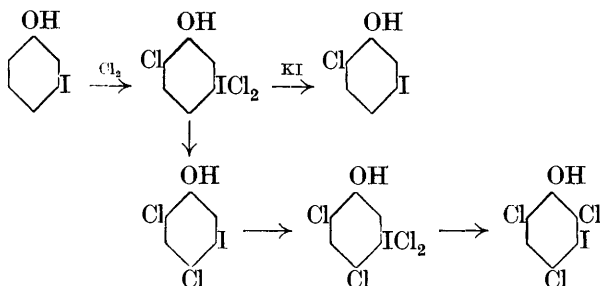


432. *The Chlorination of Iodophenols. Part V.*
m-Iodophenol.

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m-IODOPHENOL in carbon tetrachloride solution, when subjected to the action of chlorine, gave rise to a series of unstable iododichlorides and ring-substituted decomposition products very similar to those obtained from the *p*- and *o*-isomerides (Brazier and McCombie, J., 1912, **101**, 913; Buchan and McCombie, J., 1931, 137). The iododichlorides of *o*- and *p*-iodophenol decompose to give chloriodophenols, whilst that from *m*-iodophenol gives 4 : 6-dichloro-3-iodophenol. To obtain 6-chloro-3-iodophenol, the iododichloride from the chlorination of *m*-iodophenol was treated with potassium iodide solution. Chlorination of the 4 : 6-dichloro-3-iodophenol yielded another iododichloride decomposing to give 2 : 4 : 6-trichloro-3-iodophenol, which, having both ortho-positions relative to the iodine occupied, gave no iododichloride.

As a whole the iododichlorides obtained from the derivatives of *m*-iodophenol were of the same order of stability as those from the



p- and *o*-isomerides. The most notable example of increased instability was *m*-iodophenyl dibromopropyl ether iododichloride, which decomposed over-night, whereas in the ortho-series it remained stable for a month and in the para for several months. In several compounds, *e.g.*, *m*-iodophenol, *m*-iododiphenyl ether, and *m*-iodophenyl phenylcarbamate, chlorination led to the formation of iododichlorides of the monochloro-substituted compounds. In these cases substitution in the nucleus occurred by the decomposition in solution of the first-formed iododichlorides.

6-Chloro-3-iodophenol was prepared by Kray in 1926 (Diss., Amsterdam). 4-Chloro-3-iodophenol was prepared from 2-iodo-4-nitroaniline. The structure of 4:6-dichloro-3-iodophenol was established by synthesis from 4:6-dichlorophenyl *p*-toluenesulphonate. The constitution of the 2:4:6-trichloro-3-iodophenol was proved by McCombie and Ward (J., 1913, 103, 1995).

When *m*-iodophenol was chlorinated at 60–70° for a prolonged period, three products were isolated—2:4:6-trichloro-3-iodophenol, 2:4:5:6-tetrachloro-3-iodophenol, and pentachlorophenol.

EXPERIMENTAL.

m-Iodophenol was prepared from *m*-nitroaniline by Hodgson's method (B.P. 200,716; 1922). In the last stage of the prep., the steam-distilling of the *m*-iodophenol from acid solution, the whole distillate was extracted with Et₂O. The product solidified after distillation in vac. *Acetate*, colourless plates, m. p. 38°, from petroleum (b. p. 40–60°) (Found: I, 48.7. C₆H₇O₂I requires I, 48.5%). The iododichloride was unstable and decomposed over 7 days; m. p. 91–92° (decomp.). *Benzyl ether*, colourless plates, m. p. 52°, from petroleum (Found: I, 41.1. C₁₃H₁₁OI requires I, 40.9%). The iododichloride decomposed over 2 days; m. p. 70° (decomp.). *Benzoate*, white prisms, m. p. 72–73°, from petroleum (Found: I, 39.1. C₁₃H₉O₂I requires I, 39.2%). The *iododichloride* was stable, m. p. 106° (decomp.) (0.1498 gave 0.2002 AgI + AgCl. C₁₃H₉O₂Cl₂I requires 0.1899). *p-Toluenesulphonate*, white needles, m. p. 60–61°, from petroleum (Found: I, 33.8. C₁₃H₁₁O₃IS requires I, 33.9%). The *iododichloride* was stable, m. p. 97–99° (decomp.) (0.1340 gave 0.1580

