TETRA- AND TRI-CHLOROALKANES AND RELATED COMPOUNDS

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The present Review is a brief account of investigations carried out by the authors during recent years in collaboration with Ye. J. Vasil'eva, R. G. Petrova, V. N. Kost, Sh. A. Karapetyan, N. A. Semenov, A. B. Belyavsky, and T. A. Kost on reactions of polychlorohydrocarbons.[1-27]

In these investigations we were chiefly concerned with the changes in

[1] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, *Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 717.

[2] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *ibid.*, 1951, **81**, 199.

[3] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, 505.

[4] A. N. Nesmeyanov and L. I. Zakharkin, *ibid.*, 1953, 988.

[5] A. N. Nesmeyanov, L. I. Zakharkin, and R. Kh. Freidlina, *ibid.*, 1954, 34.

[6] A. N. Nesmeyanov, L. I. Zakharkin, and R. G. Petrova, *ibid.*, p. 253.

[7] A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina, *ibid.*, p. 258.

[8] *Idem, ibid.*, p. 604.

[9] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 87.

[10] *Idem, ibid.*, 1954, **97**, 91.

[11] *Idem, ibid.*, 1954, **99**, 781.

[12] A. N. Nesmeyanov, L. I. Zakharkin, and R. Kh. Freidlina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 40.

[13] A. N. Nesmeyanov and L. I. Zakharkin, *ibid.*, p. 224.

[14] R. Kh. Freidlina, V. N. Kost, and A. N. Nesmeyanov, *ibid.*, p. 233.

[15] R. Kh. Freidlina and Ye. I. Vasil'eva, *Doklady Akad. Nauk S.S.S.R.*, 1955, **100**, 85.

[16] A. N. Nesmeyanov, L. I. Zakharkin, and T. A. Kost, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 657.

[17] A. N. Nesmeyanov, V. N. Kost, and R. Kh. Freidlina, *Doklady Akad. Nauk S.S.S.R.*, 1955, **103**, 1029.

[18] A. N. Nesmeyanov, R. Kh. Freidlina, and V. N. Kost, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, in the press.

[19] L. I. Zakharkin, *ibid.*, 1955, 1009.

[20] (*a*) A. N. Nesmeyanov, R. Kh. Freidlina, and N. A. Semenov, *ibid.*, p. 993; (*b*) R. Kh. Freidlina and N. A. Semenov, *ibid.*, 1956, in the press.

[21] L. I. Zakharkin, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 985.

[22] A. N. Nesmeyanov, R. Kh. Freidlina, L. I. Zakharkin, and A. B. Belyavsky, *Zhur. obshchei Khim.*, 1956, **26**, 130.

[23] L. I. Zakharkin, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1956, 314.

[24] A. N. Nesmeyanov, Sh. A. Karapetyan, and R. Kh. Freidlina, *Doklady Akad. Nauk. S.S.S.R.*, 1956, in the press.

[25] (*a*) A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, U.S.S.R. Pat. 98449/1954; (*b*) R. Kh. Freidlina and L. I. Zakharkin, U.S.S.R. Pat. 99484/1954;

αααω-tetrachloroalkanes and ααα-trichloroalkanes, which became readily available by the telomerisation of ethylene and carbon tetrachloride or ethylene and chloroform, a reaction due to Joyce, Hanford, and Harmon.[28–30]

In a number of cases we have investigated polyhalogeno-derivatives obtained by adding carbon tetrachloride or halogeno-derivatives to olefins and to vinyl ethers as well as by condensing halogeno-derivatives with halogeno-olefins in the presence of aluminium chloride.

Our aim has been to work out general methods of synthesis of various organic compounds, starting with those involving, for example, the following radicals :

$$CCl_3— \quad CCl_3{\cdot}CHCl— \quad CCl_3{\cdot}C{=}C\diagup \quad CCl_2{=}CH— \quad CCl_2{=}C(\mathrm{I})—C(\mathrm{I})\cdot OR$$

The investigation also involved the examination of some rearrangements in the series of unsaturated polychlorohydrocarbons. In the course of our investigation we have synthesised a great number of substances, some data being listed in Tables 3—9.

Reactions of the Trichloromethyl Group in Saturated Compounds

The Determination of the Character of the Trichloromethyl Group as an Orientant.—The investigation of the orienting action of the trichloromethyl group on the electrophilic substitution in the aromatic nucleus has led to ambiguous results. Thus, the trichloromethyl group in benzotrichloride orients to the *meta*-position in nitration, but to the *para*-position in chlorination.[31]

Kharasch and his co-workers [32] failed to determine the orienting influence of the trichloromethyl group on the electrophilic addition of hydrogen bromide to 3 : 3 : 3-trichloropropene, these authors having dealt in their investigation with 1 : 1 : 2-trichloroprop-1-ene, mistakenly thought by them to be 3 : 3 : 3-trichloroprop-1-ene (see p. 339).

Study of the reaction of the true 3 : 3 : 3-trichloropropene with hydrogen bromide showed that the reaction does not take place in the absence of catalysts, and that when aluminium trichloride is present 3 : 3 : 3-trichloroprop-1-ene is isomerised to 1 : 1 : 3-trichloroprop-1-ene.[1–3]

Two of us and V. N. Kost have studied the conjugated addition of chlorine to 3 : 3 : 3-trichloropropene in glacial acetic acid or concentrated sulphuric acid, 2 : 3 : 3 : 3-tetrachloropropyl acetate having been obtained

(*c*) A. N. Nesmeyanov, R. Kh. Freidlina, L. I. Zakharkin, *et al.*, *Trudy Vsesoyuz, Soveshch. Kompleksnoi Pererab. Naft. Gazov* ; (*d*) R. Kh. Freidlina and Ye. I. Vasil'eva. U.S.S.R. Pat. Appl. ; (*e*) R. Kh. Freidlina and L. I. Zakharkin, U.S.S.R. Pat. 100341/1955.

[26] A. N. Nesmeyanov, R. Kh. Freidlina, and R. G. Petrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, in the press.

[27] Ye. I. Vasil'eva and R. Kh. Freidlina, *ibid.*, p. 177.

[28] R. M. Joyce, W. F. Hanford, and J. Harmon, *J. Amer. Chem. Soc.*, 1948, **70**, 2429.

[29] R. M. Joyce and W. F. Hanford, *ibid.*, 1950, **72**, 2213.

[30] W. F. Hanford and R. M. Joyce, U.S.P. 2,440,800/1948.

[31] W. M. Latimer and C. W. Porber, *J. Amer. Chem. Soc.*, 1930, **52**, 206.

[32] M. S. Kharasch, E. Rossin, and E. K. Fields, *ibid.*, 1941, **63**, 2558.

in the former and a corresponding sulphate in the latter. The structure of the acetate and sulphate were proved by hydrolysis to 2 : 3 : 3 : 3-tetrachloropropanol, identical with the alcohol synthesised according to the following scheme : [18]

$$CCl_2{:}CH{\cdot}CH_2Cl + CH_3{\cdot}CO_2K \xrightarrow{AcOH} CCl_2{:}CH{\cdot}CH_2{\cdot}OAc \xrightarrow{CH_3{\cdot}OH}$$
$$CCl_2{:}CH{\cdot}CH_2{\cdot}OH \xrightarrow[HCl]{Cl_2} CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH$$

Carrying out the reactions of conjugated addition of chlorine to propene in glacial acetic acid or concentrated sulphuric acid gives the corresponding esters of 1-chloropropan-2-ol.[33]

Comparing the reactions one finds the orienting action of the trichloromethyl group to be opposite to that of the methyl group, the electron-attracting character of the trichloromethyl group being thereby proved :

$$CH_3{\cdot}CH{:}CH_2 + Cl_2 \xrightarrow{AcOH} CH_3{\cdot}CH(OAc){\cdot}CH_2Cl \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH_2Cl$$
$$CCl_3{\cdot}CH{:}CH_2 + Cl_2 \xrightarrow{AcOH} CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}OAc \longrightarrow CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH$$

3 : 3 : 3-Trichloropropene also adds hypobromous acid in the reverse order to propene :

$$CH_2{:}CH{\cdot}CCl_3 + HOBr \longrightarrow HO{\cdot}CH_2{\cdot}CHBr{\cdot}CCl_3$$
$$CH_2{:}CH{\cdot}CH_3 + HOBr \longrightarrow BrCH_2{\cdot}CH(OH){\cdot}CH_3$$

