210. *Some Derivatives of* 1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-*chlorophenyl*)*ethane* (DDT).

By O. G. Backeberg and J. L. C. Marais.

1 : 1-Dichloro-2 : 2-di-(4-chlorophenyl)ethylene (II) is oxidised in acetic acid solution, either by fuming nitric acid or by chromic acid, to 4 : 4′-dichlorobenzophenone, while fuming nitric acid alone forms 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone (III); 1 : 1-dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethylene (IV) is obtained from the corresponding DDT compound (V) by the action of alcoholic potash.

Nitration of DDT with fuming nitric-sulphuric acid mixture forms 3 : 3′ : 5 : 5′-tetranitro-DDT (VI); under similar conditions. 1 : 1-Dichloro-2 : 2-di-(4-chlorophenyl)ethylene forms the corresponding tetranitrobenzophenone (VII); 1 : 1-dichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)ethylene (VIII) is obtained from tetranitro-DDT either by the action of alcoholic potash or by heating a nitrobenzene solution containing a trace of ferric chloride.

Bromine converts 1 : 1-dichloro-2 : 2-diphenylethylene into 1 : 1-dichloro-2 : 2-di-(4-bromophenyl)ethylene (XI).

Since Zeidler (*Ber.*, 1874, **7**, 1181) first described the preparation of 1 : 1 : 1-trichloro-2 : 2-di-(4-chlorophenyl)-ethane (DDT) (I), very little has been published in connection with the chemistry of this compound; quite

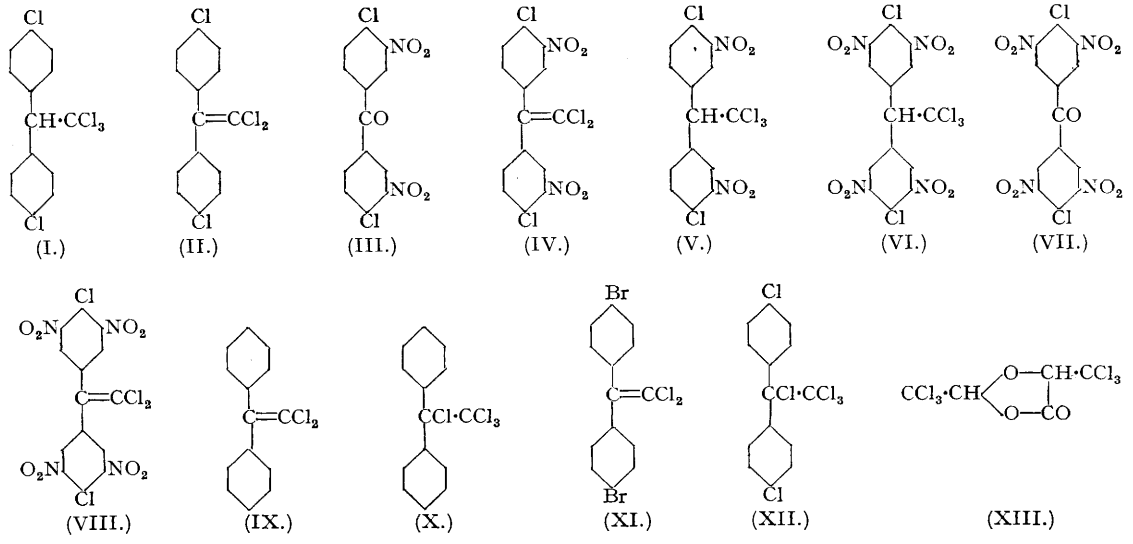
recently, however, two publications have appeared (Schechter and Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2129; Grummitt, Buck, and Jenkins, *ibid.*, 1945, **67**, 155), which became available only after the experiments now described had been completed.

