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PHOTOSUBSTITUTION REACTIONS OF NITRONAPHTHALENES LEADING TO CHLORONAPHTHALENES

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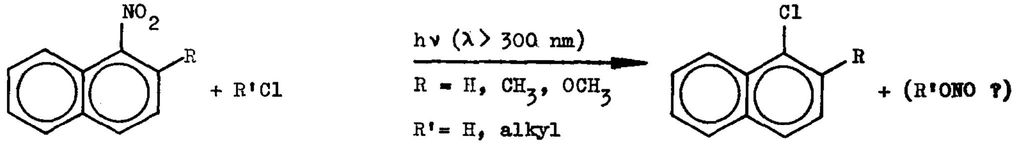
As an extension of the investigations on aromatic photosubstitution[1] 1-nitronaphthalenes were irradiated in alkylchlorides, allylchloride, dichloromethane, $CHCl_3/HCl$, CCl_4/HCl, acetic acid/HCl, hexane/HCl. The following reaction was observed



Starting with a 10^{-4} molar nitronaphthalene solution the absorption curves, taken at various reaction times, showed remarkably clear isosbestic points; the reactions proceed to practically 100% conversion. In experiments on a preparative scale (10^{-3} mol. conc.) the solutions tend to turn yellow; the yields obtained are ~ 90% (1-chloronaphthalene) +), ~ 80% (1-chloro-2-methylnaphthalene) *), ~ 20% (1-chloro-2-methoxynaphthalene) +).

2-Nitronaphthalene under the same conditions reacts much more slowly to give relatively low yields of 2-chloronaphthalene together with other, as yet unidentified, products. With nitrotoluene and nitromesitylene no corresponding chlorocompounds could be detected in the mixtures obtained upon irradiation. 1,5- and 1,8-Dinitronaphthalene show smooth reaction; in preparative experiments illumination of the 1,5-dinitronaphthalene in $CHCl_3/HCl$ gave 1,5-dichloronaphthalene in 85% yield; the 1,8-dinitro compound yielded a mixture in which 1,8-dichloronaphthalene and a trichloronaphthalene were the main products.

+) in $CHCl_3/HCl$

*) in tert.-butylchlorid (HCl)

Although the photosubstitution of 1,5-dinitronaphthalene is a fast and clean reaction, no isosbestic points are observed in the spectra during the reaction. Evidently, the formation of the 1,5-dichloro product proceeds via the formation of 1-chloro-5-nitronaphthalene, which accumulates in appreciable amounts in the course of the reaction. The values determined for the quantum yields for the various substrates are of the order of 0.01 in alkylchlorides and amount to 0.1 - 0.5 in the HCl containing media ($CHCl_3$/HCl, etc.).

The data available at the moment do not allow to make any definite conclusions as to the mechanism of this reaction. It would appear that we have to do with a new type of aromatic photosubstitution, occurring in media of relatively low dielectric constants. Most probably the reaction cannot be described as a substitution whereby NO_2^- is displaced by free chloride ions. A free radical type reaction does not seem probably either. A kind of "concerted" reaction mechanism between the photo-excited nitro aromatic and R'Cl leading to the chloronaphthalene in its ground state might be considered.

The fact that the reaction occurs in the naphthalene and not in the benzene series suggests that the reaction starts from the lowest triplet state, which is according to some authors, may have π,π^* character for nitronaphthalene and n,π^* character for nitrobenzene [2].

Finally it seems appropriate to call attention to the cleanliness of the reaction and to the high yields obtainable, which suggest synthetic utility.

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