The structure of 2-bromo-3 : 3 : 3-trichloropropanol was proved by dechlorination with alcoholic alkali to 2-bromo-1 : 1-dichloro-3-hydroxyprop-1-ene. The electron-accepting inductive effect of the trichloromethyl

TABLE 1. *Dissociation constants in water.*

Acid	Dissociation constants	Temp. (° C)	Ref.
$CCl_3{\cdot}[CH_2]_2{\cdot}CO_2H$	$6{\cdot}2 \times 10^{-5}$	20	12
$CH_3{\cdot}[CH_2]_2{\cdot}CO_2H$	$1{\cdot}53 \times 10^{-5}$	18	34
$CH_2Cl{\cdot}[CH_2]_2{\cdot}CO_2H$	3×10^{-5}	25	35
$CF_3{\cdot}[CH_2]_2{\cdot}CO_2H$	$6{\cdot}98 \times 10^{-5}$	25	36
$CCl_3{\cdot}[CH_2]_3{\cdot}CO_2H$	$3{\cdot}0 \times 10^{-5}$	20	12
$CH_3{\cdot}[CH_2]_3{\cdot}CO_2H$	$1{\cdot}51 \times 10^{-5}$	18	34
$CH_2Cl{\cdot}[CH_2]_3{\cdot}CO_2H$	$2{\cdot}04 \times 10^{-5}$	25	35
$CF_3{\cdot}[CH_2]_3{\cdot}CO_2H$	$3{\cdot}2 \times 10^{-5}$	25	36

group is shown again in the increased strength of the carboxylic acids containing a trichloromethyl group. The dissociation constants of the acids $CCl_3{\cdot}[CH_2]_n{\cdot}CO_2H$ are greater than those of the unchlorinated carboxylic acids containing the same number of carbon atoms and are greater than those

[33] A. I. Titov and F. O. Maklyayev, *Zhur. obshchei Khim.*, 1954, **24**, 1860.
[34] E. Larson and B. Adell, *Z. phys. Chem.*, 1931, **156**, 352.
[35] D. M. Lichty, *Annalen*, 1901, **219**, 369.
[36] A. L. Henne and Ch. J. Fox, *J. Amer. Chem. Soc.*, 1953, **75**, 2323, 5750.

of corresponding ω-chloro-carboxylic acids.[12] The difference in the influence of the trichloromethyl and trifluoromethyl groups decreases with the increase in the number of methylene groups and is already negligible with trihalogenovaleric acids (see Table 1).

The Action of Electrophilic Reagents on Saturated Compounds containing a Trichloromethyl Group.—We have studied the action of sulphuric and nitric acid as electrophilic reagents causing hydrolysis of the trichloromethyl to the carboxyl group as well as the action of aluminium and ferric chlorides leading to the splitting off of hydrogen chloride at the expense of the chlorine of the trichloromethyl group.

Hydrolysis. Hydrolysis to the carboxyl group is the principal reaction of the trichloromethyl group, as it permits passage from chlorine derivatives involving this grouping to the corresponding carboxylic acids.

Previously the only way of effecting hydrolysis of the trichloromethyl group in saturated compounds was by heating with concentrated (92—95%) sulphuric acid.[13, 28, 37, 38] By this procedure tetrachloroalkanes $CH_2Cl{\cdot}[CH_2]_n{\cdot}CCl_3$ (where $n = 4, 6, 8$) were converted into 5-chloropentanoic, 7-chloroheptanoic, and 9-chlorononanoic acid,[25, 37] and the corresponding higher ααaω-tetrachloroalkanes yielded 11-chloroundecanoic, 13-chlorotridecanoic, and 15-chloropentadecanoic acids.[13]

One must, however, note that whilst hydrolysis of lower tetrachloroalkanes can be effected with almost quantitative yield of the corresponding acids, hydrolysis of higher tetrachloroalkanes with sulphuric acid proceeds with marked "slurrying" or tar formation and the yields are greatly reduced. Thus, the yield of 13-chlorotridecanoic acid amounted to 42% and that of 15-chloropentadecanoic acid to 24%.[13]

Compounds containing a chlorine atom in the α-position to the chloromethyl group are only slowly attacked by concentrated sulphuric acid, the reaction starting only at 160—170° and being accompanied by considerable slurrying.

One of us and Ye. J. Vasil'eva have now shown that nitric acid (s.g. 1·51—1·52) reacts with saturated polychloroalkanes containing a trichloromethyl group even at room temperature to give the corresponding carboxylic acids;[15] to complete the reaction the mixture is heated at 60—90° for 1—3 hours. This procedure was employed[15] to prepare in high yields acids from tetrachloroalkanes containing 5, 7, 9, and 11 carbon atoms as well as for the hydrolysis of 1 : 1 : 1-trichlorotridecane, 1 : 1 : 1-trichloropentadecane, and 1 : 1 : 1-trichloroheptadecane. This method is particularly useful for obtaining the higher carboxylic acids as the reaction proceeds readily without slurrying.

When trichloroalkanes are hydrolysed with nitric acid the yields of acids containing 13, 15, and 17 carbon atoms amount to 61, 66, and 40% of theory, respectively. Those containing chlorine in the α-position to the trichloromethyl group also undergo hydrolysis rather readily when heated with fuming nitric acid. In this case the reaction is carried out at 120—130°.

[37] R. M. Joyce, U.S.P. 2,398,430.
[38] H. J. Prins, *J. prakt. Chem.*, 1914, **89**, 414.

Thus, from 1 : 1 : 1 : 2 : 5-pentachloropentane was obtained 2 : 5-dichloropentanoic acid. With 50—60% nitric acid there is virtually no reaction; 90% nitric acid reacts with αααω-tetrachloroalkanes but the yields of acids containing the same number of carbon atoms are in this case lower. Unlike hydrolysis by sulphuric or nitric acid which takes place only with concentrated acids perchloric acid as dilute as 70% hydrolyses αααω-tetrachloroalkanes, the yields being, however, substantially lower than with the procedures mentioned above.[25d]

Phosphoric acid does not hydrolyse the trichloromethyl group.

Dehydrochlorination of αααω-tetrachloroalkanes and ααα-trichloroalkanes. Among chemical reactions of polychloro-derivatives an important place is to be allotted to dehydrochlorination as constituting a route to unsaturated polychloro-derivatives.

Dehydrochlorination of higher tetrachloroalkanes has been described in patent literature,[39, 40] where it is suggested that catalytic removal of hydrogen chloride and the removal by alkali take place at the expense of the chlorine in the trichloromethyl group and result in trichloroalkenes, $CCl_2{:}CH{\cdot}[CH_2]_n{\cdot}Cl$. Actually, it has been found that dehydrochlorination with alcoholic alkali yields a mixture of products which is difficult to separate.

One must also note that the constants for trichloroalkenes described in the patent literature, *e.g.*, those of 1 : 1 : 5-trichloropent-1-ene, proved to be inaccurate as shown by a divergence between the values found and the calculated molecular refraction (MR).

The literature reports dehydrochlorination of polychloro-derivatives under the action of aluminium chloride to give, *e.g.*, hexachloropropene from heptachloropropane,[41] tetrachloroethylene from pentachloroethane,[42] etc.[43] There are examples of dehydrochlorination by heating with anhydrous ferric chloride,[44] *e.g.*, DDT. These reactions are, however, known to have been carried out at a comparatively high temperature, the scope of the procedure being thereby limited.

αααω-Tetrachloroalkanes and ααα-trichloroalkanes have now been found to split off hydrogen chloride under the action of a small quantity of aluminium chloride and particularly of anhydrous ferric chloride even at room temperature;[4] the reaction is brought to completion by a short period of heating at 40—60°, yielding dichlorovinyl derivatives, $Cl{\cdot}[CH_2]_n{\cdot}CH{:}CCl_2$ and $CH_3{\cdot}[CH_2]_n{\cdot}CH{:}CCl_2$. Under these conditions by-products are not formed nor does isomerisation of the paraffin chain take place. The method was used to give 1 : 1 : 5-trichloropent-1-ene, 1 : 1 : 7-trichlorohept-1-ene, 1 : 1 : 9-trichlorononon-1-ene, 1 : 1-dichloropent-1-ene, and 1 : 1-dichlorohept-1-ene.

