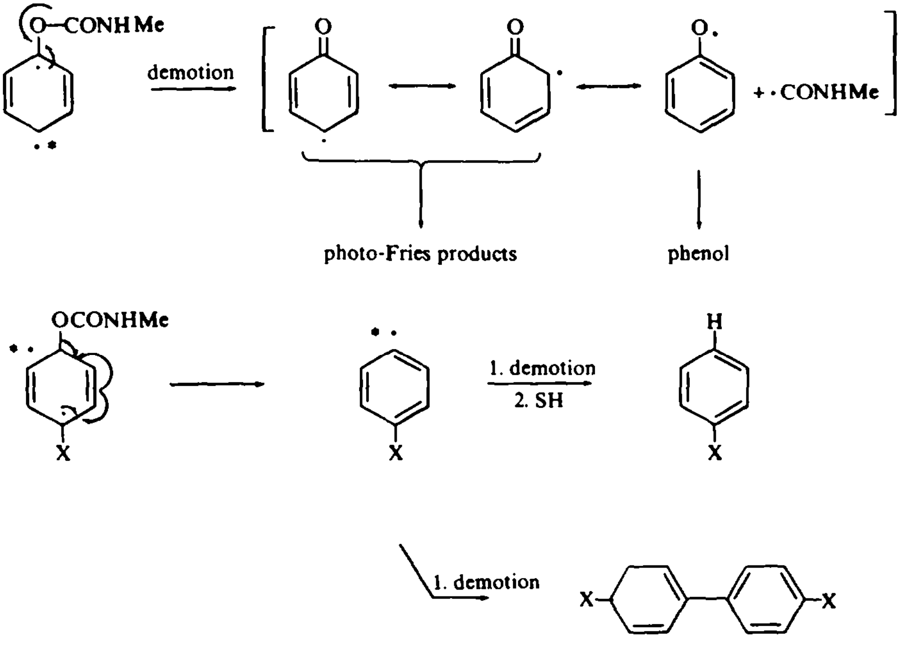
The terms, alpha and beta cleavages, have been used sporadically in literature to represent the bond rupture between the aromatic ring and the attaching atom of the substituent and between the attaching atom and the next, respectively, see **19**. With no reason for changing it, this nomenclature will be used herein.

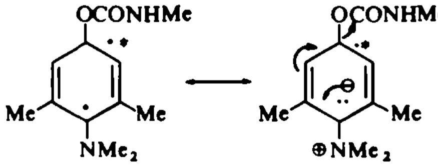


**19**

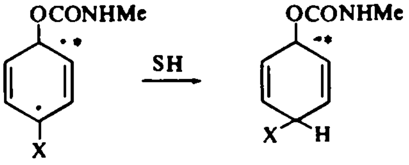
Using the concepts, the carbamate results can readily be explained as a set of two competing reaction pathways from the excited state of the benzene ring (Scheme 1). With the well-known ability of *p*-amino and *p*-phenyl substituents to shift the benzene chromophore to longer wavelengths, an alternative charge transfer process may well be occurring to promote a heterolytic alpha-cleavage, **20**. This is attractive since it explains phenyl and amine participation without the requirement of having the p-orbital of the nitrogen in an overlap position with the aromatic pi-orbitals, a condition which is virtually eliminated with **17**.

