270. *The Nuclear Chlorination of Toluene:* 2 : 3 : 4- *and* 2 : 3 : 6-*Trichlorotoluene.*

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Nuclear chlorination of toluene or *o*-chlorotoluene to the trichloro-stage in the presence of an iron catalyst is shown to yield 2 : 4 : 5- and 2 : 3 : 6-trichlorotoluene together with small amounts of 2 : 3 : 4-trichlorotoluene and not, as previously recorded, 2 : 4 : 5- and 2 : 3 : 4-trichlorotoluene only. The m. p. of 2 : 3 : 6-trichlorobenzoic acid is 124—126° and not 163—164° as hitherto recorded.

In connection with another research, it was necessary to prepare authentic samples of all the possible chlorinated derivatives of benzaldehyde and benzoic acid. These preparations, with two exceptions, were carried out without difficulty by methods described in the literature. The exceptions were the 2 : 3 : 4- and 2 : 3 : 6-trichloro-derivatives, and it became clear that the literature on these compounds was seriously in error. According to Seelig (*Annalen*, 1887, **237**, 129) and Prenntzell (*ibid.*, 1897, **296**, 181) chlorination of toluene or *o*- or *p*-chlorotoluene in the presence of an iron catalyst to the trichloro-stage gives mainly a mixture of 2 : 3 : 4- and 2 : 4 : 5-trichlorotoluene. We have now found that the major products obtained from toluene and *o*-chlorotoluene are 2 : 3 : 6- and 2 : 4 : 5-trichlorotoluene, the 2 : 3 : 4-isomer occurring only to a limited extent. We have found that the trichlorobenzoic acids are the most satisfactory derivatives for characterising the trichlorotoluenes.

The constitution of 2 : 4 : 5-trichlorotoluene was not in doubt and it was readily separated from the mixture by sulphonation and fractional desulphonation (Prenntzell, *loc. cit.*). The problem, therefore, was the identification of the 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene. For this purpose authentic samples of the corresponding benzoic acids were required. 2 : 3 : 6-Trichlorobenzoic acid, m. p. 124—126°, was prepared (*a*) from 3 : 6-dichloroanthranilic acid by the Sandmeyer reaction, (*b*) by direct oxidation of 2 : 3 : 6-trichlorotoluene with nitric acid, and (*c*) by oxidation of 2 : 3 : 6-trichlorobenzaldehyde with potassium permanganate or nitric acid. 2 : 3 : 6-Trichlorotoluene was prepared in two ways: from 3-amino-2 : 6-dichlorotoluene by the Sandmeyer reaction (Cohen and Dakin, *J.*, 1902, **81**, 1331), and by chlorination of toluene-*p*-sulphonyl chloride followed by hydrolysis of the resulting 2 : 3 : 6-trichlorotoluene-4-sulphonyl chloride (D.R.-P. 210856; "Friedländer," **9**, 104). 2 : 3 : 6-Trichlorobenzaldehyde was obtained by exhaustive chlorination of the trichlorotoluene side-chain to the benzylidene chloride, followed by hydrolysis of the latter. This method has the advantage that traces of isomeric trichlorotoluenes, other than those substituted in the 2- and the 6-position, are converted into the corresponding benzotrichlorides and benzoic acids and readily separated from the 2 : 3 : 6-trichlorobenzaldehyde.

The 2 : 3 : 6-trichlorobenzaldehyde so prepared had m. p. 87—88°, in agreement with D.R.-P. 199,943 ("Friedländer," **9**, 204); it was then obtained from 3-amino-2 : 6-dichlorobenzaldehyde by replacement of the amino-group with chlorine. The remote possibility that we were dealing with the 2 : 3 : 4-isomers was disproved by the unambiguous synthesis of and comparison with 2 : 3 : 4-trichloro-benzaldehyde and -benzoic acid. Cohen and Dakin (*loc. cit.*) record the m. p. of 2 : 3 : 6-trichlorobenzoic acid as 163—164°; this is clearly an error.

