

CCCCVI.—*The Interaction of Thiocarbonyl Chloride and Chloro-substituted Anilines and the Inhibitory Action of ortho-Substituents.*

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THE formation of arylthiocarbimides by Hofmann's method (*Annalen*, 1846, **57**, 256) is greatly inhibited by the presence of one nuclear halogen atom in the aniline and almost completely inhibited by two; indeed the only dihalogenated arylthiocarbimides hitherto synthesised, *viz.*, 2:4-dichloro- and 2:4-dibromo-phenylthiocarbimides (Chattaway, Hardy, and Watts, J., 1924, **125**, 1552), were obtained with considerable difficulty by acid hydrolysis of the corresponding *s*-phenylarylthiocarbamides. These facts led the present authors to extend the synthesis of thiocarbimides by means of thiocarbonyl chloride (Rathke, *Ber.*, 1872, **5**, 799; Dyson and George, J., 1924, **125**, 1702; Dyson and Hunter, *J. Soc. Chem. Ind.*, 1926, **45**, 83T) to the chloro-substituted arylthiocarbimides.

The desired reaction proceeded readily with *m*-chloroaniline and even more readily with *p*-chloroaniline, sluggishly with *o*-chloroaniline, readily with 3:4- and 3:5-dichloroanilines, slowly with 2:4- and 2:5-dichloroanilines, and not at all with 2:6-dichloroaniline; evidently it is inhibited greatly by one *o*-chlorine atom and completely by two. In accordance with this deduction, 2:3:5:6-tetrachloroaniline and pentachloroaniline, and also 2:6-dibromo- and 2:4:6-tribromo-anilines, did not react with thiocarbonyl chloride.

Thiocarbonyl chloride reacted with 3:4:5- and with 3:4:6-trichloroaniline to give the corresponding trichlorophenylthiocarbimides—the first trihalogenated arylthiocarbimides to be isolated.

All the thiocarbimides synthesised in this work were characterised in the form of the corresponding thiocarbamides, which are well-defined, crystalline substances.

EXPERIMENTAL.

The thiocarbimides described below were prepared as follows: Thiocarbonyl chloride (1 mol.) was completely suspended in cold

water (10 vols.) by vigorous stirring during the addition of the chloroaniline (0.75 mol.), dissolved in chloroform (5 vols.). After $\frac{1}{2}$ hour's stirring, the chloroform layer was removed and dried with calcium chloride and the solvent was evaporated on a steam-bath; the thiocarbimide was obtained by fractionally distilling the residual oil.

The chlorophenylthiocarbamides, $\text{NHAr}\cdot\text{CS}\cdot\text{NH}_2$, were prepared from the respective thiocarbimides and warm alcoholic ammonia, and the *s*-dichlorophenylthiocarbamides, $\text{CS}(\text{NHAr})_2$, from the thiocarbimides (1 mol.) and the corresponding chloroanilines (1 mol.) in chloroform; they were usually crystallised from dilute alcohol.

The following compounds were prepared: *o*-Chlorophenylthiocarbimide, a pale yellow oil, b. p. $260\text{--}262^\circ/760$ mm., having a pungent odour and lachrymatory properties (Found: S, 18.9%). *o*-Chlorophenylthiocarbamide (prepared at 15° , since heating produces a brown tar which apparently contains *o*-aminophenylthiocarbamide), short needles, m. p. 146° (Found: S, 17.0%). *s*-Di-*o*-chlorophenylthiocarbamide, needles, m. p. 129° (Found: S, 11.1%).

m-Chlorophenylthiocarbimide, a colourless, highly refractive oil, b. p. $249\text{--}250^\circ/760$ mm., having a pungent odour (Found: S, 19.0%). *m*-Chlorophenylthiocarbamide, long, flat plates, m. p. 140° (Found: S, 17.1%). *s*-Di-*m*-chlorophenylthiocarbamide, small prisms, m. p. 131° (Found: S, 10.8%).

p-Chlorophenylthiocarbimide, broad, shining plates, m. p. 45° , having the odour of aniseed (Found: S, 18.6%). *p*-Chlorophenylthiocarbamide, broad, glistening plates, m. p. 174° (Found: S, 17.3%). *s*-Di-*p*-chlorophenylthiocarbamide, glistening needles, m. p. 176° (Found: S, 10.7%).

2:3-Dichlorophenylthiocarbimide, a highly refractive oil, b. p. $256\text{--}258^\circ/760$ mm. (Found: S, 16.0. $\text{C}_7\text{H}_3\text{NCl}_2\text{S}$ requires S, 15.7%). 2:3-Dichlorophenylthiocarbamide, needles, m. p. 148° (Found: S, 14.7. $\text{C}_7\text{H}_6\text{N}_2\text{Cl}_2\text{S}$ requires S, 14.5%). *s*-Di-2:3-dichlorophenylthiocarbamide, thin laminae, m. p. 140° (Found: S, 8.8. $\text{C}_{13}\text{H}_8\text{N}_2\text{Cl}_4\text{S}$ requires S, 8.7%).

2:4-Dichlorophenylthiocarbimide, small prisms, m. p. 39.5° , b. p. $260^\circ/760$ mm., having the odour of aniseed (Found: S, 16.1%). 2:4-Dichlorophenylthiocarbamide, small crystals, m. p. 160° (Found: S, 14.4%). *s*-Di-2:4-dichlorophenylthiocarbamide, needles m. p. 169° (Found: S, 8.8%).

