# 66. *Chemical Investigations of the Insecticide "DDT" and its Analogues. Part I. Reactions of "DDT" and Associated Compounds.*

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The components of technical samples of the insecticide "DDT" have been separated and identified, and their reactions have been investigated. In addition to the main physiologically active product, 1 : 1 : 1-trichloro-2 : 2-di-(4-chlorophenyl)ethane ("pure DDT"), there are always present the very feebly insecticidal isomer 1 : 1 : 1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane ("*iso*-DDT") and small quantities of the physiologically inert "half condensation product," 1 : 1 : 1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane. When crude chloral has been used for the manufacture of DDT there is also present 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethane ("DDD"), which has only one-third of the insecticidal activity of "pure DDT." Methods of analysis of technical DDT have been developed.

The reduction of DDT affords an example of a reversed benzil–benzilic acid transformation, there being produced "DDD," 1 : 1-*di*-(4-*chlorophenyl*)*ethane* and 4 : 4′-dichlorostilbene.

The nitration reactions of DDT, *iso*-DDT, and DDD have been studied. In each case the nitro groups enter the positions 3 and 5 in the aromatic nuclei.

AT the time when the insecticide "DDT" was first introduced for use on the large scale by the Allied Nations, comparatively little was known of either its chemical or its physiological properties, and a series of investigations into these subjects was therefore put in hand on behalf of the Ministry of Production. Since numerous publications dealing with the physiological activity and technological applications of DDT have appeared within the past two years (see, *inter alia*, Läuger, Martin, and Müller, *Helv. Chim. Acta*, 1944, **27**, 892; Campbell and West, *Chem. and Ind.*, 1944, 319; *Manufacturing Chemist*, 1945, **15**, 312; Buxton, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1945, **38**, 367; Busvine, *Nature*, 1945, **156**, 169) it is now possible to give an account of chemical investigations which were completed in 1943—1944 in a research department of the Ministry of Supply.* Related physiological investigations will appear elsewhere.

*Components of Technical DDT.*—"Pure DDT" (I), prepared by Zeidler's method (*Ber.*, 1874, **7**, 1181) by condensing chlorobenzene with chloral, or chloral hydrate, in concentrated sulphuric acid, crystallises from alcohol, petrol, and many other solvents, in long, white needles of m. p. 108—109°, but the uncrystallised technical product, obtained by the large-scale operation of the same general process, is a white powder of decidedly lower setting-point (75—95°), and of inferior physiological potency. It was therefore important

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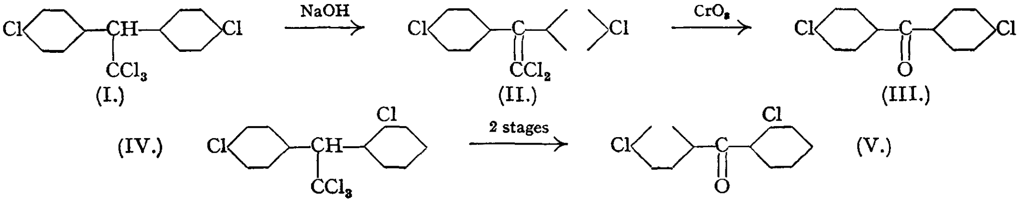
* After this work had been completed, and accounts circulated to Official Allied Authorities, descriptions of the following compounds were published by other investigators: tetranitro-DDT (Schlechter and Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2130); *iso*-DDT, DDD, and the corresponding ethylenes, tetranitro-*iso*-DDT, tetranitro-DDD, dinitro-*iso*-DDT, dinitro-DDD, and the dinitrophenylhydrazones of 4 : 4′- and 2 : 4′-dichlorobenzophenones (Haller, Bartlett, *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1591).

to separate the components of technical DDT, and examine in detail each pure substance, after first verifying its structural formula.

Fortunately, the most potent insecticide in crude DDT is (I), which always forms most of the material. Its structural formula, which was correctly inferred by Zeidler, has been confirmed rigorously by us, by degradation, through the dichloro-ethylene (II), to 4 : 4′-dichlorobenzophenone (III), which was shown to be identical with synthetic material.

By careful crystallisation, and reduced pressure distillation of the more soluble residues from the alcohol crystallisation of crude DDT, there was obtained 1 : 1 : 1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)-ethane (" *iso*-DDT ") (IV), which is almost devoid of insecticidal activity (Busvine, *loc. cit.*). The structure of (IV) was established by carrying out a similar degradation, through the dichloro-ethylene, to 2 : 4′-dichlorobenzophenone, which was synthesised independently from *o*-chlorobenzoyl chloride and chlorobenzene (cf. Montagne, *Rec. Trav. chim.*, 1906, **25**, 384 ; Norris and Tweig, *Amer. Chem. J.*, 1903, **30**, 397).



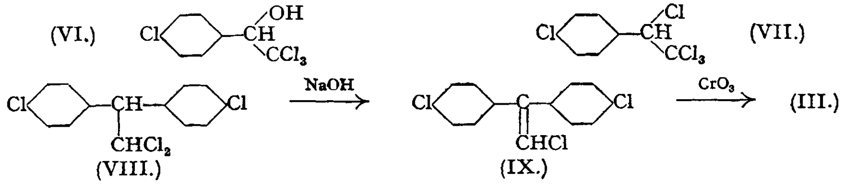
Technical DDT normally contains over 90% of these two isomers in the approximate ratio of 4 parts of (I) to 1 part of (IV), but much smaller quantities of certain other products may also be present.

The 2 : 2′-dichloro-isomer should, in theory, be present to the amount of 1—2% in crude DDT, but we have not succeeded in isolating it.

