FREE RADICAL ADDITION REACTIONS—II[1]

THE REACTION OF TRICHLOROMETHANESULPHONYL CHLORIDE WITH STYRENE, AND CHEMISTRY OF THE ADDUCTS[2]

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Abstract—Trichloromethanesulphonyl chloride reacts with styrene to give 1-phenyl-1,3,3,3-tetrachloropropane and 1,3-diphenyl-1,5,5,5-tetrachloropentane, together with sulphur dioxide.

Hydrolysis of 1-phenyl-1,3,3,3-tetrachloropropane to cinnamic acid (90% yield) is catalysed by ferric chloride, and occurs under conditions that do not markedly affect 1,1,1,3-tetrachlorooctane. Acetolysis of 1-phenyl-1,3,3,3-tetrachloropropane gives largely 1-phenyl-3,3,3-trichloropropyl acetate; reduction of this compound with lithium aluminium hydride gives 1-phenylpropanol, confirming the position of the acetate group. A mechanism is proposed to account for the formation of 1,1-dimethoxy-1-phenylprop-2-yne in the reaction of 1-phenyl-1,3,3,3-tetrachloropropane with excess methanolic potassium hydroxide.

Reduction of 1,3-diphenyl-1,5,5,5-tetrachloropentane with lithium aluminium hydride provides a synthesis of 1,3-diphenylpentane.

The reaction of trichloromethanesulphonyl chloride with alkenes has been shown[1] to proceed by a free radical mechanism and to give selectively the 1:1-adduct[4] formed *via* the more stable intermediate radical, sulphur dioxide being eliminated, e.g.

$$RCH{=}CH_2 \rightarrow RCH{\cdot}{-}CH_2CCl_3 \rightarrow RCHCl{-}CH_2CCl_3$$
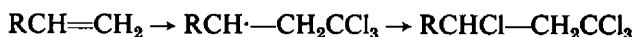
A similar 1:1-adduct is formed in the corresponding initiated carbon tetrachloride-olefine reaction,[5] though satisfactory evidence of homogeneity has not always been forthcoming in this case. Trichloromethanesulphonyl chloride emerges as the preferred[6] reagent for the synthesis of these 1:1-adducts as the weakness of the S—Cl and C—S bonds leads to efficient chain transfer with correspondingly high yields of essentially pure compounds; this is further evidenced by the fact that an excess of

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[1] Part I, H. Goldwhite, M. S. Gibson and C. Harris, *Tetrahedron* **20**, 1613 (1964).

[2] Part of this work has appeared in a preliminary communication: H. Goldwhite and C. Harris, *Chem. & Ind.* 1721 (1962).

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[4] The term '1:1-adduct' is here used to describe the product obtained from the addition of the radicals CCl₃· and Cl· to the double bond; the product is assumed to contain both possible structural isomers until evidence of homogeneity has been adduced. Cf. Ref. 1, footnote 7.

[5] C. Walling, *Free Radicals in Solution* p. 247. J. Wiley, New York (1957); and Refs. there cited.

[6] Cf. *British Patent* 649,555 (1951) to U.S. Rubber Co.

olefine is not deleterious in any of the reactions.[1] The related reaction of trichloro-methanesulphonyl chloride with a more easily polymerizable olefine, styrene, is explored in the present communication.

The formation of 1:1-adducts from trichloromethanesulphonyl chloride and various alkenylaromatics, including styrene, has been reported in the patent literature.[7] Thus styrene is said to react with a molar excess of trichloromethanesulphonyl chloride in benzene solution to give, after 24 hours, a 1:1-adduct in 10% yield; benzoyl peroxide is an optional additive. The adduct was regarded as 1-phenyl-1,3,3,3-tetrachloropropane (I) though no proof of structure was given, nor was the material shown to be homogeneous; in particular, the presence of the isomeric phenyltetrachloropropane (II) was not excluded.

$$PhCHCl—CH_2CCl_3 \qquad\qquad PhCH(CCl_3)—CH_2Cl$$
$$I \qquad\qquad\qquad\qquad\qquad II$$
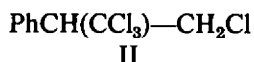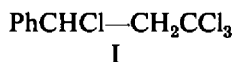
Preliminary experiments showed that the published conditions could be considerably improved. As with alkenes,[1] the use of an excess of the sulphonyl chloride was undesirable, and the quoted reaction times were far too long. It was found that, using a small excess of styrene in place of benzene, reaction proceeded smoothly in the temperature range 80–170° and, judged by the cessation of sulphur dioxide evolution, was essentially complete after only two hours. Fractionation of the reaction mixture gave the previously reported 1:1-adduct in much improved yield (40–45%), together with a 1:2-adduct, $C_{17}H_{16}Cl_4$ (25–30%; yields based on sulphonyl chloride employed), which is discussed later in this paper.