3:4-Dichlorophenylthiocarbimide, a pale yellow oil, b. p. $262^\circ/760$ mm., which solidified (Found: S, 15.7%). 3:4-Dichlorophenylthiocarbamide, needles, m. p. 164° (Found: S, 14.5%). *s*-Di-3:4-dichlorophenylthiocarbamide, large, broad plates, m. p. 144° (Found: S, 8.7%).

3 : 5-Dichlorophenylthiocarbimide, long needles, m. p. 45—50°, b. p. 274°/760 mm. (Found : S, 16·0%). 3 : 5-Dichlorophenylthiocarbamide, slender needles, m. p. 155° (Found : S, 14·4%). *s*-Di-3 : 5-dichlorophenylthiocarbamide, small prisms, m. p. 142° (Found : S, 7·1%).

3 : 4 : 5-Trichlorophenylthiocarbimide, an oil, b. p. 280° (decomp.). *s*-Di-3 : 4 : 5-trichlorophenylthiocarbamide, short needles, m. p. 140° (Found : S, 7·5. $C_{13}H_6N_2Cl_6S$ requires S, 7·3%).

3 : 4 : 6-Trichlorophenylthiocarbimide, an oil, b. p. 280°, which slowly solidified (Found : S, 14·0. $C_7H_2NCl_3S$ requires S, 13·4%). 3 : 4 : 6-Trichlorophenylthiocarbamide, needles, m. p. 162° (Found : S, 13·0. $C_7H_5N_2Cl_3S$ requires S, 13·4%).

2 : 6-Dichloroaniline.—Beilstein and Kurbatow's method (*Annalen*, 1879, **196**, 216) being unsatisfactory, this substance was prepared as follows (compare Heinichen, *Annalen*, 1889, **253**, 275; Orton and Pearson, J., 1908, **93**, 735) : A neutral solution of sulphanilic acid (1 mol.) in 25% aqueous sodium hydroxide was diluted until the concentration of sulphanilic acid was approximately 1%, and into it, cooled in ice, the calculated quantity of chlorine diluted with carbon dioxide (10 vols.) was passed. The crude 2 : 6-dichloro-sulphanilic acid obtained by evaporating the filtered solution after treatment with animal charcoal was mixed with 98% sulphuric acid (10 parts) and treated with steam at 180°. The 2 : 6-dichloro-aniline that distilled crystallised from dilute alcohol in slender needles, m. p. 39° (yield, 15—20%). It was recovered unchanged after being heated with thiocarbonyl chloride in a sealed tube at 180—200°.

3 : 5-Dichloroaniline.—*s*-Trinitrobenzene in alcoholic solution was reduced with ammonium sulphide and the 3 : 5-dinitroaniline produced was diazotised and boiled with a solution of cuprous chloride in concentrated hydrochloric acid. Distillation with steam at 140° then removed 3 : 5-dinitrochlorobenzene; the residue in the flask gave, after recrystallisation, a 15—20% yield of 3 : 3' : 5 : 5'-tetranitrodiphenyl. The dinitrochlorobenzene was reduced with ammonium sulphide, and the 5-chloro-*m*-nitroaniline obtained was converted into 3 : 5-dichloronitrobenzene in the usual way. Reduction in alcoholic solution with iron dust and a trace of hydrochloric acid then gave an 80% yield of 3 : 5-dichloroaniline in slender needles, m. p. 50° (Witt, *Ber.*, 1875, **8**, 145; Beilstein and Kurbatow, *Annalen*, 1875, **176**, 219).

3 : 4 : 5-Trichloroaniline.—2 : 6-Dichloro-4-nitroaniline (prepared by the action of potassium chlorate on a solution of *p*-nitroaniline in dilute hydrochloric acid) (1 mol.) was dissolved in acetic acid (10 vols.) and concentrated sulphuric acid (2 mols.), cooled to 0°,

and treated with methyl nitrite. The diazotised solution was heated with a solution of cuprous chloride in concentrated hydrochloric acid, and the trichloronitrobenzene isolated by steam distillation. Reduction with tin and hydrochloric acid then gave 3 : 4 : 5-trichloroaniline in white needles, m. p. 89°.

3 : 4 : 6-Trichloroaniline.—The methods of Lesimple (*Annalen*, 1866, 137, 125), Beilstein and Kurbatow (*ibid.*, 1879, 196, 232), and Gleube and Rostowzein (*Ber.*, 1901, 34, 211) having proved inconvenient, this compound was prepared by chlorinating *m*-chloroacetanilide until the increase in weight corresponded with the introduction of two molecules of chlorine; on hydrolysis the trichloroaniline was obtained in small crystals, m. p. 95°.

2 : 3 : 5 : 6-Tetrachloroaniline.—The methods of Beilstein and Kurbatow (*Annalen*, 1879, 196, 236) and Hentschel (*Ber.*, 1898, 31, 248) are unsatisfactory.

A solution of 50 g. of 1 : 2 : 4 : 5-tetrachlorobenzene in warm fuming nitric acid (150 c.c.) was poured into water and the orange product, which contained tetrachlorobenzoquinone, was collected and extracted three times with boiling light petroleum. The extracts were evaporated on a steam-bath; on recrystallising the residue from alcohol, tetrachloronitrobenzene was obtained in pale yellow needles, m. p. 99°. Reduction with tin and hydrochloric acid gave 12 g. of 2 : 3 : 5 : 6-tetrachloroaniline, m. p. 90°.

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