SUMMARY

Starting from [2.2.2.2.2.2]metacyclophane the synthesis of [2.2.2.2.2.2]metacyclophane-*all-trans*-hexaene *via* dodecabromo-[2.2.2.2.2.2]metacyclophane is described. The structure of the new ring system was confirmed by UV.-, IR.-, NMR.-, and mass spectra analyses.

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267. Photoreactions of Aromatic Molecules[1]

by **E. Havinga, R. O. de Jongh** and **M. E. Kronenberg**

(28 VI 67)

Chemistry to-day is in a state of rapid evolution. In this evolution photochemistry plays a stimulating role. If we survey the field of photochemistry of aromatic molecules we feel, if not in a brave, then certainly in a new world. To begin with, let us just mention the spectacular transformation and addition reactions that the benzene ring system itself has been found to undergo upon illumination with ultraviolet light. The aromatic nucleus, known for its rigidity in the ground-state, becomes an extremely flexible and extrovert acrobat when being doped with a light quantum! It is clear that a very interesting new field has been opened by the light-induced rearrangements discovered by VAN TAMELEN [1], KAPLAN [2], BURGSTAHLER [3], BRYCE-SMITH [4], FARENHORST [5], and others.

As a result of our investigations at Leiden, attention is concentrated in this review on a second type of aromatic photoreactions, *i.e.* the photosubstitutions. In this field, which we had the good luck to hit upon some 12 years ago [6], one again feels somewhat like Alice in Wonderland when comparing the phenomena with the familiar thermal reactions. Exchanges of substituents considered as very difficult or non-occurring in benzene chemistry, proceed smoothly upon irradiation under appropriate, mostly mild conditions. Thus, *p*-nitroaniline is obtained by just the opposite way to

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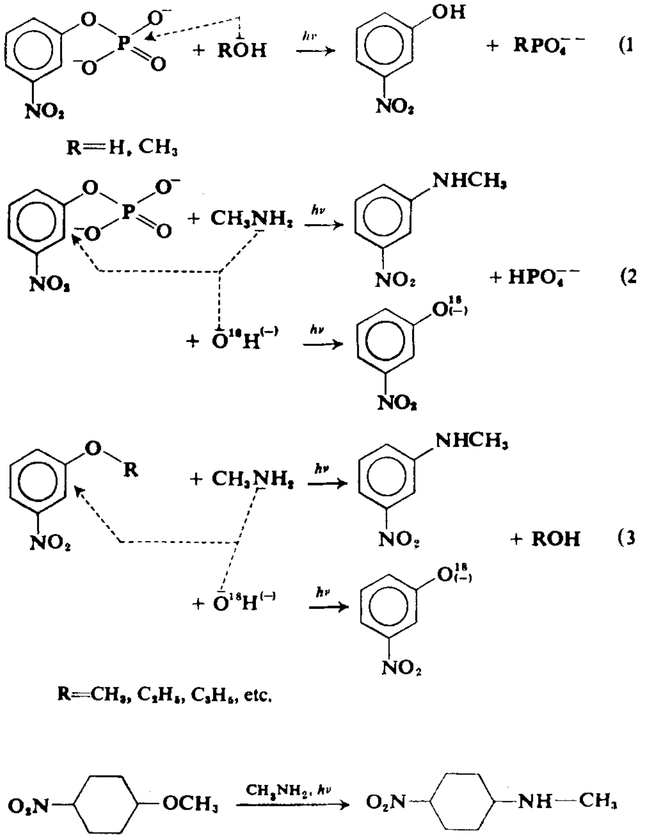
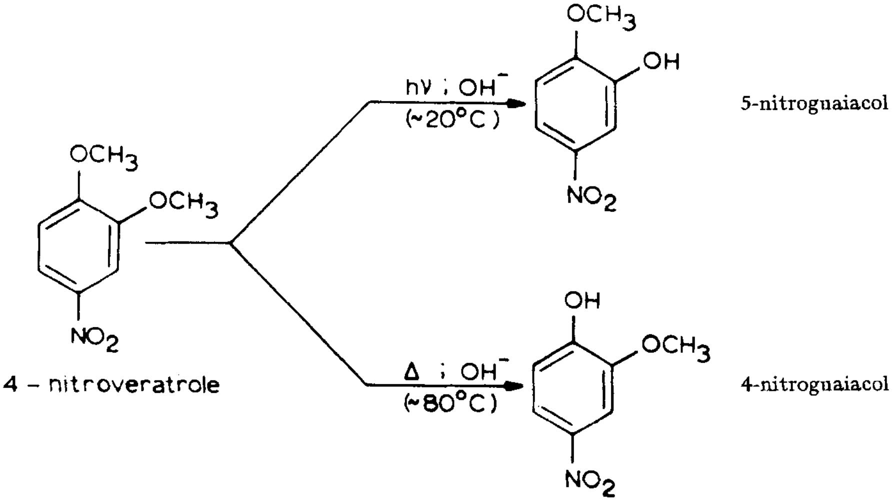
[1] Contents of a lecture given at: the Symposium on Organic Photochemistry, organized by the Swiss Chemical Society, Fribourg, 25. 2. 1967. Published by special permission of the Editorial Board.