2 : 3 : 4-Trichlorobenzoic acid, m. p. 187—188°, was prepared (*a*) by direct oxidation of 2 : 3 : 4-trichlorotoluene and (*b*) by oxidation of 2 : 3 : 4-trichlorobenzaldehyde with aqueous permanganate. 2 : 3 : 4-Trichlorotoluene was prepared by chlorination of *p*-chlorotoluene (followed by separation of the large amount of the 2 : 4 : 5-isomer) (Seelig, *loc. cit.*) and also by chlorination of 3-aminotoluene-6-sulphonamide with hydrogen peroxide and hydrochloric acid. The resulting 3-amino-2 : 4-dichlorotoluene-6-sulphonamide, on removal of the sulphonamido-group, yielded 3-amino-2 : 4-dichlorotoluene which gave 2 : 3 : 4-trichlorotoluene on replacement of the amino-group with chlorine. 2 : 3 : 4-Trichlorobenzaldehyde, m. p. 86°, was obtained by regulated side-chain chlorination of the toluene, followed by hydrolysis.

Cohen and Dakin (*J.*, 1902, **81**, 1327, 1347) record the synthesis of 2 : 3 : 4-trichlorotoluene from 2 : 3-dichlorotoluene by nitration, reduction, and replacement of the amino-group with chlorine. On oxidation of their product they obtained a trichlorobenzoic acid of m. p. 186—187°, which we confirm as the m. p. of the 2 : 3 : 4-isomer. Repetition of this synthesis, however, incorporating a vigorous purification of the dichlorotoluidine by repeated recrystallisation of its acetyl derivative, has given 2 : 3 : 6-trichlorotoluene in low yield, identified by conversion into 2 : 3 : 6-trichlorobenzaldehyde (m. p. and mixed m. p.). It thus appears that Cohen and Dakin obtained a mixture of 2 : 3-dichloro-4-nitro- and 2 : 3-dichloro-6-nitro-toluene and that their product was a mixture of 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene. We have found repeatedly that when such a mixture is chlorinated to exhaustion in the side-chain, and the products are hydrolysed, a readily separable mixture of 2 : 3 : 6-trichlorobenzaldehyde and 2 : 3 : 4-trichlorobenzoic acid results, while if the mixture is oxidised with dilute nitric acid 2 : 3 : 4-trichlorobenzoic acid results, because this acid is less soluble in water than the 2 : 3 : 6-isomer, and because 2 : 3 : 6-trichlorotoluene is less readily oxidised by dilute nitric acid.

In addition to the method mentioned above, 2 : 3 : 4-trichlorobenzaldehyde, m. p. 86°, was also obtained by side-chain chlorination of the mixture of 2 : 3 : 6- and 2 : 3 : 4-trichlorotoluene (mentioned above) by using a deficiency of chlorine, followed by hydrolysis. Its m. p. is almost coincident with that of 2 : 3 : 6-trichlorobenzaldehyde but the m. p. of a mixture of the two shows a marked depression.

Seelig (*loc. cit.*) and Cohen and Dakin (*loc. cit.*) made use of the mono- and di-nitro-derivatives for characterisation of 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene. In view of the above findings we examined these compounds. The necessary pure trichlorotoluenes were made as follows: 2 : 3 : 4-trichlorotoluene from *p*-chlorotoluene and from 3-aminotoluene-6-sulphonamide as above; 2 : 3 : 6-trichlorotoluene by a very easy Wolff–Kishner reduction of purified 2 : 3 : 6-trichlorobenzaldehyde. The mono- and di-nitro-derivatives were made by recorded methods (Cohen and Dakin, *J.*, 1902, **81**, 1327). Their m. p.s are recorded, together with those of other derivatives of 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene, in the table below.

The m. p. of 2 : 3 : 4-trichloronitrotoluene was found to be 70°; *i.e.*, 10° higher than that recorded for this substance by Cohen and Dakin (*loc. cit.*, p. 1328). The m. p.s of 2 : 3 : 4- and 2 : 3 : 6-trichlorodinitrotoluene are identical, but mixtures of the two in varying proportions show a small but definite depression of m. p.

