CCLXXVIII.—*Preparation of 3 : 5-Dihalogenophenols.*

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The whole series of 3 : 5-dihalogenophenols required in the course of a general investigation of symmetrical substitution in benzene has been prepared from 1 : 3 : 5-trinitrobenzene. Some of them and their derivatives were already known (in most cases the m. p.'s recorded in the literature have been confirmed); the new compounds are described below.

1 : 3 : 5-Trinitrobenzene was prepared by Clark and Hartmann's method (" Organic Syntheses," Vol. II, pp. 93—97), by oxidising 2 : 4 : 6-trinitrotoluene (360 g.) below 45°; a yield of 210 g. was obtained.

5-Nitro-3-aminoanisole was obtained in 85% yield by boiling a mixture of 3 : 5-dinitroanisole (30 g.), sodium trisulphide (18 g.), and alcohol (150 c.c.) for 4 hours, adding water, and extracting the precipitate with boiling dilute hydrochloric acid. It crystallised from water in orange needles, m. p. 120° (Blanksma, *Rec. trav. chim.*, 1905, **24**, 40, gives m. p. 118°; Meister, Lucius, & Brüning, D.R.-P. 22062, give 120°).

The 3-halogeno-5-nitroanisoles were obtained from the preceding compound by the Sandmeyer method, and all crystallised from alcohol in colourless needles. 3-*Iodo*-5-*nitroanisole* has m. p. 84° (Found : I, 45·2. $C_7H_6O_3NI$ requires I, 45·5%).

The 3-halogeno-5-nitrophenols were prepared by heating the 3-halogeno-5-nitroanisoles (10 g.) with concentrated sulphuric acid (30 c.c.) for 2 hours, pouring the mixture on to ice, and crystallising the 3-halogeno-5-nitrophenol from hot dilute mineral acid (yield about 70%). The benzoates crystallise from alcohol, the acetates from water or dilute alcohol, and the 2 : 4 : 6-tribromo-derivatives from dilute acetic acid or alcohol, all in colourless needles. 3-*Chloro*-5-*nitrophenyl benzoate* has m. p. 78° (Found : Cl, 12·6. $C_{13}H_8O_4NCl$ requires Cl, 12·8%), and the *acetate* has m. p. 84° (Found : Cl, 16·3. $C_8H_6O_4NCl$ requires Cl, 16·5%). 3-*Bromo*-5-*nitrophenyl acetate* has m. p. 99° (Found : Br, 30·6. $C_8H_6O_4NBr$ requires Br, 30·8%). 3-*Iodo*-5-*nitrophenol* crystallises from carbon tetrachloride or water in needles, m. p. 136° (Found : I, 47·7. $C_6H_4O_3NI$ requires I, 47·9%), the pale yellow colour of which remains unchanged after repeated crystallisations. The *benzoate* has m. p. 100·5° (Found : I, 34·1. $C_{13}H_8O_4NI$ requires I, 34·4%), and the *acetate*, m. p. 110° (Found : I, 41·1. $C_8H_6O_4NI$ requires I, 41·3%). 2 : 4 : 6-*Tribromo*-3-*iodo*-5-*nitrophenol* forms colourless plates, m. p. 176°

(0·1337 g. gave 0·2113 g. of mixed silver halides. Required, 0·2127 g.).

3-*Halogeno-5-aminoanisoles*.—The chloro- and bromo-compounds were readily prepared by reducing the corresponding nitro-compounds with tin and hydrochloric acid. The following process was more serviceable in the case of 3-iodo-5-aminoanisole : 3-Iodo-5-nitroanisole (12 g.), suspended in a mixture of water (200 c.c.) and concentrated hydrochloric acid (15 c.c.), was heated on the water-bath during the gradual addition of iron filings (24 g.). After 30 minutes, the mixture was rendered alkaline, and the 3-iodo-5-aminoanisole distilled in steam. All three compounds crystallise from light petroleum in colourless needles. 3-*Chloro-5-aminoanisole* has m. p. 33° (Found : Cl, 22·5. C_7H_8ONCl requires Cl, 22·5%), 3-*bromo-5-aminoanisole*, m. p. 52° (Found : Br, 39·4. C_7H_8ONBr requires 39·6%), and 3-*iodo-5-aminoanisole*, m. p. 86·5° (Found : I, 50·7. C_7H_8ONI requires I, 51·0%).