Scheme 1. *Photohydrolysis and photoamination of nitrophenyl esters and ethers* [8]



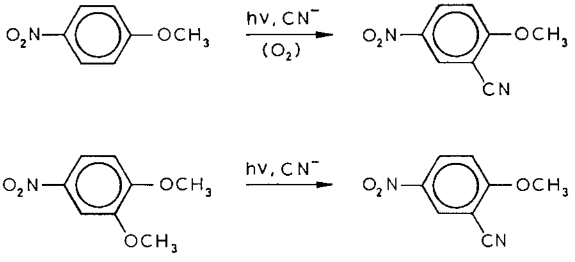
Scheme 2. *The thermal and the photohydrolysis of 4-nitroveratrole* [9]

what we are accustomed to in classical chemistry. Nitrobenzene is directly photoaminated to yield *p*-nitroaniline [7].

To give some ideas about the various types of reaction discovered up to now, a series of representative examples are shown (Schemes 1–5). First is indicated a category of reactions where 'abnormal' orientation comes to light (Scheme 1). In contradistinction to the *o/p* activation or desactivation that governs the orientation of new substituents in thermal reactions, here a *meta*- or *ortho/meta* activation is the general rule.

It is important to stress that in photochemistry one should be aware of the fact that for reactions of molecules in the excited state there is always competition between several processes: the chemical conversion leading to the final product, and the desactivations of the excited state. Thus, when we compare the photoreactions of two different molecules, say *meta*- and *para*-nitroanisole, then the fact that the *meta* compound reacts much better than the *para* isomer may be due to a greater reactivity in the excited state of the *meta* compound. It may also be due, however, to a shorter lifetime of the excited *para* isomer, not allowing efficient bimolecular reaction. We are on somewhat firmer ground if we compare the rates of reaction (quantum yields) of two positions in one and the same molecule, thus eliminating the factor 'lifetime of the excited state'. If we do so in this first class of photoreactions, we then observe the *meta* activation by a nitro substituent in the case of nucleophilic reaction [9], and the *ortho/meta* activations by electron donors such as alkyl and methoxy groupings for electrophilic substitutions (photodeuteration [10]). To make the statement more exact: as will be shown, in this class of reactions the pattern of reactivity is determined by the charge distribution in the excited state, just as in thermal reactions the pattern is governed in some cases by the charge distribution and in most cases by the localisation energies in the ground state. However, even in this seemingly straightforward statement, there is included a number of problems. Before we proceed to analyse these problems in more detail, let us first summarize some further types of photosubstitutions of the first²) category (with *m* or *o/m* activation):

2) Photoaminations of aromatic ethers in liquid NH_3 [8],
3) Photohydrolysis of a nitro substituent [13],
4) Photohydrolysis of -Br and -Cl [8d, 8g, 8h],
5) Photosubstitutions by CN^- [14] (Scheme 3),
6) An example of electrophilic substitution: photodeuteration [10] (Scheme 4).



