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PHOTOREACTIONS OF AROMATIC COMPOUNDS XI[1]

Photoinduced substitution of nitrobenzene and derivatives in liquid ammonia

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As an extension of the investigations of nucleophilic photosubstitution reactions of aromatic compounds (1), the photobehaviour of (nitro) benzene derivatives in liquid ammonia is being studied in this laboratory. We want to report the formation of nitroanilines when nitrobenzenes are illuminated in liquid ammonia in a quartz vessel by the light of a high pressure mercury arc.

Nitrobenzene itself yields ortho- and para-nitroaniline. The major product is p-nitroaniline as shown by comparing ultraviolet and infrared absorption spectra, melting point and thin layer chromatograms of an authentic sample with those of the material isolated. The ortho-isomer is formed in relatively small amounts only. No meta-isomer could be detected.

The rate of the photoinduced substitution of p-chloronitrobenzene in liquid ammonia is much lower than that of nitrobenzene under the same conditions. Substitution also occurs at the para- and ortho-positions with respect to the nitro group. p-Nitroaniline is formed by the net replacement of the chloro substituent by NH_2 and 2-nitro-5-

chloroaniline by the substitution of aromatic hydrogen. The ratio of the two products, identified by thin layer chromatography and ultraviolet spectra, is ~ 1. Again, no ''meta-isomer'' (2-chloro-5-nitroaniline) could be detected.

The pattern of the photoreaction of m-chloronitrobenzene in liquid ammonia shows the same lines as that of the para-isomer. The products are now 2-chloro-4-nitro- and 2-nitro-4-chloroaniline, apart from smaller amounts of as yet unidentified compounds.

It seems, therefore, that the photosubstitution of nitrobenzenes in liquid ammonia takes place preferentially at the 2- and 4-positions with respect to the nitro group. This is in agreement with the pattern of reaction of nitroanisoles with amines (2). The methoxy group in p-nitroanisole is efficiently substituted by methylamine, while in the otherwise highly photoreactive meta-isomer the methoxy group is very slowly replaced (2,3). However, in 4-nitroveratrole the methoxy group meta with respect to the nitro group is substituted by methylamine under illumination (4); this behaviour is in contradistinction to the trend observed with the compounds mentioned above, but is consistent with the course of the reaction of 4-nitroveratrole with OH^- (5).

1. a. Part X, J. Cornelisse and E. Havinga, *Tetrahedron Letters* *1966*, 1609.
   b. For a review and quotations of earlier publications, see: E. Havinga, Inst.intern.Chim.Solvay, 13 Conseil Chim.Brussels, *1965*, (6).
2. M.E. Kronenberg, A. van der Heyden and E. Havinga, *Rec.Trav.Chim.* **85**, 56 (1966).

3. R.O. de Jongh and [illegible] Havinga, *Rec.Trav.Chim.* **85**, 275 (1966).
4. M.E. Kronenberg, A. van der Heyden and E. Havinga, *Rec.Trav.Chim.* in the press.
5. J.L. Stratenus, Thesis Leiden (1966); cf. E. Havinga and R.O. de Jongh, *Bull.Soc.Chim.Belg.* **71**, 803 (1962).
6. Attention is drawn to the recent investigation of R.L. Letsinger and J.H. Mc. Cain, *J.Am.Chem.Soc.* **88**, 2884 (1966) of the photosubstitution by cyanide, where 4-nitroanisole is found to give 2-cyano-4-nitroanisole.