SCHEME 1





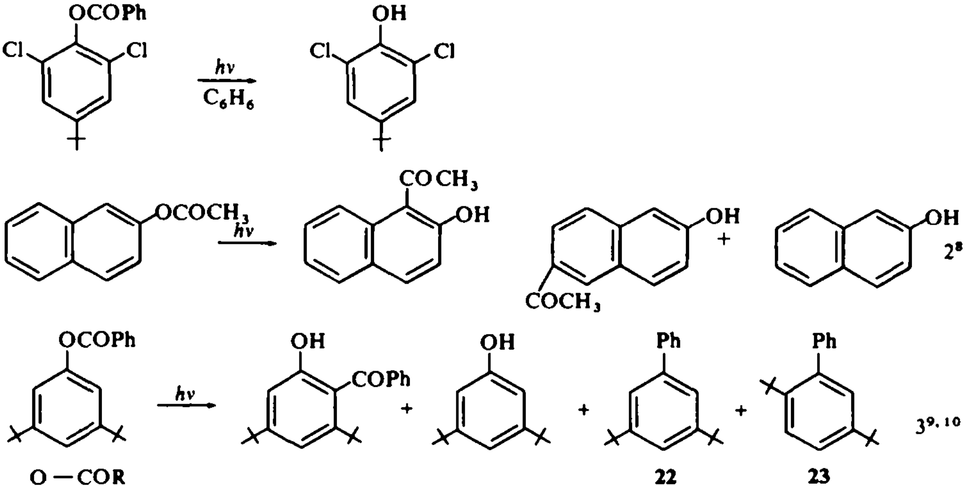
**20**



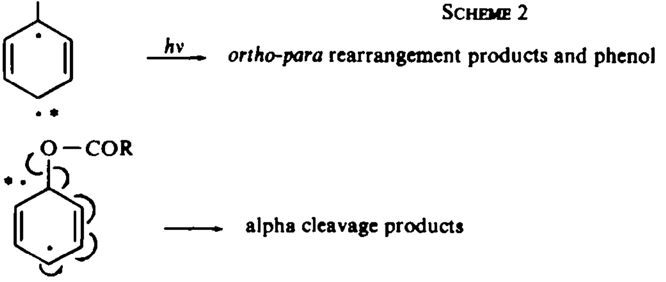
**21**

A third possibility exists where the diradical-diene can abstract a hydrogen atom and cause a heterolytic aromatic-oxygen bond rupture as well, **21**. Then a polar solvent which is also a good hydrogen atom donor would be most desirable to promote the reaction. However the opposite is found. The yield of aryl-oxygen bond cleavage products is reduced on going from methyl alcohol to isopropyl alcohol.

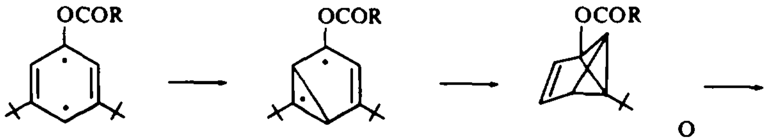
The photo-Fries reaction is a second example of where both alpha and beta cleavages occur during the irradiation of the same compounds and can now be explained in a similar manner. The photo-Fries reaction is thought to involve either $S_1$ or a short-lived $T_1$ of benzene.[2,3] Gas phase experiments reveal that the reactions are not concerted in this phase with the inference that it is also not concerted in the liquid phase.[4] However it must at least be a closely associated radical pair in a solvent cage in liquid solution. Decarboxylation occurs as a side reaction.

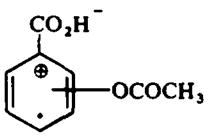


SCHEME 2



The reactions 1-3 can be rationalized in accordance with Scheme 2. The diene-diradical concept is consistent with the radical nature of the reaction[5] and the lack of *meta* substitution. Products **22** and **23** could arise via a benzvalene structure either concommittant with the loss of $CO_2$ or prior to it.[6]





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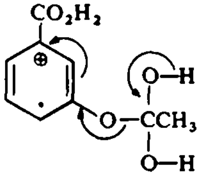
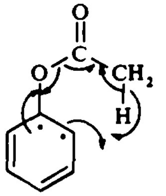


**25**



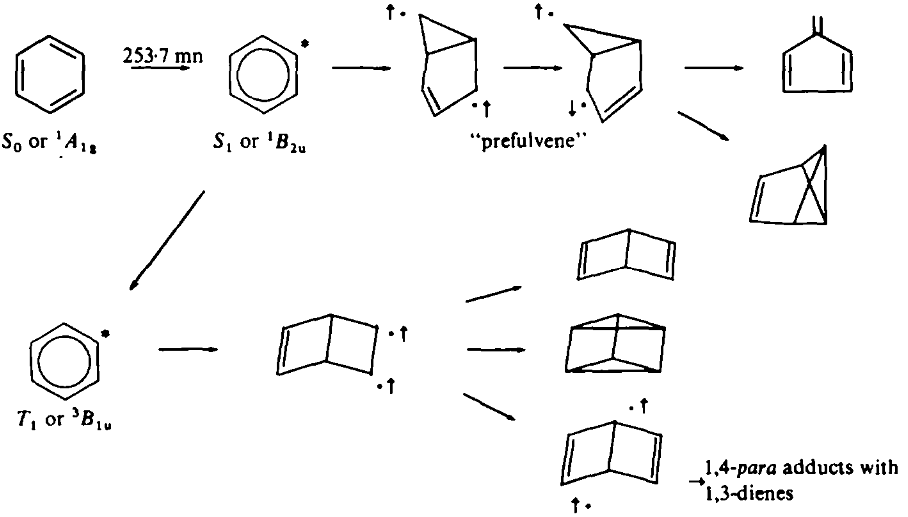
**26**

The electron-accepting ability† of the carboxyl group is probably responsible for the high proportion of phenol formation during the irradiation of *o*-, *m*- and *p*-acetoxybenzoic acids in ethanol and acetic acids, cf. **24**. A particularly favorable situation for hydrolysis is present in the *meta* isomer **25**. The formation of ketene can be rationalized according to **26**.[10]

*The isomerizations of benzene*

Benzene and substituted benzenes are isomerized into fulvene, bicyclohexadiene, benzvalene and prismane during irradiation. Intermediates of these types are used

