AROMATIC PHOTOSUBSTITUTION REACTIONS[1]

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Abstract—In this paper attention is given primarily to substitution reactions of photoexcited aromatic compounds with (non-excited) nucleophiles. At the end a brief discussion is presented on the less-well known, but no less interesting photoinduced electrophilic substitution reactions, followed by a schematic representation of the various possible ways of heterolytic reaction of an electronically excited aromatic molecule.

Nucleophilic aromatic photosubstitution nowadays comprises a great number and variety of reactions. Without ignoring traditional photochemical characteristics (singlet vs triplet reaction, $\pi \to \pi^*$ or $n \to \pi^*$ excitation etc.) the authors offer a systematization based mainly on the nature and influence of substituents (electron attracting or donating) in the aromatic system and on kinetic features.

For certain types of aromatic photosubstitution the results obtained by chemical and spectroscopic investigations permit speculation on their mechanism. The variety and subtlety of the photoinduced aromatic substitutions seem to be no less than that of their thermal counterparts notwithstanding the fact that these reactions generally proceed extremely fast (not far from encounter controlled).

As in the field of concerted processes, in heterolytic aromatic substitutions the thermal and the photochemical reactions mutually complement each other in a theoretically intriguing and practically useful way.

INTRODUCTION

Twenty years ago R. O. de Jongh, working as a student at the laboratory of organic chemistry at Leiden, observed that his measurements of the reaction rates of the nitro phenyl phosphates were hampered by a surprising heterolytic photosubstitution process. This was most strongly the case with the meta isomer.[2,3]
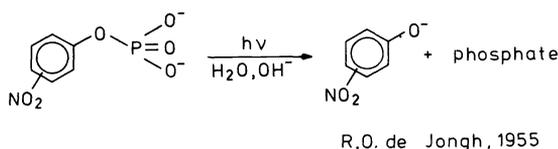
R.O. de Jongh, 1955

Fig. 1. Light-induced hydrolysis of (meta) nitrophenyl phosphate in alkaline medium (1955).

It soon became clear that with this then unorthodox photoreaction we had entered a new domain of chemistry, where the rules proved to be characteristically different from and often opposite to those prevailing in groundstate chemistry. In contrast to the well known ortho/para activation in classical aromatic substitution here meta activation by the nitro group seemed to be the rule.

Such a reversal of rules was encountered again some five years later in a different, but no less striking, form when studying the photo- and the thermal cyclisation of dienes and trienes in the vitamin-D field.[4] It may well reflect principles that govern and relate chemical phenomena occurring in the different electronic states of molecules and in passing from one state to the other. To us it certainly brought the inspiration to embark on a long term study of the photosubstitution of aromatic compounds. We hoped to gain insight into the mechanistic features of these reactions as well as to open new possibilities for synthetic chemistry.

It is not the purpose of this lecture to give a historical review or to cover the field in its current scope[5] but rather to illuminate some of the characteristic results obtained and to indicate developments for the near future.

After the first examples had been discovered, photosubstitution was soon found to occur with other aromatic esters, ethers, halogeno-compounds, etc. reacting with a variety of nucleophiles.[3,5] The reactions often proceed to a high degree of conversion resulting in good yields of easily isolated product.

Polycyclic and some heterocyclic compounds react even better than benzene derivatives (Figs. 2–4). There is a choice of (polar) solvents: water, t.-butanol/water, acetonitrile, tetrahydrofuran/water. The following lists representing results from different laboratories may illustrate the scope of the reaction.

Leaving groups in $S_N Ar^*$: OPO_3H^{2-}, OSO_3^{2-}, OR^-, NO_2^-, $F^- = Cl^- > Br^-$ ($> J^-$), H^-, N_2, SO_2^{2-}, CN^-.

Nucleophiles reacting in $S_N Ar^*$: OH^-, OR^- (CH_3O^-/CH_3OH), CN^-, NH_3, aliphatic amines, pyridine, NO_2^-, H^-, CH_3^-, CNO^-, CNS^-, Cl^-, SO_3^{2-}, CH_3COO^-, H_2O, ROH.

The number of reactions and the variation of the phenomena observed, gradually made the field (even to an organic chemist) look chaotic. However, at the moment we feel that the following empirical classification encompasses the earlier as well as the recent results and moreover gives a lead to a not too remote classification based on mechanism.

1. Nucleophilic photosubstitution of aromatic compounds activated by electron attracting substituents ($-NO_2$, $COCH_3$, $-NO$, $-CN$). Many classical examples
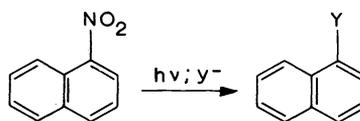
$Y^- = OCH_3^-$, CN^-, $H^-(BH_4^-)$, $Cl^-(RCl)$, $NH_2^-(NH_3)$
Some substitution reactions shown by 1-nitronaphthalene (not by nitrobenzene)
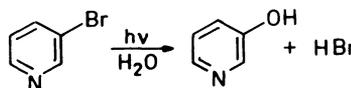
Fig. 2.

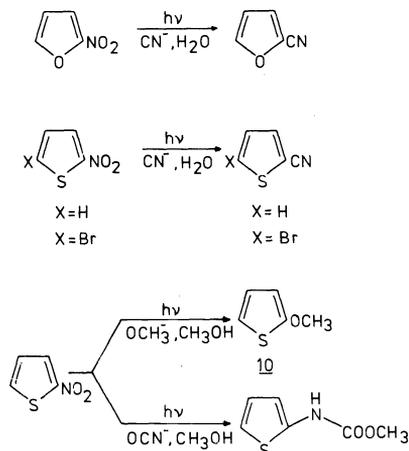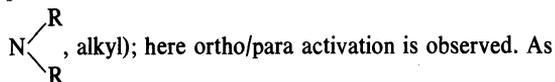Fig. 3. Photohydrolysis of 3-bromopyridine.