The Action of Nucleophilic Reagents on Saturated Compounds containing a Trichloromethyl Group.—The trichloromethyl group proved inert towards

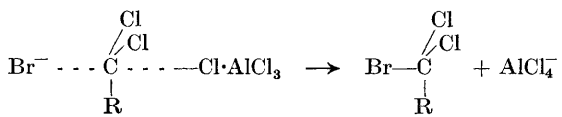
[39] B.P. 581,899; *Chem. Abs.*, 1947, **41**, 3477.
[40] R. M. Joyce, U.S.P. 2,410,541.
[41] J. Boeseken, J. van du Scheer, and J. G. Voogt, *Rec. Trav. chim.*, 1915, **34**, 78.
[42] H. J. Prins, *ibid.*, 1935, **54**, 249.
[43] *Idem*, *ibid.*, 1946, **65**, 455.
[44] E. E. Fleck and H. L. Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2095.

the action of nucleophilic reagents. Thus, 1 : 1 : 1-trichloropentane does not exchange with ammonia (heated with alcoholic ammonia at 140° for 10 hours or liquid ammonia at 140° for 5 hours) or with sodium iodide (refluxed in acetone for 18 hours), or with diethyl sodiomalonate. Other ααα-trichloroalkanes behave similarly.[9] Unlike these compounds, benzotrichloride and chloroform react with nucleophilic reagents, *e.g.*, when treated with ammonia they form benzonitrile[45] and hydrogen cyanide,[46] respectively. In the action of nucleophilic reagents on αααω-tetrachloroalkanes the trichloromethyl group also remains intact, only the chloromethyl group entering the reaction.[9] Thus, in the action of sodium iodide on 1 : 1 : 1 : 5-tetrachloropentane in acetone during 8 hours' heating 1 : 1 : 1-trichloro-5-iodopentane is formed in 90% yield. The structure of 1 : 1 : 1-trichloro-5-iodopentane was ascertained by converting it by means of sodium cyanide into the known 1 : 1 : 1-trichloro-5-cyanopentane.[5] 1 : 1 : 1 : 5-Tetrachloropentane, when heated with potassium acetate in glacial acetic acid for 18 hours (preferably in the presence of a small amount of potassium iodide), forms 5-acetoxy-1 : 1 : 1-trichloropentane in 86% yield. The structure of 5-acetoxy-1 : 1 : 1-trichloropentane was proved by converting it into 5 : 5 : 5-trichloropentan-1-ol in quantitative yield.

Ammonia,[5] diethyl sodiomalonate,[5] potassium cyanide,[5, 47] and other nucleophilic reagents react with αααω-tetrachloroalkanes similarly. It is to be noted that, depending on the basicity of the nucleophilic reagent and the reaction conditions, there takes place a varying extent of dehydrochlorination at the expense of the trichloromethyl group.[9]

Quite different is the behaviour, in a number of reactions, of 1 : 1 : 1 : 3-tetrachloropropane. Thus, in reaction with sodium cyanide, sodium sulphide, or other nucleophilic reagents, it is not possible to bring about the exchange of chlorine in the chloromethyl group; instead the dehydrochlorination reaction usually takes place with formation of a mixture of isomeric trichloropropenes and the products of their subsequent reaction. Only when rigid conditions of refluxing with an excess of aniline were employed could one obtain 1 : 1 : 1-trichloro-3-anilinopropane in a low yield.[20b]

The trichloromethyl group being inert to nucleophilic reagents, it is impossible to hydrolyse it in weakly acidic, neutral, or basic media. This is not the case in a strongly acid medium where the electrophilic qualities of the reagent come into play. Similarly, the trichloromethyl group does not undergo exchange with bromine anion under the action of hydrogen bromide but such an exchange does take place under the concurrent attack of electrophilic aluminium chloride, which can be represented as:



[45] H. Limpricht, *Annalen*, 1865, **135**, 82.
[46] A. Hofmann, *ibid.*, 1867, **144**, 116.
[47] R. Joyce, U.S.P. 2,425,426.

Thus, by introducing hydrogen bromide into 1 : 1 : 1-trichloropentane in the presence of a small amount of aluminium chloride at 4—5°, 1 : 1 : 1-tribromopentane is formed in high yield.[9] Similarly, in 1 : 1 : 1 : 5-tetrachloropentane the halogen exchange takes place initially in the trichloromethyl group, 1 : 1 : 1-tribromo-5-chloropentane being formed.[9]

It seems that the action of nucleophilic reagents on compounds containing the trichloromethyl group in concentrated acid or in the presence of an aprotic acid ($AlCl_3$ etc.) can find a wider application.

Dehydrochlorination of 1 : 1 : 1 : 3-*tetrachloropropane* [1, 3] *and of the compounds* $CCl_3{\cdot}CHCl{\cdot}CH_2X$ [14] *with alcoholic alkali.* The dehydrochlorination of 1 : 1 : 1 : 3-tetrachloropropane is of special interest as it led to the formerly unknown 3 : 3 : 3-trichloroprop-1-ene. The trichloropropene, b.p. 115°, described in the literature [32, 48–50] as having the structure $CCl_3{\cdot}CH{:}CH_2$, has been shown by Kirrmann and Ostermann [51] to possess the structure $CCl_2{:}CCl{\cdot}CH_3$. Reaction between alcoholic alkali and 1 : 1 : 1 : 3-tetrachloropropane in the cold leads to 3 : 3 : 3-trichloroprop-1-ene, 1 : 1 : 3-trichloroprop-1-ene and 1 : 1-dichloro-3-ethoxyprop-1-ene; 3 : 3 : 3-trichloropropene is readily isolated from the mixture by fractionation. The last two products are separated with difficulty and therefore it is better in some cases to carry out the reaction in ethyl cellosolve.

Data concerning 3 : 3 : 3-trichloropropene are given below (p. 339).

Polychloro-derivatives, of the structure $CCl_3{\cdot}CHCl{\cdot}CH_2X$ (where X = Ph, OMe, NEt_2, CN, or CO_2H), were dehydrochlorinated by alcoholic alkali to ascertain the influence of the type of substituent adjacent to the methylene group on the order of scission of hydrogen chloride from the particular molecules.[14] In all the examples mentioned scission occurred in accordance with Saitzeff's rule : [14]

$$CCl_3{\cdot}CHCl{\cdot}CH_2X \xrightarrow{KOH} CCl_2{:}CCl{\cdot}CH_2X \quad (\text{where X} = \text{Ph, OMe, NEt}_2)$$

When the compounds $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CN$ and $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$ were dehydrochlorinated by alcoholic alkali the reaction ran contrary to that rule : [7]

$$CCl_3{\cdot}CHCl{\cdot}CH_2X \xrightarrow{KOH} CCl_3{\cdot}CH{:}CHX$$

These observations show that the dehydrochlorination of substances $CCl_3{\cdot}CHCl{\cdot}CH_2X$ proceeds according to Saitzeff's rule when X behaves as an electron-releasing substituent, whilst, when this substituent is a pronounced electron-attracting one, Saitzeff's rule is not obeyed.[14]

The starting materials with X = Ph, CN, or CO_2H were obtained by chlorinating the corresponding compounds $CCl_2{:}CH{\cdot}CH_2X$ in carbon tetrachloride at 0—5°.[14] The compounds $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}OMe$ and $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}NEt_2$ were produced by chlorinating $CCl_2{:}CH{\cdot}CH_2{\cdot}OMe$ and $CCl_2{:}CH{\cdot}CH_2{\cdot}NEt_2$ in ether and concentrated hydrochloric acid, simultane-

[48] E. Vitoria, *Rec. Trav. chim.*, 1905, **24**, 265.
[49] J. Henry, *ibid.*, p. 342.
[50] A. L. Henne and A. M. Whaley, *J. Amer. Chem. Soc.*, 1942, **64**, 1157.
[51] A. Kirrmann and J. Ostermann, *Bull. Soc. chim. France*, 1948, **15**, 168.

ously saturating the mixture with chlorine and hydrogen chloride [14] (see page 348).

