48. *Insecticidal Activity and Chemical Constitution. Part I. Chlorinated* p-*Chloroethylbenzenes.*

By D. Woodcock.

The preparation of some chlorinated *p*-chloroethylbenzenes and *p*-chlorostyrenes is described, and relative toxicities against the grain-weevil (*Calandra granaria* L.) are given and discussed briefly.

The mode of insecticidal action of 1 : 1 : 1-trichloro-2 : 2-di-(4-chlorophenyl)ethane (D.D.T.) is not yet clearly understood. Its efficacy as an insecticide has been variously attributed to the presence in the molecule of two *p*-chlorophenyl groups as toxophores (Laüger, Martin, and Müller, *Helv. Chim. Acta*, 1944, **27**, 892), and to the loss of hydrogen chloride from the trichloroethylidene group (Martin and Wain, *Nature*, 1944, **154**, 512). In this latter concept, it is suggested that the function of the *p*-chlorophenyl residues is to increase lipoid solubility.

The active ingredient of the German insecticide formerly called " Lucex " (B.I.O.S. Final Reports, No. 1095, p. 26; No. 1480, p. 46) prepared by the side-chain chlorination of *p*-chloroethylbenzene, thus contains one lipoid-solubilising group, though the precise structure of the side-chain (said to be chlorinated to $-\mathrm{C_2HCl_4}$) has not been determined. Some of the compounds likely to be present in " Lucex " were therefore prepared for bio-assay, and a comparison of the relative toxicities to *Calandra granaria* is given in the Table. None of these compounds proved as effective as DDT, but it is not possible to give a comparable figure because the technique employed gives, with DDT, a probit mortality–dosage curve of low slope. Fuller particulars of the bio-assay method and results will be published elsewhere.

	Compound.	Toxicity.*
I	(*a*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl_2{\cdot}CCl_3}$	0·04
	(*b*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl_2{\cdot}CHCl_2}$	1·00
	(*c*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl_2{\cdot}CH_2Cl}$	0·14

	Compound.	Toxicity.*
II	(*a*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CHCl{\cdot}CCl_3}$	0·47
	(*b*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CHCl{\cdot}CHCl_2}$	0·33
	(*c*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CHCl{\cdot}CH_2Cl}$	0·05
	(*d*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CHCl{\cdot}CH_3}$	0·03

	Compound.	Toxicity.*
III	(*a*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl{:}CCl_2}$............	0·34
	(*b*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl{:}CHCl}$	0·13
	(*c*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CCl{:}CH_2}$	0·08
	(*d*) p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CH{:}CH_2}$	0·05

* Relative at L.D. 50.

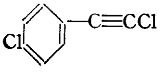
Relative potency increases with increasing chlorine content of the side-chain, though complete chlorination results in a virtually non-toxic product (I*a*), which moreover is incapable of losing hydrogen chloride (cf. Martin and Wain, *loc. cit.*). The ethylenic compounds (Series III) which were formed as intermediates in the synthetical route employed were also tested, and it was again shown that there was a direct relationship between toxicity and chlorine content. Dehydrochlorination of the compound (III*a*) in the same way as for members of the other two series is clearly impossible, and insecticidal activity here may possibly be due to liberation of hydrogen chloride by hydrolysis or to the ethylenic linkage.

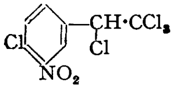
The substituted ethanes of series (II) were synthesised by the following route :

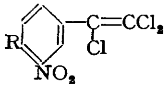
$$\text{(IV.) } p\text{-}\mathrm{Cl{\cdot}C_6H_4{\cdot}COR} \xrightarrow{\mathrm{Al(OPr^i)_3}} \text{(V.) } p\text{-}\mathrm{Cl{\cdot}C_6H_4{\cdot}CHR{\cdot}OH} \xrightarrow{\mathrm{PCl_5}} p\text{-}\mathrm{Cl{\cdot}C_6H_4{\cdot}CHRCl}$$