Hydrolysis (in aqueous acetic acid) of compounds I and II would give β-phenyl-acrylic acid (cinnamic acid) and α-phenylacrylic acid respectively, and so, if complete,[8] provide a satisfactory chemical means of establishing the nature of the 1:1-adduct. Considerable improvement in the hydrolysis procedure was possible when it was noted that the reaction was catalysed by ferric chloride. The 1:1-adduct could thus be converted to cinnamic acid in 90% yield; no trace of the isomeric α-phenylacrylic acid was detected. A neutral by-product accompanied the cinnamic acid and was particularly noticeable if ferric chloride was omitted in the hydrolysis experiments. The compound, which gave cinnamic acid on hydrolysis, contained chlorine and was seen from the IR spectrum to be an ester. This was evidently an acetolysis product and could be obtained from the 1:1-adduct (though not in a pure condition) by acetolysis with anhydrous sodium or potassium acetate in glacial acetic acid. To determine the position of the acetate group, the acetolysis product was reduced with lithium aluminium hydride to an alcohol, which was identified as 1-phenylpropanol by oxidation to propiophenone with 8N chromic acid. This reaction sequence shows that the acetolysis product is largely 1-phenyl-3,3,3-trichloropropyl acetate:
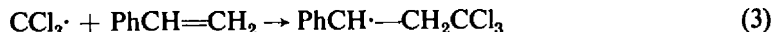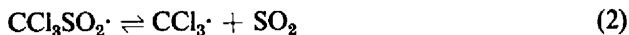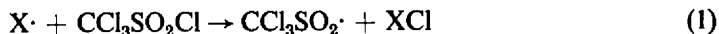
$$PhCH(OAc)CH_2CCl_3 \rightarrow PhCH(OH)CH_2CH_3 \rightarrow PhCOCH_2CH_3$$
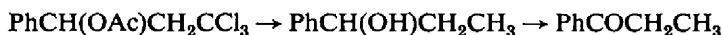
The accumulated evidence serves to show that the 1:1-adduct is essentially

[7] U.S. Patent 2,606,213 (1952), E. C. Ladd and L. Y. Kiley to U.S. Rubber Co.
[8] This is implicit in the perchloric acid-catalysed hydrolysis of e.g. the 1:1-adduct from bromo-trichloromethane and p-chlorostyrene, which gives p-chlorocinnamic acid in 90% yield; cf. M. S. Kharasch, E. Simon and W. Nudenberg, J. Org. Chem. 18, 328 (1953). Applied to the 1:1-adduct from carbon tetrachloride and styrene, however, this method gives cinnamic acid in only 35% yield; cf. M. Asscher and D. Vofsi, J. Chem. Soc. 1887 (1963).

1-phenyl-1,3,3,3-tetrachloropropane (I); the orientation of addition is determined, as in the case of alkenes, by production of the more stable (benzylic) radical in step (3):
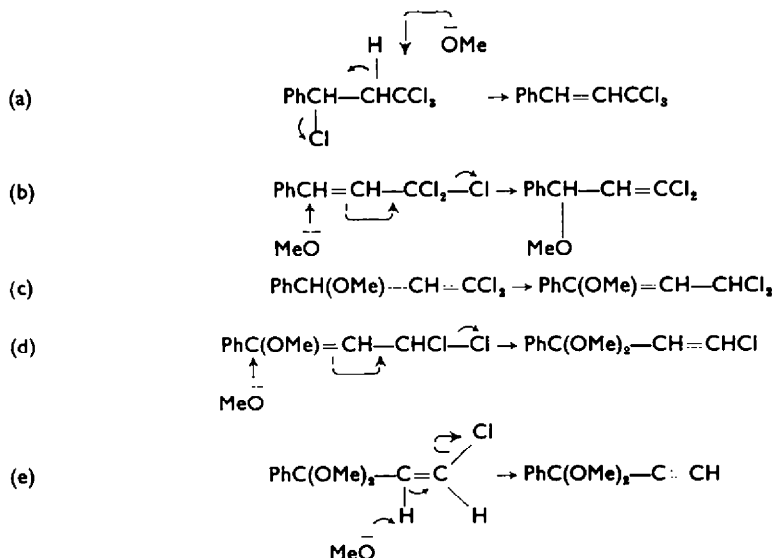
$$X\cdot + CCl_3SO_2Cl \rightarrow CCl_3SO_2\cdot + XCl \qquad (1)$$