Scheme 3. *Photosubstitution by CN^-*

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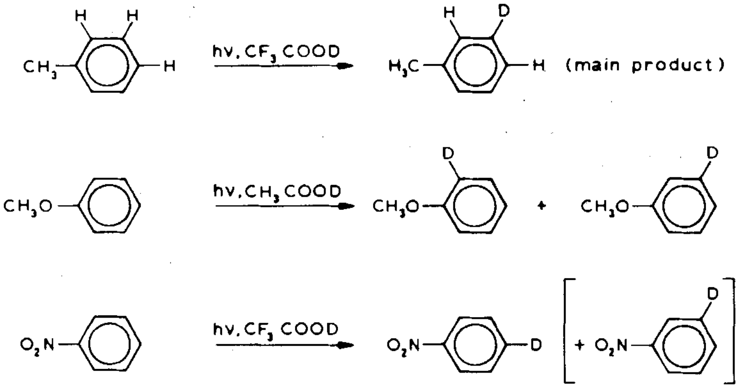
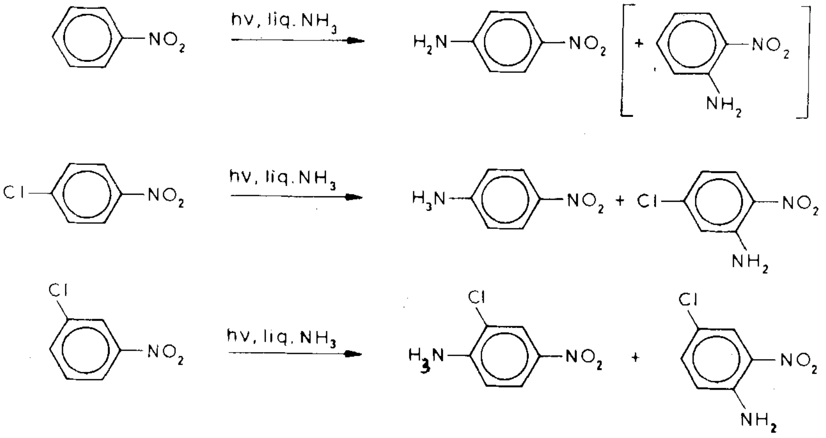
²) We take the opportunity to draw attention to somewhat related reactions studied by ZIMMERMAN, SOMASEKHARA & SANDEL [11] and by HEILBRONNER & SEILER [12].



Scheme 4. *Aromatic photodeuteration*

The second category of photosubstitutions has been discovered only very recently. These reactions are not observed in the dark; nevertheless, the orientation follows the classical pattern, familiar from extensive experience with thermal nucleophilic and electrophilic aromatic substitutions. These are the photoaminations of nitrobenzene, nitrochlorobenzenes, dinitrobenzenes (Scheme 5).



Scheme 5. *Photosubstitution in liquid* NH_3

Perhaps it is appropriate to remark that here we have to do with neutral reagents in very high concentrations.

At the present state of our knowledge it seems a matter of taste how to classify some reactions with methylamine and dimethylamine, the results of which fit in with the rules for the first as well as for the second group [8f].

It is easily seen that aromatic photosubstitutions may offer considerable advantages in solving synthetic problems. One has the impression that quite a variety of substitution reactions, difficult to perform otherwise, may be brought about photochemically. Moreover, the abnormal selectivity offers attractive possibilities.

Let us now consider whether it is possible to understand the mechanism and hence the characteristics of the first group comprising *i. a.* photohydrolysis, photoamination, photocyanation of nitrophenyl and naphthyl ethers as nucleophilic substitutions, and the photodeuteration of alkylbenzenes and alkoxybenzenes as electrophilic substitution. These are generally very clean reactions with good quantum yields. The reactions are practically temperature-independent (no activation energy), first order with regard to light intensity, and zero order with regard to the aromatic compound, as is to be expected for normal photoreactions. The quantum yield is the same for light in the first $\pi - \pi^*$ and the second $\pi - \pi^*$ band! No indications of the occurrence of triplet states or free radicals were found. $n - \pi^*$ excitation does not – or only slightly – contribute to the reaction.