The carbinols (V; R = $\mathrm{CH_3}$, $\mathrm{CH_2Cl}$, and $\mathrm{CHCl_2}$) were prepared in excellent yield from the corresponding chloroacetophenones (IV) (Gautier, *Ann. Chim.* 1888, **14**, 373, 379, 402) by reduction with aluminium *iso*propoxide and the trichloro-carbinol (V; R = $\mathrm{CCl_3}$) was obtained in 80% yield as a crystalline solid, m. p. 47—48°, by the condensation of *p*-chlorophenylmagnesium bromide and freshly distilled chloral (cf. Howard and Castles, *J. Amer. Chem. Soc.*, 1935, **57**, 2317; Haller *et al.*, *ibid.*, 1945, **67**, 1601). Treatment of the carbinols with a suspension of phosphorus pentachloride in dry benzene gave smooth conversions to the corresponding chloro-compounds (II*d*, *c*, *b*, and *a*). Dehydrohalogenation to the ethylenes (III) was generally accomplished by treatment with the calculated amount of alcoholic potassium hydroxide at room temperature, though the compound (II*d*) was stable under these conditions and required excess of this reagent at 100° for complete conversion into *p*-chlorostyrene.

Addition of chlorine to the ethylenes (III*a*, *b*, and *d*) was done in chloroform or carbon tetrachloride solution at 0°, and the resulting ethanes (I*a*, I*b*, and II*c*) were isolated by aspiration of the solvent and distillation of the residue. Attempts to prepare the compound (I*c*) from the appropriate ethylene by addition of chlorine were not successful, since even at 0° some substitution took place at the β-carbon atom in the ethylene (III*c*), and subsequent addition gave a product containing a variable amount of (I*b*). Treatment of the ketone (IV; R = CH_2Cl) with a slight excess of phosphorus pentachloride at 130°, however, gave (I*c*) in 80% yield. Nitration of this compound using fuming nitric acid resulted in the loss of chlorine with the formation of *4-chloro-3-nitrophenyl chloromethyl ketone* (VI), but confirmation of the structure was achieved by conversion into the ethane (II*b*) by dehydrochlorination and subsequent addition of chlorine, followed by comparison of the nitro-derivatives.


(VII.)


(VIII.)


(IX.)

With the exception of the hexachloro-compound (I*a*), m. p. 63—64°, the ethanes (series I) were liquids which by further successive dehydrochlorinations and additions of chlorine also gave this compound as the ultimate product.

The structure of the compound, m. p. 77—78°, obtained when excess of ethyl-alcoholic potassium hydroxide at 100° was used to dehydrohalogenate (II*b*), was confirmed as (VII) by addition of chlorine and isolation of (I*a*) in theoretical yield.

Loss of one molecule of hydrogen chloride from the ethanes (II*b* and II*c*) can take place in two ways. Biltz (*Annalen*, **1897**, **296**, 276) has reported that 1 : 1 : 2-trichloro-2-phenylethane on treatment with ethyl-alcoholic potassium hydroxide at 30—40° gave 1 : 1-dichloro-2-phenylethylene. In the 4-chlorophenyl series, however, it has now been demonstrated by mononitration of the corresponding ethanes and comparison of the appropriate nitro-derivatives that the alternative route is taken; (II*a*) gives 1 : 2-dichloro- and (II*c*) gives *1-chloro-1-(4-chlorophenyl)ethylene*.

In general, the nitro-derivatives of the ethanes (series I and II) resisted oxidation by alkaline potassium permanganate, but, after dehydrochlorination, oxidation to 4-chloro-3-nitrobenzoic acid was readily accomplished by using potassium permanganate in acetic acid solution, thus establishing the position of the nitro-group. From the nitro-derivative (VIII), either aqueous or alcoholic potassium hydroxide replaced the labile nuclear halogen by ethoxyl forming (IX; R = OEt), and subsequent oxidation gave 3-nitro-4-ethoxybenzoic acid.