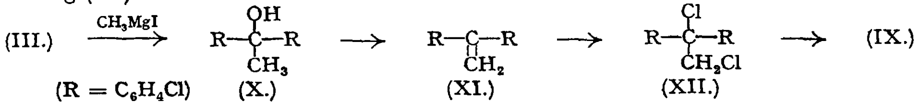
Most samples of crude DDT contain about 3% of oily material of decidedly lower boiling point (*ca.* 115°/0·5 mm. compared with *ca.* 190°/0·5 mm. for I or IV) which consists mainly of the " half-condensation product " 1 : 1 : 1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane (VI). This was isolated from crude DDT as a syrupy liquid which, after purification by hydrolysis of its acetate, was obtained as a solid identical with that prepared synthetically by another method (see Part III of this series). (VI) has no insecticidal value. Analytical evidence suggests that this fraction of technical DDT may contain, besides the 2-chloro-isomer of (VI), a little 1 : 1 : 1-trichloro-2-chloro-2-(4-chlorophenyl)ethane (VII) and also (in preparations of DDT from chloral alcoholate) 1 : 1 : 1-trichloro-2-ethoxy-2-(4-chlorophenyl)ethane, but we have not succeeded in isolating these substances in pure states.

Some samples of crude DDT have been found to contain small quantities of polychloral, or of chloralide, $C_5H_2O_3Cl_6$ (cf. Wallach, *Annalen*, 1878, **193**, 35) due to reaction under too vigorous conditions which lead to wastage of chloral. Adequately washed samples of DDT are usually free from these products, and also from free sulphuric acid, or sulphonic acids, but may contain traces of unchanged chlorobenzene.

A much more common impurity in technical DDT is 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethane (" DDD ") (VIII). This product has about one-third of the insecticidal activity of (I) (Busvine, *loc. cit.*) and can easily be prepared by condensing chlorobenzene with either dichloroacetal or dichloroacetaldehyde (cf. Fritsch, *Annalen*, 1894, **279**, 319, 337). Evidently it is formed from these impurities when technical chloral is used in the manufacturing process, and it has the effect of lowering the setting-point of technical DDT to a value not commensurate with the loss of physiological activity.



(VIII), on boiling with caustic soda in alcohol, gives 1-chloro-2 : 2-di-(4-chlorophenyl)ethylene which on oxidation with chromic acid gives 4 : 4′-dichlorobenzophenone (III) and a little *p*-chlorobenzoic acid. The structure of (IX) has been established independently by synthesis from (III), by treatment with methylmagnesium iodide to yield *1-hydroxy-1 : 1-di-(4-chlorophenyl)ethane* (X), which loses water when sublimed in a vacuum, giving *1 : 1-di-(4-chlorophenyl)ethylene* (XI). This adds on chlorine in carbon tetrachloride solution, giving *1 : 2-dichloro-2 : 2-di-(4-chlorophenyl)ethane* (XII) which loses hydrogen chloride when the solution is evaporated, leaving (IX).



$$\text{(III.)} \xrightarrow{CH_3MgI} \underset{\text{(X.)}}{R{-}\overset{OH}{\underset{CH_3}{C}}{-}R} \longrightarrow \underset{\text{(XI.)}}{R{-}\underset{\underset{CH_2}{\|}}{C}{-}R} \longrightarrow \underset{\text{(XII.)}}{R{-}\overset{Cl}{\underset{CH_2Cl}{C}}{-}R} \longrightarrow \text{(IX.)}$$

$(R = C_6H_4Cl)$

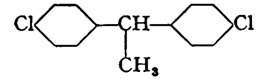
" DDD " should, of course, be produced together with its 4 : 2′-isomer, which, however, we have not yet isolated.

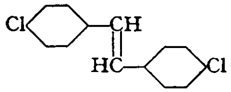
*Analysis of Technical DDT.*—It is characteristic of DDT (I), and its associated compounds, (IV) and (VIII), that on treatment with alcoholic alkali they lose one molecule only of hydrogen chloride, giving the very stable ethylenes (II, IX, etc.) which are resistant to further alkaline hydrolysis. Thus extraction with benzene or petroleum, hydrolysis of the washed (*i.e.*, salt-free) extract with alkali, and subsequent estimation of chloride, can be made the standard method of analysis of DDT, for detection of gross impurities, as well as for its estimation in insecticide sprays, or powders, or upon fabrics. The hydrolysis method does not, however, serve to differentiate between the pure compound (I) and its physiologically inert isomer (IV). Again the hydrolysable chlorine content of DDD (11·1%) is so little more than that of DDT (10·0%) that this analysis cannot be used as a sensitive test for the presence of DDD. Estimation of total chlorine (44·3% for DDD; 50·1% for DDT) is much more indicative of this contamination, though unfortunately impracticable for rapid routine testing purposes. High hydrolysable chlorine figures (over 10·5%) are indicative of appreciable contamination by the " half-product " (VI), since this, on boiling, neutralises nearly 4 equivalents of alkali, liberating 3 equivalents of chloride per mol.

We have shown, however, by the following experimental procedure, that the ratio between the amounts of the 4 : 4′ and 2 : 4′-isomers produced remains very closely constant, both for the reaction between chlorobenzene and pure chloral or chloral hydrate, and for reactions with crude chloral containing a high percentage of dichloroacetal, over a wide range of reaction temperatures, concentrations, and operating times. Weighed samples of technical DDT were hydrolysed to the corresponding mixed ethylenes, which were then extracted and oxidised with chromic acid in glacial acetic acid solution, yielding a mixture of the dichlorobenzophenones (III) and (V). The mixtures were precipitated quantitatively with water, washed with alkali, dried, and their setting points were taken. The " half-condensation products " (VI, VII, etc.) by this procedure yielded *p*-chlorobenzoic acid, which is sufficiently insoluble in water for quantitative precipitation from the alkaline washings by mineral acid. A wide range of samples of technical DDT, of different origin, yielded ketone mixtures of setting point 132° ± 2°, which corresponds to a mixture containing 26% of 2 : 4′-isomer (compare fig.). This is, of course, a maximum value for the *iso*-DDT content.