SCHEME 3



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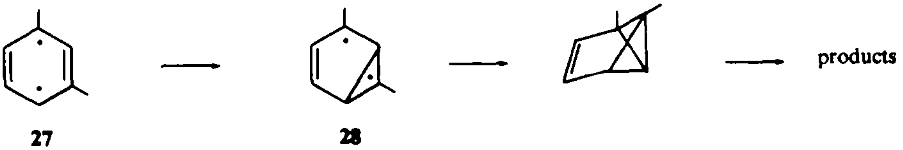
† See discussion on $pK_a$ of $S_0$ and $S_1$ of napthoic acids.

in rationalizing some of the positional isomerizations of alkylbenzenes. Bryce-Smith and Longuet-Higgens[12] have explained these isomerizations in terms of the "prefulvene" diene-diradical concept of Scheme 3. This is consistent with the known fact that substituents on benzene isomerize during irradiation with concomitant changes in the ring carbons.[13]

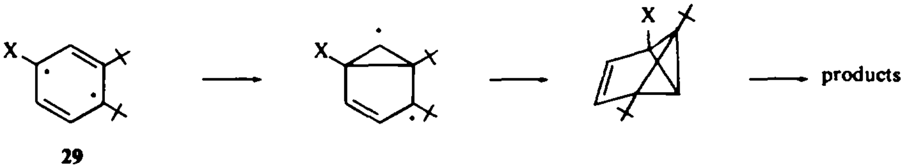
The concepts of the excited states of benzene described herein differ significantly in description but the consequences are the same and the rationalization of existing reactions requires little or no modification. However, explanations of hitherto unexplained phenomena can now be offered.

1. The preference of *meta*-xylene over the *ortho* and *para* isomers to rearrange.[14]



Structure 27 rearranges to the diradical 28 which has more stabilized radicals.

2. *Ortho*-di-t-butylbenzene rearranges but *p*-nitro-, *p*-MeO and *p*-acetyl-*o*-di-t-butylbenzene rearrangements are strongly inhibited.[15]



The driving force for the rearrangement of *ortho*-di-t-butylbenzene is thought to be the steric repulsion of the two *ortho* bulky t-butyl groups. With the *para* substituents, the diradical structure 29 contribution to the excited state is enhanced and the rearrangement is discouraged.

3. Since the CT process is not expected to be important in these rearrangements, it is not surprising that the quantum yields are independent of the solvent.[14]

Invoking the secondary concept 4, it is expected that these isomerizations only occur on relatively unreactive compounds.

### *The acidity of organic molecules*

The strongest evidence for the intramolecular CT concept comes from the changes of p$K$'s of phenols, aromatic amines and acids during excitation. Two trends appear significant: (1) dramatic changes in p$K_a$'s occur on excitation to $S_1$, and (2) the p$K_a$'s of $T_1$ are nearly the same as those of the ground states for most compounds. cf. Table 1. Therefore for the compounds of this table a major change in the electronic environment of the functional groups occurred on going from $S_0$ to $S_1$, but the difference in this environment is minimal between $S_0$ and $T_1$.† However, this is not necessarily always true.

The compounds which alter p$K_a$ values on being excited to $S_1$ can be grouped into two types depending on whether they become more or less acidic during excitation. Further if the ammonium ions are considered in their conjugate base forms then these two groups correlate with electron withdrawing and donating substituents on the aromatic ring, respectively. Thus phenols, naphthol and 2-naphthylammonium cation become more acidic in their respective $S_1$ excited states and the acridinium ion, 1-naphthoic acid, its acidium cation and 2-naphthoic acid more basic.

For both of the two types, the phenomena can be adequately explained by the CT process concepts 2a and 2b. The inherent dilemma of the excited state acting as both an electron donor to an acceptor group and a receiver of an electron from a donor group is resolved by recognizing that it is the high energy electron in the antibonding orbital which is transferred to the acceptor group and the electron-deficient pi-system which accepts an electron from a donor group.

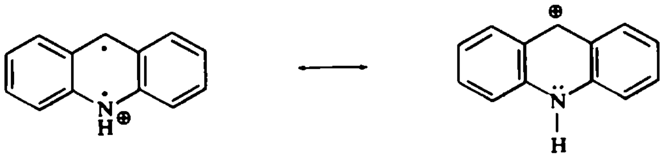
In regard to the triplet states of the molecules, insufficient energy is present to allow much intramolecular charge-transfer character. An interesting test case for the future is that of the aromatic nitro compounds where the charge-transfer phenomena appears to be possible in the triplet state.

TABLE I. THE p$K$ VALUES OF THE GROUND STATE AND EXCITED STATES[16, 17]

| Compound† | p$K_a$($S_0$) | p$K_a$ ($S_1$) | p$K_a$ ($T_1$) |
|---|---|---|---|
| group 1 | | | |
| *p*-Cresol | 10·3 | 4·4 | 8·6 |
| *p*-Bromophenol | 9·4 | 3·0 | 7·7 |
| *m*-Methoxyphenol | 9·7 | 3·8 | |
| 2-Naphthol | 9·5 | 3·1 | 7·9 |
| 2-Naphthyl ammonium cation | 4·1 | −2 | 3·2 |
| group 2 | | | |
| 2-Naphthoic acid | 4·0 | 10–12 | 4·1 |
| 1-Naphthoic acid | 3·7 | 10–12 | 4·2 |
| Acridinium cation | 5·5 | 10·6 | 5·6 |
| 1-Naphthylacidium cation | −6·9 | 1·5 | |

† Where there are several reported values for a datum, an average is recorded.