The structures of the dehydrochlorination products were ascertained as follows. The compound $CCl_2{:}CCl{\cdot}CH_2Ph$ was identified as the product of the reaction:

$$CCl_2{:}CCl{\cdot}CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} CCl_2{:}CCl{\cdot}CH_2{\cdot}C_6H_5$$

To the samples of phenyltrichloropropene obtained by following the two routes we added chlorine and determined the m.p. of the mixed sample of phenylpentachloropropane [14] ($CCl_3{\cdot}CCl_2{\cdot}CH_2Ph$). The compound $CCl_2{:}CCl{\cdot}CH_2{\cdot}OMe$ proved by its constants to be identical with that obtained in the reaction [14]

$$CCl_2{:}CCl{\cdot}CH_2Cl + Me{\cdot}ONa \longrightarrow CCl_2{:}CCl{\cdot}CH_2{\cdot}OMe$$

The hydrochloride of the compound $CCl_2{:}CCl{\cdot}CH_2{\cdot}NEt_2$ was identified by mixed m.p. determination [14] as the substance obtained by the reaction:

$$CCl_2{:}CCl{\cdot}CH_2Cl + NHEt_2 \longrightarrow CCl_2{:}CCl{\cdot}CH_2{\cdot}NEt_2,HCl$$

The acid from the nitrile, obtained when $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CN$ was dehydrochlorinated, showed constants identical with those of the known [52] $\gamma\gamma\gamma$-trichlorocrotonic acid, obtained when $\beta\gamma\gamma\gamma$-tetrachlorobutyric acid was dehydrochlorinated, and exhibited no depression of the melting point when it was mixed with authentic $\gamma\gamma\gamma$-trichlorocrotonic acid.

Attack by Radicals on the Trichloromethyl Group in Saturated Polychlorohydrocarbons.—We have investigated homolytic reactions involving a trichloromethyl group with phenylmagnesium bromide in the presence of cobaltous chloride, under the action of Raney nickel and finely ground copper. In all cases reaction took place at the expense of the trichloromethyl group, the monochloromethyl group remaining unchanged.[9]

In the absence of cobaltous chloride, 1 : 1 : 1 : 5-tetrachloropentane does not react with phenylmagnesium bromide. In the presence of cobaltous chloride, which is known [53] to direct the reaction of organomagnesium compounds with halogen derivatives along the radical mechanism, 1 : 1 : 1 : 5-tetrachloropentane and phenylmagnesium bromide formed a mixture from which were isolated two main products, diphenyl and 1 : 5 : 5 : 6 : 6 : 10-hexachlorodecane, no products arising from reaction of the chloromethyl group having been found.

According to Kharasch [53] the reaction runs as follows:

$$\begin{aligned} PhMgBr + CoCl_2 &\longrightarrow Ph{\cdot} + CoCl + MgClBr \\ 2Ph{\cdot} &\longrightarrow Ph{\cdot}Ph \\ Cl{\cdot}[CH_2]_4{\cdot}CCl_3 + CoCl &\longrightarrow Cl{\cdot}[CH_2]_4{\cdot}CCl_2{\cdot} + CoCl_2 \\ 2Cl{\cdot}[CH_2]_4{\cdot}CCl_2{\cdot} &\longrightarrow Cl{\cdot}[CH_2]_4{\cdot}CCl_2{\cdot}CCl_2{\cdot}[CH_2]_4{\cdot}Cl \end{aligned}$$

Refluxing of 1 : 1 : 1 : 5-tetrachloropentane with Raney nickel in ethyl alcohol for 2 hours gives 1 : 5 : 5 : 6 : 6 : 10-hexachlorodecane along with some starting material. Finely ground copper when heated has the same

[52] K. Auwers and H. Wissebach, *Ber.*, 1923, **56**, 731.
[53] M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2316.

effect on 1 : 1 : 1 : 5-tetrachloropentane.[9] In the presence of platinum, palladium, or Raney nickel catalyst and bases hydrogen acts selectively on the trichloromethyl and does not affect the monochloromethyl group, resulting in hydrodimerisation at the expense of the former group,[16 54, 55] with the formation of the compounds (II).

$$\underset{\text{(I)}}{Cl\cdot[CH_2]_n\cdot CCl_3} \longrightarrow \underset{\text{(II)}}{(Cl\cdot[CH_2]_n\cdot CCl_2\cdot)_2} \longrightarrow \underset{\text{(III)}}{(Cl\cdot[CH_2]_n\cdot CCl{:})_2} \longrightarrow \underset{\text{(IV)}}{(Cl\cdot[CH_2]_n\cdot CH_2\cdot)_2}$$

The next step of the hydrogenation has been shown [16] to be dechlorination to form a compound involving a symmetrical dichlorovinyl group, subsequently reduced to the disubstituted alkane. The reduction to the end product (IV) is, of necessity, carried out through the isolation of an intermediate compound of the type (II) as, being carried out continuously in one step, the process runs very slowly and results in a poor yield of end product. The higher tetrachloroalkanes containing 7, 9, and 11 carbon atoms behave towards nucleophilic and radical reagents just as does 1 : 1 : 1 : 5-tetrachloropentane.

Conclusions.—From the above account one can make conclusions about the chemical reactions of the trichloromethyl group in saturated polychlorohydrocarbons.

The trichloromethyl group is inert to nucleophilic reagents; this seems to be due to the screening of the central carbon atom from nucleophilic attack by the three chlorine atoms. Electrophilic reagents behave in reactions with ααα-trichloroalkanes and αααω-tetrachloroalkanes oppositely to nucleophilic reagents in that they attack in the first place the trichloromethyl and leave unaffected the monochloromethyl group.

Radical reagents also selectively attack the trichloromethyl group.

It is interesting to note that the heterolytic reactions of nucleophilic substitution of chlorine in the monochloromethyl group and of attack by electrophilic reagents on the trichloromethyl group in the polychlorohydrocarbons under study result in a high yield of product. Homolytic changes of the trichloromethyl group are much more complex, a number of products being formed.

The introduction of a chlorine atom into the α-position to a trichloromethyl group considerably retards the attack by electrophilic reagents.

Reactions of the Trichloromethyl Group in Compounds containing the Grouping $CCl_3\cdot\overset{|}{C}=C<$

Synthesis and Properties of 3 : 3 : 3-Trichloropropene.[1, 3]—Chemical changes which have been studied most thoroughly were those of the simplest compound of this class, namely 3 : 3 : 3-trichloropropene.

[54] B.P. 652,768; *Chem. Abs.*, 1952, **46**, 1577.
[55] E. C. Ladd and H. Sargent, U.S.P. 2,651,664.

For a long time, the trichloropropene, b.p. 114—115°, $n_D^{20} = 1{\cdot}4827$, $d_4^{20} = 1{\cdot}369$, first obtained by dehydrating 3 : 3 : 3-trichloropropanol, was mistakenly postulated to have the structure 3 : 3 : 3-trichloropropene. Actually it is the 1 : 1 : 2-trichloroprop-1-ene.[51] The mistaken assumption has led to a number of wrong suggestions as to the properties and chemical behaviour of 3 : 3 : 3-trichloropropene as well as to the structures of many compounds related to 1 : 1 : 2-trichloroprop-1-ene. 3 : 3 : 3-Trichloropropene was obtained by the action of potassium hydroxide on 1 : 1 : 1 : 3-tetrachloropropane at 0—5°; the reaction also yields 1 : 1 : 3-trichloroprop-1-ene. 3 : 3 : 3-Trichloropropene is a liquid, b.p. 101—102°, $n_D^{20} = 1{\cdot}4680$, $d_4^{20} = 1{\cdot}3292$ (Found, MR 30·37; calc., MR 30·20).

The structure of this trichloropropene was proved by its yielding chloral when ozonised.

Contrary to the prevailing literature reports that 3 : 3 : 3-trichloropropene is,[50] supposedly, inert, it proved to be a rather reactive substance. In particular, it readily undergoes allylic rearrangement, adds chlorine and bromine, and also, in the presence of benzoyl peroxide, adds hydrogen bromide. It can be dimerised and polymerised by peroxides, and condensed with benzene in the presence of aluminium chloride. Allylic rearrangement of 3 : 3 : 3-trichloroprop-1-ene into 1 : 1 : 3-trichloroprop-1-ene results when the former is heated in a steel tube up to 150° or when a small amount of aluminium chloride is added to it at 0°.