All this leads to the conclusion, that we can best describe the reactions as starting from a low vibrational level of the first excited singlet (S_1) state. This is corroborated by the fact that chloride and, in particular, bromide ions, which are known to catalyse the $S_1 \rightarrow T_1$ transformation, diminish the quantum yields of these reactions, when present in high concentration.

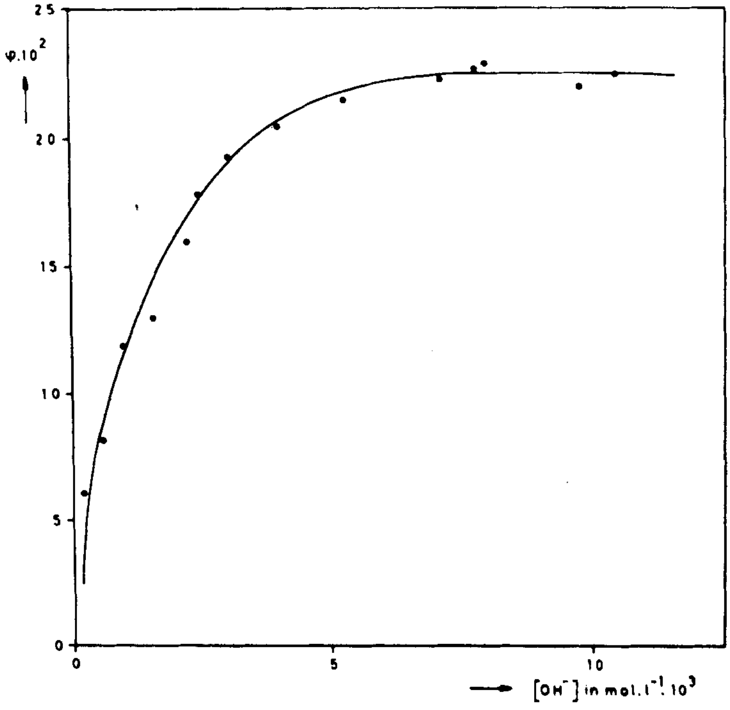


Fig. 1. *Quantum yield as a function of concentration of reagent*

Similar suggestive data are gained from a study of the influence of the concentration of the reagent. The reagent has to be present in rather high concentrations (10^{-3} to 10^{-2} M or higher) in order to obtain a substantial quantum yield. This is consistent with the idea of a bimolecular reaction with the aromatic compound in a short-lived excited state. The quantum yield increases with increasing concentration, levelling off at concentrations of 0,1–1 M towards a constant and maximum value (mostly in between 0,1 and 0,5). This suggests a competition between the (spontaneous) desactivations (fluorescence, internal conversion) of the excited molecules and their encounters with the reaction partner. However, even if the latter is present in such a high concentration that the spontaneous desactivation can no longer compete, the quantum yield remains significantly below 1. This means that encounters between excited molecule and reaction partner lead to reaction for a certain percentage and to quenching for the remaining percentage.

In order to rationalize all experimental data we may set up a tentative scheme that includes our knowledge of the mechanism of aromatic substitution in the ground state (Fig. 2). As a useful example we choose the deuteron-proton exchange, because this reaction is fairly simple and symmetrical. In the ground state reaction curve the intermediate σ-complex is accounted for, whilst the – probably not essential – presence of π complexes is also indicated.

Starting from the S_1 state a molecule may:

1. become desactivated by fluorescence or internal conversion (k_0),
2. encounter a CF_3COOD molecule and *a*) become quenched (k_q), or *b*) react (k_c).