In view of the importance of DDT as an insecticide, it appeared of interest to investigate its conversion into related compounds. Zeidler (*loc. cit.*) described its nitration to the 3 : 3′-dinitro-compound (V) and its conversion into 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene (II) by the action of alcoholic potash. The behaviour of (II) with fuming nitric acid has been studied; in acetic acid solution it formed 4 : 4′-dichlorobenzophenone, thus fixing the 4-position of the two nuclear chlorine atoms in 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene therefore in DDT. With fuming nitric acid alone the product was 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone (III), identical with the compound described by Montagne (*Ber.*, 1915, **48**, 1030). It was not found possible to nitrate 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene without at the same time oxidising it to the corresponding ketone, but 1 : 1-dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethylene (IV), was readily prepared by the action of alcoholic potash on dinitro-DDT; the compound, (IV), was reduced to the corresponding *amine*, 1 : 1-dichloro-2 : 2-di-(4-chloro-3-aminophenyl)ethylene, while fuming nitric acid oxidised it to the ketone (III) referred to above.

The more vigorous nitration of DDT and 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene to tetranitro derivatives was accomplished by the action of fuming nitric–sulphuric acid mixture. In the former case the product was 1 : 1 : 1-trichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)ethane (VI), confirming the result of Schechter and Haller (*loc. cit.*), although its m. p. was found to be significantly lower than reported by these authors; in the latter case, however, the product was 4 : 4′-dichloro-3 : 3′ : 5 : 5′-tetranitrobenzophenone (VII) and not 1 : 1-dichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)-ethylene, as stated by these authors (who described the product as having m. p. 224·5—225·5°, but did not give any analytical data for it); here too, therefore, oxidation to the ketone occurred during nitration. 1 : 1-Dichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)ethylene (VIII), m. p. 247° was, however, readily obtained from tetranitro-DDT either by the action of alcoholic potash or by heating a nitrobenzene solution containing a trace of ferric chloride; this compound (VIII), on warming with fuming nitric acid, was oxidised to the tetranitro-ketone (VII).

The oxidation of 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene to 4 : 4′-dichlorobenzophenone by the action of chromic acid in acetic solution (a reaction first carried out on this type of compound by Brand and Busse-Sundermann, *Ber.*, 1942, **75**, 1819), as well as its conversion into 1 : 1 : 1 : 2-tetrachloro-2 : 2-di-(4-chlorophenyl)-ethane (XII) by the action of chlorine, was also carried out. The results obtained were substantially the same as those described by Grummitt, Buck, and Jenkins (*loc. cit.*). In this connection, Biltz (*Ber.*, 1893, **26**, 1966) investigated the action of chlorine and of bromine on 1 : 1-dichloro-2 : 2-diphenylethylene (IX); his observation that the product in the former case was the tetrachloroethane derivative (X) formed by addition, was confirmed both by analysis and by its reconversion into the compound (IX) by the action of zinc dust; but the interesting observation was made that bromine formed, not the addition compound as stated by Biltz, but the substitution product, 1 : 1-dichloro-2 : 2-di-(4-bromophenyl)ethylene (XI).

Details for the large-scale preparation of DDT are contained in E.P. 547,871 and 547,874; for the preparation of small quantities (*ca.* 10—20 g.) Zeidler's reaction conditions and quantities were slightly modified, and the product, after one crystallisation from alcohol, had m. p. 108°. Examination of a local commercial product, prepared on a small scale, gave a substance which on investigation proved it to be chloralide (XIII), m. p. 114°. Enquiry showed that higher temperatures had been used in an attempt to speed up the reaction and to increase the yield—the reaction mixture had, in fact, been refluxed for some time. In such circumstances chloralide may thus be a by-product of the reaction (compare Gabrowski, *Ber.*, 1875, **8**, 1433).



Experimental.

(A standardised, short-stem Anschütz thermometer was used for all m. p. determinations.)