The acridinium ion must be considered as a special case. Both as the free base and as the ammonium ion, the nitrogen is a part of the aromatic bonding skeleton in contrast to 2-naphthylamine. This special system perhaps allows a CT process of a different type to occur in the ammonium ion form, cf. **30**, with the consequence of enhanced basicity of the nitrogen atom in $S_1$ acridine.



**30**

### *Nucleophilic aromatic substitution*

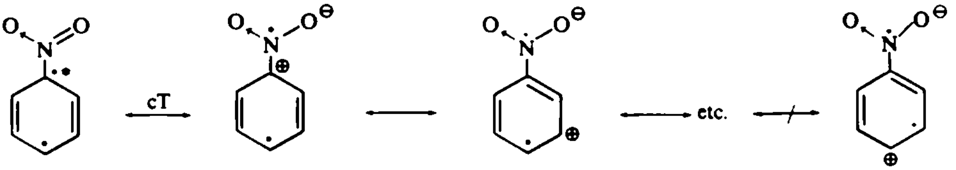
One of the most perplexing problems of photochemistry has been the rationalization of the complex results of nucleophilic aromatic substitution reactions. Some of these reactions occur with *ortho–para* addition and others with *meta*. However, the functional groups cannot be categorized into *ortho–para* directors and *meta* directors readily. Further the course of these reactions are often influenced by the polarity of the solvents.

At the present time, aromatic nucleophilic substitution reactions caused by light involve either nitro, acetyl, or cyano electron-withdrawing groups on the aromatic ring. Of these three, the most detailed studies have been done on the nitrobenzenes. As a consequence, the following discussion dwells on these.

Mechanistically, two categories of aromatic nucleophilic substitution are apparent: (1) those reactions of nitrobenzene where the nucleophilic attack is on the 3 and 5 or *meta* positions and (2) those where the attack is at the 1,2,4 and 6 positions.

### 3,4 (meta) *Substitution*

Using the diene-diradical concept of the excited state of nitrobenzene and incorporating the CT process, the principal contributing structures to the excited state are those of **31**. It is then readily apparent that nucleophilic attack will occur on the *meta* positions. The following reactions[4–12] can now be rationalized.



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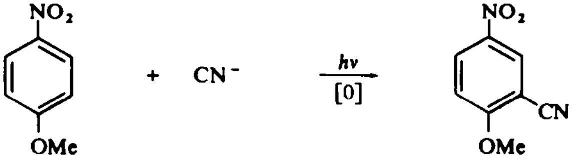
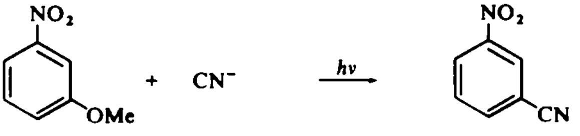


4[18–20,21]



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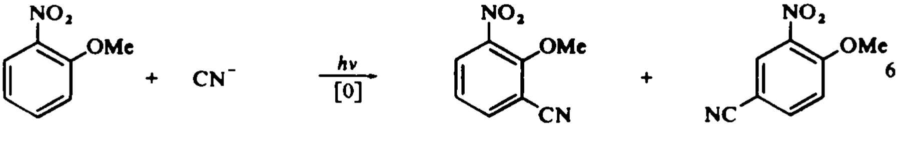

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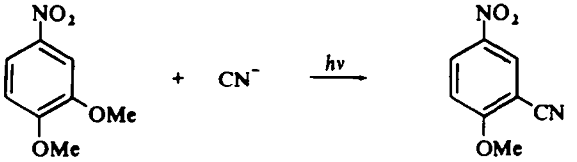

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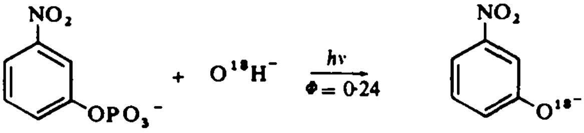

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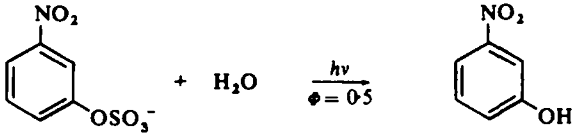

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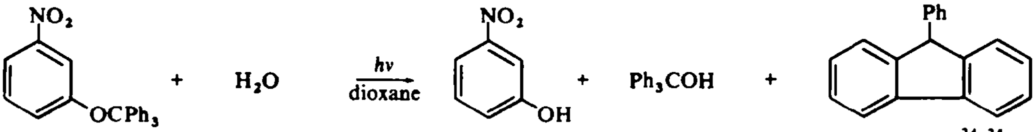