EXPERIMENTAL.

(M. p.s are uncorrected; C, H, and N microanalyses are by Drs. Weiler and Strauss.)

2 : 2 : *2-Trichloro-1-(4-chlorophenyl)ethanol* (V; R = CCl_3).—This was prepared according to Haller *et al.* (*loc. cit.*). The colourless viscous liquid solidified completely on standing, and crystallised from light petroleum (b. p. 40—60°) in aggregates of large colourless rhombic prisms, m. p. 47—48° (Found: C, 37·2; H, 2·2; Cl, 54·6. Calc. for $C_8H_6OCl_4$: C, 36·9; H, 2·3; Cl, 54·6%). Howard and Castles (*loc. cit.*) and Haller *et al.* (*loc. cit.*) give only the b. p. The acetate crystallised from methyl alcohol in large prisms, m. p. 123—124°. Howard and Castles (*loc. cit.*) give m. p. 120—121°; Wain (unpublished) gives m. p. 125°.

1 : 1 : 1 : *2-Tetrachloro-2-(4-chlorophenyl)ethane* (II*a*).—Prepared according to Haller *et al.* (*loc. cit.*), this was a water-white, pleasant smelling liquid, b. p. 157—159°/14 mm., $n_D^{18°}$ 1·5833. Treatment with excess of fuming nitric acid at 100° for 5 minutes gave 1 : 1 : 1 : 2-tetrachloro-2-(4-chloro-3-nitrophenyl)-ethane (VIII) which crystallised from light petroleum (b. p. 40—60°) in aggregates of large colourless prisms, m. p. 72—73° (Found: Cl, 54·1. Calc. for $C_8H_4O_2NCl_5$: Cl, 54·8%). Haller *et al.* give m. p. 73°. On several occasions nitrations done under apparently identical conditions gave a product, m. p. 117—119°, which crystallised from ether in colourless monoclinic prisms, m. p. 120—121° (Found: C, 30·0; H, 1·3; N, 5·2; Cl, 54·7. $C_8H_4O_2NCl_5$ requires C, 29·7; H, 1·2; N, 4·3; Cl, 54·8%). This *substance* depressed the m. p. of (VIII), and, although the two are isomeric, no evidence of dimorphism could be obtained since solutions could not be mutually seeded. It is being further investigated.

1 : 1 : *2-Trichloro-2-(4-chloro-3-nitrophenyl)ethylene* (IX; R = Cl).—The above nitro-compound (VIII), m. p. 72—73°, was refluxed for 2 hours with excess of 10% aqueous sodium hydroxide. The product (0·3 g.), isolated by extraction with ether, crystallised from methyl alcohol in pale yellow needles, m. p. 81—81·5° (Found: C, 33·2; H, 1·1; N, 5·0; Cl, 48·7. $C_8H_3O_2NCl_4$ requires C, 33·4; H, 1·1; N, 4·9; Cl, 49·5%). This *compound* was also produced in attempts to oxidise (VIII) by alkaline potassium permanganate.

1 : 1 : *2-Trichloro-2-(3-nitro-4-ethoxyphenyl)ethylene* (IX; R = OEt).—The compound (VIII) (1·0 g.) was treated with excess of ethyl-alcoholic potassium hydroxide at 100° for 0·5 hour, and the excess of alcohol distilled off. The *product* (0·75 g.), isolated with ether, crystallised from ethyl alcohol in prisms, m. p. 103—104° (Found: C, 40·6; H, 2·8; N, 4·8; Cl, 35·8. $C_{10}H_8O_3NCl_3$ requires C, 40·5; H, 2·7; N. 4·7; Cl, 35·9%). Treatment with excess of fuming nitric acid at 100° for 0·25 hour gave 3 : 5-

dinitro-4-ethoxybenzoic acid (0·5 g.) which crystallised from acetone–light petroleum (b. p. 40—60°) (1 : 1) in stout prisms, m. p. 194—195° (Found : C, 42·5; H, 3·1; N, 10·9; equiv., 246. Calc. for $C_9H_8O_7N_2$: C, 42·2; H, 3·1; N, 10·9%; equiv., 256). Jackson and Ittner (*Amer. Chem. J.*, 1897, **19**, 215) give m. p. 192°.