Derivative of:	2 : 3 : 4-Trichloro-, m. p.	2 : 3 : 6-Trichloro-, m. p.
Toluene	43—44°	43—44°
Nitrotoluene	70	59—60
Dinitrotoluene	143	143
Benzylidene chloride	—	78—80
Benzaldehyde	86	87—88
Benzoic acid	187—188	124—126

2 : 3 : 6-Trichloro-benzaldoxime, -benzylamine, and -benzyl alcohol have also been prepared.

EXPERIMENTAL.

(M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.)

2 : 3 : 6-*Trichlorotoluene*.—(1) 3-Amino-2 : 6-dichlorotoluene (37·2 g.; m. p. 52°) was diazotised at 0—5° in hydrochloric acid (*d* 1·18; 93 c.c.) and water (93 c.c.) by the slow addition of powdered sodium nitrite (14·8 g.). The cold filtered solution of the diazonium salt was added, during 15 minutes, to a solution of cuprous chloride (46·5 g.) in 15% hydrochloric acid (370 c.c.) at 25°. The temperature rose to 40° during the addition. After 15 minutes, the trichlorotoluene was distilled in steam from the reaction mixture, separated, and dried at room temperature, giving waxy cubes (31·0 g.), m. p. 39—40°. On chlorination of the side-chain at 180—200°, a solid benzylidene chloride (needles, m. p. 78—80°, from ethanol) was obtained which gave 2 : 3 : 6-trichlorobenzaldehyde, m. p. 87—88°, on hydrolysis.

(2) Crude toluene-*p*-sulphonyl chloride (1000 g.) was washed with water (1500 c.c.) at 75°, and the oil separated, dried ($CaCl_2$), and screened through a 200-mesh gauze yielding the purified material (850 g.). This was heated to 70—80°, antimony trichloride (25 g.) added, and chlorine passed into the stirred mixture until a gain in weight of 460 g. was obtained (7½ hours). The product (1335 g.) was added during 1 hour to 86% sulphuric acid (200 g.) kept at 230—240° in a steam-distillation apparatus supplied with steam superheated to 240—250°. Crude 2 : 3 : 6-trichlorotoluene collected in the receiver. It was washed with water at 70° and redistilled in superheated steam. The crude material was further washed with water until it was neutral to litmus (yield, 600 g.). It was purified by distillation *in vacuo* through a column equivalent to 50 theoretical plates; the distillate (385 g.; b. p. 118°/18 mm.) crystallised in waxy needles, m. p. 40—42°, from ethanol or methanol. On oxidation with 60% nitric acid at 150° it yielded 2 : 3 : 6-trichlorobenzoic acid, m. p. 124—126°, and on chlorination of the side-chain behaved in the same way as the sample prepared from 3-amino-2 : 6-dichlorotoluene.

(3) Dry toluene (or *o*-chlorotoluene) was chlorinated to the trichloro-stage in the presence of ½—1% of iron filings. The temperature was allowed to rise from 10° to 15° during the introduction of the first chlorine atom, then held at 20° until near completion, and the final 5% of chlorine introduced at 20—40°. The crude chlorinated toluenes (981 g.) were added with stirring to 23% oleum (1930 g.). The

temperature rose to 70—80° and was kept thereat for a further 45 minutes. 33% Sulphuric acid (1800 g.) was added cautiously, the temperature being allowed to rise to 130—140°. The mixture was then distilled in superheated steam. The temperature was gradually raised as the distillation proceeded. From 160° to 200°, crude 2 : 4 : 5-trichlorotoluene collected in the receiver (463 g. *ex* toluene, or 330 g. *ex* *o*-chlorotoluene). Between 200° and 210° small amounts (80—90 g.) of liquid chlorotoluenes were collected, and between 210° and 230° impure 2 : 3 : 6-trichlorotoluene (405 g. *ex* toluene; 543 g. *ex* *o*-chlorotoluene) containing *ca.* 2—3% of 2 : 3 : 4-trichlorotoluene and higher chlorinated toluenes. The last fraction was washed with warm water and fractionally distilled *in vacuo* through a column equivalent to 50 theoretical plates. 2 : 3 : 6-Trichlorotoluene was obtained, of b. p. 118°/18 mm., m. p. 39—40°, containing 3—4% of the 2 : 3 : 4-isomer. It constituted 62% of the material fractionated in the case of toluene and 81% in the case of *o*-chlorotoluene. If the temperature in the initial stages of chlorination was allowed to rise to 30—40° the 2 : 3 : 6-trichlorotoluene fraction was smaller and the proportion of 2 : 4 : 5-trichlorotoluene increased.