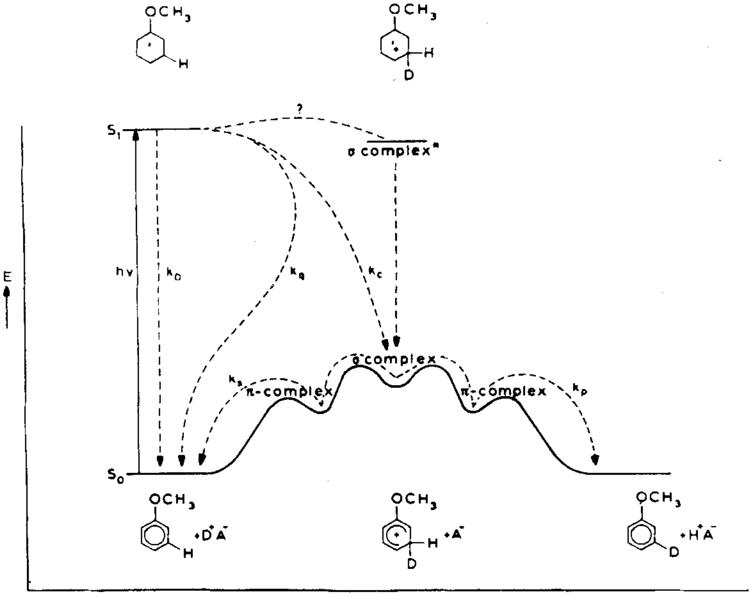


Fig. 2. *Possible energy relationships and reaction paths of photodeuteration of anisole*

It seems improbable that this reaction of the molecule in the S_1 state would require some non-negligible activation energy and proceed *e.g.* towards an excited product or an excited σ-complex at a higher level than that of S_1 (+ CF_3COOD), as this would ask for longer lifetime than an S_1 state can have ($10^{-8} - 10^{-9}$ s). Let us assume therefore that the system either passes to a relatively low lying excited σ-complex (if existent) and then very rapidly to the ground state σ-complex, or that (more probably) it cascades down directly to the σ-complex in the ground state. In this latter case one could consider the reaction as a kind of internal conversion from the excited S_1 state to the ground state σ-complex. From the σ-complex the system comes further down to product (k_p) or returns to the starting situation (k_s) along pathways normally trodden in ground state substitution reactions. It is easy to deduce that this mechanism leads to the following relation between the reciprocal values of the quantum yield and the concentration of the reagent R:

$$1/\varphi = \frac{k_s + k_p}{k_p} \frac{k_o}{k_c[\mathrm{R}]} + \frac{k_s + k_p}{k_p} \frac{k_q + k_c}{k_c} .$$

Such a linear relationship between $1/\varphi$ and $1/[\mathrm{R}]$ has been found to exist in all cases investigated. This linear relationship is in agreement with the picture developed for the reaction path, but of course constitutes no proof of it. As a further attractive feature, one may remark that the results are reasonable from a quantitative point of view.

For the alkaline hydrolysis of *m*-nitroanisole the following values were found:

$$\frac{k_s + k_p}{k_p} \frac{k_q + k_c}{k_c} = 3{,}6; \quad \frac{k_s + k_p}{k_p} \frac{k_o}{k_c} = 0{,}005 \text{ mole/l}; \quad \frac{k_o}{k_c + k_q} = 1{,}4 \cdot 10^3 \text{ mole/l}.$$

At a concentration of $1{,}4 \cdot 10^{-3}$M of OH^- spontaneous desactivation and interaction with OH^- are in equilibrium. The not unreasonable assumption $k_q \simeq k_c$ and $k_s \simeq k_p$ fits the equations found, together with $k_o/k_c = 2{,}5 \cdot 10^{-3}$ mole/l.