$$CCl_3SO_2\cdot \rightleftharpoons CCl_3\cdot + SO_2 \qquad (2)$$

$$CCl_3\cdot + PhCH{=}CH_2 \rightarrow PhCH\cdot{-}CH_2CCl_3 \qquad (3)$$

$$PhCH\cdot{-}CH_2CCl_3 + CCl_3SO_2Cl \rightarrow PhCHClCH_2CCl_3 + CCl_3SO_2\cdot \qquad (4)$$

The facile hydrolysis of 1-phenyl-1,3,3,3-tetrachloropropane suggests a useful additional route to β-arylalkenoic acids. The process is intimately concerned with the β-site of the phenyl group relative to the trichloromethyl group, and probably involves the conjugated 1-phenyl-3,3,3-trichloropropene as intermediate. Collateral evidence is provided by the extreme resistance to hydrolysis of 1,1,1,3-tetrachlorooctane. Hydrolysis of the latter compound was eventually accomplished, though with some decomposition, by the fuming nitric acid method[9] but this is not a recommended route to β-chlorooctanoic acid.

In the past, base-catalysed dehydrohalogenation has often been used in structural work on 1:1-adducts of the type under discussion, but such reactions frequently give complex mixtures of products.[9] 1-Phenyl-1,3,3,3-tetrachloropropane behaves in this way, giving products in various stages of dehydrochlorination, when treated with sodium hydroxide ($<$ 4 equiv.) in ethanolic solution. When, however, an excess of methanolic potassium hydroxide is used, a chlorine-free acetylenic compound is isolable from the reaction mixture. This has been identified as 1,1-dimethoxy-1-phenylprop-2-yne by acidic hydrolysis to the known[10] phenyl ethynyl ketone:

$$PhCHClCH_2CCl_3 \rightarrow PhC(OMe)_2C{\equiv}CH \rightarrow PhCOC{\equiv}CH$$

The transposition of groups in this unusual reaction strongly suggests a sequential

(a)   PhCH—CHCCl₃   → PhCH=CHCCl₃

(b)   PhCH=CH—CCl₂—Cl → PhCH—CH=CCl₂
              MeO   MeO

(c)   PhCH(OMe)—CH=CCl₂ → PhC(OMe)=CH—CHCl₂

(d)   PhC(OMe)=CH—CHCl—Cl → PhC(OMe)₂—CH=CHCl
              MeO

(e)   PhC(OMe)₂—C=C⟨Cl/H → PhC(OMe)₂—C≡CH
                        MeO

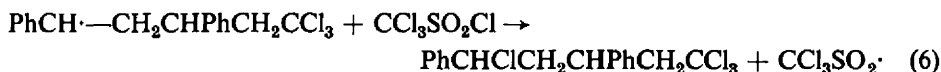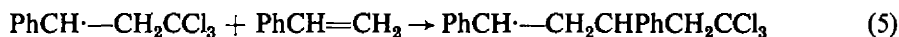[9] Cf. A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharin, *Quart. Rev.* **10**, 330 (1956).
[10] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).