AgCl + AgI. $C_{13}H_{11}O_3Cl_2IS$ requires 0.1572). *Ethyl carbonate*, prepared by the action of ethyl chlorocarbonate in dil. $NaHCO_3$ aq., was obtained as an oil, b. p. 163—164°/11 mm. (Found : I, 43.8. $C_9H_9O_3I$ requires I, 43.8%). The *iododichloride* was obtained by the addition of light petroleum to a chlorinated solution of the carbonate in CCl_4 . It remained stable for 4 months, m. p. 79—80° (decomp.) (0.2094 gave 0.3025 AgCl + AgI. $C_9H_9O_3Cl_2I$ requires 0.3011). *Iodophenyl carbonate* crystallised from C_6H_6 in white plates, m. p. 141° (Found : I, 54.7. $C_{13}H_9O_3I_2$ requires I, 54.5%). The *bisiododichloride* was stable, m. p. 115° (decomp.) (0.2098 gave 0.3576 AgCl + AgI. $C_{13}H_9O_3Cl_4I_2$ requires 0.3603). *Methyl ether* separated as an oil, b. p. 123°/14 mm. (Found : I, 54.6. C_7H_7OI requires I, 54.3%). The *iododichloride* was very unstable and was prepared by gentle chlorination of redistilled *m*-iodoanisole at 0°; m. p. 74° (decomp.) (0.1889 gave 0.3270 AgCl + AgI. $C_7H_7OCl_2I$ requires 0.3233). More vigorous chlorination led to the formation of chloro-*m*-iodoanisole iododichloride. *Ethyl ether*, an oil, b. p. 133—134°/15 mm. (Found : I, 51.3. C_8H_9OI requires I, 51.2%). An unstable iododichloride was prepared, m. p. 64° (decomp.), while more vigorous chlorination gave the iododichlorides of chloriodophenetole, m. p. 75° (decomp.), and dichloriodophenetole, m. p. 82—83° (decomp.). *Allyl ether*, an oil, b. p. 154—156°/11 mm. (Found : I, 49.2. C_9H_9OI requires I, 48.9%). On prolonged chlorination in conc. $CHCl_3$ solution traces of an iododichloride were obtained, m. p. 86—87°. In CCl_4 solution the action of Cl resulted in *m*-iodophenyl dichloropropyl ether being pptd. as an oil. *Dibromopropyl ether*, an oil (0.2596 gave 0.3789 AgBr + AgI. $C_9H_9OBr_2I$ requires 0.3777). The iododichloride was pptd. from $CHCl_3$ solution and decomposed over-night; m. p. 78° (decomp.). *Phenylcarbamate*, white needles, m. p. 138°, from C_6H_6 (Found : I, 37.3. $C_{13}H_{10}O_2NI$ requires I, 37.5%). The *iododichloride* was moderately stable, m. p. 120° (decomp.). Analysis showed the presence of one Cl atom in the nucleus (0.1112 gave 0.1672 AgCl + AgI. $C_{13}H_9O_2NCl_3I$ requires 0.1665).

3-Iododiphenyl ether. 3-Nitrodiphenyl ether was prepared by condensing *m*-bromonitrobenzene with $PhONa$ in presence of acetone-washed Cu powder. The ether was distilled under reduced press., b. p. 189—200°/14 mm. Reduction of the nitro-group was effected by means of $SnCl_2$ in Et_2O . The sulphate of the base was diazotised with $NaNO_2$, and KI aq. added. *3-Iododiphenyl ether* was obtained pure as an oil, b. p. 185°/14 mm. (Found : I, 43.0. $C_{12}H_9OI$ requires I, 42.9%). The *iododichloride* was obtained by adding light petroleum to a chlorine-saturated solution of the ether in $CHCl_3$. It decomposed over 2 days, m. p. 58°. Analysis showed that one Cl atom entered the ring (0.0625 gave 0.1048 AgCl + AgI. $C_{12}H_9OCl_3I$ requires 0.1035).

ω -3'-Iodophenoxyacetophenone, white needles, m. p. 104°, from light petroleum (Found : I, 37.7. $C_{14}H_{11}O_2I$ requires I, 37.6%). The iododichloride, which was almost white, was pptd. from $CHCl_3$ solution; m. p. 94°. It decomposed over a period of several days.