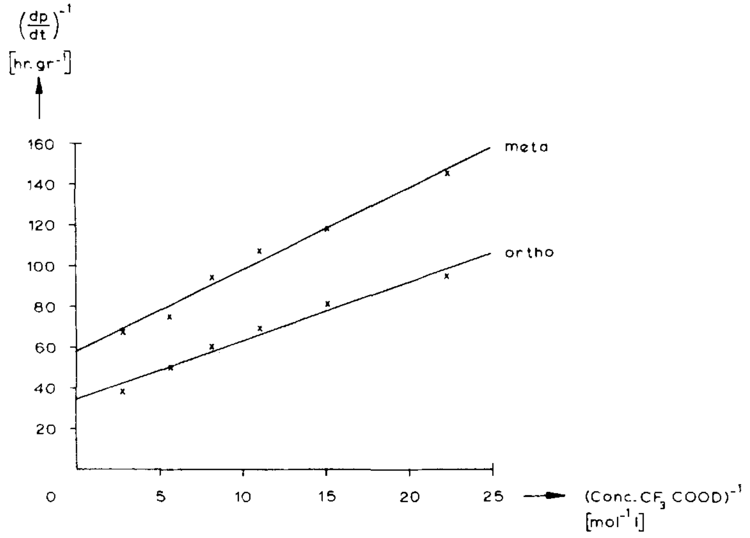


Fig. 3. *Photodeuteration of anisole with CF_3COOD in tetrahydrofuran*

Even more informative are the data obtained for the photodeuteration of anisole with CF_3COOD in tetrahydrofuran (Fig. 3). The equations for *ortho* and *meta* substitution (*para* substitution does not occur!) are:

$$1/\varphi^o = \frac{k_0}{k_c^o\,[CF_3COOD]} \cdot \frac{k_s^o + k_p^o}{k_p^o} + \frac{k_q + k_c^m + k_c^o}{k_c^o} \cdot \frac{k_s + k_p^o}{k_p^o} = \frac{0{,}64}{[CF_3COOD]} + 8,$$

$$1/\varphi^m = \frac{k_0}{k_c^m\,[CF_3COOD]} \cdot \frac{k_s^m + k_p^m}{k_p^m} + \frac{k_q + k_c^m + k_c^o}{k_c^m} \cdot \frac{k_s^m + k_p^m}{k_p^m} = \frac{1{,}0}{[CF_3COOD]} + 14 \cdot$$

For a substitution by deuteration it seems likely that

$$\frac{k_p^o}{k_s^o + k_p^o} \simeq \frac{k_p^m}{k_s^m + k_p^m}\,.$$

Assuming an isotope effect of the order $\frac{k_p^o}{k_s^o} \simeq \frac{k_p^m}{k_s^m} \simeq 4$,

we obtain $\frac{k_0}{k_c^o} = \sim 0{,}5$ mol/l and $\frac{k_0}{k_c^m} = \sim 0{,}8$ mol/l, yielding $\frac{k_c^o}{k_c^m} \sim 1{,}6$.

This seems, – within a considerable range of uncertainty –, in agreement with the value 1,7 derived from the intercepts.

The examples discussed reveal several interesting general points:

1. Comparison of quantum yields, even in the favourable case of two reaction centres in one and the same excited molecule, does not give a straigthforward answer to the question of the reactivities. However, in the rather symmetrical reaction of replacement of a proton by a deuteron we may with some confidence relate the quantum yields with relative rates of reaction (k_c^0 and k_c^m) at the various positions of the excited aromatic nucleus. It is seen that the relative rates ($o:m:p = 1{,}7:1:0$) significantly reflect the charge distribution of the anisole molecule in S_1: $o = -0{,}112$, $m = -0{,}108$, $p = +0{,}054$.