Fig. 4. Nucleophilic photosubstitutions of 2-nitrofuran and of 2-nitrothiophene.

belong to this group. A characteristic meta activation obtains.

2. Nucleophilic photosubstitution of aromatic compounds activated by electron donating groups (OH, OR, N$\diagdown^{R}_{R}$, alkyl); here ortho/para activation is observed. As an illustrative example may be mentioned the reactions of para-fluoro- or para-chloroanisole, where (isolated) yields of more than 90% substitution product are obtained (Fig. 5).[6,7] To round off this introductory survey it should be
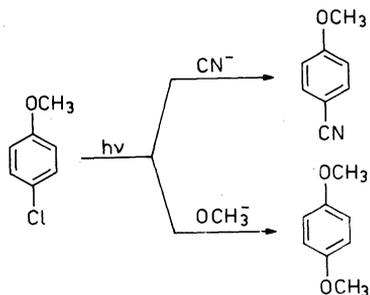

Fig. 5. Photosubstitution reactions of para chloroanisole.

stated that meta activation by electron withdrawing groups (1) and ortho/para activation by electron-donating substituents (2) are complemented by two additional directing effects.

(3) "α-reactivity" in polycyclic aromatics. Other things being equal naphthalenes and azulenes react preferably at
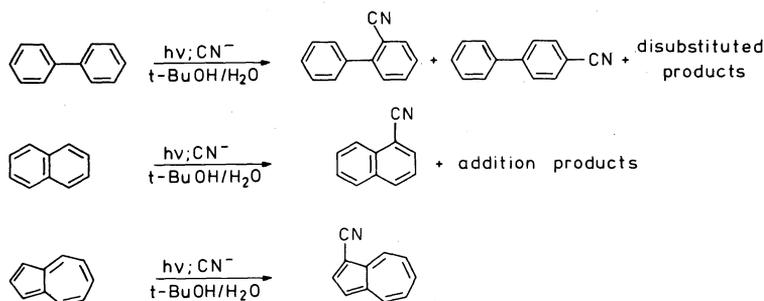
the 1 position, biphenyls at the 4 and 2 position, phenanthrene at the 9 position.

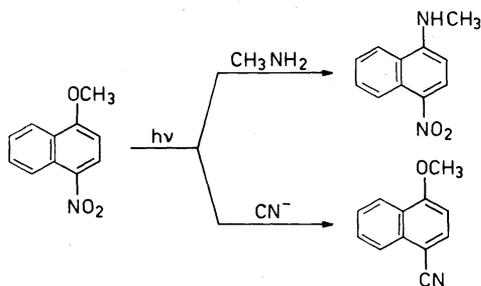(4) Merging (resonance) stabilisation in product formation. An example is given in Fig. 7.

Fig. 7. Directing influence of merging (resonance) stabilisation.

Judicious handling of these four orientation principles enables us to predict the product composition of photoinduced nucleophilic photosubstitution reactions in a given system.

After this short introduction let us have a more detailed look and discussion of the reactions of categories 1 and 2.

1. Reactions activated by electron attracting substituents.

(a) *Qualitative description*

As we will see later in the discussion the fact that meta nitrophenyl phosphate shows a more rapid and clean photosubstitution than the ortho- and the para-isomer is in itself no proof of real meta activation. It may be due just as well to a longer lifetime. More reliable indications are derived from the reactions of compounds like 4-nitroveratrole, where the meta and the para position in one and the same molecule are compared. (Fig. 8). Reactions with different nucleophiles indicate that in photosubstitution it is the group in the meta position indeed that is the most reactive (Fig. 9). A clear meta activation ("extended" meta activation in polycyclic
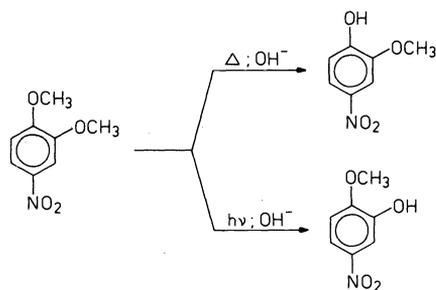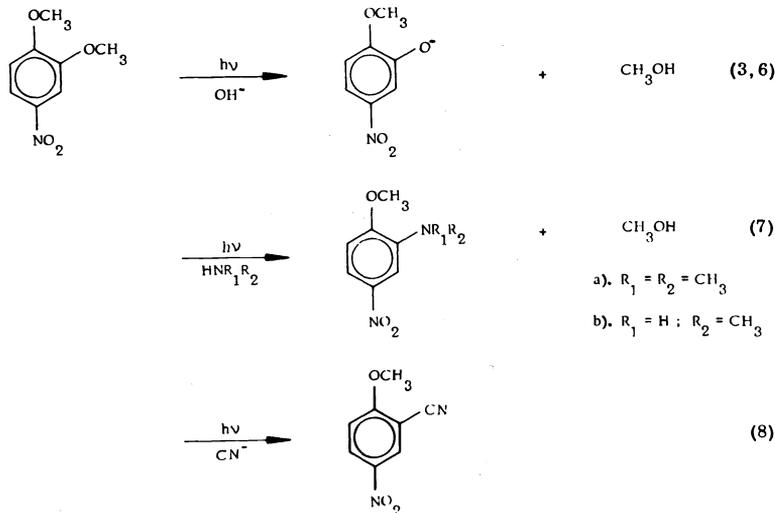

Fig. 8.

Fig. 6. "α-Reactivity". Photocyanation of biphenyl, naphthalene and azulene.

