8. *Direct Introduction of Deuterium into the Aromatic Nucleus. Part II. Orientation by Certain Substituents.*

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In agreement with the hypothesis that nuclear deuteration in aromatic compounds is an electrophilic substitution, it has been shown that phenol and aniline are substituted exclusively in the ortho- and para-positions.

The hypothesis that aromatic deuteration is an electrophilic substitution is supported by considerable experimental evidence concerning relative velocities of nuclear exchange in various monosubstituted benzenes (Ingold, Raisin, and Wilson, J., 1936, 1637). It has been shown that substituents which accelerate deuteration are those which are known to promote nitration or coupling processes. For example, hydrochloric acid, under prescribed conditions, induced considerable nuclear exchange in dimethylaniline, appreciably less in anisole, and none at all in benzene.

It is well established that substituents such as the dimethylamino- or methoxy-group accelerate electrophilic substitution principally by activation of the ortho- and para-positions. In compounds containing such groups deuteration should, therefore, cease or almost cease when these three nuclear positions are exchanged. It is known that three and only three nuclear positions are exchanged with facility in anisole, phenol (*idem, ibid.* Cf. also Small and Wolfenden, J., 1936, 1811), dimethylaniline (Kharasch, Brown, and McNab, *J. Org. Chem.*, 1937, **2**, 41), and aniline (Harada and Titani, *Bull. Chem. Soc. Japan*, 1936, **11**, 554) and in each of these instances it has been assumed (*locc. cit.*), without direct proof, that the deuterium enters the ortho- and para-positions. We have therefore oriented deuterated phenol and aniline by converting each into a 1 : 3 : 5-tribromo-derivative. The latter was free from deuterium, thus demonstrating that, under the conditions of exchange, the meta-positions remain unaffected.

EXPERIMENTAL.

Phenol.—Phenol (15 g.), sodium hydroxide (3 g.), and dilute deuterium oxide (excess density 2141 p.p.m., 74 g.) were heated in a sealed bulb at 100° for 96 hours. It has already been shown (Ingold, Raisin, and Wilson, *loc. cit.*) that under these conditions the hydrogen of the phenol, reckoned as a whole, attains an isotopic composition corresponding with about 900 p.p.m. in excess water density. The alkaline solution from the above experiment was acidified, and the phenol precipitated with bromine water. The tribromophenol was filtered off, dissolved in ether, and shaken with distilled tap water to 'normalise' the hydroxyl hydrogen, and then dried and burnt in the usual manner. The water produced had the same density as the standard water to within the limit of accuracy of the pyknometer (1 p.p.m.).

Aniline.—Harada and Titani (*loc. cit.*) have described nuclear exchange between water and aniline hydrochloride. The latter (26 g.) and water (excess density 2141 p.p.m., 36 g.) were heated at 100° in a sealed bulb for 30 hours. The solvent was evaporated in a vacuum, the residue dissolved in 'normal' water and made alkaline, and the aniline was extracted with ether. The ethereal solution was further shaken with 'normal' water, and the aniline distilled. Half of it was burnt, giving water which had an excess density of 599 p.p.m., and the remainder was dissolved in acid and converted into the tribromo-derivative. Combustion of the latter gave a water sample having a density 1 p.p.m. less than the standard.

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