Oxidation in aqueous acetic acid with potassium permanganate gave 3-nitro-4-ethoxybenzoic acid which crystallised from acetone–benzene (1 : 3) in plates, m. p. 200—201° (Found : C, 51·2; H, 4·5; N, 6·9. Calc. for $C_9H_9O_5N$: C, 51·2; H, 4·3; N, 6·6%). King and Murch (*J.*, 1925, 2632) give m. p. 200—201°.

1 : 1 : 2-*Trichloro*-2-(4-*chlorophenyl*)*ethylene* (III*a*).—The ethane derivative (II*a*) (3·1 g.) was refluxed with a solution of sodium hydroxide (0·45 g., 1 mol.) in ethyl alcohol (20 c.c.) for 0·5 hour, water (20 c.c.) added, and the alcohol distilled off. The residual fragrant-smelling water-insoluble yellow oil was extracted with ether, the extract dried, and the solvent removed. Distillation of the residue gave 2·4 g., b. p. 136°/16 mm., $n_D^{15^\circ}$ 1·6019. One specimen of the *compound* after several months solidified completely (prisms), and then had m. p. 24—26° [Found : C, 36·7; H, 1·9; Cl, 58·8; *M* (Rast), 235; $C_8H_4Cl_4$ requires C, 36·5; H, 1·7; Cl, 58·6%; *M*, 241·8].

1 : 1 : 1 : 2 : 2-*Pentachloro*-2-(4-*chlorophenyl*)*ethane* (I*a*).—The ethylene (III*a*) (2·4 g.) was dissolved in carbon tetrachloride (5 c.c.), saturated with dry chlorine at 0°, and left overnight at the same temperature. After removal of the solvent by aspiration, the residue was distilled, and the distillate (2·4 g., b. p. 176—178°/17 mm.) solidified completely on cooling. The *product* crystallised from methyl alcohol in prismatic plates, m. p. 63—64° (Found : C, 30·6; H, 1·6; Cl, 67·5. $C_8H_4Cl_6$ requires C, 30·7; H, 1·3; Cl, 68·0%). Treatment with excess of fuming nitric acid as previously described gave 1 : 1 : 1 : 2 : 2-*pentachloro*-2-(4-*chloro*-3-*nitrophenyl*)*ethane* which crystallised from ethyl alcohol in long monoclinic prisms, m. p. 95—96° (Found : C, 26·7; H, 1·1; N, 4·1; Cl, 58·4. $C_8H_3O_2NCl_6$ requires C, 26·8; H, 0·8; N, 3·9; Cl, 59·5%).

4-*Chlorophenyl Dichloromethyl Ketone* (IV; R = $CHCl_2$).—4-Chloroacetophenone, prepared according to Gautier (*Ann. Chim.*, 1888, **14**, 373) (25 g.) was heated in an oil-bath at 110—120° for 3 hours during the rapid passage of chlorine. On cooling, the product solidified; it crystallised from ethyl alcohol in massive prisms (27 g.), m. p. 61—62·5° (Found : Cl, 47·3. Calc. for $C_8H_5OCl_3$: Cl, 47·6%). Gautier (*ibid.*, p. 402) gives m. p. 51°. Attempts to prepare a 2 : 4-dinitrophenylhydrazone led to an orange-red product which crystallised from glacial acetic acid in prisms, m. p. 300—301° (decomp.) (Found : C, 45·6; H, 2·8; N, 19·8; Cl, 7·5, 7·8%). The constitution of this substance has not yet been elucidated.