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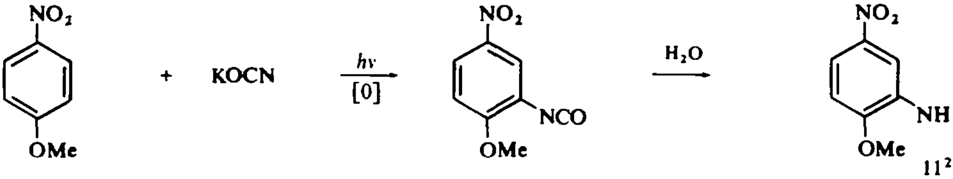

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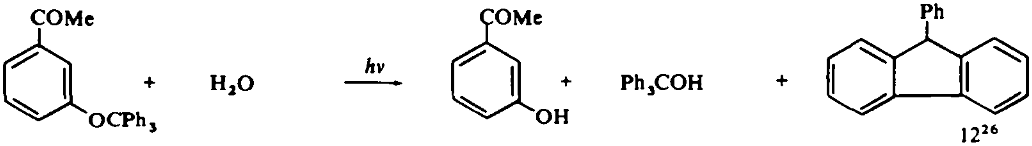

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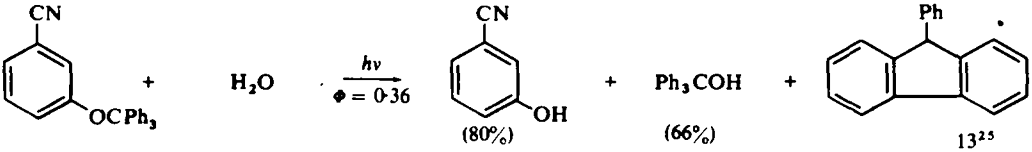
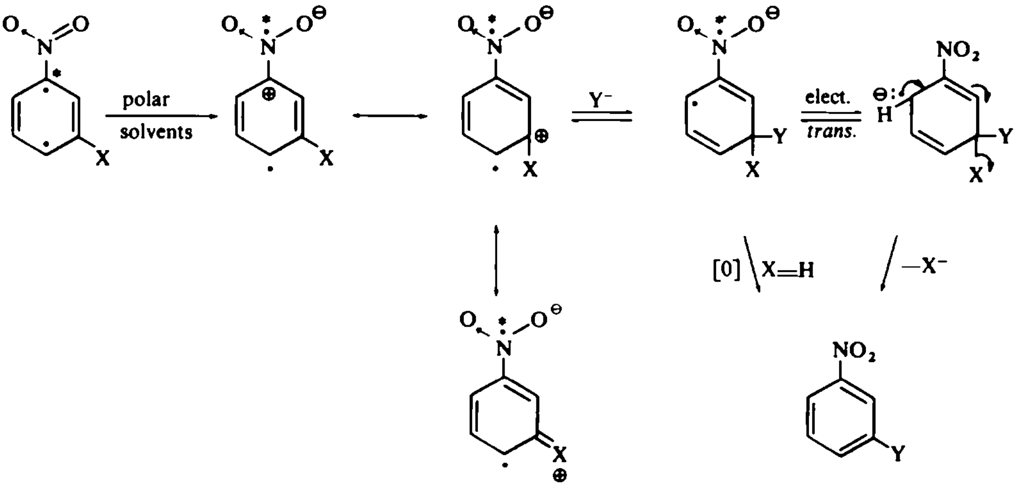


13[25]

The reactions, 4–13, can be placed into two subgroups in accordance with whether or not an oxidizing agent is needed. If the leaving group is hydrogen, then an oxidizing agent is required. If one such as oxygen is not provided, the nitroaromatic acts as its own oxidizing agent and complex reaction mixtures result.[18, 27, 28] Mechanistically, the substitutions are illustrated in a general way in Scheme 4. Electron donating *meta* substituents encourage the CT process in the manner illustrated.

SCHEME 4



The excitation represented in Scheme 4 is $\pi\pi^*$ and the active spin state is $S_1$. *Meta* substitution has not been sensitized as yet, is quenched by $Br^-$ and to a lesser extent by $Cl^-$,[20, 23] is insensitive to oxygen[19, 20, 22, 29] and is independent of whether $S_1$ or $S_2$ is formed.[21, 24, 26, 30] Therefore the conclusion that *meta* substitution occurs from the $S_{1\pi\pi^*}$ state is likely correct.[20, 23, 25, †]

### 1,2,4,6 (1, ortho, para) *Substitution*

The substitution pattern is altered from the *o,p* classification already suggested since replacement of the electron withdrawing group is associated with the reactions in which *ortho* and *para* substitution occur. However, a case can also be made that the substitution at position 1 can occur with the 3,5 group reactions since the carbon holding this group becomes positive with the CT process, cf. Scheme 4. Consequently it would not be surprising if substitution at $C_1$ would occur in some of the *meta* group reactions.