Fig. 9. Meta activation by the nitro group in the photosubstitution of 4-nitroveratrole by various nucleophiles.

$$(3,6)$$

$$(7)$$

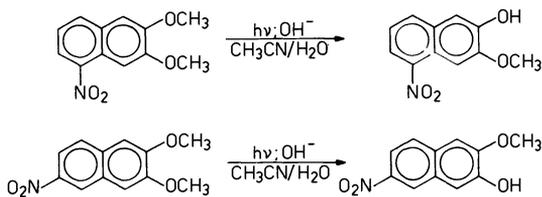a). $R_1 = R_2 = CH_3$

b). $R_1 = H$; $R_2 = CH_3$

$$(8)$$

Fig. 10. "Extended" meta activation in photosubstitution of 5- and 6-nitro-2,3-dimethoxynaphthalenes.

aromatics, Fig. 10) can thus be observed in the photostimulated molecule, contrasting to the ortho/para activation in the ground state. These reactivities parallel the charge distribution calculated for the molecule in its lowest $\pi \to \pi^*$ state (singlet or triplet) and in the ground state (Fig. 11). The quantum yield is mostly independent of the wavelength (interesting exceptions are found e.g. with azulenes) and increases with the nucleophile concentration. At concentrations of $10^{-3} \to 10^{-1}\,M$ nucleophile the extent of increase is diminished and ϕ reaches a constant upper value that is smaller than 1 (often 0.1–0.6) (Fig. 12). These characteristics suggest a pathway of reaction as indicated in a simplified manner in Fig. 13. The required linear relationship between $1/\phi$ and $1/_{[N]}$ has been observed in very many cases (Fig. 14). Starting from this simple picture as a basis we now want to learn the nature of the reacting excited species, the values of the various rate constants, the intermediates, and the mechanism of the reaction steps.

Fig. 12. Photoamination of meta nitroanisole.

Schematic representation of $S_N2\,Ar^*$ [(3)]

$$\phi = \phi_{isc} \frac{k_1[N]}{k_1[N] + k_2[N] + k_d}$$

$$\phi^{-1} = \phi_{isc}^{-1} \frac{k_1 + k_2}{k_1} + \frac{k_d}{k_1\,[N]}$$

Fig. 13.

	S_0	S_1	S_2
	+ 0.001	+ 0.053	+ 0.021
	+ 0.011	+ 0.036	+ 0.048
	+ 0.011	+ 0.030	+ 0.121
	0.000	+ 0.127	- 0.002

Calculated charge densities on carbon atoms 2 and 3 in 2,3-dimethoxy-5-nitro- and -6-nitro-naphthalene in the ground state and the first and second excited π,π^* singlet state.
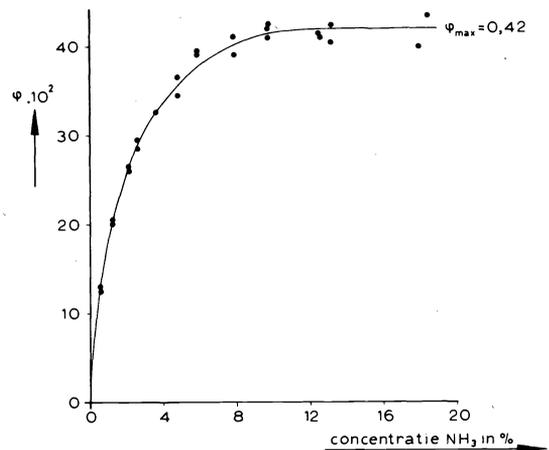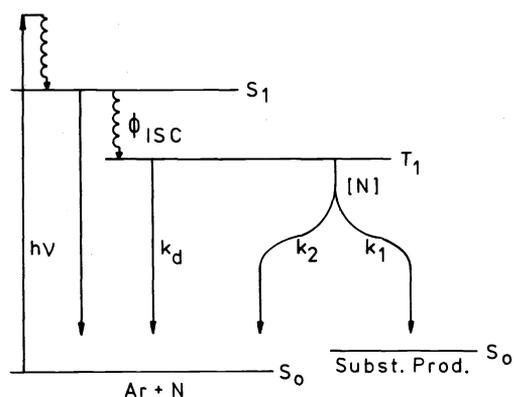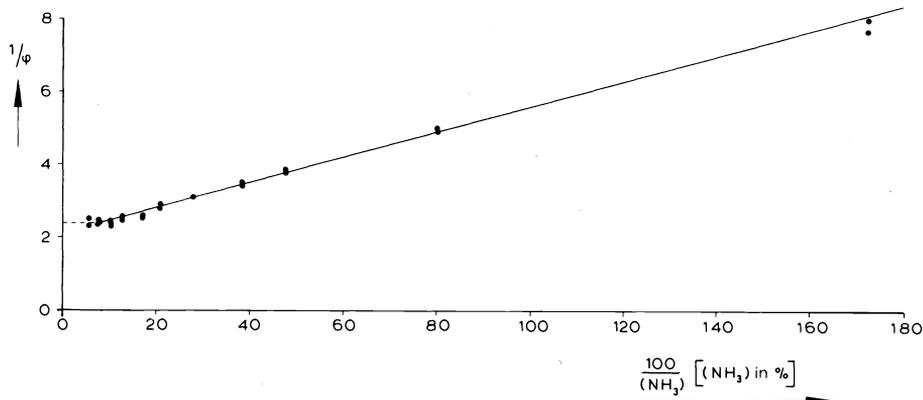
Fig. 11.

Fig. 14.

(b) Quantitative data; the nature of the reacting excited species[8,9]

In order to satisfy the primary requirement for quantitative mechanistic studies, i.e. clean reaction with completely known product composition, systems were chosen on the basis of the rules presented in the introduction of this paper. We used naphthalene derivatives, substituted at the α-position by good leaving groups (F and OCH$_3$). Extra activation was effected by a nitro group at the 3- or 6-position. The reactions were performed in acetonitrile/H$_2$O, 1:1, applying hydroxide ion and methylamine as nucleophiles. The photosubstitution
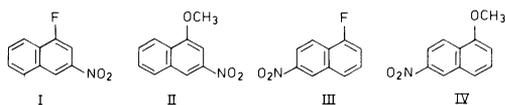
Nucleophiles: OH$^-$, CH$_3$NH$_2$ (in CH$_3$CN/H$_2$O 1:1)