By using pure chemicals, a DDT mixture containing 75—80% of (I) (assessed by fractional crystallisation from alcohol) can regularly be obtained as the direct reaction product before crystallisation. Samples of still higher purity can be obtained by fractionally precipitating the condensation mixture (a solution in excess of concentrated sulphuric acid) with water, thereby leaving many impurities in solution, but this can be effected only with loss in total yield, and is in no way indicative of any variability in the *ortho–para* ratio in the condensation itself.

(XIII.)



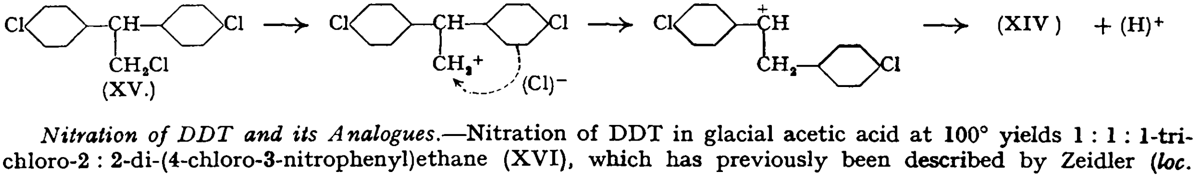


(XIV.)

The production of a ketone mixture of constant setting point is to be expected on theoretical grounds if the intrinsic *ortho* and *para* directive powers of chlorobenzene govern the course of each condensation. It indicates, moreover, that that insecticidal activity of technical DDT of hydrolysable chlorine content 10·0—10·5% should not vary to any serious extent according to the method of manufacture.

*Reduction Products of DDT.*—DDT is resistant to mild reducing agents, but when treated in boiling alcoholic solution with zinc and concentrated hydrochloric acid it yields three products: (*a*) " DDD " (VIII); (*b*) 1 : 1-*di*-(4-*chlorophenyl*)*ethane* (XIII), and (*c*) 4 : 4′-dichlorostilbene (XIV).

The structure of (XIII) is substantiated by oxidation to 4 : 4′-dichlorobenzophenone (III). (XIV), in contrast, oxidises easily to *p*-chlorobenzoic acid, and gives no trace of ketone. Moreover it readily yields a dibromo addition compound. (VIII) also gives a mixture of both (XIII) and (XIV) on further reduction. Analogous products are obtained on reduction of 1 : 1 : 1-trichloro-2 : 2-diphenylethane (" DT "). Other examples of transformations of DDT analogues to stilbene derivatives have been noted by Elbs (*J. pr. Chem.*, 1889, **39**, 300; 1894, **47**, 66) and by Harris and Frankforter (*J. Amer. Chem. Soc.*, 1926, **48**, 3144). A molecular rearrangement equivalent to a reversed benzil–benzilic acid change is involved. This is most probably a Wagner–Meerwein rearrangement of a cation, closely similar to the process whereby *iso*bornyl chloride yields camphene, occurring at the reduction stage of 1-chloro-2 : 2-di-(4-chlorophenyl)ethane (XV):



(XV.)

*Nitration of DDT and its Analogues.*—Nitration of DDT in glacial acetic acid at 100° yields 1 : 1 : 1-trichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethane (XVI), which has previously been described by Zeidler (*loc. cit.*). This is resistant to direct oxidation, but when boiled with pyridine it gives 1 : 1-*dichloro*-2 : 2-*di*-(4-*chloro*-3-*nitrophenyl*)*ethylene* which can be oxidised by chromic acid in glacial acetic acid to 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone (XVII) of m. p. 134°. This substance, the direct nitration product of 4 : 4′-dichlorobenzophenone, has been reported as having m. ps. between 120° (Consonno, *Gazzetta*, 1904, **34**, 376) and 132° (Montagne, *Rec. Trav. chim.*, 1902, **21**, 26). For confirmation of structures, we have repeated the nitration of (III). The reaction product, initially of indefinite m. p. 120—130°, after repeated recrystallisation eventually yielded crystals of m. p. 132°, which did not depress the m. p. of the oxidation product of (XVI)

1 : 1-Dichloro-2 : 2-di-(4-chlorophenyl)ethylene (II) could not be nitrated. It is oxidised by a warm mixture of concentrated nitric and glacial acetic acids yielding 4 : 4′-dichlorobenzophenone (III) in over 80% yield, and a lachrymatory product (possibly dichlorodinitromethane).

Nitration of DDT in fuming nitric/sulphuric acid mixture at 100° gives 1 : 1 : 1-trichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)ethane (XVIII). This reacts smoothly with aniline in hot alcoholic solution to give 1 : 1 : 1-*trichloro*-2 : 2-*di*-(3 : 5-*dinitro*-4-*anilinophenyl*)*ethane* (XIX), which was also prepared from the bromo-analogue of DDT. Again, 4 : 4′-dichloro-3 : 3′-dinitro-benzophenone (XVII), on prolonged refluxing with aniline, gives 3 : 3′-*dinitro*-4 : 4′-*dianilinobenzophenone*, whilst both 1 : 1-dichloro-di-(4-chloro-3-nitrophenyl)-ethylene and (XVI) on prolonged boiling in pyridine yield a brown *di-pyridinium* salt. These reactions confirm the positions assigned to the nitro groups in (XVI) and (XVII).

*iso*-DDT (IV) reacts in a similar manner, giving a dinitro-compound when nitrated in a mixture of concentrated nitric acid and glacial acetic acid, and a tetranitro-compound when nitrated with fuming nitric acid and concentrated sulphuric acid at 100°. The tetranitro-compound also yields a *dianilide*, so that evidently the nitro groups are in the 3 and 5 positions in each ring. The di- and tetra-nitration products of both DDT and *iso*-DDT have almost identical m. ps.; they are nevertheless quite distinct substances, each of which depresses the m. p. of the other.