3 : 3 : 3-Trichloropropene readily adds chlorine when its solution in carbon tetrachloride is saturated with gaseous chlorine at room temperature to give a liquid pentachloropropane, b.p. 64—65°/8 mm., $n_D^{20} = 1{\cdot}5105$, $d_4^{20} = 1{\cdot}6117$ (Found, MR 40·16; calc., MR 40·39). This pentachloropropane must be 1 : 1 : 1 : 2 : 3-pentachloropropane because of the route by which it was obtained. Its properties differ markedly from those of the crystalline pentachloropropane, b.p. 170—180°, described in the literature as having this structure.

The latter compound, obtained [48, 49] by adding chlorine to 1 : 1 : 2-trichloropropene, b.p. 115°, is probably 1 : 1 : 1 : 2 : 2-pentachloropropane.

Addition of bromine to 3 : 3 : 3-trichloropropene gives a liquid dibromotrichloropropane, b.p. 76—70°/3 mm., $n_D^{20} = 1{\cdot}5640$, $d_4^{20} = 2{\cdot}1712$ (Found, MR 45·75; calc., MR 46·18), apparently 2 : 3-dibromo-1 : 1 : 1-trichloropropane.[1, 3] The crystalline dibromotrichloropropane described in the literature as melting at 210° and supposed to be the 2 : 3-dibromo-1 : 1 : 1-trichloropropane owing to its being obtained [48, 49] by adding bromine to the trichloropropene, b.p. 115°, is actually 1 : 2-dibromo-1 : 1 : 2-trichloropropane.

For the synthesis from 3 : 3 : 3-trichloropropene of a number of halogeno-propanes and -propenes containing fluorine, chlorine, and bromine, see references 1—3, 56.

The Action of Nucleophilic Reagents.—(a) *On* 3 : 3 : 3-*trichloropropene.* In all cases studied the action of nucleophilic compounds on 3 : 3 : 3-trichloropropene takes place with allylic rearrangement, giving products

[56] R. N. Haszeldine, *J.*, 1953, 3371.

identical with those obtained by reaction of the same reagents with 1 : 1 : 3-trichloroprop-1-ene.[7]

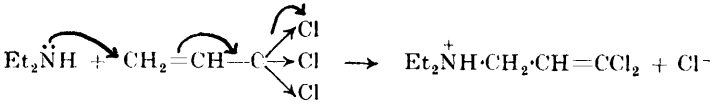
As nucleophilic reagents diethylamine, diethyl sodiomalonate, sodium sulphide, and sodium methoxide were used. In reactions with 1 : 1 : 3-trichloroprop-1-ene the allyl chlorine was substituted. These reactions can be illustrated :

$$\left.\begin{matrix}CCl_3{\cdot}CH{:}CH_2\\ CCl_2{:}CH{\cdot}CH_2Cl\end{matrix}\right\}\begin{cases}+\ Et_2NH \longrightarrow CCl_2{:}CH{\cdot}CH_2{\cdot}NEt_2\\ +\ NaCH(CO_2Et)_2 \longrightarrow CCl_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2\\ +\ Na_2S \longrightarrow (CCl_2{:}CH{\cdot}CH_2)_2S\\ +\ MeONa \longrightarrow CCl_2{:}CH{\cdot}CH_2{\cdot}OMe\end{cases}$$

The identity of the dichlorodiethylaminopropenes obtained from the two trichloropropenes by reaction with diethylamine is proved by mixed m.p. determination of the hydrochlorides.

The structure and identity of the products of the reaction of diethyl sodiomalonate and the trichloropropenes were proved by their conversion into glutaric acid by hydrolysis and decarboxylation. The identity of the bisdichloropropenyl sulphide derived from the two trichloropropenes was indicated by the boiling point of a mixture of the sulphones obtained from the two sulphides. The action of sodium methoxide on either 3 : 3 : 3-trichloropropene or 1 : 1 : 3-trichloroprop-1-ene gave the same compound, apparently 1 : 1-dichloro-3-methoxyprop-1-ene.

It is to be stressed that the reactions of nucleophilic reagents with 3 : 3 : 3-trichloropropene give good yields under conditions which exclude its preliminary isomerisation into 1 : 1 : 3-trichloroprop-1-ene. One can suppose that the centre of the nucleophilic attack in 3 : 3 : 3-trichloropropene is the methylene group, the carbon atom of the trichloromethyl group being strongly screened by chlorine atoms, and, consequently, these reactions of 3 : 3 : 3-trichloropropene belong to the type taking place with " transfer of reaction centre ".[57] The reaction of 3 : 3 : 3-trichloropropene with, say, diethylamine may be shown to take place as follows :



Similar results were obtained in the reaction of nucleophilic reagents with 3 : 3 : 3-trichloro-2-methylprop-1-ene.[58] de la Mare and Vernon [58] found that when 3 : 3 : 3-trichloro-2-methylprop-1-ene reacts with sodium thiophenoxide, there takes place a second-order reaction, only one compound, with the structure $CCl_2{:}CMe{\cdot}CH_2{\cdot}SPh$, being formed. This led the authors to conclude that the reaction was exclusively of S_N2' type. The

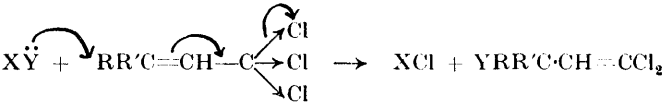
[57] (*a*) A. N. Nesmeyanov, *Uch. Zap. Mosk. Univ.*, 1950, No. 132, 5 ; (*b*) A. N. Nesmeyanov and M. I. Kabachnik, *Zhur. obshchei Khim.*, 1955, **25**, 41 ; (*c*) A. N. Nesmeyanov, R. Kh. Freidlina, and A. Ye. Borisov, *Yubileinyi Sbornik Akad. Nauk S.S.S.R.*, 1947, p. 658.

[58] P. B. D. de la Mare and C. A. Vernon, *J.*, 1952, 3628.

same authors [59] have also found that the reaction of 3 : 3-dichloroprop-1-ene with nucleophilic reagents follows two paths—with and without isomerisation. For the overall reaction, a second order having been found, the authors believe the reaction to follow S_N2' and S_N2 mechanisms.

On compounds $CCl_3{\cdot}CH{:}CRR'$.[22] Judging from the reported behaviour of 3 : 3 : 3-trichloropropene toward nucleophilic reagents one would expect the reactivity of the compounds $CCl_3{\cdot}CH{:}CRR'$ to be greatly influenced by the character of substituents R and R' directly bound to the centre of nucleophilic attack.

The influence of these substituents has been studied by us in collaboration with A. B. Belyavsky by using $CCl_3{\cdot}CH{:}CHMe$, $CCl_3{\cdot}CH{:}CHPh$, $CCl_3{\cdot}CH{:}CMe_2$, and $CCl_3{\cdot}CH{:}CH{\cdot}CMe_3$. The synthesis and proof of structure of these compounds and their allylic isomers $CCl_2{:}CH{\cdot}CHCl{\cdot}Me$ and $CCl_2{:}CH{\cdot}CClMe_2$ has been given.[22] As nucleophilic reagents ammonia and amines, alcohols in the presence of alkali, sodium alkoxides, and potassium acetate were used among others. In all cases studied the reactions proceeded with transfer of the reaction centre according to the scheme:



the following peculiarities being noted: 1 : 1 : 1-trichloro-4 : 4-dimethylpent-2-ene does not react with diethylamine and only extremely slowly with sodium methoxide; this seems to result from steric hindrance due to the *tert.*-butyl group directly adjacent to the centre of nucleophilic attack.

The reactions of $Me{\cdot}CH{:}CH{\cdot}CCl_3$ and $Ph{\cdot}CH{:}CH{\cdot}CCl_3$ with diethylamine in alcoholic media result in mixtures of the corresponding alkoxy- and diethylamino-derivatives; in the case of $Me_2C{:}CH{\cdot}CCl_3$ only alkoxy-derivatives are formed whereas under the same conditions $CH_2{:}CH{\cdot}CCl_3$ forms only diethylamino-derivatives. When the reaction with diethylamine is carried out in the absence of alcohol, $Me{\cdot}CH{:}CH{\cdot}CCl_3$ and $Ph{\cdot}CH{:}CH{\cdot}CCl_3$ react in the usual way, giving diethylamino-derivatives, whereas $Me_2C{:}CH{\cdot}CCl_3$ does not react even at 100—110°, slurrying taking place at a higher temperature. The reaction of $Me_2C{:}CH{\cdot}CCl_3$ with ammonia and piperidine in alcohol leads to negligible quantities of amino-derivatives.