The 3 : 5-*dihalogenoanisoles* were prepared from the 3-halogeno-5-aminoanisoles by the Sandmeyer method. 3-*Chloro-5-iodoanisole* is a liquid, b. p. 267—268°, which solidifies at 0° (0·1882 g. gave 0·2672 g. of silver halides. Required, 0·2652 g.). The others all crystallise from light petroleum in colourless aggregates. 3 : 5-*Di-iodoanisole* has m. p. 85° (Found : I, 70·5. $C_7H_6OI_2$ requires I, 70·5%), 3-*chloro-5-bromoanisole*, m. p. 33° (0·1026 g. gave 0·1535 g. of silver halides. Required, 0·1534 g.), and 3-*bromo-5-iodoanisole*, m. p. 54° (0·1219 g. gave 0·1660 g. of silver halides. Required, 0·1646 g.).

3 : 5-*Dihalogenophenols*.—It was found more convenient to hydrolyse the 3-halogeno-5-aminoanisoles with concentrated sulphuric acid as described above and to apply the Sandmeyer process to the diluted diazotised solution than to replace the amino-group by halogen and hydrolyse the 3 : 5-dihalogenoanisole.

The 3 : 5-dihalogenophenols are moderately easily volatile in steam and crystallise from light petroleum in colourless needles. The benzoates, acetates, and tribromo-derivatives all crystallise from alcohol or dilute alcohol in colourless needles. 3 : 5-*Dichlorophenyl benzoate* has m. p. 55° (Found : Cl, 26·5. $C_{13}H_8O_2Cl_2$ requires Cl, 26·6%), and the *acetate*, m. p. 38° (Found : Cl, 34·3. $C_8H_6O_2Cl_2$ requires Cl, 34·6%).

3 : 5-Dibromophenol has m. p. 81° (Blau, *Monatsh.*, 1886, **7**, 630, gives m. p. 76·5°; Blanksma, *Rec. trav. chim.*, 1892, **12**, 254, gives 81°). The *benzoate* has m. p. 77° (Found : Br, 44·8. $C_{13}H_8O_2Br_2$ requires Br, 44·9%), and the *acetate*, m. p. 53° (Found : Br, 54·5. $C_8H_6O_2Br_2$ requires Br, 54·4%). 3 : 5-*Di-iodophenyl benzoate* has m. p. 93° (Found : I, 56·2. $C_{13}H_8O_2I_2$ requires I,

56·4%). 2 : 4 : 6-*Tribromo*-3 : 5-*di-iodophenol* has m. p. 226—228° (0·1166 g.; 0·2059 g.; 0·2068 g.*).

3-*Chloro*-5-*bromophenol* has m. p. 70° (0·0728 g.; 0·1157 g.; 0·1162 g.), the *benzoate* m. p. 62° (0·1016 g.; 0·1072 g.; 0·1080 g.), and the *acetate* m. p. 45° (0·0716 g.; 0·0911 g.; 0·0950 g.). 3-*Chloro*-2 : 4 : 5 : 6-*tetrabromophenol* has m. p. 205° (0·0657 g.; 0·1312 g.; 0·1323 g.). 3-*Chloro*-5-*iodophenol* has m. p. 60° (0·1273 g.; 0·2385 g.; 0·2393 g.), the *benzoate* m. p. 54° (0·1793 g.; 0·2387 g.; 0·2393 g.), and the *acetate* m. p. 47° (0·1483 g.; 0·2395 g.; 0·2393 g.). 3-*Chloro*-2 : 4 : 6-*tribromo*-5-*iodophenol* has m. p. 195° (0·1229 g.; 0·2350 g.; 0·2356 g.).

3-*Bromo*-5-*iodophenol* has m. p. 82·5° (0·1013 g.; 0·1430 g.; 0·1432 g.), the *benzoate* m. p. 76° (0·1066 g.; 0·1108 g.; 0·1119 g.), and the *acetate* m. p. 46° (0·0723 g.; 0·0884 g.; 0·0896 g.). 2 : 3 : 4 : 6-*Tetrabromo*-5-*iodophenol* has m. p. 220—221° (0·1072 g.; 0·1962 g.; 0·1974 g.).

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