Since the same electron withdrawing species can cause 1,2,4,6 substitution in one instance and 3,5 in another, a new intermediate is warranted for the former group of reactions. Because 3,5 substitution generally occurs with highly reactive nucleophiles as $CN^-$, it can be assumed that the formation of the 1,2,4,6 intermediate is relatively slow on the reaction time scale. Though the triplet state can give rise to this inter-

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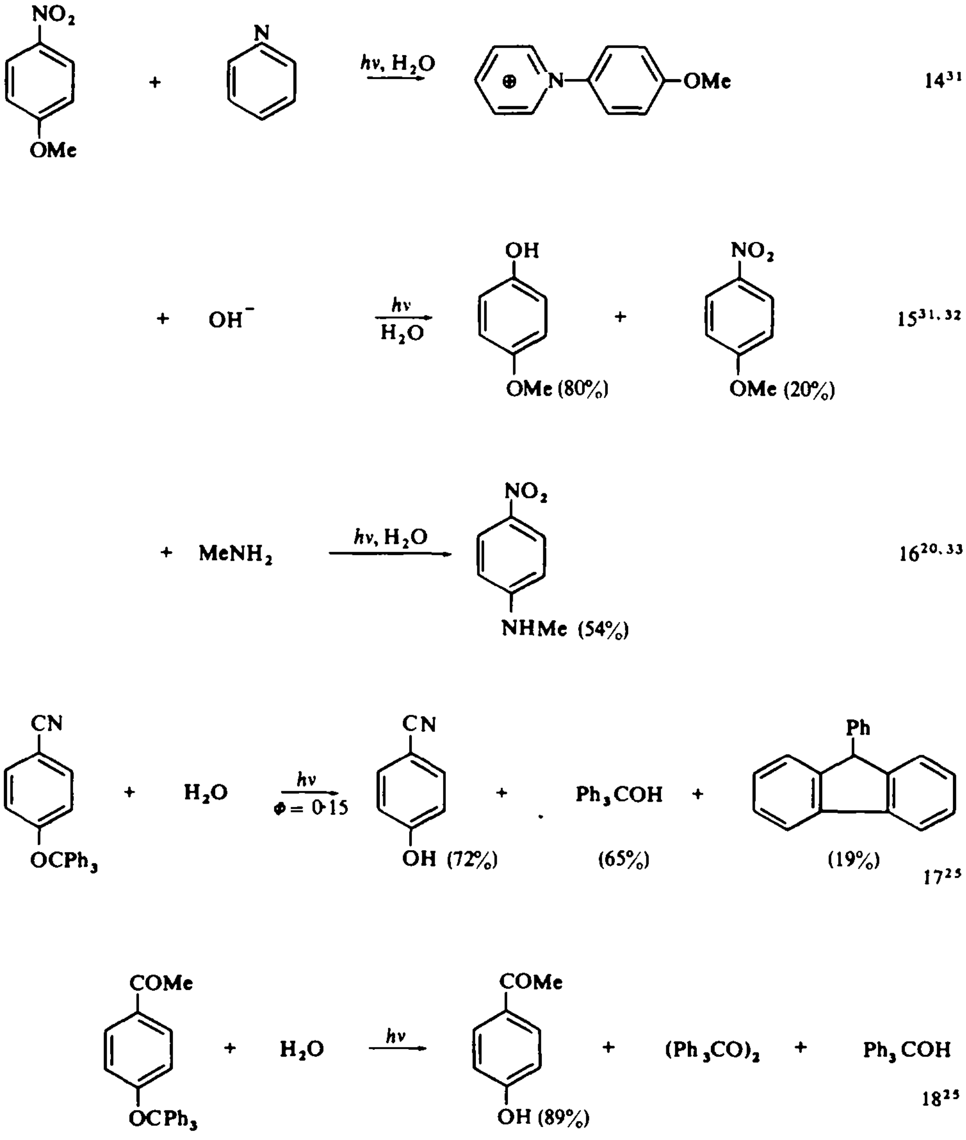
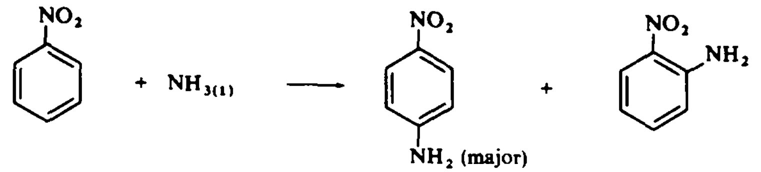
[†] See the discussion on $pK_a$ of phenols.

mediate,[30] so can the singlet state. One of the 1,2,4,6 reactions can be sensitized by $Ph_2CO$ and the sensitized reaction quenched by oxygen. However, the same reaction on direct irradiation is not quenched by oxygen.[30]