Sensitizers : benzophenone, triphenylene

Quenchers : tetramethyl diazetine dioxide,
            9-fluorenone

Fig. 15.

of all naphthalenes with both nucleophiles could be triplet sensitized with the curious exception of the photohydrolysis of 1-methoxy-3-nitronaphthalene. The reactions that take place upon direct light absorption may therefore be, but are not necessarily, triplet reactions. A decisive indication comes from experiments with triplet quenching. We present in the following the data obtained using tetramethyl diazetine dioxide (TMDD; $E_T = 40$, $E_S = 94$ Kcal/mol). (From Fig. 16 one sees that in the case of a 100% triplet process the following relation is obeyed:
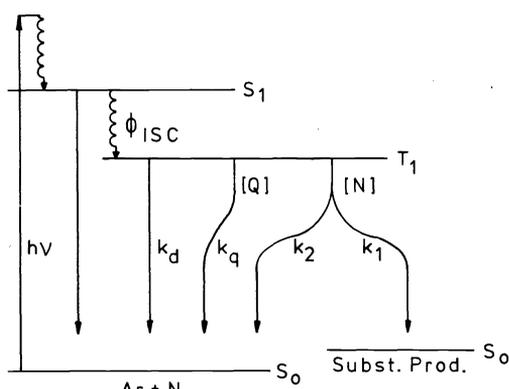
$$\phi^{-1} = \phi_{isc}^{-1}\left\{\frac{k_1+k_2}{k_1} + \frac{k_d}{k_1[N]} + \frac{k_q[Q]}{k_1[N]}\right\}.$$

These relations appeared to hold for the reactions of compounds I, II and III. Interestingly the reactions of 1-methoxy-6-nitronaphthalene could not be quenched and therefore seem to constitute an example where the compound reacts in the singlet state.

The results of the rate measurements are summarized in Tables 1 and 2. From the data we can draw some significant conclusions even though the value of ϕ_{isc}, amounting to 0·73 for 3-nitro-1-fluoronaphthalene, is not yet exactly known for the methoxy compound.

(1) The fact that the data for the 3-nitro- and 6-nitro-1-

Schematic representation of S_N2 Ar* [3] in the presence of quencher Q

$$\phi = \phi_{isc}\frac{k_1[N]}{k_1[N] + k_2[N] + k_q[Q] + k_d}$$

$$\phi^{-1} = \phi_{isc}^{-1}\left\{\frac{k_1}{k_1+k_2} + \frac{k_q[Q]}{k_1[N]} + \frac{k_d}{k_1[N]}\right\}$$

Fig. 16.

fluoronaphthalene are similar confirms in a striking manner that the meta-activation by a nitro group extends practically undiminished into the other ring.[10] This is another element of difference from what obtains in ground state chemistry.

(2) The rates of reaction of the triplet excited aromatics with both nucleophiles (k_1 values) are very great and not more than one or two orders of magnitude smaller than the diffusion controlled rate of triplet quenching ($K_q \simeq 10^{10}$ l/mol/s).

The reactivity of the methoxy compound is somewhat larger than that of the corresponding fluoro compound.

(3) The fact that, at not too large nucleophile concentration, higher quantum yields of substitution are found for 1-fluoro-3-nitronaphthalene than for 1-methoxy-3-nitronaphthalene stems from the considerably longer lifetime (~100 x) of the fluoro compound (k_d values). This overcompensates the lower reactivity (k_1).

These conclusions are particularly illustrative.

For the interpretation of quantitative data in photochemical processes it is essential to break down the values for the quantum yields in terms of intersystem crossing

Table 1. Kinetic data on nucleophilic photosubstitution of 1-fluoro-3-nitronaphthalene and 1-methoxy-3-nitronaphthalene
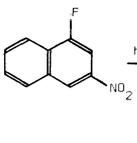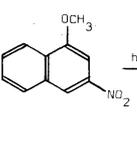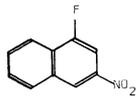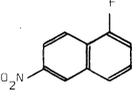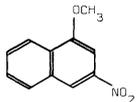
$$\phi^{-1} = \phi_{isc}^{-1}\left[\frac{k_1+k_2}{k_1} + \frac{k_d}{k_1}[N]^{-1} + \frac{k_q}{k_1}\frac{[Q]}{[N]}\right]$$

$\phi^{-1} = 2.4 + 0.057\,[OH^-]^{-1} + 130\dfrac{[TMDD]}{[OH^-]}$

$\phi^{-1} = 3.6 + 0.046\,[CH_3NH_2]^{-1}$

$\phi^{-1} = 10.0 + 1.84\,[OH^-]^{-1} + 70\dfrac{[TMDD]}{[OH^-]}$

$\phi^{-1} = 10.0 + 1.62\,[CH_3NH_2]^{-1} + 40^{*)}\dfrac{[TMDD]}{[CH_3NH_2]}$

Table 2. Rate constants and lifetimes of the reacting triplets in the photosubstitution of nitrofluoro- and nitromethoxynaphthalenes

	Φ_{isc}	k_1	k_2	$\tau = 1/k_d$
+ OH⁻	0·8	$1\cdot1.10^8$	$1\cdot0.10^8$	2.10^{-7}
+ CH₃NH₂	0·8	$1\cdot3.10^8$	$2\cdot5.10^8$	2.10^{-7}
+ OH⁻	0·8	$1\cdot0.10^8$	$1\cdot4.10^8$	$2\cdot5.10^{-7}$
+ OH⁻	0·3?	6.10^8	$1\cdot2.10^9$	$\sim3.10^{-9}$
+ CH₃NH₂	0·3?	1.10^9	2.10^9	$\sim2.10^{-9}$

efficiency, lifetime of the reacting excited species, and its specific rate of reaction.