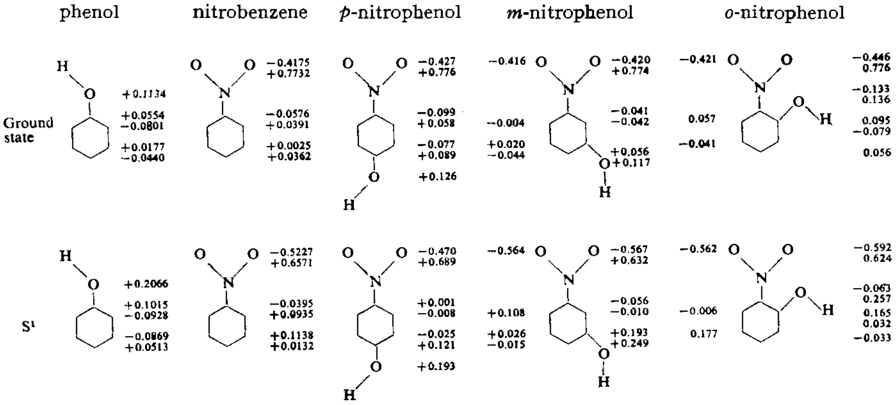


Fig. 4. *Charge distribution in the ground state and the lowest excited singlet states originating from* $\pi \rightarrow \pi^*$ *transitions*3)

Another striking example is *p*-nitroanisole, which is deuterated in the dark at position 2 only, but in the light to the same extent at positions 2 and 3, in harmony with calculated charge densities. In addition, the charge distribution of the first excited singlet state of *p*-nitroanisole (∼*p*-nitrophenol) also makes it clear why nucleophilic reagents attack both at C-1 and C-4.

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3) The calculations according to the PARISER-PARR-POPLE method were made by Drs. J. J. C. MULDER of the Department of Theoretical Organic Chemistry (Head: Prof. Dr. L. J. OOSTERHOFF). The calculations were rounded off by including the configuration interaction of all singly excited singlets.

This correlation of quantum yield with charge distribution is in agreement with the idea that these reactions do not require thermal activation. The reaction seems to be 'diffusion controlled', the electrostatic interaction between the deuteron and the charges at the *ortho, meta* and *para* positions bringing about the selectivity. The attraction or repulsion influences the probability of approach of the deuteron towards the *ortho, meta,* or *para* position, respectively, where once arrived it has a great chance to react.

We have to keep in mind that this dominating influence of the charge distribution may be changed and perhaps even overruled by the influence of the ratio k_p/k_s. This may be the case in the second class of aromatic photosubstitution, where we see amination of nitrobenzenes predominantly at the *para* (and *ortho*) position.

It might be that here the k_c's at the various positions are of the same order, since the neutral attacking reagent (NH_3) is not so strongly influenced in its approach to the excited nitrobenzene by the charge densities. Hence, σ-complexes will be formed at *ortho, meta,* and *para* in not too divergent ratios. Here the light energy has more or less the function of an elevator that brings the system to a high level from which the three possible σ-complex levels are filled without much discrimination. The selectivity then originates from the percentage that goes to final product for each of the 3 σ-complexes (*o, m* and *p*). It is clear that here the *para* compound will preponderate because of the influence of the resonance stabilisation that will be considerable in the transition state leading to the favoured *p*-nitroaniline; *o*-nitroaniline will be produced to a lesser extent, whereas *m*-nitroaniline will be hardly formed.

Of course there are other possibilities such as:

2. A reaction in the high vibrationally activated levels of the ground state, during internal conversion (seems rather improbable, notwithstanding the fact that very high concentrations are found to be necessary for this type of reactions).
3. A reaction starting by excitation of (charge transfer) complexes.
4. A reaction starting with electron uptake by the excited nitrobenzene and subsequent reaction of C_6H_5–NO_2^- and the NH_3^+ radical ion[4]).
5. A reaction in the n-π^* state; this can be excluded on experimental and theoretical grounds.

At the moment, the first possibility (σ-complex reaction decisive) seems the most attractive for this type of photoinduced aromatic substitution. It brings the various categories of photosubstitution together in one coherent and consistent picture presented in Fig. 2. In the first category the primary reactivity or charge at the reaction centre of the aromatic compound in its first singlet state (k_c) is dominating; in the second category the product forming reactions of the intermediate ground state σ-complex (k_p/k_s) are decisive.

