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PRELIMINARY COMMUNICATION

The direct introduction of the diazonium group into aromatic nuclei

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THE conversion of an aromatic hydrocarbon into a diazonium salt, normally involves three steps, nitration, reduction to the amine, and diazotisation with nitrous acid. However, it has long been known that in certain instances it is possible to obtain diazonium salts directly from reactive aromatic compounds. The best known example is the formation of diazonium salts as by-products in the preparation of nitroso-phenols (quinone-monoximes). If phenols are treated with excess nitrous acid for long periods, the nitroso-derivatives first formed react further to yield diazonium salts.[1-4] Another reaction in which a diazonium group is directly introduced into aromatic nuclei, is the treatment of reactive aromatic compounds with a solution of nitrous acid in trifluoroacetic anhydride.[5] The method only gives moderate yields of diazonium salt and very expensive trifluoroacetic anhydride is required.

It has now been shown that these two examples are special instances of a general reaction by which diazonium salts can be prepared directly from a variety of aromatic compounds by the action of nitroxyl derivatives of the type NO·X (X = Cl, HSO_4, ClO_4, CF_3COO, etc.). The reaction almost certainly involves the initial nitrosation of the aromatic nucleus followed by the conversion of the nitroso compound so formed into the diazonium salt.

$$\mathrm{ArH} \xrightarrow[\mathrm{HX}]{\mathrm{HNO_2}} \mathrm{ArNO} \xrightarrow[\mathrm{HX}]{\mathrm{HNO_2}} \mathrm{ArN_2^{+}X^{-}}$$

The most reactive compounds, e.g. phenols, can be converted into diazonium salts in good yield by treating the aromatic compound in aqueous ethanol solution with hydrogen chloride and excess ethyl nitrite. By this method, phenol and *m*-cresol have been converted into the corresponding diazonium salts in 80 per cent and 45 per cent yields respectively. Tertiary amines can also be converted into diazonium salts by these reagents, small yields of the corresponding diazonium salts having been isolated from dimethyl and diethyl anilines. Polyalkyl benzenes and phenol ethers are converted into the corresponding diazonium salts by treating the aromatic compounds dissolved in nitrobenzene with nitrosyl sulphuric acid (either prepared separately from nitric acid and sulphur dioxide, or in situ by dissolving sodium nitrite in excess sulphuric acid before adding the nitrobenzene solution of the hydrocarbon). By this means diazonium salts have been prepared from anisole (48 per cent), mesitylene (78 per cent), and *m*-xylene (43 per cent). Low yields of diazonium salts have also been obtained from toluene and benzene by the direct reaction of solutions of sodium nitrite in sulphuric acid on the hydrocarbons. The diaxonium salts so obtained are the derivatives of nitrotoluene and nitrobenzene and not the simple hydrocarbons. Thus evidence for a general reaction by the following equation

$$\mathrm{ArH} + 2\mathrm{HNO_2} \longrightarrow \mathrm{ArN_2^{+}\ OH^{-}} + \mathrm{H_2O} + 2[\mathrm{O}]$$

has been established. For certain compounds, namely phenols, phenol ethers and polyalkyl benzenes, the yields of diazonium salt obtained during the present exploratory work, are sufficiently large to suggest the reaction has considerable preparative value. However, the reaction appears likely to give

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only poor yields with toluene and benzene and does not take place at all with aromatic compounds containing deactivating groups. For such compounds considerable adaptation of the basic reaction is necessary in order to obtain significant yields of diazonium salt. Only one of several possible routes has so far been investigated.

In collaboration with G. Theaker a method for introducing a diazonium group directly into deactivated aromatic nuclei has been developed. The reaction involves the use of a mercury catalyst and is based on the earlier work of Bamberger,[6] and on the investigations of "Oxynitration" by Westheimer,[7] and Carmack.[8] The aromatic compound, dissolved in sulphuric acid, is treated with nitrosyl sulphuric acid (prepared in situ by the addition of sodium nitrite) and a catalytic amount of mercuric sulphate (1/100 mole). Using this method moderate yields of diazonium salt have been prepared from aromatic sulphonic acids [benzene sulphonic acid 20 per cent; *p*-toluene sulphonic acid 53 per cent], carboxylic acids [*p*-toluic acid 21 per cent; α-naphthoic acid 20 per cent] and aromatic nitro-compounds [*p*-nitro anisole 74 per cent; *p*-nitro toluene 37 per cent].

Full details of this work together with a discussion of the mechanism of the reactions will be submitted for publication shortly.

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