6-Chloro-3-iodophenol. *m*-Iodophenol in CCl_4 was chlorinated under ice-cooling. The iododichloride was separated, washed with light petroleum, and dissolved in AcOH, and KI aq. added. The iodine liberated was removed with bisulphite, and the *chloriodophenol* pptd. as an oil by H_2O and crystallised from light petroleum, forming white plates, m. p. 56° (0.0989 gave 0.1490 AgCl + AgI. C_6H_4OClI requires 0.1475). The *acetate* was obtained as an oil by the decomp. of *m*-iodophenyl acetate iododichloride; b. p. 149°/11 mm.

(0.1772 gave 0.2242 AgCl + AgI. $C_8H_6O_2ClI$ requires 0.2262). The iododichloride, m. p. 89° (decomp.), decomposed after 2 days. The *benzyl ether* was prepared by decomp. from the iododichloride of *m*-iodophenyl benzyl ether; b. p. $250-260^\circ/11$ mm. (0.2888 gave 0.3180 AgCl + AgI. $C_{13}H_{10}OClI$ requires 0.3173). The iododichloride, m. p. 72° (decomp.), decomposed after 2 days.

4-Chloro-3-iodophenol was prepared from 2-iodo-4-nitroaniline. The latter compound was diazotised and chlorine introduced by a Sandmeyer reaction. The chloriodonitrobenzene was then reduced with $SnCl_2$ in Et_2O , the tin double salt decomposed with 30% NaOH aq., and the base extracted with Et_2O . The hydrochloride was pptd. with HCl and diazotised, and the diazo-solution boiled. White needles, m. p. 78° , from light petroleum (0.2412 gave 0.3570 AgCl + AgI. C_6H_4OClI requires 0.3587).

4 : 6-Dichloro-3-iodophenol. *m*-Iodophenol, dissolved in CCl_4 , was chlorinated at 0° , and the iododichloride, m. p. 59° (decomp.), filtered off. The iododichloride decomposed over-night, giving a clean decomp. product crystallising from light petroleum in white needles, m. p. 104° (0.1166 gave 0.2116 AgCl + AgI. $C_6H_3OCl_2I$ requires 0.2106). The iododichloride from this, m. p. $68-69^\circ$ (decomp.), decomposed after 2 days, giving 2 : 4 : 6-trichloro-3-iodophenol. The constitution of 4 : 6-dichloro-3-iodophenol was established from 4 : 6-dichloro-3-nitrophenyl 2-nitro-*p*-toluenesulphonate (Groves, Turner, and Sharp, J., 1929, 512). Both nitro-groups were reduced by boiling for 10 hr. with $SnCl_2$ in Et_2O , the base diazotised, and iodine introduced. The product was heated, without further purification, with piperidine for 5 hr. at 100° , NaOH aq. added, and the filtered solution acidified, the dichloroiodophenol being pptd. The *acetate* formed white needles, m. p. 95° , from light petroleum (0.2288 gave 0.3575 AgCl + AgI. $C_6H_3O_2Cl_2I$ requires 0.3609). The iododichloride was stable, m. p. 104° (decomp.). *Benzyl ether*, white needles, m. p. 82° , from aq. EtOH (0.1500 gave 0.2056 AgCl + AgI. $C_{13}H_9OCl_2I$ requires 0.2066). The iododichloride decomposed after several days, m. p. 86° (decomp.).

2 : 4 : 6-*Trichloro-3-iodophenol* was prepared by chlorinating *m*-iodophenol in the cold and allowing the iododichloride to decompose either in solution or after filtration. White needles, m. p. 104° , from light petroleum (0.1966 gave 0.4060 AgCl + AgI. $C_6H_2OCl_3I$ requires 0.4044). No iododichloride was obtained with the trichloroiodophenol or its derivatives. *Acetate*, m. p. 87° . *Benzyl ether*, white needles, m. p. $80-81^\circ$, from light petroleum (0.1834 gave 0.2960 AgCl + AgI. $C_{13}H_8OCl_3I$ requires 0.2951).

m-Iodophenol, dissolved in dry CCl_4 , was chlorinated at $60-70^\circ$ for 5 hr. The product was almost pure 2 : 4 : 6-trichloro-3-iodophenol. This was redissolved in the solvent and further chlorinated for 30 hr. The solvent was again removed and the oil, which had a penetrating camphor-like smell, extracted with light petroleum. Tetrachloroiodophenol separated in white needles, m. p. 171° ; *acetate*, m. p. 141° (McCombie and Ward, *loc. cit.*). When distilled in steam, pentachlorophenol, which was only slightly volatile, distilled; m. p. 187° .

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