2 : 2-*Dichloro*-1-(4-*chlorophenyl*)*ethanol* (V; R = $CHCl_2$).—The above ketone (IV; R = $CHCl_2$) was reduced by means of aluminium *iso*propoxide as described in " Organic Reactions," Vol. II, p. 198. Cleaned aluminium foil (4·0 g.) was dissolved by refluxing with *iso*propyl alcohol (80 c.c.) in the presence of mercuric chloride (0·2 g.) and carbon tetrachloride (0·8 c.c.), solution being complete in 2 hours. The ketone (18·9 g.), also dissolved in *iso*propyl alcohol (80 c.c.), was added, and the solvent distilled off slowly, acetone being no longer detectable in the distillate after 2—3 hours. Any remaining solvent was removed, and the residual viscous mass was cooled, treated with 2N-hydrochloric acid, and extracted with ether. Removal of the solvent from the dried extract and distillation of the residue gave the carbinol as a colourless liquid (18·4 g.), b. p. 158°/14 mm. (Found : Cl, 46·4. Calc. for $C_8H_7OCl_3$: Cl, 47·2%) (cf. Haller *et al.*, *loc. cit.*). Acetylation by refluxing with excess of acetic anhydride and fused sodium acetate gave the *acetate*, b. p. 115—117°/0·3 mm., $n_D^{9^\circ}$ 1·5430 (Found : Cl, 39·1. $C_{10}H_9O_2Cl_3$ requires Cl, 39·8%). Attempts to prepare crystalline *p*-nitro- or 3 : 5-dinitro-benzoates were unsuccessful.

1 : 1 : 2-*Trichloro*-2-(4-*chlorophenyl*)*ethane* (II*b*).—The carbinol (V; R = $CHCl_2$) (7·7 g.) in dry benzene (10 c.c.) was added in small amounts with cooling and shaking to a suspension of phosphorus pentachloride (7·5 g.; 1 mol.) in dry benzene (10 c.c.), and the solution finally heated at 60—70° for 0·25 hour. After cooling, water (20 c.c.) was added, the benzene layer washed with sodium hydrogen carbonate solution and dried, and the benzene removed. Distillation of the residue gave a colourless pleasant-smelling liquid (7·5 g.), b. p. 99—101°/0·2 mm. (Found : Cl, 57·3. $C_8H_6Cl_4$ requires Cl, 58·2%). Treatment of this *tetrachloro*-compound with fuming nitric acid gave 1 : 1 : 2-*trichloro*-2-(4-*chloro*-3-*nitrophenyl*)*ethane* which crystallised from methyl alcohol in rosettes of pale yellow prisms, m. p. 97—98° (Found : C, 34·0; H, 2·1; N, 5·0; Cl, 47·7. $C_8H_5O_2NCl_4$ requires C, 33·2; H, 1·7; N, 4·8; Cl, 49·1%).

1 : 1-*Dichloro*-2-(4-*chlorophenyl*)*ethylene* (III*b*).—A solution of (II*b*) (4·0 g.) in ethyl alcohol (5 c.c.) was added in 4 portions with shaking to ethyl-alcoholic potassium hydroxide (1 g. in 5 c.c.), the temperature being kept below 50°. After 4 hours at 20° the alcohol was removed under reduced pressure, water (10 c.c.) added, and the *product* extracted with ether. Distillation of the oil left after removal of the solvent from the dried extract gave a colourless liquid (3·6 g.), b. p. 85—87°/0·6 mm. (Found : Cl, 50·9. $C_8H_5Cl_3$ requires Cl, 51·3%). After several days the liquid became cloudy and gradually deposited *p*-chlorobenzoic acid, m. p. 234—235° undepressed by admixture with an authentic specimen.