(4) 2 : 3 : 6-Trichlorobenzaldehyde, m. p. 78° (21 g.), was added to a solution of hydrazine hydrate (50%; 20 c.c.) in ethylene glycol (200 c.c.). The solution was warmed to 90° and set aside for 1 hour The temperature was then raised to 80°, and powdered sodium hydroxide (12 g.) added. The temperature rose to 100° with a brisk evolution of nitrogen. The mixture was heated to 110° for 10 minutes, allowed to cool somewhat, and poured into water (500 c.c.), and the whole distilled in steam. 2 : 3 : 6-Trichlorotoluene (15·2 g.) collected in the receiver and was filtered off and dried at room temperature; it formed waxy cubes melting sharply at 43—44°. Recrystallisation from ethanol or methanol gave waxy white needles of unchanged m. p. This material was used to prepare mono- and di-nitro-derivatives.

(5) 2 : 3-Dichloronitrotoluene was prepared by Cohen and Dakin's method (*J.*, 1902, **81**, 1347). 2 : 3-Dichlorotoluene (70 g.; f. p. 6°) was added to nitric acid (*d* 1·5; 84 c.c.) at 10—20° with stirring; the mixture was kept for 1 hour, then poured into water (400 c.c.), and the precipitate was filtered off; the product (88 g.; m. p. 49—52°) was a waxy solid; its m. p. was unaffected by recrystallisation from ethanol. 2 : 3-Dichloronitrotoluene (85 g.) was added during 1½ hours to a well-stirred solution of stannous chloride (290 g.) in hydrochloric acid (*d* 1·16; 290 c.c.) at 70—80°. The temperature was then raised to 95° and kept thereat for 20 minutes. The clear solution was poured into water, made alkaline with aqueous sodium hydroxide, and distilled in steam. Crude amino-2 : 3-dichlorotoluene, m. p. 40° (63 g.), was collected. This base (60 g.) was acetylated by stirring it for 1 hour at 45° with water (300 c.c.) and acetic anhydride (42 g.). The solid was collected and twice crystallised from ethanol–water. This material (27 g.), m. p. 131—133°, was boiled with 65% sulphuric acid (150 c.c.) for 2 hours. The clear solution was cooled, poured into water, basified with aqueous sodium hydroxide, and distilled in steam. Crude amino-2 : 3-dichlorotoluene (20 g.), m. p. 35° (not sharp), was collected. It was diazotised at 0° with hydrochloric acid (*d* 1·16; 48 c.c.), water (500 c.c.), and sodium nitrite (8·0 g.). The clear solution of the diazonium chloride was added at 0° to a solution of cuprous chloride (25 g.) in hydrochloric acid (*d* 1·16; 95 c.c.) and water (95 c.c.). The mixture was kept for 1 hour, and the trichlorotoluene (6·2 g.) distilled from it in steam. The product was a waxy solid, m. p. 35°, which could not be purified by crystallisation from methanol or ethanol, but was shown to consist largely of 2 : 3 : 6-trichlorotoluene by chlorination of the side-chain at 180—200° followed by hydrolysis of the solid benzylidene chloride formed, giving 2 : 3 : 6-trichlorobenzaldehyde (isolated in good yield *via* the bisulphite compound), m. p. 87—88°, identical (mixed m. p.) with material obtained from authentic 2 : 3 : 6-trichlorotoluene. The crude aldehyde contained only traces of alkali-soluble material.