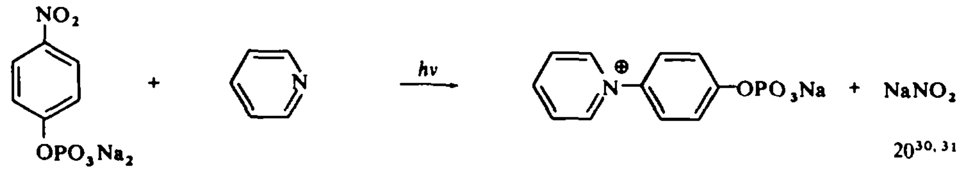
The nature of the 1,2,4,6 intermediate can be surmised from the reaction products it gives, cf. reactions 14–20. A good candidate is the bicyclohexadiene **32**. Nucleophilic attack on **32** would be expected to occur at positions 1,2,4,6 as illustrated in Scheme 5. This concept is in conformity with the experimental observations that the preferred attack is at the 1 and 4 positions.

SCHEME 5

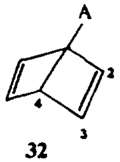




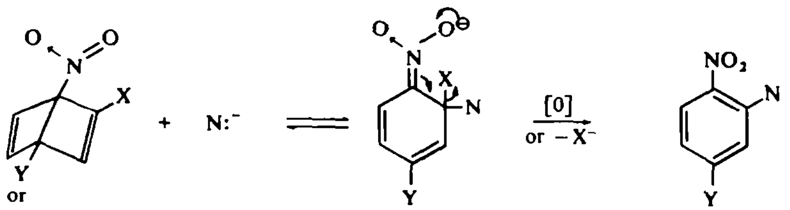
19[20]

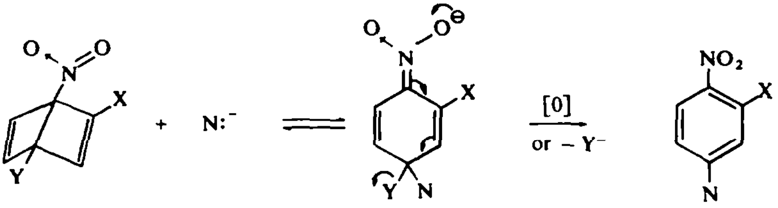


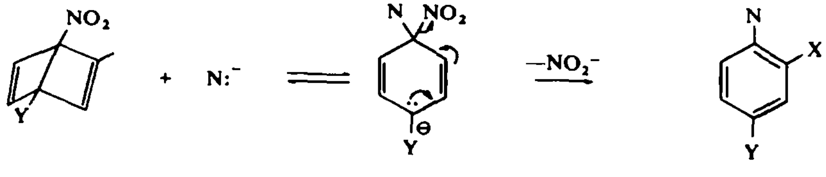
20[30, 31]



**32**

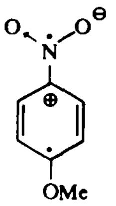






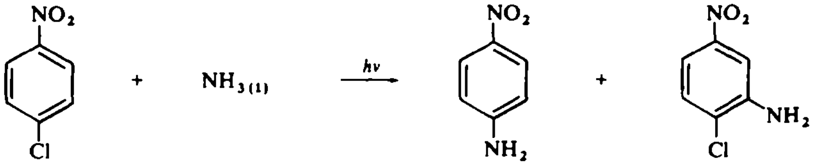
The bicyclohexadiene intermediate formation rate and the lifetime of the cyclohexadiene-diradical species is expected to be less influenced by solvent change than the CT process. In nonpolar solvents the CT state is of higher energy and reaction product yields from it should be correspondingly reduced. This is consistent with the observation that the reaction rate of *p*-methoxynitrobenzene with the cyanide ion in 95% $CH_3CN$–5% $H_2O$, reaction 4, is 1/50 that of the same reaction in water. However solvent effects are complex and can affect the ground states and transition states as well.

Letsinger and Hautula[18] have observed that nitrobenzene is unreactive to nucleophiles under the conditions where *p*-methoxynitrobenzene reacts. This is the consequence of a substituent stabilizing effect on the excited state, 33. Letsinger and McCain[19] also report that *p*-hydroxynitrobenzene is unreactive under these same conditions. Since phenols are known to increase in acidity during irradiation,[29] the resulting charge transfer into the aromatic ring reduces its reactivity to attacking nucleophiles which accounts for the observation. It is obvious that the OH group differs remarkably from the methoxy group in its ability to transfer an electron into the aromatic ring. This is attributed to the ability of the H atom to be stabilized by other basic species in the reaction media which is in agreement with Weller's experiments on the absorption-phosphorescence of salicyclic acid and its methyl ether.[32]