1-*Chloro*-2-(4-*chlorophenyl*)*acetylene* (VII).—The chloro-compound (II*b*) (4·0 g.) was refluxed for 0·5 hour with excess of ethyl-alcoholic potassium hydroxide, and the product isolated as described above. Crystallisation of the residue from a small amount of light petroleum (b. p. 40°) gave large prismatic plates (0·4 g.), m. p. 77—78° (Found : C, 55·4; H, 2·5; Cl, 42·2. $C_8H_4Cl_2$ requires C, 56·1; H, 2·3; Cl, 41·5%). The mother liquors contained a large proportion of (III*b*). A solution of the above *product* (VII) in carbon tetrachloride was saturated with chlorine at 0° and left for 18 hours at the same temperature. Removal of the solvent by aspiration gave a residue which crystallised from methyl alcohol in plates, m. p. 59—60°, undepressed by admixture with the previously prepared 1 : 1 : 1 : 2 : 2-pentachloro-2-(4-chlorophenyl)ethane (I*a*).

1 : 1 : 2 : 2-*Tetrachloro*-1-(4-*chlorophenyl*)*ethane* (I*b*).—The ethylene derivative (III*b*) (5·2 g.) was dissolved in chloroform (5 c.c.), cooled to 0°, and saturated with dry chlorine. After 18 hours at 0°, the solvent was removed by aspiration; distillation of the residue gave a colourless liquid (5·9 g.), b. p. 103—105°/0·6 mm., $n_D^{9^\circ}$ 1·5907 (Found : Cl, 62·7. $C_8H_5Cl_5$ requires Cl, 63·7%). Treatment of

this *pentachloro*-compound with fuming nitric acid as already described gave 1 : 1 : 2 : 2-*tetrachloro*-1-(4-*chloro*-3-*nitrophenyl*)*ethane*, which crystallised from methyl alcohol or a mixture of ether–light petroleum (b. p. 40—60°) in pale yellow prisms, m. p. 109—110° (Found : C, 29·4; H, 2·6; N, 4·6; Cl, 54·6. $C_8H_4O_2NCl_5$ requires C, 29·7; H, 2·2; N, 4·4; Cl, 54·9%).

4-*Chlorophenyl Chloromethyl Ketone* (IV; R = CH_2Cl).—Prepared according to Gautier (*Ann. Chim.*, 1888, **14**, 395) this ketone was collected from the reaction mixture in high yield as large prismatic plates, m. p. 98—100°, and after being washed with a little ethyl alcohol was sufficiently pure for reduction (Found : Cl, 37·6. Calc. for $C_8H_6OCl_2$: Cl, 37·6%). Gautier (*loc. cit.*) gives m. p. 101°. The 2 : 4-*dinitrophenylhydrazone*, prepared in ethyl-alcoholic solution, crystallised from glacial acetic acid in small red prisms, m. p. 205—206° (Found : C, 45·2; H, 2·8; N, 14·2; Cl, 17·9. $C_{14}H_{12}O_4N_4Cl_2$ requires C, 45·3; H, 3·2; N, 15·1; Cl, 19·1%).

Treatment with excess of fuming nitric acid at 0° gave 4-*chloro*-3-*nitrophenyl chloromethyl ketone* (VI) which crystallised from a small amount of methyl alcohol in pale yellow monoclinic prisms, m. p. 84—85° (Found : C, 41·4; H, 2·1; N, 6·0; Cl, 30·0. $C_8H_5O_3NCl_2$ requires C, 41·0; H, 2·4; N, 6·3; Cl, 30·3%).

2-*Chloro*-1-(4-*chlorophenyl*)*ethanol* (V; R = CH_2Cl).—Prepared as described for the corresponding 2 : 2-dichloro-compound (V; R = $CHCl_2$), this *compound* was obtained as a colourless liquid, b. p. 95—97°/0·1 mm., which solidified on standing. It crystallised from ether–light petroleum (b. p. 40—60°) in aggregates of prisms, m. p. 39—41° (Found : C, 50·3; H, 4·4; Cl, 37·1. $C_8H_8OCl_2$ requires C, 50·3; H, 4·2; Cl, 37·2%). Späth (*Monatsh.*, 1914, **35**, 472) only records b. p. Attempts to prepare the phenylurethane or the 3-nitrophthalic ester in a crystalline form were unsuccessful. The *acetate* was a colourless liquid, b. p. 160—162°/16 mm., $n_D^{10^\circ}$ 1·5329 (Found : Cl, 29·7. $C_{10}H_{10}O_2Cl_2$ requires Cl, 30·5%).