2 : 3 : 6-*Trichlorobenzaldehyde.*—2 : 3 : 6-Trichlorotoluene (20 g.), prepared by any of the above methods, was chlorinated at 180—220° until no further absorption of chlorine occurred, an uptake corresponding to 2 atoms of chlorine being obtained in 24 hours. On cooling, the reaction mixture solidified. (A small portion of this material on crystallisation from ethanol had m. p. 78—80°.) It was added gradually with good stirring to 98% sulphuric acid (100 g.) at 75°. When evolution of hydrogen chloride slackened (1 hour) the temperature was raised to 95° and kept thereat for 30 minutes. After cooling to room temperature, the mixture was poured on ice and water, and the light cream-coloured solid filtered off and purified by distillation in steam; the product (20·2 g.; m. p. 84—85°) recrystallised from ethanol–water or light petroleum (b. p. 80—100°) in needles, m. p. 87—88°. If the 2 : 3 : 6-trichlorotoluene used contained any of the 2 : 3 : 4-isomer, the yield was somewhat lower and the chlorine uptake slightly greater, since 2 : 3 : 4-trichlorotoluene is readily chlorinated to the benzotrichloride stage. The 2 : 3 : 4-trichlorobenzoic acid, m. p. 187—188°, was isolated by extraction of the crude aldehyde with dilute aqueous sodium carbonate.

2 : 3 : 6-*Trichlorobenzoic Acid.*—(1) 2 : 3 : 6-Trichlorobenzaldehyde (2·1 g.) was stirred with a 1% aqueous solution of potassium permanganate (105 c.c.) at 90—95°. When the permanganate was decolorised, the hot suspension was filtered, the filtrate acidified with hydrochloric acid, and 2 : 3 : 6-trichlorobenzoic acid precipitated by addition of sodium chloride. It was collected and recrystallised from water; it (0·54 g.) had m. p. 124—126°. This acid is more soluble in water than the 2 : 3 : 4-isomer and corresponds with the description given by Seelig (*loc. cit.*) for " 2 : 3 : 4"-trichlorobenzoic acid.

(2) 2 : 3 : 6-Trichlorobenzaldehyde (50 g.) was stirred vigorously at 95° with 30% nitric acid (1450 g.) until a test portion showed almost complete solubility in dilute aqueous sodium hydroxide (5 hours). The reaction mixture was then cooled and basified with sodium hydroxide, and the faintly turbid solution clarified by extraction with benzene, treated with carbon, filtered, and slowly acidified with dilute hydrochloric acid with stirring. The precipitated 2 : 3 : 6-trichlorobenzoic acid was collected, washed with water, and dried at room temperature, giving a product (50 g.) of m. p. 124—126°.

(3) 3 : 6-Dichloroanthranilic acid (8·0 g.), m. p. 153° (Villiger, *Ber.*, 1909, **42**, 3539), was dissolved in an aqueous solution (120 c.c.) of an equivalent of sodium carbonate, and sodium nitrite (2·8 g.) added. This solution was added at 0—5° to 12% hydrochloric acid (85 c.c.). The resulting solution of the

diazonium chloride was added to a solution of cuprous chloride (4·0 g.) in 15% hydrochloric acid (100 c.c.) at −25°. The mixture was allowed to warm to room temperature, and then heated momentarily to the b. p. The suspension was cooled, the solid was filtered off and extracted with dilute sodium carbonate solution, and the filtered extracts were acidified. The crude 2 : 3 : 6-*trichlorobenzoic acid* was recrystallised from water (yield 0·4 g.), m. p. 124—126° (Found : C, 37·5; H, 1·6; Cl, 47·0. $C_7H_3O_2Cl_3$ requires C, 37·25; H, 1·3; Cl, 47·2%).

(4) 2 : 3 : 6-Trichlorotoluene (2·6 g.) was heated for 6 hours at 150° with 60% nitric acid (40 c.c.) in a sealed tube. The resulting mixture was diluted with water and evaporated to dryness on the steam-bath. The crude 2 : 3 : 6-trichlorobenzoic acid was extracted with aqueous sodium hydrogen carbonate, and the solution treated with carbon, filtered, and acidified (yield, 1·3 g.; m. p. 124° raised to 124—126° on recrystallisation from water). This acid was identical (mixed m. p.s) with that obtained by methods (1), (2), and (3), above (Found : C, 36·95; H, 1·45; Cl, 46·7%).