The nitration of 1 : 1-di-(4-chlorophenyl)ethane (XIII) takes a similar course, giving the *di*-(4-*chloro*-3-*nitro*)-compound, and then the *di*-(4-*chloro*-3 : 5-*dinitro*)-compound which again yields a *dianilide*. DDD (VIII) also gives a dinitro-derivative on heating to 100° in a mixture of glacial acetic and concentrated nitric acids, and a tetranitro-derivative on heating to 100° with fuming nitric and concentrated sulphuric acids, and the latter product again gives a dianilide.

*Other Reactions of DDT.*—In the hope of discovering a reaction applicable for micro-chemical estimation of pure DDT, interactions with a number of other reagents have been studied. Reactions involving the –CCl$_3$ group offered the best hope of success, but in DDT, *iso*-DDT, DDD, and analogous compounds, this group is surprisingly inert. Hydrogen chloride can be eliminated easily by treatment with alcoholic sodium hydroxide, or by refluxing with pyridine, quinoline, or aniline, but not by treatment with alcoholic ammonia or 2 : 4-dinitrophenylhydrazine. Sodium carbonate in boiling aqueous alcohol removed hydrogen chloride only very slowly. The resultant dichloroethylenes resist attack by all these reagents and also by fused sodium hydroxide, though sodium ethoxide does react further under extremely drastic conditions (cf. Harris and Frankforter, *loc. cit.*).

DDT and its analogues also lose hydrogen chloride when heated to high temperatures (200° or over). The thermal stability is dependent upon the purity of the product; for example, dry DDT is decomposed readily at its m. p. by addition of a trace of ferric chloride with quantitative formation of the ethylene (II) (compare Fleck and Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2095; Balaban and Sutcliffe, *Nature*, 1945, **155**, 755).

DDT is decomposed by boiling with anhydrous zinc chloride in glacial acetic acid solution, giving (II) and a little *di*-(4-*chlorophenyl*)*acetic acid*, which was identified by conversion into its *ethyl* ester, and by oxidation to (III).

Red products are formed by fusing DDT or its isomer with phenol, naphthols, or diphenylamine, in the presence of anhydrous zinc chloride, but their colours are not sufficiently intense to be of value for colorimetric analysis.

## EXPERIMENTAL.

*Separation of Components of Technical DDT (Typical Examples).*—(i) *Material of* 50% (±0·5%) *total chlorine content.* 500 G. of crude material were dissolved in 1500 ml. of light petroleum (b. p. 40—60°), separated from a small aqueous layer (which usually gave positive tests for chloral), and filtered hot. On cooling, 200 g. of DDT, m. p. 107—108°, separated. One recrystallisation gave a pure product, m. p. 109°. The residue was stripped from petrol, warmed with 400 ml. of methyl alcohol, and kept for 24 hours. It deposited a further 75 g. of DDT, and, after a further 24 hours, 42 g. of a solid, m. p. 50—60° (*a*).

The remaining liquid was stripped from solvent by heating under reduced pressure, and was then fractionated through a short Vigreux column. It gave (*b*) 25 g. of an oil, b. p. 115—135°/0·5 mm., and (*c*) 75 g. of an oil, b. p. 175—195°/0·5 mm. At temperatures above this, some decomposition set in with evolution of hydrogen chloride. Fraction (*b*), after redistillation, gave 20 g. (= 4%) of a viscous liquid, b. p. 114—116°/0·5 mm., consisting essentially of 1 : 1 : 1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane (VI) (Found : C, 37·4; H, 2·3; Cl, 54·2. Calc. for C$_8$H$_6$OCl$_4$ : C, 37·0; H, 2·3; Cl, 54·6%).

Fraction (*c*) redistilled at 190—191°/1 mm. and formed a thick gum on cooling. This was dissolved in light petroleum (b. p. 40—60°) and kept at 0° until crystallisation occurred (*ca.* 2 days). The white solid, m. p. 67—71°, on repeated recrystallisation from petrol and methyl alcohol, was obtained in rhombs, m. p. 76°, and proved to be *iso*-DDT (IV). Solid (*a*) contained substantially the same material (Found : C, 47·6; H, 2·4; Cl, 50·1. Calc. for C$_{14}$H$_9$Cl$_5$ : C, 47·4; H, 2·7; Cl, 50·03%).

(ii) *Material of under* 49% *total chlorine content.* 400 G. of crude material were dissolved in 1000 ml. of boiling methyl alcohol and the solution was allowed to cool slowly, when 245 g. (= 61%) of DDT, m. p. 108—109°, separated in clusters of white needles. The filtrate was concentrated at reduced pressure and then distilled at less than 4 mm.

pressure, giving (*a*) 7 g., b. p. 100—180°, and (*b*) 140 g., b. p. 180—198°. Fraction (*b*) became viscous on cooling, and when treated with cold methyl alcohol deposited 62 g. of a solid, m. p. 105°. This on recrystallisation from methyl alcohol yielded stout white prisms of " DDD," (VIII), m. p. and mixed m. p. 110° (Found : C, 52·4; H, 3·2; Cl, 44·3. Calc. for $C_{14}H_{10}Cl_4$ : C, 52·5; H, 3·1; Cl, 44·4%).

*Direct Synthesis of " DDD."*—94 G. of dichloroacetal (0·5 mol.) were mixed with 112 g. of chlorobenzene (1·0 mol.), and 250 ml. of concentrated sulphuric acid were added slowly with vigorous shaking at 30°. A crystalline solid separated after keeping at room temperature. The brown acid liquors were poured off, and the solid was washed with cold dilute alcohol, leaving 74 g. of crude material which, when recrystallised twice from methyl alcohol, gave 59 g. of pure DDD, m. p. and mixed m. p. 110°. The same product was obtained by condensing dichloroacetaldehyde with chlorobenzene at 80° for 1 hour.