The same is true of the reaction with sodium sulphide in alcoholic solution, $CCl_3{\cdot}CH{:}CH_2$ yielding only the sulphide $(CCl_2{:}CH{\cdot}CH_2)_2S$ and $CCl_3{\cdot}CH{:}CMe_2$ yielding only an alkoxy-derivative.

The results are listed in Table 2 (overleaf).

As is seen from the Table, the substances investigated can be arranged in the series $CCl_3{\cdot}CH{:}CH_2$, $CCl_3{\cdot}CH{:}CHMe$, $CCl_3{\cdot}CH{:}CHPh$, $CCl_3{\cdot}CH{:}CH{\cdot}CMe_3$, $CCl_3{\cdot}CH{:}CMe_2$, in which the ability of the compound to be alkylated on the nitrogen atom is decreasing and to be alkylated on the oxygen atom increasing.

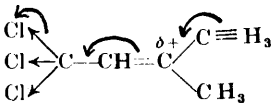
[59] P. B. D. de la Mare and C. A. Vernon, *J.*, 1952, 3325.

TABLE 2. *The action of nucleophilic reagents on* $CCl_3{\cdot}CH{:}CRR'$.

Compound	RONa in alc.	Et_2NH	Et_2NH in alc.	Na_2S in alc.
$CCl_3{\cdot}CH{:}CH_2$	O	N	N	S
$CCl_3{\cdot}CH{:}CHMe$	O	N	O and N	O and S
$CCl_3{\cdot}CH{:}CHPh$	O	N	O and N	—
$CCl_3{\cdot}CH{:}CMe_2$	O	does not substitute	O	O
$CCl_3{\cdot}CH{:}CH{\cdot}CMe_3$	O	—	O	—

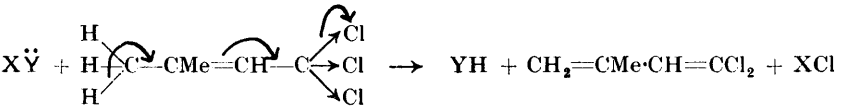
O denotes formation of $CCl_2{:}CH{\cdot}CRR'{\cdot}OR''$; N formation of $CCl_2{:}CH{\cdot}CRR'{:}NR''_2$; and S formation of $(CCl_2{:}CH{\cdot}CRR')_2S$.

If one considers the electrophilicity of the γ-carbon atom in the above series of trichloromethyl derivatives to decrease, being the least with the trichlorodimethylpropene (see *X*), then the observed relation can be explained as follows : as the electrophilicity of the γ-carbon atom decreases, the rate of reaction of alkylation of the oxygen atom increases and that of the nitrogen atom decreases. It must however be borne in mind that

X 

the initial trichloromethyl compounds being compared differ not only in their electrophilicity but also in steric hindrance at the carbon atom, the influence of each of these factors taken separately being unknown.

We now consider some other reactions of these substances.[22] The reaction of $CCl_3{\cdot}CH{:}CMe_2$ with alcoholic potassium hydroxide, diethylamine, or piperidine gives, in addition to the main product, $CCl_2{:}CH{\cdot}CMe_2X$, a small quantity of 1 : 1-dichloro-3-methylbuta-1 : 3-diene, possibly as a result of the isomerisation of the trichloromethyl compound to 1 : 1 : 3-trichloro-3-methylbut-1-ene followed by dehydrochlorination, or as a result of a direct attack of the nucleophilic reagent on the $\sigma\pi\sigma$ conjugated system, according to the scheme :



The latter suggestion is preferred for, whilst $CCl_3{\cdot}CH{:}CMe_2$ under the action of alcoholic alkali gives mainly 3-alkoxy-1 : 1-dichloro-3-methylbut-1-ene and only a little 1 : 1-dichloro-3-methylbuta-1 : 3-diene, under the same conditions $CCl_2{:}CH{\cdot}CMe_2$ is wholly converted into 1 : 1-dichloro-3-methylbuta-1 : 3-diene, which suggests that preliminary isomerisation does not take place.

The reactions of the trichloromethyl group in $Ph{\cdot}CH{:}CH{\cdot}CCl_3$ are in some respects similar to those of the same group in benzotrichloride. Thus,

the compound was hydrolysed readily when heated for 30 minutes with 90% acetic acid to give cinnamic acid in 95% yield. It is easily disproportionated when heated with chloroacetic acid, yielding chloroacetyl chloride.

The Attack of Radicals on 3 : 3 : 3-Trichloropropene.—*The rearrangement of the radical* $CCl_3{\cdot}CH{\cdot}CH_2X$ (X = Br *or* CCl_3) *in solution.*[2] When studying the addition of bromotrichloromethane and hydrogen bromide to 3 : 3 : 3-trichloropropene in the presence of benzoyl peroxide, we observed a rearrangement which we interpret [2] to be the rearrangement of the free radical. The addition of bromotrichloromethane to 3 : 3 : 3-trichloropropene in the presence of benzoyl peroxide should lead to the compound $CCl_3{\cdot}CHBr{\cdot}CH_2{\cdot}CCl_3$. Actually the reaction was more complex and yielded a number of products some of which we isolated and identified as the compounds $CCl_3{\cdot}CH_2{\cdot}CH{:}CCl_2$, $CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_2Br$, and $ClCH_2{\cdot}CHCl{\cdot}CCl_2Br$.

The formation of 1-bromo-1 : 1 : 2 : 4 : 4 : 4-hexachlorobutane can be understood when allowance is made for rearrangement in the intermediate radical $CCl_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CCl_3$. The reaction can be represented :

$$(Ph{\cdot}CO_2)_2 \longrightarrow Ph{\cdot} + CO_2 + Ph{\cdot}CO{\cdot}O{\cdot} \quad . \quad . \quad (1)$$

$$Ph{\cdot} + BrCCl_3 \longrightarrow PhBr + CCl_3{\cdot} \quad . \quad . \quad . \quad (2)$$

$$CCl_3{\cdot} + CH_2{:}CH{\cdot}CCl_3 \longrightarrow CCl_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CCl_3 \quad . \quad . \quad (3)$$

$$CCl_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CCl_3 \longrightarrow CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2{\cdot} \quad . \quad . \quad (4)$$

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2{\cdot} + BrCCl_3 \longrightarrow CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_2Br + CCl_3 \quad (5a)$$

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2{\cdot} + CH_2{:}CH{\cdot}CCl_3 \longrightarrow CCl_3{\cdot}CH_2{\cdot}CH{:}CCl_2 + ClCH_2{\cdot}\dot{C}H{\cdot}CCl_3 \quad . \quad (5b)$$

$$ClCH_2{\cdot}\dot{C}H{\cdot}CCl_3 \longrightarrow ClCH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2 \quad . \quad . \quad . \quad (6)$$

$$ClCH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2 + BrCCl_3 \longrightarrow ClCH_2{\cdot}CHCl{\cdot}CCl_2Br + CCl_3{\cdot} \quad (7)$$

$$2CCl_3{\cdot} \longrightarrow C_2Cl_6 \quad . \quad . \quad . \quad . \quad (8)$$

It will be seen that step (4) suggests isomerisation of the radical $CCl_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CCl_3$ to $CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}\dot{C}Cl_2$. An alternative apparent mechanism would have consisted in the phenyl radical, formed during the decomposition of the peroxide, reacting not with bromotrichloromethane but with trichloropropene and abstracting the labile chlorine from the trichloromethyl group according to the scheme :

$$CH_2{:}CH{\cdot}CCl_3 + Ph{\cdot} \longrightarrow CH_2{:}CH{\cdot}\dot{C}Cl_2 + PhCl$$

giving rise to the radical $CH_2{:}CH{\cdot}CCl_2{\cdot}$, which could have been the starting point for the same products as the first mechanism.

In a special study of the decomposition of a 50 g. sample of benzoyl peroxide in a mixture of bromotrichloromethane and trichloropropene, bromobenzene was the only halogenobenzene formed ; that is, the phenyl radical takes up bromine from bromotrichloromethane, which result definitely indicates against the second reaction mechanism.