(c) *Intermediates in* $S_N2Ar^{*11,12}$

In the study of the very fast photoreactions, where a decisive part of the process may often be described as an internal conversion, a transition from the one molecular potential surface to the other, or as a thermal relaxation, we have to reckon with the drawback that the invaluable tool in thermal reactions, transition state theory, cannot be applied. On the other hand the nature of the initiation of a photochemical process together with the high rate of the reaction, offers possibilities of studying short lived intermediates much more efficiently than with most thermal reactions. By throwing a short flash of light of sufficient intensity into the system a large percentage of all reactant molecules is brought into the reactive excited state almost instantaneously and their fate can be followed.

We chose as one of the systems to study by flash techniques the $S_NAr^{*(3)}$ of 3,5-dinitroanisole (dNA) with various nucleophiles. Most experiments were done on the alkaline photohydrolysis to dinitrophenolate (dNP), a clean reaction that has a good quantum yield ($\phi_{max} = 0\cdot51$) and that can be efficiently followed e.g. by UV absorption. Using a nitrogen discharge flash ($t \sim 10^{-6}$ sec.)

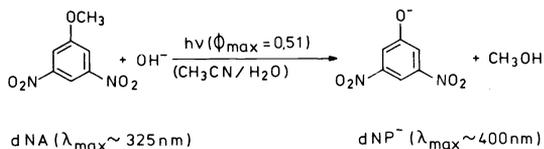dNA ($\lambda_{max} \sim 325\,nm$)   dNP⁻ ($\lambda_{max} \sim 400\,nm$)

Fig. 17. Nucleophilic photosubstitution of 3,5-dinitroanisole (dNA).

a short lived species with a broad absorption band at ~550 nm and a half life time of 40 ms could be traced. E.S.R. and other methods proved it to be the radical anion dNA⁻, a species that sometimes had been considered as a possible intermediate in the S_NAr^* reactions. However it now appeared from inspection of the UV spectra that formation of the product dNP⁻ ($\lambda_{max} \sim 410\,nm$) is completed within the shortest time measurable with this N₂ discharge ($\sim 10^{-6}$ s). Most probably the radical anion upon protonation reacts to form reduction products (azoxy benzenes) that indeed are found in small percentage in the crude reaction mixtures. Evidently the complete S_NAr^* reaction is over within 10^{-6} s. Upon initiating the reaction with a nanosecond flash (frequency doubled ruby laser, $t = 6.10^{-9}$ s) two very short lived intermediates could be traced. The one, with a UV absorption maximum around 412 nm, is only formed in the
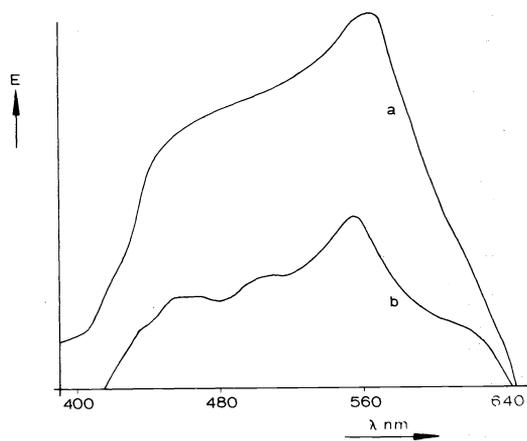
Fig. 18. Absorption spectrum of short lived species (radical anion) observed upon flashing 3,5-dinitroanisole in the presence of hydroxide ion (a) or methylamine (b).
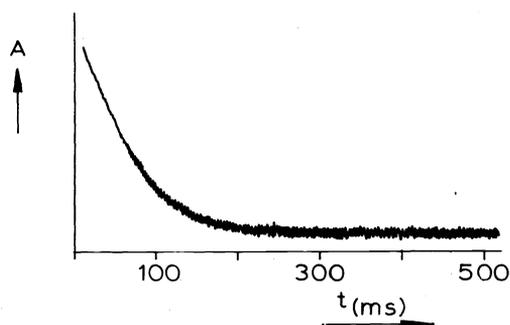

Fig. 19. Decrease of absorption at 555 nm as a function of time.

presence of a nucleophilic reaction partner. It has a lifetime of ~400 ns and converts (partly) to the radical anion and probably also to the substitution product. This latter transition could not be seen directly in the UV due to the coincidence of the position of absorption bands of

complex and dNP⁻ but the product is clearly present as soon as the intermediate has disappeared. Taking all evidence together we assume the 412 nm intermediate to be a complex (σ-complex?, exciplex?) formed from dNA* and nucleophile.

Finally there appears to be a very short lived intermediate ($t_{1/2} \sim 20$ ns; λ_{max} 475 nm) that is formed upon illumination of dNA even in the absence of nucleophile. Its lifetime, that depends on nucleophile concentration, agrees with the value found for the reacting triplet by quenching experiments.

The results obtained by the flash techniques (Fig. 21) thus bring more concreteness to the picture of Fig. 13 that was derived primarily from qualitative features.
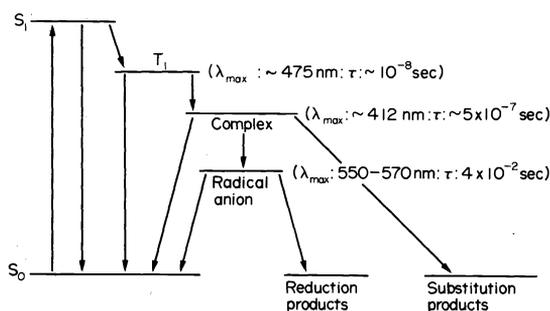

Fig. 21.