*Analysis of Technical DDT by Oxidation. General Procedure.*—(*a*) 25 G. of technical DDT were dissolved in warm alcohol (200 ml.) and refluxed for ½ hour with a solution of sodium hydroxide (8 g.) in water (50 ml.). The excess of alcohol was evaporated on the water-bath, and the residue diluted with water and acidified with hydrochloric acid. When cold, the aqueous layer was decanted from the gummy solid, extracted with chloroform, and the chloroform extract evaporated.

(*b*) The brown gum, together with the residue from the chloroform extraction, was dissolved in hot, glacial acetic acid (*ca.* 75 ml.), using the same flask as before, and a saturated solution of chromium trioxide (50 g.) was added gradually. The mixture was refluxed for 4 hours, diluted, whilst still hot, with water (*ca.* 500 ml.), and allowed to cool.

(*c*) The cold product was extracted with chloroform, and the extract washed 4 times with small quantities of dilute ammonia and finally with distilled water. The alkaline aqueous extracts were evaporated to small bulk, filtered, and acidified, and the precipitate (= Y) was collected and weighed in a Gooch crucible.

(*d*) The washed chloroform extract was dried over calcium chloride, and the ketone mixture (= X) was collected quantitatively by evaporation of the filtered solution. The residue was heated above its m. p. to remove traces of chloroform, and was then cooled and weighed. The setting point of the mixture was taken.

Analytical results, exemplified by the Table below, can be calculated from theoretical equations, from which it may be deduced that 25 g. of (DDT + analogues) should give 17·7 g. of mixed ketones (X), whilst 25 g. of " half products " (VI, etc.) should give 15 g. of acids (Y) Several ultimate analyses confirmed that X was in fact a mixture of isomeric dichlorobenzophenones.

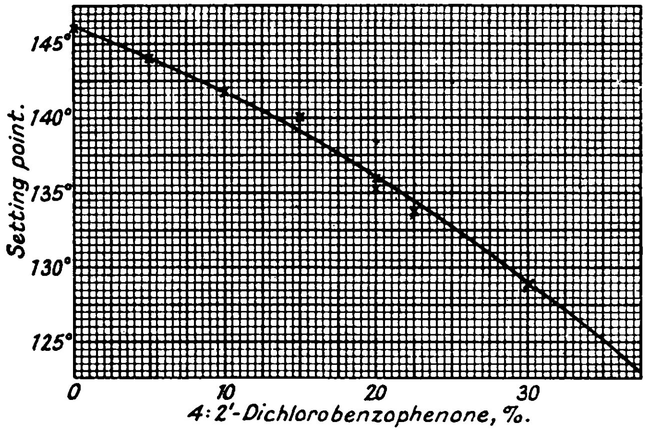
*Analyses of Technical DDT (showing range of variability)*

| Sample. | G 43. | S 617. | S 657. | D 62. | H 156. |
|---|---|---|---|---|---|
| Setting point | 91° | — | 80° | 67° | 78° |
| DDT (I), % * | 76 | 56 | 65 | 48 | 59 |
| Hydrolysable Cl, % | 10·2 | 11·4 | 10·6 | 11·4 | 10·6 |
| Total Cl, % | 49·2 | 50·7 | 48·9 | 48·0 | 50·3 |
| DDT cpds. (I, IV, VIII), % calc. from weight of ketones | 88, 89 | 84 | 85 | 90 | 91 |
| Setting point of ketones | 133° | 130° | 134° | 134° | 130° |
| " Half products " (VI, VII), % | 3·2 | 2·2 | 2·6 | 2·4 | 3·0 |
| Probable % DDD (VIII) | 2 | 27 | 16 | 37 | 22 |
| Maximum % *iso*-DDT + *iso*-DDD | 29 | 22 | 25 | 11 | 23 |

* Estimated by crystallisation from alcohol.

The setting point curve of mixtures of the ketones (III) and (V) is given in the figure.

*Setting points of* 4 : 4′*-dichlorobenzophenone plus* 4 : 2′*-dichlorobenzophenone.*



Most technical samples of DDT fall between the range represented by specimens G 43 and S 657, and have setting points above 75°.

*Reduction of DDT.*—100 G. of pure DDT were dissolved in 1200 ml. of industrial spirit, 75 g. of granulated zinc and 200 ml. of concentrated hydrochloric acid were added, and the whole was refluxed for 8 hours. The mixture was filtered and the filtrate concentrated under reduced pressure until an oily solid remained. This was taken up in chloroform, washed with water, dried ($CaCl_2$), concentrated and then diluted with light petroleum (b. p. 40—60°), when it gave 21 g. of solid, m. p. 90—140°, and a soluble residue. On fractional crystallisation of the solid from methyl alcohol there were obtained, (*a*) 4 : 4′-dichlorostilbene (XIV), m. p. 178° (Found : C, 67·4; H, 3·87; Cl, 28·2; *M*, (Rast) 236, (F.P. in benzene) 224. Calc. for $C_{14}H_{10}Cl_2$ : C, 67·4; H, 4·05; Cl, 28·5%; *M*, 249) and (*b*) 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethane (VIII), m. p. 110° (total yield *ca.* 10 g.).

The petroleum-soluble residue was fractionally distilled in a vacuum and yielded (*c*) 42 g. of solid, b. p. 160°/3 mm. and (*d*) 24 g., b. p. 179—186°/0·9 mm. On repeated crystallisation from petrol, (*c*) proved to be mainly compound (VIII), whilst (*d*) yielded 1 : 1-*di*-(4-*chlorophenyl*)*ethane* (XIII) which crystallised from methyl alcohol in fine, white prisms, m. p. 56° (Found : C, 66·8; H, 4·8; Cl, 28·0. $C_{14}H_{12}Cl_2$ requires C, 66·9; H, 4·8; Cl, 28·3%).