1 : 2-*Dichloro*-1-(4-*chlorophenyl*)*ethane* (II*c*).—Prepared in 85% yield by the addition of a solution of the above carbinol (V; R = CH_2Cl) in benzene to a suspension of phosphorus pentachloride (1 mol.) in benzene, this *compound*, isolated as previously described for the 1 : 1 : 2-trichloro-analogue (II*b*), was obtained as a colourless liquid, b. p. 137—138°/18 mm. (Found : Cl, 50·5. $C_8H_7Cl_3$ requires Cl, 50·8%). Nitration with fuming nitric acid in the usual way gave 1 : 2-*dichloro*-1-(4-*chloro*-3-*nitrophenyl*)*ethane* as a pale yellow solid which crystallised from ether–light petroleum (b. p. 40—60°) (1 : 4) as triangular prisms, m. p. 52—53° (Found: C, 37·5; H, 2·5; N, 5·7; Cl, 39·1. $C_8H_6O_2NCl_3$ requires C, 37·7; H, 2·4; N, 5·5; Cl, 41·8%).

1-*Chloro*-1-(4-*chlorophenyl*)*ethylene* (III*c*).—The ethane (II*c*) (3·1 g.) was added gradually to a solution of potassium hydroxide (0·83 g.; 1 mol.) in ethyl alcohol (5 c.c.), the temperature being kept below 50°. After 3 hours the alcohol was removed under reduced pressure, water (20 c.c.) added, and the product extracted with ether. Removal of the solvent from the dried extract and distillation of the residue gave a colourless liquid *product* (2·0 g.), b. p. 108—110°/18 mm. (Found : Cl, 40·9. $C_8H_6Cl_2$ requires Cl, 41·0%). After some days the liquid gradually deposited crystals of *p*-chlorobenzoic acid, m. p. 235—236°, undepressed by admixture with an authentic specimen.

With excess of alcoholic alkali at 100° the product was again the compound (III*c*).

1 : 1 : 2-*Trichloro*-1-(4-*chlorophenyl*)*ethane* (I*c*).—The ketone (IV; R = CH_2Cl) (5·0 g.) and phosphorus pentachloride (6·25; 1·1 mols.) were heated in an oil-bath at 130—140° for 1 hour, then allowed to cool and treated with water (20 c.c.). The *product*, isolated with ether and washed with sodium hydrogen carbonate solution, was obtained as a colourless liquid (4·8 g.), b. p. 87—90°/0·3 mm., $n_D^{19^\circ}$ 1·5949 (Found : Cl, 53·1, 53·0, 54·0. $C_8H_6Cl_4$ requires Cl, 58·2%). When excess of fuming nitric acid was added to a small amount cooled in ice, a strongly exothermic reaction took place momentarily. From various nitrations carried out in this way, two products have been isolated : (*a*) crystallises from ether–light petroleum (b. p. 40—60°) in rosettes of pale yellow prisms, m. p. 83—84°, undepressed by admixture with 4-chloro-3-nitrophenyl chloromethyl ketone previously described, whilst (*b*) crystallises from ether–light petroleum (b. p. 40—60°) (1 : 5) in colourless stout prisms, m. p. 92—93° (Found : C, 41·9; H, 2·1; N, 5·3; Cl, 31·4. $C_8H_5O_3NCl_2$ requires C, 41·4; H, 2·1; N, 6·0; Cl, 30·4%). This *substance* depressed the m. p. of product (*a*) and is being further investigated.