(d) $S_N 1$ Ar* processes

As a transition to the discussion of category 2 of nucleophilic photosubstitutions (activated by electron donating substituents) it is appropriate to look at a few photosubstitutions that may be indicated as $S_N 1$ Ar* processes. Among the very first examples of photosubstitution, there was one queer exception to the usual bimolecular characteristic. Meta nitrophenylsulphate showed an efficient photohydrolysis with a quantum yield ($\phi = 0.51$) that did not increase with increasing hydroxide ion concentration. The same exceptional behaviour was observed several years later with 5-chloro-3-nitro-
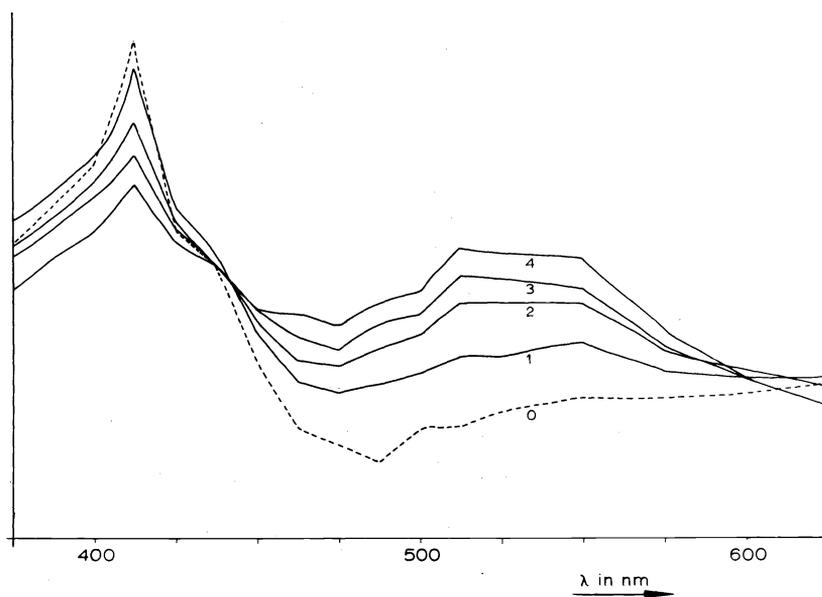

Fig. 20. Absorption spectra of alkaline solutions of 3,5-dinitroanisole (in CH_3CN/H_2O) in course of time following excitation by laser flash (347 nm).

Table 3. Quantum yields of photohydrolysis of some halogenopyridines as a function of pH

		Ph	14	13	7	6	4	3	2·4	2·1	1·2
2-Cl-pyridine	Φ_{OH}			0·07	0·07						
2-Br-pyridine	Φ_{OH}			0·32	0·31	0·31	0·29				0·20
2-I-pyridine	Φ_{OH}			0·14	0·15		0·18				
3-Br-pyridine	Φ_{OH}		0·14	0·13	0·14	0·14	0·12	0·09	0·03	0	
4-Br-pyridine	Φ_{OH}			0·2	0·2						
2-Br-quinoline	Φ_{OH}			0·02	0·02					0·02	

phenylphosphate, which is the more intriguing since 3-nitrophenylphosphate itself had been the classical example of the second order S_N2Ar^*.

A few more photohydrolyses that are independent of hydroxide ion concentration in a large pH region, were encountered in the heterocyclic field. Most halogenopyridines showed this behaviour. It was with the study of five membered heterocyclics that we encountered a revealing case which proved amenable to a simple rationalisation.[13] Let us compare the photosubstitution (by cyanide) of 2-nitrothiophene and 2-nitrofuran (Fig. 4).

2-Nitrothiophene shows orthodox $S_N2 Ar^{*(3)}$ behaviour. Its rate of disappearance increases with cyanide concentration accompanied by formation of an equivalent amount of 2-cyanothiophene. With 2-nitrofuran the dependence of the formation of 2-cyanofuran on the cyanide concentration is completely normal, ϕ approaching the value 0·51 at ~1M cyanide. However the quantum yield of disappearance of the nitrofuran is independent of the nucleophile concentration and has the value 0·51 even if no cyanide is present at all. Evidently 2-nitrofuran upon excitation reacts efficiently with cyanide not only but also with water. Indeed we could demonstrate the presence of γ-butenolide as the product of this reaction. Taking all evidence together one arrives at the conclusion that here we most probably have to do with a quantum yield determining dissociation in a $S_N1 Ar^*$ type reaction. The positive (carbenium ?) ion formed reacts with water and with other nucleophiles, the product composition depending on the concentrations and reactivities of the various reaction partners (Fig. 22). Of course one should be cautious in assuming that the mechanism proposed in Fig. 22 may be applied to other reactions where the quantum yield of conversion of the starting material seems to be independent of nucleophile concentration. It may quite well be that in some of the reactions mentioned a moment ago, the excited aromatic species (triplet) is so agressive that it undergoes direct substitution for 100% even by the weak nucleophile water. The observed quantum yield may then possibly represent the efficiency of formation of the reacting triplet.

Category 2 reactions
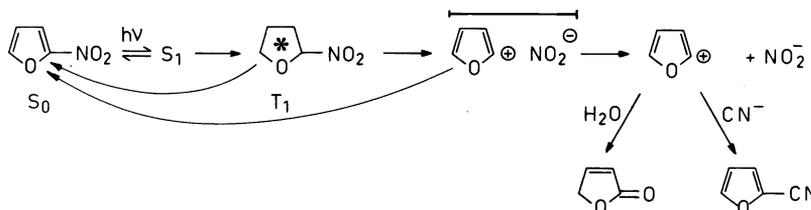
The first question that needs a clear answer is whether

we really have to do here with ortho/para activation by electron donating substituents like methoxy groups a.o. Figures 23, 24, 25 show some of the results that establish this at first glance peculiar phenomenon. The data on the complete series of dimethoxy- and trimethoxybenzenes especially seem convincing.

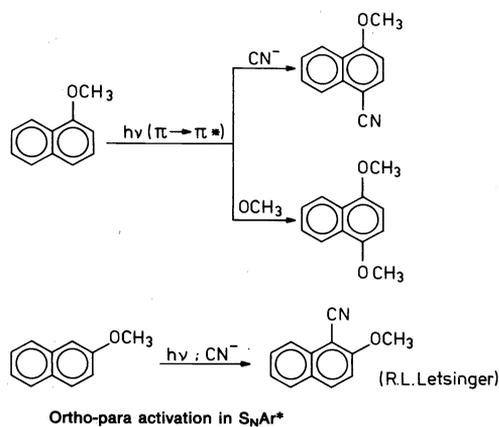Ortho-para activation in S_NAr^*

Fig. 23.

