44. 2 : 4 : 6-*Trichloroaniline.*

By F. D. Chattaway and Harry Irving.

The preparation of 2 : 4 : 6-trichloroaniline in any quantity is difficult and no really satisfactory procedure has been described. The difficulty is due to the circumstance that, in the presence of even a small quantity of water, the amino-group is displaced by hydroxyl; if the chlorination be prolonged, octachlorohexenone is finally obtained.

When moisture is carefully excluded, the chlorination of a suspension of 2 : 4-dichloroaniline hydrochloride in dry chloroform gives a practically quantitative yield of 2 : 4 : 6-trichloroaniline; 80% of the theoretical amount may similarly be obtained by starting with aniline hydrochloride.

2 : 4 : 6-Trichloroaniline forms a well-crystallised crimson *picrate* and a colourless *phthalanil* and N-*dichloroacetyl* derivative. 2 : 4 : 6-Trichloroacetanilide, m. p. 207—208°, yields 2 : 4 : 6-*trichlorodiacetanilide*, m. p. 80·5—81·5°, when heated with an excess of acetic anhydride.

The substance obtained by Fels (*Z. Kryst.*, 1903, **37**, 465) and considered by him to be a molecular compound, $x\mathrm{C_6H_2Cl_3{\cdot}NH_2},y\mathrm{CH_3{\cdot}COCl}$ (although no analysis is given), appears to have been 2 : 4 : 6-trichlorodiacetanilide, since its m. p., given as 80—81°, and its crystallographic constants agree closely with those of this compound. In repeating Fels's work, under a wide range of experimental conditions we have always obtained only 2 : 4 : 6-trichloroacetanilide.

Similarly, the "molecular compound" of acetyl chloride and 2 : 4 : 6-tribromoaniline, m. p. 128·5—129·5°, described by Fels (*loc. cit.*) appears to be in reality 2 : 4 : 6-tribromodiacetanilide; the variations in crystal habit reported by Fels have not been observed.

Preparation of 2 : 4 : 6-*Trichloroaniline.*—A solution of 50 g. of aniline in 750 c.c. of $\mathrm{CHCl_3}$ (free from EtOH and dried over $\mathrm{CaCl_2}$) was saturated with dry HCl, moisture being carefully excluded. Through the suspension of aniline hydrochloride formed, a stream of Cl was passed, the temp. being maintained between 0° and 10°. When Cl was no longer absorbed, the excess of halogen was removed by aspirating dry air through the mixture, the colourless suspension of 2 : 4 : 6-trichloroaniline hydrochloride freed from $\mathrm{CHCl_3}$ with the aid of a pump, and the base itself obtained by crystn. from EtOH. The 2 : 4 : 6-trichloroaniline may if necessary be further purified by converting it into its monoacetyl derivative and hydrolysing this by suspending it in

H_2O (6 parts by wt.) and adding conc. H_2SO_4 (18 parts) rapidly with very vigorous stirring. The temp. rises to 130—140° and the solution becomes clear. When the cold liquid is poured over twice its wt. of ice, pure trichloroaniline separates as a colourless flocculent solid.

2 : 4 : 6-*Trichlorophthalanil*, obtained from trichloroaniline (1 mol.) and phthalic anhydride (1 mol.) at 150° (30 min.), separated from boiling EtOH (moderately sol.) in colourless pearly leaflets, m. p. 175—176° (Found : Cl, 32·8. $C_{14}H_6O_2NCl_3$ requires Cl, 32·6%).

2 : 4 : 6-*Trichloroanilinium picrate*, obtained from trichloroaniline and picric acid (eq. mol.) in warm EtOH, crystallised from boiling EtOH (very readily sol.) in fine, deep crimson prisms, m. p. 81·5—82·5°, which develop a green shade on keeping (Found : Cl, 25·15. $C_{12}H_7O_7N_4Cl_3$ requires Cl, 25·0%).

2 : 4 : 6-*Trichlorodichloroacetanilide*, $C_6H_2Cl_3\cdot NH\cdot CO\cdot CHCl_2$, obtained by refluxing the trichloroaniline with a slight excess of dichloroacetyl chloride at 170° for 15 min., crystallised from boiling EtOH (moderately sol.) in very slender, colourless prisms, m. p. 184—184·5° (Found : Cl, 57·35. $C_8H_4ONCl_5$ requires Cl, 57·7%).

2 : 4 : 6-*Trichlorodiacetanilide*, $C_6H_2Cl_3\cdot NAc_2$, prepared by refluxing the trichloroaniline (4 g.), Ac_2O (5 c.c.), and conc. H_2SO_4 (3 drops) for 4 hr. and pouring the mixture into H_2O, crystallised from EtOH or acetone, in which it is very sol., in small compact prisms, m. p. 81—82° (Found : Cl, 38·0. $C_{10}H_8O_2NCl_3$ requires Cl, 38·0%).

Measurements of selected crystals (from acetone at room temp.) showed that the forms *a* (100), *b* (010), *l* (110), *m* ($1\bar{1}0$), *n* ($1\bar{2}0$), *r* (101), and *q* (011) were represented. The identity of this 2 : 4 : 6-trichlorodiacetanilide with Fels's alleged molecular compound is shown by comparing the corresponding interfacial angles :

Angle.	Fels's cmpd.	$C_6H_2Cl_3\cdot NAc_2$.	Angle.	Fels's cmpd.	$C_6H_2Cl_3\cdot NAc_2$.	Angle.	Fels's cmpd.	$C_6H_2Cl_3\cdot NAc_2$.
bl	42° 5½′	42° 7½′	*qr*	34° 10′	34° 10′	*qa*	80° 50′	80° 53′
la	29° 42½′	30° 0′	*ra*	54° 59′	54° 41′	*qb*	59° 27′	59° 43′
am	42° 1½′	42° 4′	*rm*	67° 18′	67° 36½′	*ql*	67° 41½′	68° 16′
mn	26° 32½′	26° 27′	*rn*	81° 7′	81° 20′			

THE QUEEN'S COLLEGE, OXFORD.

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