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PHOTOREACTIONS OF AROMATIC COMPOUNDS VIII
A PHOTOCHEMICAL SUBSTITUTION OF HALOGEN IN 2-BROMO-(CHLORO)-4-NITROANISOLE

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As a result of the discovery of the photoreactivity of nitrophenylesters and nitroanisoles (1,2), it was deemed interesting to extend the study to the photobehaviour of substituted nitroanisoles. An alkaline solution of 2-bromo-4-nitroanisole turns yellow rapidly when illuminated with ultraviolet light. A plot of ultraviolet absorption spectra taken at various intervals during the reaction shows the occurrence of isosbestic points. In the dark no reaction takes place.

To isolate the products a solution of 1 g of 2-bromo-4-nitroanisole (m.p. 106-107° (3)) in 600 ml of purified tetrahydrofuran and 2400 ml of 0,1 N NaOH was illuminated at room temperature with the light of a Hanau Q 81 high pressure mercury arc, filtered through pyrex glass.

After illumination the presence of halogen ions could be demonstrated with silvernitrate. Two compounds and a tarry product were detected on a thin layer chromatogram with the aid of ultraviolet light.

The reaction mixture was partly neutralized with hydrochloric acid and evaporated under reduced pressure on a waterbath (temp. 40°C). The residue (100 ml) was extracted with ether to remove unreacted anisole. Then the solution was neutralized completely and again extracted with ether. After distilling the ether the solid residue was treated with boiling petroleum ether, b.p. 40-60° (2 x 30 ml) and with boiling petroleum ether, b.p. 80-100° (1 x 100 ml). An insoluble tarry product remained. From the higher boiling petroleum ether fraction a product crystallized which after recrystallization melted at 103-104,5° and which proved to be identical with 5-nitroguaiacol (4) (mixed melting point, ultraviolet- and infrared absorption spectra and analysis). The product which crystallized from the lower boiling petroleum ether fraction was chromatographed on a neutral aluminumoxide column (50 x 2,5 cm) with a benzene-alcohol mixture (9:1) as eluent. Two compounds were isolated: 5-nitroguaiacol (44 % isolated) and a compound which after crystallization from petroleum ether (40-60°) melted at 108,5-110° and which proved to be identical with 2-bromo-4-nitrophenol (5) (mixed melting point, ultraviolet- and infrared absorption spectra). The yield of 2-bromo-4-nitrophenol is small in comparison with the yield of 5-nitroguaiacol.

It thus seems that the main photoreaction of 2-bromo(chloro)-4-nitroanisole in alkaline solution is a substitution of bromine by hydroxyl. Substitution of the methoxygroup also takes place. Whether an attack at carbon-4 (6,7) is occurring could not yet be established.

Similarly, 2-chloro-4-nitroanisole on illumination yields 5-nitroguaiacol (48 % isolated) besides a tarry product and a small amount of 2-chloro-4-nitrophenol.

When 2-bromo-4-nitroanisole is illuminated in a water-methanol-methylamine solution several products are formed. One of them has been isolated and proved to be N-methyl-2-bromo-4-nitroaniline (8).

A photosubstitution of the bromosubstituent by OH^- could not be established with 3-nitrobromobenzene, 3,5-dinitrobromobenzene, 2- and 4-bromoanisole. The substitution of the halogen in 2-bromo- and 2-chloro-4-nitroanisole by OH^- thus seems to be a rather specific reaction. Its scope and kinetic features are being investigated (9).

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