4 : 4′-Dichlorostilbene (XIV), on oxidation with chromic acid in acetic acid, or with hot alkaline permanganate, yielded *p*-chlorobenzoic acid, m. p. and mixed m. p. 238°. Bromination of (XIV) with an equal weight of bromine in carbon tetrachloride yielded αβ-dibromo-4 : 4′-dichlorostilbene, m. p. 229° (Found : C, 40·4; H, 2·56. Calc. for $C_{14}H_{10}Cl_2Br_2$ : C, 40·1; H, 2·45%).

"DDD" (VIII), on oxidation with chromic acid in acetic acid, gave a little *p*-chlorobenzoic acid, but the main product was (III). 1·0 G. on further reduction with zinc and alcoholic hydrochloric acid yielded (XIV) (0·15 g.) and (XIII) (0·50 g.). On refluxing with alcoholic sodium hydroxide DDD yielded 1-chloro-2 : 2-di-(4-chlorophenyl)ethylene (IX), which crystallised from methyl alcohol in long, white needles, m. p. 68° (Found : C, 59·2; H, 3·47; Cl, 37·7. Calc. for $C_{14}H_9Cl_3$ : C, 59·2; H, 3·2; Cl, 37·6%). DDD was not attacked by boiling alcoholic solutions of aniline, phenylhydrazine, or 2 : 4-dinitrophenylhydrazine.

1 : 1-Di-(4-chlorophenyl)ethane (XIII), on oxidation with chromic acid in acetic acid, yielded 4 : 4′-dichlorobenzophenone, m. p. 147°, quantitatively. Oxidation could not be effected with alkaline permanganate solution.

2·0 G. of (XIII) were nitrated at 100° with a mixture of 30 ml. each of concentrated sulphuric and concentrated nitric (*d*, 1·46) acids. The product, when crystallised from acetic acid, gave small pale yellow needles of 1 : 1-*di*-(4-*chloro*-3 : 5-*dinitrophenyl*)*ethane*, m. p. 261° (Found : C, 39·0; H, 1·74; N, 13·0. $C_{14}H_8O_8N_4Cl_2$ requires C, 39·0; H, 1·9; N, 13·0%). This on heating with aniline in alcoholic solution gave, in good yield, bright red crystals of 1 : 1-*di*-(3 : 5-*dinitro*-4-*anilinophenyl*)*ethane*, m. p. 203° (Found : C, 57·1; H, 3·75; N, 15·5. $C_{26}H_{20}O_8N_6$ requires C, 57·3; H, 3·71; N, 15·4%).

2·0 G. of (XIII) were also nitrated by dissolving in a mixture of 40 ml. of glacial acetic and 30 ml. of fuming nitric (*d*, 1·5) acids and heating to 100° for 5 hours. The mixture was then cooled and poured on ice, and the solid was separated, washed with water and crystallised from methyl alcohol, giving 1 : 1-*di*-(4-*chloro*-3-*nitrophenyl*)*ethane* (XX), m. p. 92—93° (Found : C, 48·9; H, 3·14; N, 8·1. $C_{14}H_{10}O_4N_2Cl_2$ requires C, 49·2; H, 2·9; N, 8·2%). On oxidation with chromic anhydride in glacial acetic acid, (XX) yielded 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone (XVII), m. p. 132°, identical with the products obtained (i) from "dinitro-DDT" and (ii) by direct nitration of (III) (see below).

*Synthesis of* 1-*Chloro*-2 : 2-*di*-(4-*chlorophenyl*)*ethylene* (IX).—(i) 5 G. of 4 : 4′-dichlorobenzophenone (III) in 200 ml. of dry ether were added slowly to the Grignard reagent prepared from 0·45 g. of magnesium and 4·0 g. of methyl iodide in 150 ml. of dry ether. The mixture was kept over-night, heated on the water-bath for 1 hour, cooled, and finally decomposed with dilute sulphuric acid. The ethereal extract was washed, dried, and evaporated, and the residue was treated with light petroleum (b. p. 40—60°) when clusters of rod-like needles of 1-*hydroxy*-1 : 1-*di*-(4-*chlorophenyl*)*ethane*, m. p. 70—71°, separated (Found : C, 63·4; H, 4·36; Cl, 26·9. $C_{14}H_{12}OCl_2$ requires C, 62·8; H, 4·49; Cl, 26·6%).

(ii) The above product was heated in a vacuum at 160—180° when a white solid sublimed. This on recrystallisation from methyl alcohol had m. p. 86° and was 1 : 1-*di*-(4-*chlorophenyl*)*ethylene* (Found : C, 67·5; H, 4·05; Cl, 28·4. $C_{14}H_{10}Cl_2$ requires C, 67·4; H, 4·02; Cl, 28·5%). Reduction of this compound to (XIII) could not be effected with zinc and hydrochloric acid.

(iii) 1 G. of 1 : 1-di-(4-chlorophenyl)ethylene was treated with 1·2 mol. of chlorine in cold carbon tetrachloride and the solvent was evaporated, when hydrogen chloride was eliminated with the vapours. The oily residue, on recrystallisation from methyl alcohol, gave fine white needles of (IX), m. p. 68—69°, unchanged on admixture with a specimen prepared as above from DDD.

*Nitration Products of DDT.*—1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-*chloro*-3-*nitrophenyl*)*ethane* (XVI). 5 G. of DDT were dissolved in a mixture of 80 ml. of acetic acid and 80 ml. of fuming nitric acid (*d*, 1·5), and the solution was heated on the water-bath for 3—4 hours. The mass was cooled and poured into cold water, and the solid product after washing was crystallised from alcohol, giving 5·2 g. of small yellow needles, m. p. 145—146° (Zeidler, *loc. cit.*, gives m. p. 145°).