2 : 3 : 4-*Trichlorotoluene*.—(1) *p*-Chlorotoluene was chlorinated in the presence of 1% of iron filings below 30°. Slightly more than the theoretical gain in weight for the production of trichlorotoluene was obtained. The product was washed with water until neutral, separated, and dried. The crude trichlorotoluene (370 g.) was sulphonated and fractionally desulphonated as previously described for the preparation of 2 : 3 : 6-trichlorotoluene from toluene or *o*-chlorotoluene. The distillation in superheated steam from sulphuric acid yielded : at 160—180°, impure 2 : 4 : 5-trichlorotoluene (236 g.); at 190—210°, a liquid of unknown composition (64 g.); and at 210—230°, a white crystalline solid (42 g.). The last fraction, on distillation, all boiled at 244°/760 mm. The distilled material was recrystallised from ethanol giving 2 : 3 : 4-trichlorotoluene in white needles (25 g.), m. p. 43—44°.

(2) 3-Aminotoluene-6-sulphonamide, m. p. 168° (Backeberg and Marais, *J.*, 1943, 78) (26·6 g.), was dissolved in a mixture of hydrochloric acid (*d* 1·16; 300 c.c.) and water (450 c.c.) at 60°. At this temperature a solution of hydrogen peroxide (100-vol.; 30 c.c.) in water (30 c.c.) was added in four equal portions during 30 minutes with good stirring. The mixture was stirred for a further 30 minutes at 60° and then cooled to 25°. The precipitated solid was filtered off and washed with a solution of hydrochloric acid (*d* 1·16; 25 c.c.) in water (75 c.c.) and then with water. The wet filter cake was recrystallised from the minimum of hot glacial acetic acid, the mixture filtered, and the residue washed cautiously with cold acetic acid and dried at 90°; 3-*amino*-2 : 4-*dichlorotoluene*-6-*sulphonamide* (17 g.), formed faintly pink crystals, m. p. 184—185° (Found : C, 33·3; H, 3·4; Cl, 27·3; N, 11·0. $C_7H_8O_2N_2Cl_2S$ requires C, 32·95; H, 3·1; Cl, 27·8; N, 11·0%). 3-Amino-2 : 4-dichlorotoluene-6-sulphonamide (80 g.) was heated at the boil for 2 hours with 70% sulphuric acid (400 c.c.). The reaction mixture was cooled, poured into water (1700 c.c.), and distilled in steam. 3-Amino-2 : 4-dichlorotoluene solidified in the receiver. The distilland contained some unchanged starting material, which was filtered off from the cooled solution and again heated with 70% sulphuric acid, and the dichloroaminotoluene isolated as above. The 3-*amino*-2 : 4-*dichlorotoluene* (total yield, 50 g.) formed white crystals, m. p. 37—38° not raised by recrystallisation from light petroleum (b. p. 80—100°) (Found : C, 47·5; H, 4·05; Cl, 40·7; N, 8·1. $C_7H_7NCl_2$ requires C, 47·7; H, 4·0; Cl, 40·3; N, 7·95%). Its p-*nitrobenzoyl* derivative, needles from ethanol, had m. p. 246° (Found : C, 52·2; H, 3·3; N, 8·35; Cl, 22·6. $C_{14}H_{10}O_3N_2Cl_2$ requires C, 51·7; H, 3·1; N, 8·6; Cl, 21·8%).

3-Amino-2 : 4-dichlorotoluene (22 g.) was dissolved in a hot mixture of hydrochloric acid (*d* 1·16; 290 c.c.) and water (185 c.c.), and the solution cooled quickly; a finely divided suspension was obtained. To this was added, during 1 hour at 10—15°, sodium nitrite (9·0 g.). The filtered solution of the diazonium chloride was added in a thin stream to a boiling solution of cuprous chloride (26·5 g.) in hydrochloric acid (*d* 1·16; 114 c.c.) and water (114 c.c.) in a steam-distillation apparatus, steam being passed through the mixture simultaneously. 2 : 3 : 4-Trichlorotoluene collected in the receiver. It was separated and dried at room temperature (yield, 19 g.; m. p. 36°). Crystallisation from ethanol yielded white needles (8·3 g.), m. p. 42—43°, and a further recrystallisation raised this m. p. to 43—44°. This material did not depress the m. p. of the 2 : 3 : 4-*trichlorotoluene* obtained from *p*-chlorotoluene when admixed with it (Found : C, 43·1; H, 2·6; Cl, 54·0. $C_7H_5Cl_3$ requires C, 42·95; H, 2·6; Cl, 54·5%).