Oxidation of 1 : 1-*Dichloro*-2 : 2-*di*-(4-*chlorophenyl*)*ethylene*.—The compound (2 g.) in 20 c.c. glacial acetic acid was heated on the water-bath for 3 hours with 10 c.c. nitric acid (*d* 1·47) and poured into water; a colourless solid (1·5 g.) separated which, after crystallisation from alcohol, had m. p. 146·5°, identical with an authentic specimen of 4 : 4′-dichlorobenzophenone.

4 : 4′-*Dichloro*-3 : 3′-*dinitrobenzophenone* (III).—(a) 1 : 1-Dichloro-2 : 2-di-(4-chlorophenyl)ethylene (2 g.) was dissolved in nitric acid (20 c.c., *d* 1·47) in small portions at a time, the solution warmed on the water-bath for 30 minutes and poured into water. A pale yellow granular solid separated, m. p. 131·5° after crystallisation from alcohol or acetic acid. The m. p. was unchanged by admixture with a specimen prepared by the nitration of 4 : 4′-dichlorobenzophenone according to Consonno (*Gazz.*, 1904, **34**, 374), who, however, reported m. p. 120°. This compound was later prepared by Montagne (*loc. cit.*), who established its constitution unambiguously and reported m. p. 132·5°. The identity of the ketone was further established by its reduction to the corresponding diamine, m. p. 167·5° (cf. Montagne, *loc. cit.*). (b) 2 : 2-Dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)-ethylene (IV) (1 g.) was heated on the water-bath with nitric acid (5 c.c. *d* 1·5) for 15 minutes and poured into water. The yellow solid had m. p. 131·5° after crystallisation from alcohol, identical with a specimen prepared as above.

1 : 1-*Dichloro*-2 : 2-*di*-(4-*chloro*-3-*nitrophenyl*)*ethylene* (IV).—Dinitro-DDT (V) (20 g.), dissolved in absolute alcohol, was refluxed with a solution of potassium hydroxide (3 g. in absolute alcohol) for 2 hours. The filtered solution was left at 0° and the product (12 g.) was obtained as pale yellow, stout prisms, m. p. 118·5°. A further quantity (6 g.) was recovered from the mother liquor (Found : N, 7·0. $C_{14}H_6O_4N_2Cl_4$ requires N, 6·9%).

1 : 1-*Dichloro*-2 : 2-*di*-(4-*chloro*-3-*aminophenyl*)*ethylene*.—1 : 1-Dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethylene (3 g.) in acetic acid (30 c.c.) was heated under reflux and a concentrated aqueous solution of sodium hydrosulphite (15·8 g.) added dropwise during 1 hour. The hot solution was filtered, and on cooling, the *amine* crystallised in colourless plates, m. p. 143—144° (Found : N, 8·2. $C_{14}H_{10}N_2Cl_4$ requires N, 8·05%). The *diacetyl* derivative crystallised from dilute acetic acid in colourless prisms, m. p. 202° (Found : N, 6·7. $C_{18}H_{14}O_2N_2Cl_4$ requires N, 6·5%).

1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-*chloro*-3 : 5-*dinitrophenyl*)*ethane* (VI).—Concentrated sulphuric acid (30 c.c.) was slowly added to DDT (2 g.) dissolved in nitric acid (30 c.c., *d* 1·5), and the mixture heated on the water-bath for 4 hours, during which the oil, which initially separated, solidified. The reaction mixture was poured into water, and the solid separated, washed and crystallised from dioxan; it was obtained in small cream prisms with a greenish tinge, m. p. 218·5—219·5°. With alcoholic potash a purple colour was formed which changed to reddish brown on warming (Found : N, 10·4. Calc. for $C_{13}H_5O_8N_4Cl_5$: N, 10·5%) (Schechter and Haller, *loc. cit.*, reported m. p. 223·5—224·5°). The similar nitration of dinitro-DDT (V) formed the same product.