The structure of the pentachlorobutane has been confirmed by its hydrolysis to succinic acid. The structure of the bromohexachlorobutane as

1-bromo-1 : 1 : 2 : 4 : 4 : 4-hexachlorobutane has been indicated by the reactions :

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_2Br \xrightarrow{H_2SO_4} HO_2C{\cdot}CH{:}CH{\cdot}CO_2H$$

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_2Br \xrightarrow{KOH} CCl_2{:}CH{\cdot}CCl{:}CCl_2$$

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_2Br \xrightarrow{Zn} CCl_3{\cdot}CH_2{\cdot}CH{:}CCl_2 \longrightarrow HO_2C{\cdot}[CH_2]_2{\cdot}CO_2H$$

The structure of 1-bromo-1 : 1 : 2 : 3-tetrachloropropane was proved by its conversion by the action of alcoholic alkali into $ClCH_2{\cdot}CCl{:}CCl_2$, which was identified as the known 1 : 1 : 2-trichloro-3-diethylaminoprop-1-ene hydrochloride.

When hydrogen bromide is added to 3 : 3 : 3-trichloropropene in the presence of benzoyl peroxide there is a ready formation in good yield of a product, $C_3H_4Cl_3Br$, which proved to be 3-bromo-1 : 1 : 2-trichloropropane. This could also have been formed by isomerisation of the intermediate radical :

$$Br + CH_2{:}CH{\cdot}CCl_3 \longrightarrow BrCH_2{\cdot}\dot{C}H{\cdot}CCl_3 \longrightarrow BrCH_2{\cdot}CHCl{\cdot}CCl_2{\cdot}$$

$$BrCH_2{\cdot}CHCl{\cdot}CCl_2{\cdot} + HBr \longrightarrow BrCH_2{\cdot}CHCl{\cdot}CHCl_2 + Br$$

Dechlorination of the compound with alcoholic alkali at 0° is accompanied by removal of hydrogen bromide to form a compound, b.p. 126—127°, $n_D^{20} = 1{\cdot}4840$, $d_4^{20} = 1{\cdot}3843$ (Found, MR 30·07; calc. for $C_3H_3Cl_3$, MR 30·18).

The resulting trichloropropene differs in physical constants from the four known of the six possible trichloropropenes. The two unknown trichloropropenes have the structure $CH_2{:}CCl{\cdot}CHCl_2$ and $CHCl{:}CH{\cdot}CHCl_2$.

The trichloropropene obtained was ozonised and the ozonide decomposed by water without further oxidation to yield an acid (b.p. 92—94°/13 mm.; dichloroacetic acid has b.p. 91—92°/12 mm.) which was converted through the chloride into the anilide, m.p. 116—117°. The mixture with αα-dichloroacetanilide melted at 116·5—117°. Thus, the trichloropropene had the structure $CH_2{:}CCl{\cdot}CHCl_2$, and the parent bromotrichloropropane would seem to be $CH_2Br{\cdot}CHCl{\cdot}CHCl_2$.

Such behaviour of the trichloromethyl group adjacent to the carbon atom carrying a free valency is formally similar to its behaviour in the dehydration of 1 : 1 : 1-trichloropropan-2-ol, which proceeds with rearrangement and formation of 1 : 1 : 2-trichloroprop-1-ene. The reaction can be represented by a cationic rearrangement :

$$CCl_3{\cdot}CH(OH){\cdot}CH_3 \longrightarrow CCl_3{\cdot}\overset{+}{C}H{\cdot}CH_3 \longrightarrow \overset{+}{C}Cl_2{\cdot}CHCl{\cdot}CH_3 \longrightarrow CCl_2{:}CCl{\cdot}CH_3$$

Other reactions of 3 : 3 : 3-*trichloropropene of homolytic type.*[7] When butylmagnesium bromide reacts either with 3 : 3 : 3-trichloropropene or with 1 : 1 : 3-trichloroprop-1-ene the main product is 1 : 1-dichlorohept-1-ene, the structure of which has been proved by hydrolysis to heptanoic acid. When the reaction was carried out with phenylmagnesium bromide, in addition to 1 : 1-dichloro-3-phenylprop-1-ene some diphenyl was produced. It is to be noted that these reactions, as is usually the case with

homolytic reactions, proceed with formation of a number of other products, not investigated in detail. These reactions can be represented by the following scheme:

$$2RMgX \longrightarrow R{\cdot}R + 2MgX \quad . \quad . \quad . \quad (1)$$

$$CH_2{:}CH{\cdot}CCl_3 + MgX \longrightarrow CH_2{:}CH{\cdot}\dot{C}Cl_2 + MgXCl \quad . \quad (2)$$

$$CH_2{:}CH{\cdot}\dot{C}Cl_2 + RMgX \longrightarrow R{\cdot}CH_2{\cdot}CH{:}CCl_2 + MgX \quad . \quad (3)$$

Under the action of Raney nickel in ethanol 3 : 3 : 3-trichloropropene yielded a tetrachlorohexadiene which apparently has the structure $[CCl_2{:}CH{\cdot}CH_2]_2$ since, when hydrolysed in the presence of concentrated sulphuric acid, it gave adipic acid, though in a low yield.

Thus, reactions which are likely to be homolytic also proceed with 1 : 1 : 3-trichloroprop-1-ene at the expense of allylic chlorine and in the case of 3 : 3 : 3-trichloropropene with allylic rearrangement.[7]

Consequently, in homolytic reactions 3 : 3 : 3-trichloropropene appears to undergo two types of rearrangement: (*a*) allylic and (*b*) with shift of a chlorine atom from the trichloromethyl group to the adjacent carbon atom. One may suppose the type of rearrangement to depend on the mechanism of the reaction. Reaction with allylic rearrangement takes place when the radical attacks the trichloromethyl group and that with chlorine shift when the radical attacks the methylene group.

The Electrophilic Reagent Attack on 3 : 3 : 3-Trichloropropene.—*Friedel–Crafts catalysts.*[1, 3] Under ordinary conditions 3 : 3 : 3-trichloropropene is not in tautomeric equilibrium with its allylic isomer, 1 : 1 : 3-trichloroprop-1-ene. Small quantities of such electrophilic reagents as aluminium chloride, ferric chloride, and antimony pentachloride produce isomerisation of 3 : 3 : 3-trichloropropene to 1 : 1 : 3-trichloroprop-1-ene. This isomerisation induced by the action of, *e.g.*, aluminium chloride can be represented:

$$CH_2{:}CH{\cdot}CCl_3 + AlCl_3 \longrightarrow (CH_2{:}CH{\cdot}CCl_2)^+AlCl_4^- \longrightarrow Cl{\cdot}CH_2{\cdot}CH{:}CCl_2 + AlCl_3$$

The reverse isomerisation of 1 : 1 : 3-trichloroprop-1-ene to 3 : 3 : 3-trichloropropene is unknown.

The reaction of compounds $CCl_3{\cdot}CH{:}CRR'$ *with aromatic compounds in the presence of aluminium chloride.* 3 : 3 : 3-Trichloropropene condenses extremely readily with benzene in the presence of small quantities of aluminium chloride at 0—5°, giving in good yield a product of the composition $C_6H_5{\cdot}C_3H_3Cl_2$, b.p. 93—94°/6 mm., $n_D^{20} = 1{\cdot}5490$, $d_4^{20} = 1{\cdot}2032$ (Found, MR 49·45; calc., MR 49·43). In the presence of aluminium chloride the reaction has thus proceeded with allylic rearrangement, and the product has the structure $PhCH_2{\cdot}CH{:}CCl_2$. Indeed, the reaction of benzene with 1 : 1 : 3-trichloroprop-1-ene under the same conditions yielded the same product.[1, 3] Hydrolysis of this substance with 70% perchloric acid gave β-phenylpropionic acid.[25d] This reaction may be of interest as a synthetical method permitting the introduction into the aromatic molecule of the reactive grouping $CH_2{\cdot}CH{:}CCl_2$, which. in particular, is readily

converted into the propionic acid residue. Two of us in collaboration with N. A. Semenov have investigated the reaction of 3 : 3 : 3-trichloropropene with chlorobenzene, bromobenzene, anisole, phenol, aniline, and methyl- and dimethyl-aniline.[20a, b]