2 : 3 : 4-*Trichlorobenzaldehyde*.—(1) 2 : 3 : 4-Trichlorotoluene (12·0 g.) was chlorinated at 180—200° until an increase in weight corresponding to the uptake of two chlorine atoms was obtained. The crude liquid benzylidene chloride was hydrolysed with 98% sulphuric acid, and the crude aldehyde isolated in the same way as for the 2 : 3 : 6-isomer. It was dissolved in ether, and the solution shaken with concentrated (40%) sodium hydrogen sulphite solution. The bisulphite compound separated, and was filtered off, washed with ether, and dissolved in water, and the aldehyde was precipitated by addition of excess of sodium carbonate. The aldehyde (3·0 g.), m. p. 83°, was crystallised from ethanol–water; it formed needles, m. p. 86°; mixed m. p. with 2 : 3 : 6-trichlorobenzaldehyde, 60—70°. On oxidation with dilute aqueous potassium permanganate it yielded 2 : 3 : 4-trichlorobenzoic acid, m. p. 187—188°.

(2) The mixture of 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene obtained by chlorinating toluene or *o*-chlorotoluene was chlorinated at 180—200°, the chlorination being stopped when the gain in weight corresponded to the uptake of one chlorine atom. The reaction mixture was hydrolysed with 98% sulphuric acid at 70—90°, and the whole was poured into water, and the gummy solid filtered off. It was then extracted with ether, and the filtered ethereal solution shaken with 40% sodium hydrogen sulphite solution, yielding the aldehyde *via* the bisulphite compound as above. The yield was low and depended on the composition of the starting material, which in turn depended on the conditions of nuclear chlorination.

2 : 3 : 4-*Trichlorobenzoic Acid*.—(1) 2 : 3 : 4-Trichlorotoluene (2·0 g.) was boiled for 16 hours under reflux with 60% nitric acid (50 c.c.). On cooling, 2 : 3 : 4-trichlorobenzoic acid separated. It was collected and dissolved in dilute sodium carbonate solution, from which unchanged toluene was extracted

with ether. On acidification with hydrochloric acid, 2 : 3 : 4-trichlorobenzoic acid was precipitated; it formed needles, m. p. 187—188° (Found : C, 37·5; H, 1·5. Calc. for $C_7H_3O_2Cl_3$: C, 37·3; H, 1·3%).

(2) The mixture of 2 : 3 : 4- and 2 : 3 : 6-trichlorotoluene (above) was chlorinated at 180—200° until no more chlorine was absorbed. The resulting mixture of 2 : 3 : 6-trichlorobenzylidene chloride and 2 : 3 : 4-trichlorobenzotrichloride was hydrolysed with 98% sulphuric acid at 70—90°, and poured into water, and the crude benzaldehyde–benzoic acid mixture dissolved in ether and filtered. The filtered ethereal solution was shaken with concentrated (40%) sodium hydrogen sulphite solution, and the bisulphite compound of 2 : 3 : 6-trichlorobenzaldehyde separated. It was filtered off, and the ethereal portion of the filtrate extracted with aqueous sodium carbonate to obtain 2 : 3 : 4-trichlorobenzoic acid; recrystallised from water, this had m. p. 187—188°. The yield of acid was low and depended on the composition of the starting material.

2 : 3 : 4- *and* 2 : 3 : 6-*Trichloronitrotoluenes.*—These were made by the same method : the toluene (2·0 g.) was added slowly to nitric acid (*d* 1·5; 4 c.c.) at 0—20°. The mixture was kept for one hour, then poured into water, and the precipitated solid was filtered off and recrystallised from ethanol. 2 : 3 : 4-Trichloromononitrotoluene had m. p. 70° (Found : C, 35·2; H, 2·0; Cl, 44·2; N, 6·0. Calc. for $C_7H_4O_2NCl_3$: C, 34·9; H, 1·7; Cl, 44·3; N, 5·8%). The 2 : 3 : 6-trichloromononitrotoluene had m. p. 59—60°.