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mechanism involving elimination, S_N2' substitution,[11] prototropic shift,[11] S_N2' substitution, and finally elimination. Dehydrochlorination mixtures from simple 1,1,1,3-tetrachloroalkanes have been shown to contain compounds of the type produced in steps (a) and (b) above.[9]
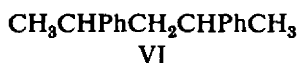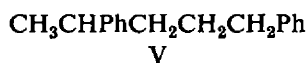
The ^1H NMR spectrum of $C_6H_5CHClCH_2CCl_3$ displays some unusual features. By analogy with other polychloroalkanes prepared in this series[1] the —CHCl—CH$_2$— grouping would have been expected to give rise to an ABX type of spectral pattern. The observed spectrum at 60 Mc/s is much simpler than this, and consists of a triplet, centred at $\tau = 4.76$, with J = 6 c/s, and a pair of peaks centred at $\tau = 6.50$, with J = 6 c/s., the low-field component of which is a singlet, and the high-field component a close doublet (J ~ 1 c/s). The triplet at $\tau = 4.76$ may be assigned to the —CHCl— group, and the pair of peaks at $\tau = 6.50$ to the —CH$_2$— group; there is also a complex multiplet at $\tau = 2.65$, assignable to the hydrogen atoms attached to the benzene ring. At present the reasons for the apparent simplicity of this spectrum are not clear. It is possible that accidental coincidence of a number of spectral line positions leads to the observed spectrum, and further study of the spectrum will be undertaken to investigate this possibility.

The 1:2-adduct

The sequence (1)–(4) leading to the 1:1-adduct (1-phenyl-1,3,3,3-tetrachloropropane) involves the formation of the more stable radical in step (3), and its subsequent reaction (chain transfer) in step (4). Styrene, however, may compete with trichloromethanesulphonyl chloride for this radical, and so lead to 1:2-adduct, or telomer, formation. On the assumption that the more stable (secondary, benzylic) radical is again produced in the addition step (5), the likely structure of the 1:2-adduct, formed by chain transfer in step (6), emerges as 1,3-diphenyl-1,5,5,5-tetrachloropentane:

$$PhCH\cdot—CH_2CCl_3 + PhCH=CH_2 \rightarrow PhCH\cdot—CH_2CHPhCH_2CCl_3 \qquad (5)$$

$$PhCH\cdot—CH_2CHPhCH_2CCl_3 + CCl_3SO_2Cl \rightarrow$$
$$PhCHClCH_2CHPhCH_2CCl_3 + CCl_3SO_2\cdot \quad (6)$$

For experimental evidence on this point, the 1:2-adduct was reduced with lithium aluminium hydride to the corresponding diphenylpentane, $C_{17}H_{20}$. Since this is unlikely to have caused any rearrangement in the carbon skeleton of the compound,[1] the only reasonable structures to be considered for the hydrocarbon on the basis of the four possible 1:2-adduct formulations are (III)–(VI), with a strong preference for (III) on mechanistic grounds:

$$PhCH_2CH_2CHPhCH_2CH_3 \qquad\qquad CH_3CHPhCHPhCH_2CH_3$$
III   IV

$$CH_3CHPhCH_2CH_2CH_2Ph \qquad\qquad CH_3CHPhCH_2CHPhCH_3$$
V   VI

The ^1H NMR spectrum of the hydrocarbon consists of a triplet at $\tau = 9.27$, J = 7 c/s., associated with 3 hydrogen atoms, a complex region of absorption covering the range $\tau = 7.3$ to $\tau = 8.8$, associated with 7 hydrogen atoms, and a further

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[11] Cf. G. W. Wheland, *Advanced Organic Chemistry* (3rd Edition) Chap. 13. J. Wiley, New York (1960); and Refs. there cited, particularly P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.* 3325 (1952).

complex region at $\tau = 2\cdot7$ to $\tau = 3\cdot1$, associated with 10 hydrogen atoms (on the two phenyl groups). The triplet at $\tau = 9\cdot27$ indicates unambiguously the presence of the grouping CH_3—CH_2— in the compound, thereby eliminating structures V and VI from consideration. Compound IV contains the grouping CH_3—$CH<$ which would be expected[12] to give rise to a doublet at about $\tau = 8\cdot8$, associated with 3 hydrogen atoms. No such doublet is observed, and so structure III is confirmed for the hydrocarbon. The chlorinated precursor of the 1,3-diphenylpentane was, consequently, 1,3-diphenyl-1,5,5,5-tetrachloropentane, formed as indicated in steps (5) and (6) above.

The mass spectrum of 1,3-diphenylpentane displays expected features, viz. strong peaks at 224 (1,3-diphenylpentane), 119 (and 120) (PhCH—CH_2CH_3) and 105 (PhCH$_2$CH$_2$) from fission of the molecule between C-2 and C-3, 91 (PhCH$_2$) and 77 (Ph).