1 : 1-*Dichloro*-2 : 2-*di*-(4-*chloro*-3-*nitrophenyl*)*ethylene*. 4 G. of (XVI) were boiled with 50 ml. of pyridine for 3 hours. After reaction had ceased the dark solution was poured into excess of cold, dilute, nitric acid when an oil separated, and solidified on cooling. On crystallisation from acetic acid, and then from alcohol, it gave 4·0 g. of large yellow plates, m. p. 121—122° (Found : C, 41·4; H, 1·68; N, 6·8; Cl, 34·2. $C_{14}H_6O_4N_2Cl_4$ requires C, 41·2; H, 1·47; N, 6·9; Cl, 34·8%). This *compound* was oxidised by boiling for 2 hours with excess of chromium trioxide in glacial acetic acid. On dilution, the solid which separated was 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone (XVII), m. p. 133—134° (Found : C, 45·5; H, 1·76; N, 8·3; Cl, 21·3. Calc. for $C_{13}H_6O_5N_2Cl_2$ : C, 45·7; H, 1·75; N, 8·2; Cl, 20·8%).

(iii) Direct nitration of (II) was attempted as follows : 5 g. were dissolved in a mixture of fuming nitric and glacial acetic acids (80 ml. of each) and maintained at 40—50° for 2½ hours and then at 60° for 1 hour. A steady evolution of nitrous fumes occurred. On pouring into water, the characteristic smell and typical lachrymatory effects of chloronitromethanes were noted. The solid which separated was recrystallised from alcohol and proved to be 4 : 4-dichlorobenzophenone (III) (yield 3·5 g. = 80%).

(iv) 1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-*chloro*-3 : 5-*dinitrophenyl*)*ethane* (XVIII). 4 G. of (XVI) were heated at 100° for 8 hours with 50 ml. of concentrated sulphuric acid and 30 ml. of fuming nitric acid (*d*, 1·5) and finally the temperature was raised to 150° for ½ hour. The product, after cooling, was poured on ice, and the resulting solid was washed and recrystallised from glacial acetic acid, giving small yellow plates, m. p. 223° (Found : N, 10·4. Calc. for $C_{14}H_5O_8N_4Cl_5$ : N, 10·5%).

(v) 1 : 1 : 1-*Trichloro*-2 : 2-*di*-(3 : 5-*dinitro*-4-*anilinophenyl*)*ethane* (XIX). This *compound* was obtained in the form of deep orange-red needles, m. p. 231°, by refluxing (XVIII) (0·5 g.) in alcohol (100 ml.) and aniline (1·0 g.) for 2 hours. It crystallised well from glacial acetic acid (Found : C, 48·6; H, 2·64; N, 13·1. $C_{26}H_{17}O_8N_6Cl_3$ requires C, 48·4; H, 2·65; N, 13·0%). The same product was obtained from 1 : 1 : 1-trichloro-2 : 2-di-(4-bromophenyl)ethane, m. p. 141° (Zeidler, *Ber.*, 1874, **7**, 1180), which gives a tetranitro-derivative, m. p. 224°, when heated with nitric/sulphuric acid.

(vi) 1 : 1-Dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethylene when boiled in pyridine for 12 hours and then poured into cold, dilute hydrochloric acid gave a residue which crystallised from hot water in small yellow-brown needles, m. p. 222—223°. This was evidently a *dipyridinium* salt (Found : N, 10·8. $C_{24}H_{16}O_4N_4Cl_2,2HCl$ requires N, 9·9; the base, $C_{24}H_{16}O_4N_4Cl_2$, requires N, 11·3%).

(vii) 4 : 4′-Dichloro-3 : 3′-dinitrobenzophenone (XVII), was boiled for 4 hours with an excess of aniline (5 mols.). The product was poured into dilute hydrochloric acid and gave an orange-yellow powder which, after repeated crystallisation from glacial acetic acid and then chlorobenzene, followed by washing with cold alcohol, gave small crystals of the *dianilide*, m. p. 224° (Found : C, 65·8; H, 3·64; N, 12·0. $C_{25}H_{18}O_5N_4$ requires C, 66·1; H, 3·97; N, 12·3%).

(viii) 4 : 4′-Dichlorobenzophenone (III) was nitrated at 100° in a mixture of nitric and sulphuric acids. The product was crystallised repeatedly from acetic acid, when its m. p., at first indefinite at 120—130°, rose to 132°, and this product did not depress the m. p. of (XVII) obtained from DDT as described above.

*Other Reactions of DDT.*—(1) *Action of alkaline reagents.* (i) DDT, dissolved in alcohol, was refluxed for 15 minutes with sodium hydroxide (1 mol.). The solution was diluted with water, precipitating quantitatively 1 : 1-dichloro-2 : 2-di-(4-chlorophenyl)ethylene (II) which crystallised from methyl alcohol in white, shining plates, m. p. 89° (Found : C, 52·8; H, 2·40; Cl, 44·8. Calc. for $C_{14}H_8Cl_4$ : C, 52·8; H, 2·52; Cl, 44·7%). The same product was obtained after prolonged refluxing of DDT with excess of sodium hydroxide or sodium ethoxide, or by fusion with sodium hydroxide. Partial conversion of DDT into (II) was effected by refluxing for ½ hour with sodium carbonate in aqueous alcohol.

(ii) Quantitative conversion of DDT into (II) was effected by refluxing for 2 hours in pyridine, quinoline, or aniline (in the absence of another solvent). DDT was not attacked when boiled for 3 hours with a 1 : 1 mixture of ammonia (*d*, 0·88) and alcohol and did not react with 2 : 4-dinitrophenylhydrazine in boiling alcohol.