Finally, what are the possibilities for checking the picture given? To this end, we are studying isotope effects of photosubstitution reactions. Furthermore, suggestive results have been obtained by flashing the mixtures of reactants and looking for intermediates formed upon the flash.

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[4]) *Note added in proof:* Recent E.S.R. experiments by Drs. A. VAN VLIET of this laboratory showed the rapid building up, during illumination of the systems nitrobenzene/liq. NH_3 and *m*-nitroanisole/liq. NH_3, of a strong, rather long-lived signal, perhaps due to the radical anion of the aromatic nitro compound.

Through the help of Professor G. J. HOIJTINK at Amsterdam and Professor S. CLAESSON of Uppsala we could perform various flash experiments mainly with the classical system of *m*-nitroanisole and 3,5-dinitroanisole in 0,05 N NaOH. In both cases intermediates were observed that had relatively long wavelength absorption bands (~4000 Å for the dinitro compound and ~5000 Å for the mononitro compound). Intermediates with a lifetime of ~0,1 s and of several seconds were traced. After 30 seconds the only product remaining was the nitrophenolate, in harmony with the outcome of the photochemical reactions described before. Moreover, no intermediates were observed in blank experiments with solutions lacking the OH^-, or in solutions containing bromide, which suppresses the photolyses [15].

Of course, a much more detailed study is necessary. It looks as if here we have a clue to a direct study of the intermediates, possibly the σ- and π-complexes, in 'Reinkultur'. In this respect the otherwise rather elusive photoreactions offer a great advantage. It may even prove possible in this way to study the σ- and π-complexes that play an important role in photoreactions and in thermal aromatic substitutions.

SUMMARY

1. Aromatic substitutions can generally be effected by simple photochemical methods.

2. The photoinduced substitution reactions follow their own rules, usually different from those of the normal thermal reactions.

3. In many cases the charge distribution in the photo-excited state is the directive factor. In other cases a ground state orientation pattern is followed; here the light activation may serve the purpose of bringing the system into a high enough energy state and of producing rather indiscriminately ground state σ-complexes. The reaction patterns of the *ortho*, *meta*, and *para* complexes then determine the composition of the product.

4. It seems feasible to study directly the photochemically formed intermediates with a view to a better understanding of the photochemical as well as the classical thermal aromatic substitutions.

5. Last but certainly not least: Aromatic photosubstitutions offer elegant possibilities to the synthetic chemist.

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268. Une fonction d'onde autocohérente (self-consistent) sans restriction de symétrie pour l'état $X^3\Pi$ de la molécule BN

par **J. L. Masse** et **M. Masse-Bärlocher**

(13 XI 67)

1° *Introduction.* Dans un travail antérieur [1] nous avons calculé les orbitales moléculaires, combinaisons linéaires autocohérentes (self-consistent) d'orbitales atomiques (SCF-LCAO-MO) pour la molécule BN dans l'état $a\ {}^1\Sigma^+$. Nous avons pris la distance internucléaire à l'équilibre: 1,281 Å, et calculé les énergies électroniques et le moment dipolaire en utilisant comme orbitales atomiques de base celles de Slater [2] des atomes B et N.

Dans cet article nous présentons les résultats obtenus dans la même approximation pour l'état

$$(1\,\sigma)^2\,(2\,\sigma)^2\,(3\,\sigma)^2\,(4\,\sigma)^2\,(5\,\sigma)\,(1\,\pi^+)^2\,(1\,\pi^-):X^3\Pi.$$

Nous prenons la même distance B–N: 1,281 Å. La numérotation des fonctions de base X_μ est celle de [1]:

X_μ	$1\,s$	$2\,s$	$2\,p_\sigma$	$2\,p_{\pi^+}$	$2\,p_{\pi^-}$
B	1	2	3	7	9
N	4	5	6	8	10.

La solution des équations de Hartree-Fock pour cet état à «couches ouvertes» a été obtenue par une méthode développée par l'un de nous [3]. Les coefficients de $(1\,\pi^+)$ et $(1\,\pi^-)$ ne sont pas contraints à être identiques.