The reaction of styrene with trichloromethanesulphonyl chloride may thus be summarized in terms of steps (1)–(3), followed by (4) or by (5) and (6); polymerization occurs to some extent from addition of the radical produced in step (5) to further molecules of styrene. Two related free radical addition reactions have been briefly examined under essentially the same conditions. The first of these was the reaction of phenylacetylene with trichloromethanesulphonyl chloride. As with styrene, evolution of sulphur dioxide was observed, but the reaction product was polymeric. This is of particular interest, since 1:1-adduct formation has been reported in the reaction of phenylacetylene with bromotrichloromethane.[5] A similar result was obtained in the reaction of styrene with dichloromethanesulphonyl chloride, initiated by benzoyl peroxide. Sulphur dioxide was evolved; some of the acid chloride was recovered, and the residual material was polymeric.

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin.

IR spectra were measured for liquid films and, in the case of solids, mulls in Nujol and hexachlorobutadiene.

The reaction of trichloromethanesulphonyl chloride with styrene

Trichloromethanesulphonyl chloride (Eastman Kodak) had m.p. 140–141° and was used without purification; styrene was distilled prior to use.

(a) *Isolation of the* 1:1-*adduct.* Trichloromethanesulphonyl chloride (21·8 g, 0·1 mole) and styrene (13 g, 0·13 mole, n_D^{20} 1·5467) were placed in a flask fitted with reflux condenser, and the apparatus was flushed with N_2. The temp of the mixture was raised to 160° during 1 hr, and maintained at 160–170° for 1 hr; evolution of SO_2, perceptible at 80°, became vigorous at 135–140°, but had virtually ceased by the end of the reaction period. Distillation of the reaction mixture then gave fractions (i) 3·0 g, b.p. 139°/16 mm, n_D^{20} 1·5472, (ii) 9·0 g, b.p. 139–144°/16 mm, n_D^{20} 1·5563, and (iii) 2·8 g, b.p. 144–200°/16 mm, n_D^{20} 1·5653, leaving a high-boiling residue.

Redistillation of fraction (ii) gave an analytical sample of 1-phenyl-1,3,3,3-tetrachloropropane (5 g, heart cut), b.p. 135–136°/10 mm, n_D^{20} 1·5560 (lit[7] b.p. 85–87°/0·2 mm, n_D^{20} 1·5557) (Found: Cl, 54·9. Calc. for $C_9H_8Cl_4$: Cl, 55·0%); ν_{max} 3040(s), 2985, 1957, 1880, 1805, 1751, 1692, 1608, 1493(s), 1451(s), 1422(s), 1355, 1328, 1297, 1238, 1200(s), 1153, 1078(s), 1060(s), 1020(s), 1001(s), 970(s), 913(s), 854(s), 823(s), 761(s), and 696(s) cm^{-1}.

(b) *Isolation of the* 1:2-*adduct.* A similar experiment was performed using trichloromethanesulphonyl chloride (43·6 g, 0·2 mole) and styrene (30·4 g, 0·29 mole, n_D^{20} 1·5467). Distillation gave a forerun, b.p. 64·5°/9 × 10⁻³ mm, then 1-phenyl-1,3,3,3-tetrachloropropane (23 g, 45%), collected as fractions (i) b.p. 64·5–66·5°/9 × 10⁻³ mm, n_D^{20} 1·5562, (ii) b.p. 66·5–75°/5 × 10⁻³ mm, n_D^{20} 1·5562, and

[12] NMR Spectra Catalog, Varian Associates, Palo Alto, California (1962).

(iii) b.p. 75–160°/2 × 10⁻³ mm, n_D^{20} 1·5561, and finally a pale yellow viscous oil, essentially 1,3-*diphenyl*-1,5,5,5-*tetrachloropentane* (19 g, 27%), b.p. 160°/10⁻³ mm (Found: Cl, 38·1. $C_{17}H_{16}Cl_4$ requires: Cl, 39·2%); ν_{max} 3020(s), 2910, 1935, 1866, 1789, 1739, 1667, 1597, 1490(s), 1449(s), 1427, 1353, 1304, 1250, 1193, 1178, 1151, 1053(s), 1028(s), 968(s), 911, 838, 808(s), 789(s), 770(s), 756(s) and 700(s) cm⁻¹.