Confirmation of the structure of the liquid (I*c*) obtained as described above was consequently sought by conversion into 1 : 1 : 2 : 2-tetrachloro-1-(4-chlorophenyl)ethane (I*b*). Dehydrochlorination using 2N-sodium hydroxide, followed by chlorination of the resulting ethylene in carbon tetrachloride solution at 0°, gave a colourless liquid, b. p. 140°/12 mm. Treatment with fuming nitric acid gave a nitro-derivative which crystallised from methyl alcohol in stout prisms, m. p. 106—107°, undepressed by admixture with the 1 : 1 : 2 : 2-tetrachloro-1-(4-chloro-3-nitrophenyl)ethane, previously described.

4-*Chloroacetophenone* (IV : R = Me).—This was prepared in 80—90% yield by essentially the same method as that described by Gautier (*Ann. Chim.*, 1888, **14**, 373), except that the reaction mixture was refluxed for 5 hours before being poured on ice. The product, b. p. 125°/15 mm., which solidified on cooling was sufficiently pure for subsequent work.

1-(4-*Chlorophenyl*)*ethanol* (V; R = Me).—Prepared in 90% yield by reduction of the above ketone using aluminium *iso*propoxide (as already described), this *compound* was obtained as a colourless liquid, b. p. 85—86°/0·5 mm., $n_D^{16^\circ}$ 1·5460 (Found : Cl, 22·3. C_8H_9OCl requires Cl, 22·7%) [cf. Gastaldi (*Gazzetta*, 1915, **45**, II, 272) and Hanai (*J. Chem. Soc. Japan*, 1944, **62**, 1208)]. The *acetate* was a colourless liquid, b. p. 75—80°/18 mm., $n_D^{9^\circ}$ 1·5118 (Found : Cl, 17·4. $C_{10}H_{11}O_2Cl$ requires Cl, 17·9%). Phenyl *iso*cyanate only reacted in the presence of a trace of dimethylamine, giving the phenylurethane which crystallised from light petroleum (b. p. 80—100°) in large rhombic aggregates, m. p. 94—95° (Found : Cl, 13·0. Calc. for $C_{15}H_{14}O_2NCl$: Cl, 12·9%). Gastaldi (*loc. cit.*) gives m. p. 93° for the phenylurethane. The α-*naphthylurethane*, prepared by heating with α-naphthyl *iso*cyanate at 160° for 2 minutes, separated from light petroleum (b. p. 80—100°) as compact nodules, m. p. 102—103° (Found: Cl, 11·3. $C_{19}H_{16}O_2NCl$ requires Cl, 10·9%).

1-*Chloro*-1-(4-*chlorophenyl*)*ethane* (II*d*).—This was obtained in 90% yield by treating the corresponding carbinol (V; R = Me) with the calculated amount of phosphorus pentachloride; it was a colourless liquid, b. p. 63—65°/0·4 mm., $n_D^{9^\circ}$ 1·5560 (Found : Cl, 40·4. Calc. for $C_8H_8Cl_2$: Cl, 40·6%) (cf. Hanai, *loc. cit.*).

Treatment with fuming nitric acid gave 4-chloroacetophenone (oxime, m. p. 95—96°, undepressed by admixture with an authentic specimen).

p-*Chlorostyrene.*—The chloroethane (II*d*) (5·6 g.) obtained as described above was stable to ethyl-alcoholic potassium hydroxide [1·2 g. (1 mol.) in 10 c.c.] at room temperature, but, by refluxing the solution for 0·5 hour, dehydrochlorination was effected. Removal of the alcohol and extraction with ether gave a colourless liquid (4·4 g.), b. p. 57—58°/0·3 mm., $n_D^{9°}$ 1·5363 (Found : Cl, 23·7. Calc. for C_8H_7Cl : Cl, 25·6%) (cf. Staudinger, *Ber.*, 1920, **53**, 1099).

My thanks are due to Dr. H. Martin for his interest in the work, to Mr. A. Stringer, B.Sc., A.R.C.S., for the insecticidal testing, and to Mr. R. F. Batt for the chlorine analyses (Robertson's method).

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[*Received, April* 29*th*, 1948.]