4 : 4′-*Dichloro*-3 : 3′ : 5 : 5′-*tetranitrobenzophenone* (VII).—Concentrated sulphuric acid (30 c.c.) was slowly added to a solution of 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene in 30 c.c. nitric acid (30 c.c. *d* 1·5), and the mixture heated on the water-bath for 4 hours; on pouring the solution into water a solid separated which crystallised from dioxan in small, pale yellow needles, m. p. 209°. With alcoholic potash a reddish brown colour was formed which changed to brown on warming (Found : N, 13·0. Calc. for $C_{13}H_4O_9N_4Cl_2$: N, 13·0%). Consonno (*loc. cit.*) nitrated 3 : 3′-dinitro-4 : 4′-dichlorobenzophenone with potassium nitrate–sulphuric acid mixture, and the product had m. p. 202°. The same product was obtained in a similar manner from the dinitro-compound (IV) and from the dinitro-ketone (III), as well as from the tetranitro-compound (VIII) by the action of nitric acid (*d* 1·5).

1 : 1-*Dichloro*-2 : 2-*di*-(4-*chloro*-3 : 5-*dinitrophenyl*)*ethylene* (VIII).—(a) Tetranitro-DDT (VI) (1 g.), dissolved in nitrobenzene (5 c.c.) containing a small crystal of ferric chloride, was boiled gently for 5 minutes. The nitrobenzene was removed by steam distillation and the residue crystallised from dilute acetic acid in brownish yellow prisms, m. p. 247°. With alcoholic potash a purple colour was formed which changed to brown on heating (Found : N, 11·45. $C_{14}H_4O_8Cl_4$ requires N, 11·25%). (b) Tetranitro-DDT (1 g.), dissolved in acetone–absolute alcohol, was refluxed for 1 hour with potassium hydroxide (0·2 g.), the solvent evaporated and the residue, crystallised from dilute acetic acid, was identical with the product described above.

Action of Chlorine and of Bromine on 1 : 1-*Dichloro*-2 : 2-*diphenylethylene* (IX).—(a) A solution of the compound (IX) (2 g.) in chloroform (20 c.c.) was heated under reflux for 3 hours while a steady stream of dry chlorine was passed through the solution. The gummy residue obtained after removal of the solvent solidified on stirring and crystallised from acetic acid in good yield as stout, colourless prisms, m. p. 87°; the *product* (X) possessed a characteristic odour of green maize, very similar to that of the compound (XII) (Found : Cl, 44·1. $C_{14}H_{10}Cl_4$ requires Cl, 44·4%). That the product was the addition compound with chlorine and not compound (II), m. p. 88°, was shown by a mixed m. p. determination and by its reconversion into the compound (IX). For this purpose the compound (X) (0·5 g.) in absolute alcohol (5 c.c.), was refluxed with zinc dust (0·5 g.) for 6 hours. After filtration and removal of the solvent, the residue crystallised from dilute alcohol in colourless prisms, m. p. 80°, unchanged by admixture with the compound (IX). Bilz (*loc. cit.*), in describing this reaction, referred to chlorination at the ordinary temperature for 30 minutes, but did not state the weight of the compound (IX) used; he obtained a product having m. p. 85°. When the compound (IX) was thus chlorinated, almost all of it was recovered unchanged.

(b) The compound (IX) (2 g.) was dissolved in bromine (10 c.c.); hydrogen bromide was freely evolved and the solution was exposed to the atmosphere. When the excess bromine had evaporated, the product was crystallised from alcohol and obtained in colourless plates, m. p. 122°, identical with 1 : 1-dichloro-2 : 2-di-(4-bromophenyl)ethylene (XI), prepared by the action of alcoholic potash on 1 : 1 : 1-trichloro-2 : 2-di-(4-bromophenyl)ethane according to Zeidler (*loc. cit.*), who reported m. p. 120°.

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University of the Witwatersrand, Johannesburg, South Africa. [*Received, June 18th*, 1945.]