Hydrolysis of 1-*phenyl*-1,3,3,3-*tetrachloropropane.* A mixture of 1-phenyl-1,3,3,3-tetrachloro-propane (2·58 g, 0·01 mole, n_D^{20} 1·5561), ferric chloride hexahydrate (2·71 g, 0·01 mole), water (1·08 g, 0·06 mole) and glacial acetic acid (12 g, 0·2 mole) was refluxed for 6 hr, then cooled, and diluted with water (30 ml). The precipitated solid was collected, and crystallized from water, giving cinnamic acid (1·27 g, 86%), m.p. and mixed m.p. 133–134°; refrigeration of the mother liquor gave a second crop (0·06 g, 4%), m.p. 132–134°.

The above experiment when carried out in the absence of FeCl₃ afforded cinnamic acid (65–70%) together with a neutral by-product. This was isolated by removing most of the acetic acid by distillation, then dissolving the residue in ether and washing with 2 N NaOH aq to extract cinnamic acid and traces of acetic acid. Washing with water, drying and evaporation then gave a small amount of oil, whose IR spectrum was virtually identical with that of the product of acetolysis of 1-phenyl-1,3,3,3-tetrachloropropane.

Acetolysis of 1-*phenyl*-1,3,3,3-*tetrachloropropane*

(a) *Preparation of the acetolysis product and hydrolysis thereof.* A mixture of 1-phenyl-1,3,3,3-tetrachloropropane (51·5 g, 0·2 mole, n_D^{20} 1·5561), anhydrous potassium acetate (60 g, 0·6 mole) and glacial acetic acid (520 g) was refluxed for 20 hr, and then cooled. The mixture was filtered from KCl, and then concentrated to remove the bulk of the acetic acid. The residue was poured into water (500 ml) and extracted with chloroform (2 × 50 ml). The extract was washed with 2 N NaOH aq (2 × 50 ml) to remove traces of cinnamic and acetic acids, and then with water, then dried (MgSO₄) and evaporated. Distillation then gave (i) a forerun, b.p. 114–116°/1 mm, (ii) b.p. 116–119°/1 mm, n_D^{20} 1·5308, and (iii) b.p. 119–121°/1 mm, n_D^{20} 1·5308. The combined fractions (ii) and (iii), totalling 31 g, were redistilled, and the fraction (5 g), b.p. 116°/1 mm, n_D^{20} 1·5308 taken for analysis (Found: C, 49·7; H, 4·2. $C_{11}H_{11}Cl_3O_2$ requires: C, 46·9; H, 3·9%); ν_{max} 3010, 2940, 1750(s), 1590, 1490, 1447, 1368(s), 1225(s), 1040(s), 1025(s), 940, 915, 885, 850, 766(s) and 696(s) cm⁻¹.

From a similar experiment using sodium acetate, the product had b.p. 100–102°/0·4 mm, n_D^{20} 1·5296 (Found: C, 49·7; H, 4·0%); the IR spectrum was identical with that reported above.

Though impure, this product is considered to be predominantly 1-*phenyl*-3,3,3-*trichloropropyl acetate.*

The acetate (2 g, 0·007 mole, n_D^{20} 1·5308) was hydrolysed by refluxing with 90% acetic acid (11 ml) containing anhydrous FeCl₃ (0·5 g) for 15 hr. Cinnamic acid (0·75 g, 71%), isolated as in the previous case, had m.p. and mixed m.p. 132–134°. The same result was obtained by using 90% formic acid in place of acetic acid.

(b) *Location of the acetate group in the acetolysis product.* A solution of the acetate (14 g, 0·05 mole, n_D^{20} 1·5296) in dry, peroxide-free dioxan (50 ml, AnalaR grade) was added dropwise during 1¼ hr to a mixture of LiAlH₄ (12·5 g, 0·37 mole) and dioxan (100 ml) at reflux under N₂ with stirring. After a further 20 hr at reflux, the mixture was cooled, and excess LiAlH₄ decomposed by the drop-wise addition of water. The mixture was poured into 4N H₂SO₄ (500 ml) with stirring, extracted with ether (3 × 50 ml), washed with water till free from acid, and then dried (MgSO₄). After removal of ether, distillation gave (i) a forerun, b.p. 55–105°/13 mm, and (ii) an oil (2·4 g, 35%), b.p. 105–106°/13 mm, n_D^{20} 1·5202.

Redistillation of fraction (i) gave a hydrocarbon fraction (1·1 g), b.p. 60–62°/12 mm, not further investigated since it could supply no information regarding the original site of the acetate group.