As is clear even from qualitative reasoning this ortho/para activation cannot be understood on the basis of charge densities in the excited singlet or triplet. A rationalisation in terms of a primary photoionisation was adopted as a result of the elucidation of the $S_N1 Ar^*$ reaction mentioned above on the one hand and on experiences in the field of anodic substitution reactions as
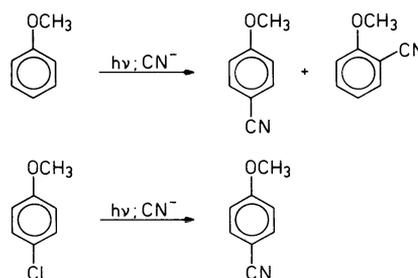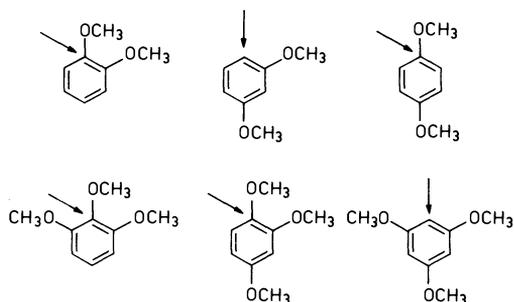

Fig. 24.

Possible $S_N1 A^{*(3)}$ reaction pathway

Fig. 22.

Fig. 25. Positions of preferential attack in photocyanation of di- and trimethoxybenzenes.

trimethoxybenzenes is particularly striking (lc. 16, page 275 and lc. 6).

Of course the situation in the case of the photochemical and electrochemical substitution is different. In the light induced reaction the aromatic partner is selectively activated; in the anodic process more than one electron can be transferred. However this may be, it is promising that experience and viewpoints from photo- and electrochemistry come together and support each other in the elucidation of the various steps of the sequence leading to substitution product.

$S_E Ar^*$ reactions

In traditional ground state chemistry electrophilic substitutions form one of the most widely used and intensively investigated classes of aromatic reaction. As if also in this respect excited state chemistry manifests seemingly opposite behaviour, electrophilic aromatic photosubstitutions until now have been relatively rare and little studied. One of the reactions of this class which, owing to its apparent simplicity and symmetry, looked promising for theoretical studies as well as for practical application, is the photoinduced exchange of hydrogen (isotopes) at aromatic carbon. However, it took quite a bit of perseverance and thorough experimental work before the complexities and difficulties of this reaction could be overcome. Only in the last few years have results from different authors begun to show consistency and mutual agreement.[17,18] It seems certain now that photostimulated

elaborated in the schools of Eberson,[14,15] Weinberg[16] a.o. on the other hand. Considering first the photosubstitution of compounds like para-chloroanisole, one might think of a photodissociation, possibly via formation of an ion pair, which is promoted by the electron, donating (methoxy) group. Alternatively formation of a radical cation by loss of an electron could be considered as the primary process. This question is currently being investigated.[6]

In the photosubstitution of (poly) methoxybenzenes and methoxynaphthalenes where hydrogen is displaced, transfer of an electron may well be the important initial step (Fig. 26). The radical cation will react with the
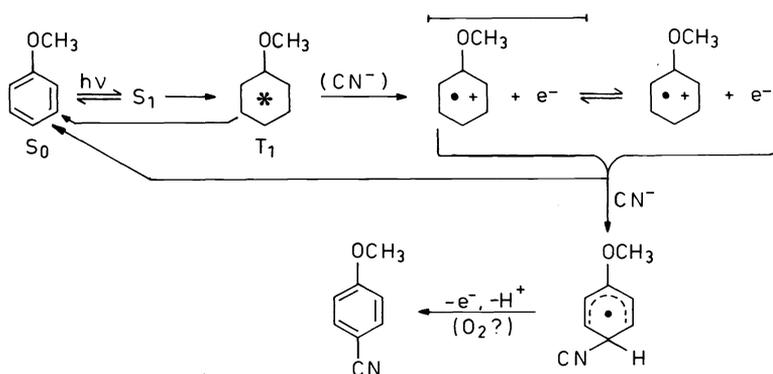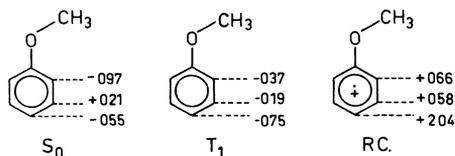

Fig. 26. Possible $S_{R^+N}1(Ar^*)$ reaction pathway.

nucleophile and the substitution product is formed via one or more oxidative steps. The favourable influence of oxygen or, far better still, persulphate is suggestive. Calculated charge distribution in the radical cation affords no contraindication against adopting it as an intermediate in ortho/para substitution (Fig. 27).

The similarity in product composition of e.g. the photoinduced and the anodic cyanation of the di- and

hydrogen isotope exchange in acid media occurs indeed; it can be characterised as an S_E2 Ar^* reaction (Fig. 28), although its precise mechanism has not yet been established.

The pattern of this substitution is markedly different from the thermal counterpart. With anisole and toluene thermal hydrogen exchange in acidic medium at the meta position is strongly disfavoured in comparison to reaction at the ortho and para positions. In contrast it can be effected reasonably well by illumination although at a somewhat lower rate than at the other positions.

Charge distribution of anisole; ground state, lowest triplet, radical cation

Fig. 27.
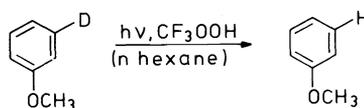
Fig. 28.

Fluorescence studies in these systems indicate that the acids used exert a significant quenching on the excited (singlet) state of the aromatic compound thereby decreasing the efficiency of the hydrogen exchange. This quenching is denoted to be of a "physical" nature, which to a chemist means that the mechanism is still obscure.