2 : 3 : 4- *and* 2 : 3 : 6-*Trichlorodinitrotoluenes.*—The toluene (2·0 g.) was heated in the steam-bath with a mixture of nitric acid (*d* 1·5; 16·0 c.c.) and sulphuric acid (*d* 1·84; 9 c.c.) for 30 minutes. The mixture was cooled and poured into water, and the product recrystallised from ethanol. Both 2 : 3 : 4- and 2 : 3 : 6-trichlorodinitrotoluenes had the same m. p., *viz.*, 143°. Mixtures of the two in varying proportions had m. p. 137—139°. 2 : 3 : 4-*Dichloro*-5 : 6-*dinitrotoluene* was analysed (Found : C, 29·8; H, 1·0; N, 9·75. $C_7H_3O_4N_2Cl_3$ requires C, 29·4; H, 1·05; N, 9·8%).

2 : 3 : 6-*Trichlorobenzaldoxime.*—2 : 3 : 6-Trichlorobenzaldehyde (63 g.) was dissolved in ethanol (600 c.c.), and anhydrous sodium carbonate (21 g.) added with stirring. The mixture was heated to 40°, and hydroxylamine hydrochloride (21 g.) in water (100 c.c.) added. The whole was then heated momentarily to the b. p., water (600 c.c.) added, and the solid filtered off and washed with water. Recrystallisation of the *oxime* (55 g.) from ethanol gave white needles, m. p. 169—170° (Found : C, 37·5; H, 1·7; N, 6·3; Cl, 47·5. $C_7H_4ONCl_3$ requires C, 37·4; H, 1·8; N, 6·2; Cl, 47·4%).

2 : 3 : 6-*Trichlorobenzylamine.*—2 : 3 : 6-Trichlorobenzaldoxime (20 g.), ethanol (100 c.c.), water (70 c.c.), and hydrochloric acid (*d* 1·16; 25 c.c.) were mixed and stirred, and zinc dust (20 g.) added during one hour. The temperature rose gradually to 40°. A further 40 c.c. of hydrochloric acid (*d* 1·16) were added in 10-c.c. portions to keep the reaction mixture strongly acid. The suspension was then heated to 60° for a few minutes, cooled, diluted with water, and filtered. The ethanol was removed from the filtrate by evaporation *in vacuo*, and the residue basified with sodium hydroxide solution. The oil which separated was extracted with ether, the ether removed from the dried ethereal solution, and the residue distilled *in vacuo*. The colourless oil (11 g.; b. p. 144°/12 mm.) gave a faintly turbid solution in dilute hydrochloric acid. It solidified on storage. It was dissolved in dilute hydrochloric acid, the solution treated with carbon and filtered, and the hydrochloride of the base precipitated by addition of sodium chloride. This was filtered off, dried, and dissolved in ethanol, the solution filtered, and the *hydrochloride* precipitated by addition of ether; it formed a white microcrystalline solid not melting below 270° (Found : C, 33·8; H, 2·7; N, 5·5. $C_7H_7NCl_4$ requires C, 34·0; H, 2·8; N, 5·7%). The base regenerated from the purified hydrochloride had m. p. 41—44° raised to 43—44° by crystallisation from light petroleum (b. p. 80—100°).

2 : 3 : 6-*Trichlorobenzyl Alcohol.*—2 : 3 : 6-Trichlorobenzylamine (20 g.) was dissolved in water (200 c.c.) and hydrochloric acid (*d* 1·16; 40 c.c.). Sodium nitrite (13·2 g.) was then added with stirring at 45°, precipitating a pale yellow gum. The mixture was cooled and extracted with ether, the ethereal solution dried, and the ether removed. The residue was distilled *in vacuo*, giving the *alcohol* (11 g.), b. p. 160—162°/12 mm., m. p. 60° raised by three recrystallisations from light petroleum (b. p. 80—100°) to 70—73° (constant) (Found : C, 40·0; H, 2·0; Cl, 50·5. $C_7H_5OCl_3$ requires C, 39·8; H, 2·4; Cl, 50·4%).

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