Fraction (ii) showed ν_{max} (principal bands) 3320, 2890, 1447, 1042, 1012, 975, 751 and 699 cm⁻¹; this fraction was characterized by conversion to the α-naphthylurethane, which crystallized from light petroleum (b.p. 80–100°) as clusters of small needles, m.p. 89–90° (lit[13] m.p. 101° for the α-naphthylurethane of 1-phenylpropanol) (Found: C, 78·6; H, 6·0; N, 4·8. Calc. for $C_{20}H_{19}NO_2$: C, 78·6; H, 6·2; N, 4·6%).

In spite of the discrepancy in m.p. recorded above, fraction (ii) was shown to be 1-phenylpropanol

[13] S. Searles, K. A. Pollart and E. F. Lutz, *J. Amer. Chem. Soc.* **79**, 948 (1957); cf. V. T. Bickel and H. E. French, *Ibid.* **48**, 747 (1926).

in the following way. To the alcohol (fraction ii, 0·75 g) in pure anhydrous acetone was added dropwise an approximately 8N CrO₃ aq until a faint yellow colour persisted in the solution. After 30 min, the solution was filtered and acetone removed by evaporation in a stream of nitrogen (water bath). The residue was dissolved in ether, dried (Na₂SO₄), and evaporated as above, giving a colourless oil (0·65 g) whose IR spectrum was identical with that of propiophenone. Identity was established by conversion to propiophenone semicarbazone, which formed needles from aqueous ethanol, m.p. and mixed m.p. 175–176° (lit[14] m.p. 176–177°), and to propiophenone 2,4-dinitrophenylhydrazone, which crystallized from a large volume of ethanol as red plates, m.p. 194–195° (lit[15] m.p. 193–194°), depressed on admixture with 2,4-dinitrophenylhydrazine (m.p. 197°).

Hydrolysis of 1,1,1,3-tetrachlorooctane. 1,1,1,3-Tetrachlorooctane[1] (12 g, n_D^{20} 1·4772) was submitted to the FeCl₃–90% acetic acid hydrolysis procedure used above; after 30 hr reflux, the tetrachlorooctane (9·5 g, 80%), b.p. 112–113°/10 mm, n_D^{20} 1·4772, was recovered.

1,1,1,3-Tetrachlorooctane (12 g, 0·048 mole, n_D^{20} 1·4763) and fuming HNO₃ (40 ml, d 1·5) were stirred vigorously at 35–45° for 2 hr, then at 45–55° for 1 hr. The homogeneous brown solution was poured onto ice–water (100 g) and extracted with chloroform (2 × 25 ml). The extract was washed with water (3 × 25 ml), dried (CaCl₂) and evaporated. The residue was distilled, and an arbitrary middle cut (1·5 g), b.p. 142–145°/12 mm, n_D^{20} 1·4517, collected. This contained chlorine (Beilstein test) and was completely soluble in 2N NaOH aq. The material was shown to consist largely of β-chlorooctanoic acid by conversion to the S-*benzylisothiuronium salt*, which crystallized from aqueous ethanol as platelets, m.p. 145–146° (Found: C, 56·2; H, 7·4. C₁₆H₂₅ClN₂O₂S requires: C, 55·7; H, 7·3%).

Reaction of 1-phenyl-1,3,3,3-tetrachloropropane with an excess of methanolic potassium hydroxide.

1-Phenyl-1,3,3,3-tetrachloropropane (19 g, 0·074 mole, n_D^{20} 1·5565) was added to a solution of KOH (42 g, 0·75 mole) in absolute methanol (250 ml), and the mixture was brought to reflux. After 3 hr, the reaction mixture was cooled, KCl removed by filtration, and the filtrate concentrated to ca. 150 ml. This was diluted with water (400 ml) and extracted with ether (2 × 40 ml). The ether solution was washed with water to remove alkali, dried and evaporated, giving a colourless oil (11·5 g). Distillation then gave (i) several drops, b.p. 109–111·5°/14 mm, $n_D^{15·5}$ 1·5158, (ii) b.p. 111·5–112°/14 mm, $n_D^{15·5}$ 1·5187, (iii) b.p. 112–112·5°/14 mm, $n_D^{15·5}$ 1·5180, and (iv) several drops, b.p. 112·5–119·5°/14 mm, $n_D^{15·5}$ 1·5219. Fractions (ii) and (iii), totalling 5·1 g, had identical IR spectra and were subsequently combined for further experiments; the fractions were separately shown to contain no chlorine (Beilstein test), and to decolorize bromine water immediately. The product, i.e. combined fractions (ii) and (iii), was seen from the IR spectrum and from subsequent transformations to be essentially 1,1-*dimethoxy*-1-*phenylprop*-2-*yne*; spectroscopic results were ν_{max}[16] 3290 (acetylenic C—H), 2940, 2830 (methyl acetal), 2115 (acetylenic C≡C), 1960, 1885, 1815, 1720, 1680, 1640, 1608, 1484, 1445(s), 1350, 1305, 1236(s), 1183, 1171, 1151, 1124(s), 1071(s), 1031(s), 1000, 970(s), 918, 821, 769(s), 736 and 703(s) cm⁻¹.