(2) *Degradation by oxidation.* DDT was recovered unchanged after refluxing for 20 hours with excess of potassium permanganate in N-alkali, and also after refluxing for 8 hours with chromium trioxide in glacial acetic acid. (II) was unaffected by boiling with sodium dichromate in acetic acid, but when boiled for 1 hour with 3 mols. of chromium trioxide in glacial acetic acid oxidation occurred giving (III) which crystallised from alcohol in needles, m. p. 146—147° (compare p. 337) (Found : C, 62·4; H, 3·5. Calc. for $C_{13}H_8OCl_2$ : C, 62·1; H, 3·7%). The m. p. of this specimen of (III) was not depressed by an authentic specimen synthesised from chlorobenzene and *p*-chlorobenzoyl chloride. The 2 : 4-dinitrophenylhydrazone of 4 : 4′-dichlorobenzophenone crystallised from acetic acid in shining red plates, m. p. 241° (Found : C, 52·8; H, 2·90; N, 12·9. Calc. for $C_{19}H_{12}O_4N_4Cl_2$ : C, 52·9; H, 2·81; N, 13·0%).

(3) *Decomposition in presence of zinc chloride.* 50 G. of DDT and 120 g. of anhydrous zinc chloride were refluxed together for 12 hours in 500 ml. of glacial acetic acid when the mixture darkened slightly and a slow stream of hydrogen chloride was evolved. The solution was then diluted well with water and extracted with chloroform. The chloroform layer, after washing with water, was extracted with dilute sodium hydroxide. The alkaline extract on acidification gave 4 g. of *di-(4-chlorophenyl)acetic acid* which crystallised from benzene–petrol in small white needles, m. p. 163—164° (Found : C, 59·5; H, 3·6; Cl, 24·8. $C_{14}H_{10}O_2Cl_2$ requires C, 59·8; H, 3·6; Cl, 25·1%). The residual chloroform extract yielded 30 g. of (II). The *ethyl* ester of di-(4-chlorophenyl) acetic acid crystallised from methyl alcohol in white needles, m. p. 88° (Found : C, 62·4; H, 4·83. $C_{16}H_{14}O_2Cl_2$ requires C, 62·1; H, 4·53%). Oxidation of the acid with sodium dichromate in acetic acid yielded (III).

*Reactions of* iso-*DDT* (IV).—(i) *Action of alkali. iso*-DDT, m. p. 76°, was refluxed for 15 minutes with alcoholic sodium hydroxide (1 mol.), cooled, and diluted. The product (yield 95—100%) crystallised from dilute methyl alcohol in white tablets, m. p. 79°, and proved to be 1 : 1-*dichloro*-2-(2-*chlorophenyl*)-2-(4-*chlorophenyl*)*ethylene* (Found : C, 53·3; H, 2·89; Cl, 44·7. $C_{14}H_8Cl_4$ requires C, 52·8; H, 2·52; Cl, 44·7%).

(ii) *Oxidation.* The ethylene, m. p. 79°, oxidised smoothly with chromium trioxide in glacial acetic acid to 2 : 4′-dichlorobenzophenone (V), which crystallised from aqueous methyl alcohol in white needles, m. p. 66° (Found : C, 62·1; H, 3·18. Calc. for $C_{13}H_8OCl_2$ : C, 62·1; H, 3·2%). This ketone gave a 2 : 4-dinitrophenylhydrazone which crystallised from acetic acid in orange-yellow needles, m. p. 230° (Found : C, 52·7; H, 2·62; N, 12·8. Calc. for $C_{19}H_{12}O_4N_4Cl_2$ : C, 52·9; H, 2·8; N, 13·0%).

(iii) *Nitration.* 3 G. of *iso*-DDT were heated at 100° for ½ hour with a mixture of 20 ml. of glacial acetic acid and 20 ml. of fuming nitric acid. The cooled mixture was poured on ice, and the resulting solid crystallised from alcohol, giving deep yellow needles, m. p. 146—147° of 1 : 1 : 1-trichloro-2-(2-chloro-5-nitrophenyl)-2-(4-chloro-3-nitrophenyl)-ethane (Found : C, 38·1; H, 1·77; N, 6·3; Cl, 39·6. Calc. for $C_{14}H_7O_4N_2Cl_5$ : C, 37·7; H, 1·57; N, 6·2; Cl, 40·0%). This product was heated for 8 hours at 100° with concentrated sulphuric and fuming nitric acids (1 : 1), cooled, and diluted with water. The solid which separated was 1 : 1 : 1-trichloro-2-(2-chloro-3 : 5-dinitrophenyl)-2-(4-chloro-3 : 5-dinitrophenyl)ethane, which crystallised from glacial acetic acid in yellow needles, m. p. 224°, and was not identical with tetranitro-DDT (XVIII) (Found : N, 10·3. Calc. for $C_{14}H_5O_8N_4Cl_5$ : N, 10·5%). Its di-anilide crystallised from acetic acid in deep red prisms, m. p. 209°.

*Nitration of DDD* (VIII).—(i) 10 G. of DDD were heated at 100° for 3 hours with 100 ml. of a 1 : 1 mixture of glacial acetic and concentrated nitric acids. The product crystallised from alcohol in pale yellow prismatic needles, and was 1 : 1-dichloro-2 : 2-di-(4-chloro-3-nitrophenyl)ethane, m. p. 176° (Found : C, 41·1; H, 2·03; N, 6·7. Calc. for $C_{14}H_8N_2O_4Cl_4$ : C, 41·0; H, 1·97; N, 6·83%). This compound was recovered unchanged after refluxing for 20 hours with aniline in ethyl alcohol.

(ii) 10 G. of DDD were dissolved, by shaking, in a mixture of 50 ml. of concentrated sulphuric and 100 ml. of fuming nitric acids. The mixture was then treated with a further 50 ml. of concentrated sulphuric acid and heated at 100° for 4 hours. After cooling it was poured on to ice, and the solid which separated was crystallised from dilute acetic acid, giving pale yellow needles of 1 : 1-dichloro-2 : 2-di-(4-chloro-3 : 5-dinitrophenyl)ethane, m. p. 220° (Found : N, 11·1. Calc. for $C_{14}H_6O_8N_4Cl_4$ : N, 11·2%). When boiled with aniline in alcohol this tetranitro-compound readily formed a di-anilide which crystallised from acetic acid in deep red needles, m. p. 175°.

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