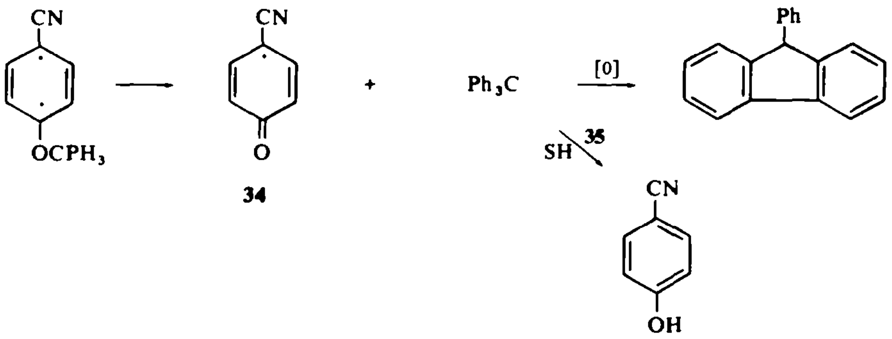


33

Since the aromatic compounds can react via (1) the diene-diradical, (2) the CT state and (3) the bicyclohexadiene, mixtures of products from different reaction types are



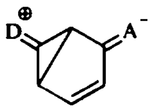
21



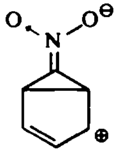
to be expected when energy factors are balanced. There are many recorded examples of where this has occurred such as reactions 17 and 21. In reaction 17, *p*-hydroxybenzonitrile and triphenylcarbinol arise through the bicyclohexadiene intermediate whereas 9-phenylfluorene arises from the diene-diradical **34** to give the relatively stable triphenylmethyl radical **35**, *cf* also reactions 12 and 13.

### *Further application, discussion and prediction*

The concepts of the resonance theory also explains the photochemistry of DArA systems including the more puzzling *meta* orientational CT effect. The "long" or "stretched" bonds of **35** previously used to explain the CT phenomena like that of **36** for explaining the *meta* orientation effects of ArA molecules can now be retired. The radical-ionic nature of excited state phenols as shown in their reactions is quite consistent with that of structure **4**.



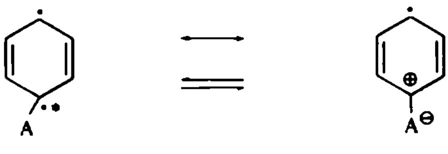
**35**



**36**

These concepts have further application on certain of the di-*pi*-methane reactions and with appropriate modifications to the heterocyclic aromatic compounds. Perhaps most exciting of all is the possibility that the practical interpretation of light absorption, fluorescence, phosphorescence and lifetimes of excited states might follow.

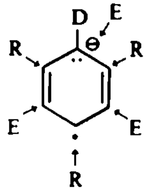
One of the most controversial points of this resonance theory of excited states has been the question of whether the CT molecules contribute stabilization to the excited state by resonance or by equilibrium, **37**. This is a theoretical point to be settled



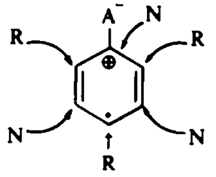
**37**

which does not bear on the applications discussed. This has been represented as resonance herein because the CT band is not wholly what the name implies. Dipole moment studies indicate partial ionic character to the CT state rather than complete charge transfer.[34] Theoretical studies[35] and absorption spectra work[36] agree.

In regard to prediction of chemical reactivity, it is necessary to take into account the nature of the substituent as well as the amount of CT character of the excited state. With a large CT contribution to either $S_1$ or $T_1$, sites of radical (R), nucleophilic (N) and electrophilic (E) reactions are to be expected as illustrated on structures **38** and **39**.



**38**



**39**

## EXPERIMENTAL

Methanol solns (5·0 ml) of the six carbamates (7 × $10^{-2}$ *M*) were deoxygenated in quartz tubes with a stream of $N_2$ and sealed. All the tubes were irradiated simultaneously using a Rayonet Photochemical Reactor with 253·7 nm lamps. The tubes were equidistant from the lamps and were continuously rotated during the 72 hr irradiation. The reaction solns were analyzed for alpha cleavage products by GLPC (Beckman GC-5 gas chromatograph equipped with dual flame ionization detectors). Chromatographic columns used were A, 20 ft × 0·125 in. 5% KOH-20% Carbowax 20 M-60-80 mesh Chromosorb W; B, 6 ft × 0·125 in. SE-30; C, 8 ft × 0·125 in. Poropak QS. Retention times on two or more of the above columns and spiking techniques were used to identify the alpha cleavage products. All yields are based on recovered starting material. Recovered starting material was determined by preparative TLC (Silical Gel HF-254) using diethyl ether as eluent.

*Acknowledgements*—The National Science Foundation Traineeship (D.R.D.) and the Career Development Award (V.I.S.), National Institutes of General Medical Sciences, 1-K4-GM-9888) were invaluable for this work. The hospitality of Imperial College during my Leave-of-Absence (V.I.S.) and the discussions of these concepts with Profs. D. H. R. Barton, G. Porter, Drs. P. Magnus, P. Sammes, O. L. Chapman and D. Widdowson are gratefully appreciated. The detailed review of this manuscript and its contents by Dr. J. Wing was especially helpful.

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