The acetylenic acetal (5·1 g) and 4N H₂SO₄ (30 ml) were heated on a steam bath for 30 min, and the mixture then distilled in steam. The preliminary distillate deposited a pale yellow solid, which was collected and dried. The solid (1·2 g) had m.p. 46·5–50°, raised by crystallization from 90% ethanol to 48·5–50·5°, and was identified as phenyl ethynyl ketone (lit[10] m.p. 50–51°); ν_{max} 3320, 3030, 2120, 1672(s), 1610, 1590, 1466, 1326, 1256(s), 1245(s), 1178, 1033, 1008(s), 744, 722 and 704(s) cm⁻¹.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate as orange needles, m.p. 212·5–214° (lit[10] m.p. 214° dec); the aniline adduct, 1-anilino-3-phenylpropen-3-one, crystallized from methanol as lemon-yellow needles, m.p. 141° (lit[17] m.p. 140–141°).

Preparation of 1,3-diphenylpentane. A solution of 1,3-diphenyl-1,5,5,5-tetrachloropentane (24 g, 0·066 mole) in dry, peroxide-free dioxan (50 ml) was added during 1 hr to a mixture of LiAlH₄ (11 g, 0·29 mole) and dioxan (100 ml) at reflux under N₂, with stirring. After a further 17 hr at reflux, the mixture was cooled, and excess LiAlH₄ decomposed by the dropwise addition of water. The

[14] M. A. T. Rogers, *J. Chem. Soc.* 2784 (1956).

[15] F. Ramirez and A. F. Kirby, *J. Amer. Chem. Soc.* **75**, 6026 (1953).

[16] Cf. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (2nd Edition) Chaps. 4 and 7. Methuen, London (1958).

[17] K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 45 (1946).

mixture was poured into 4N H_2SO_4 (500 ml), stirred for 3 hr, and then extracted with light petroleum (3 × 75 ml, b.p. 60–80°). The extract was washed with water till free from acid, dried (Na_2SO_4) and evaporated. Distillation then gave (i) a forerun, b.p. 93–95°/0·15 mm, n_D^{20} 1·5486, followed by 1,3-*diphenylpentane* (7·5 g) collected as fractions (ii) b.p. 95–97°/0·15 mm, n_D^{20} 1·5507 and (iii) b.p. 97–104°/0·15 mm, n_D^{20} 1·5507. A yellow involatile wax remained, which contained chlorine (Beilstein test), and which gave no further 1,3-diphenylpentane on recycling with $LiAlH_4$. Redistillation gave an analytical sample (2 g), b.p. 166–168°/11 mm, n_D^{20} 1·5507 (Found: C, 91·1; H, 8·8. $C_{17}H_{20}$ requires: C, 91·1; H, 8·9%).[18] Spectroscopic data were: ν_{max} 2995, 2950, 2865, 2825, 1595, 1488, 1447, 1029, 903, 750 and 697 cm^{-1}.

[18] Reaction of benzene with polyvinyl alcohol at 80–90° in the presence of aluminium chloride gives, in addition to polymers, a hydrocarbon, b.p. 80–82°/2 mm, n_D^{20} 1·6008; cf. P. Losev and O. V. Smirnova, *J. Gen. Chem. U.S.S.R.* (English translation) **28**, 968 (1958). This hydrocarbon was described as 1,3-diphenylpentane, though its relative volatility seems to be inconsistent with this view; a more serious objection is the absence of a satisfactory mechanism for the formation of 1,3-diphenylpentane in this reaction.