More generally "physical" quenching of electronically excited species by the commonly used electrophiles may well constitute one of the causes for the inefficiency of S_EAr^* reactions experienced thus far. Another reason may be that the $\pi \rightarrow \pi^*$ excited compound tends to yield an electron to the electrophilic medium (compare the discussion of the S_{R^+N} reaction). The remaining radical cation by its nature will show little tendency for reaction with electrophiles. A third feature that makes it difficult to perform efficient S_EAr^* reactions may reside in the fact that a high concentration of reactive electrophile, as required for a sufficient encounter frequency with very short lived species, is hard to realize in the commonly used systems.

Notwithstanding these difficulties a few interesting cases of what probably are S_EAr^* reactions—besides the acidic hydrogen exchange—have been found. We mention the light induced protodeboronation of pyridine boronic acids and nitrophenyl boronic acids (Fig. 29).[19] Also the photoacylation of anisole observed as a result of irradiation of anisole in solutions containing acetic acid[17] may well represent an electrophilic photosubstitution (Fig. 30). Although evidently the number of electrophilic aromatic photosubstitutions known at this moment is low, this little trodden field certainly deserves more fundamental investigation.
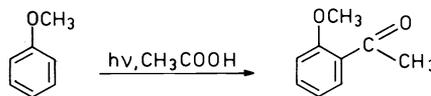
Fig. 30. Photoacylation of anisole.

CONCLUSION

In this lecture an attempt has been made to picture the charms and the challenges in the field of aromatic photosubstitution. This field is inviting because of its unorthodox features to the theoretician, to the chemist interested in reaction mechanism and intermediates, and to the synthetic chemist. At the moment it is not yet justified to classify the light induced substitution reactions of aromatic compounds in terms of detailed pathways and mechanisms. We hope, however, that through the lecture you may have perceived that the time to bring such a classification and rationalisation in this field is almost here and we cannot resist presenting speculation on what such a classification might look like. For the sake of simplicity the reactions considered are limited to those starting from the lowest $\pi \rightarrow \pi^*$ triplet. We have to keep in mind that reactions of molecules in other electronically excited states or those occurring during thermal relaxation in the ground state are no less interesting. The $(\pi \rightarrow \pi^*)$ $A^{*(3)}$ molecule, when compared to a ground state cousin has: (1) a very high energy content, (2) a loosely bound electron as well as an electron hole. It therefore can be expected to undergo,—besides returning to the ground state without chemical reaction and besides homolytic reaction—the following processes that may lead to nucleophilic substitution (Fig. 31):

heterolytic dissociation under formation of a positive (carbenium) ion, direct substitution by a nucleophile, probably via initial complex formation, transfer of an electron to the medium under formation of a radical cation (S_{R^+N}), uptake of an electron under formation of a radical anion (S_{R^-N})[20]†. A comparable scheme can be presented for electrophilic substitution and a photostimulated S_{EA} process (Fig. 32). It is significant that for each of the classes enumerated we can at the present stage already write down an experimentally found reaction as a
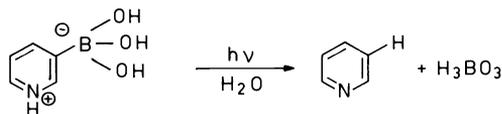
$S_E 1 Ar^*$

Fig. 29.

†For the synthetically important "$S_{RN}1$" reactions, l.c.[20]
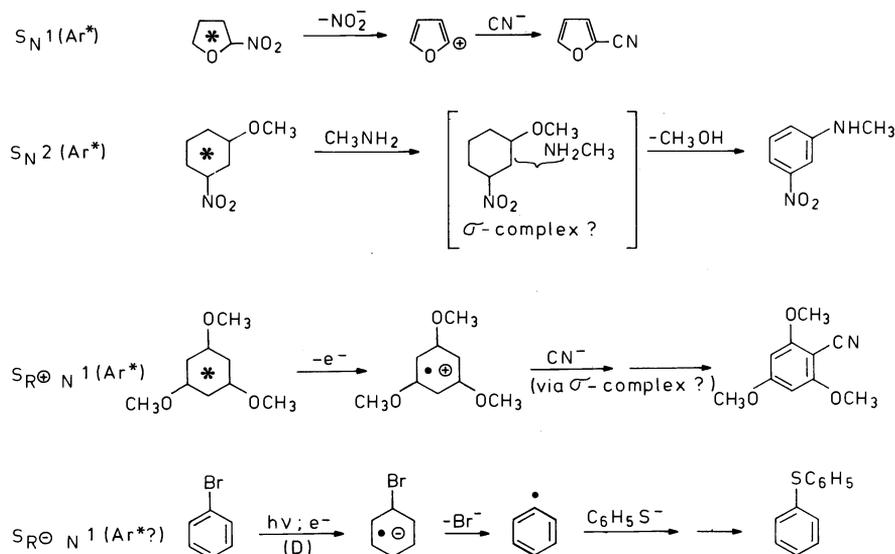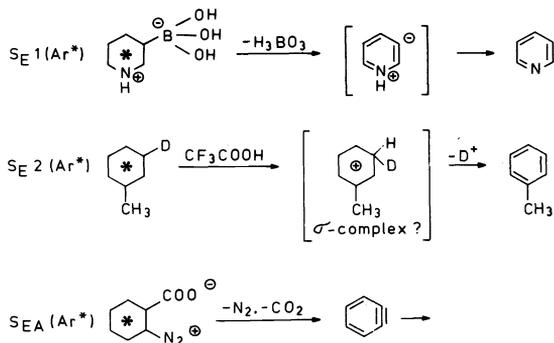
Fig. 31.

Fig. 32.

good candidate. The investigations of the next one or two years will bring proof of the correctness of this speculative scheme or indicate the additions and correction that have to be made. However this may turn out to be, it seems certain that the diverse manifold of reactions of excited aromatic molecules will remain a source of excitement to chemists for a long period to come.

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