Bromobenzene and chlorobenzene react violently with 3 : 3 : 3-trichloropropene in the presence of aluminium chloride with evolution of heat, the main products being 3-*p*-bromophenyl- and 3-*p*-chlorophenyl-1 : 1-dichloroprop-1-ene, respectively. The structure of these products has been proved by hydrolysing them with concentrated sulphuric acid, giving in good yield *β*-*p*-bromophenyl- and *β*-*p*-chlorophenyl-propionic acid. 1 : 1-Dichloro-3-*p*-chlorophenylprop-1-ene and 3-*p*-bromophenyl-1 : 1-dichloroprop-1-ene add chlorine yielding 1 : 1 : 1 : 2-tetrachloro-3-*p*-chlorophenylpropane and 3-*p*-bromophenyl-1 : 1 : 1 : 2-tetrachloropropane. Anisole and phenol react less readily with 3 : 3 : 3-trichloropropene in the presence of aluminiun chloride than do chloro- and bromo-benzene, requiring several hours at 80—90° to bring the reaction to completion. Anisole gave 1 : 1-dichloro-3-*p*-methoxyphenylprop-1-ene, the structure being ascertained by oxidation with 5% potassium permanganate solution to anisic acid. 3 : 3 : 3-Trichloropropene condenses with phenols when heated, even in the absence of aluminium trichloride ; it is better, however, to carry out the reaction in the presence of aluminium chloride, obtaining a mixture of 1 : 1-dichloro-3-*o*- and 1 : 1-dichloro-3-*p*-hydroxyphenylprop-1-ene. The structure of these compounds has been proved by alkylating them with dimethyl sulphate to the corresponding methoxyphenyl compounds, which were oxidised to *o*-methoxybenzoic acid and anisic acid, respectively. Hydrolysis of 1 : 1-dichloro-3-*p*-methoxyphenylprop-1-ene with concentrated sulphuric acid yielded sulphonated *β*-*p*-methoxyphenylpropionic acid, obtained as barium salt. The reaction of 3 : 3 : 3-trichloropropene with aqueous sodium phenoxide gave products of both *C*- and *O*-alkylation, resulting in a mixture of 1 : 1-dichloro-3-*o*-, 1 : 1-dichloro-3-*p*-hydroxyphenylprop-1-ene, and 1 : 1-dichloro-3-phenoxyprop-1-ene. The same products were obtained when the above mentioned aromatic compounds reacted with 1 : 1 : 3-trichloroprop-1-ene but the reaction then proceeded less readily and the yields were lower than with the reaction with 3 : 3 : 3-trichloropropene.

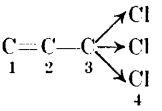
Such trichloromethyl derivatives as CCl_3·CH:CHMe, CCl_3·CH:CHPh, and CCl_3·CH:CMe_2 also condense with benzene in the presence of aluminium chloride, yielding the compounds Ph·CHMe·CH:CCl_2, Ph_2CH·CH:CCl_2, and Ph·CMe_2·CH:CCl_2.[22] The structure of the last was proved by oxidising it with potassium permanganate to *αα*-dimethylphenylacetic acid.

Chlorination of 3 : 3 : 3-*trichloropropene in acids.*[18] As distinct from the reactions of 3 : 3 : 3-trichloropropene with electrophilic reagents we have just discussed, the conjugated addition of chlorine to 3 : 3 : 3-trichloropropene in glacial acetic and concentrated sulphuric acid proceeds, as has been already shown (p. 331), without isomerisation, yielding, in addition to 1 : 1 : 1 : 2 : 3-pentachloropropane, 2 : 3 : 3 : 3-tetrachloropropyl sulphate and acetate. Hydrolysis of these esters gave 2 : 3 : 3 : 3-tetrachloropropanol.

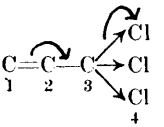
In this case absence of isomerisation may be due to the fact that it was

not the trichloromethyl group that has been subjected to electrophilic attack but the carbon atom situated in the centre of the chain.

Conclusions.—The investigation of the reactivity of compounds involving the system of linkages shown in (*A*) toward nucleophilic, electrophilic, and radical reagents has thus shown these reactions to proceed with rearrangements in all cases when one can assume that the first or the fourth atom



(*A*)



(*B*)

of the chain is subjected to the attack. If the central atoms of this system are attacked, there is no rearrangement. These relations demonstrate strikingly the occurrence of $\sigma\pi$ conjugation in the system, which can be represented as in (*B*). Because of the screening of the carbon atom of the trichloromethyl group, the only centre for nucleophilic attack in this particular system is at the first atom, which is supplied along the chain of $\sigma\pi$ conjugation with electrophilicity from the carbon atom of the trichloromethyl group; reaction of nucleophilic reagents with compounds of this type therefore always proceeds with allylic rearrangement. Depending on the character of the reagent, electrophilic attack can take place either at the second or the fourth atom of the system. The second atom being attacked, reactions proceed without isomerisation; when the fourth atom is attacked there is allylic rearrangement.

Radical reagents, when attacking the first atom of the system, cause rearrangement with shift of chlorine from the trichloromethyl group to the adjacent carbon atom. Attack on the fourth atom leads to allylic rearrangement.

Reactions of the 2 : 2-Dichlorovinyl Group

Compounds containing the 2 : 2-dichlorovinyl group (CCl_2:CH·) are now readily available. They may be produced by dehydrochlorination of $\alpha\alpha\alpha$-trichloroalkanes and $\alpha\alpha\alpha\omega$-tetrachloroalkanes (see p. 334) as well as by the action of Grignard reagent on 3 : 3 : 3- or 1 : 3 : 3-trichloropropene. Compounds of the type CCl_2:CH·CHCl·OR are readily prepared by dehydrochlorination of the products of the addition of carbon tetrachloride to alkyl vinyl ethers,[10, 60, 61] and compounds of the type CCl_2:CH·CRR′:X by both nucleophilic and some other reagent attack on the compounds CCl_3·CH:CRR′ (see p. 341), as well as in other ways.

Hydrolysis.—Hydrolysis of compounds containing the 2 : 2-dichlorovinyl group with concentrated sulphuric acid yields carboxylic acids. This reaction is carried out under similar conditions to the hydrolysis of the trichloromethyl group. In contrast with the action of fuming nitric acid

[60] S. A. Glickman, U.S.P. 2,560,219.
[61] E. Lewas and E. Lewas, *Compt. rend.*, 1950, **230**, 1670.

on the trichloromethyl group,[15] this acid acts on 2 : 2-dichlorovinyl compounds to yield neutral nitrogenous compounds. Hot 70% perchloric acid hydrolyses the dichlorovinyl group as has been shown by two of us in collaboration with Ye. J. Vasil'eva by obtaining ω-chlorovaleric and 7-chloroheptanoic acid from 1 : 1 : 5-trichloropent-1-ene and 1 : 1 : 7-trichlorohept-1-ene. The reaction is, however, accompanied by slurrying and gives moderate yields. 1 : 1-Dichloro-3-phenylprop-1-ene and 70% perchloric acid yield β-phenylpropionic acid. Since hydrolysis of aromatic compounds containing the trichloromethyl or dichlorovinyl group by sulphuric acid is often accompanied by nuclear sulphonation, hydrolysis of such compounds with perchloric acid is of some preparatory value.[25d]

Oxidation.[25a]—Compounds containing the 2 : 2-dichlorovinyl group evolve hydrogen chloride on storage and acquire a strong pungent odour but, if a little quinol is added, the compounds do not undergo decomposition. It is thus evident that dichloroalkenes gradually oxidise when stored. A number of dichloroalkenes having been saturated with oxygen at 100—110° furnished acids in 40—50% yield : α-chlorovaleric acid from 1 : 1-dichloropent-1-ene, $\alpha\delta$-dichlorovaleric acid from 1 : 1 : 5-trichloropent-1-ene, and 2 : 7-dichloroheptanoic acid from 1 : 1 : 7-trichlorohept-1-ene.

The oxidation by oxygen of compounds containing the dichlorovinyl group is already known, as illustrated by several simple instances, to give dichloro-carboxylic acids.[62]

Chlorination.[14, 18]—In collaboration with V. N. Kost we have shown that addition of chlorine to the double bond of the compounds $CCl_2{:}CH{\cdot}[CH_2]_n{\cdot}Cl$ and $CCl_2{:}CH{\cdot}[CH_2]_n{\cdot}CH_3$ in a neutral medium is usually accompanied by a varying amount of chlorination of the saturated part of the molecule. We have studied the reaction between chlorine and compounds of the structure $CCl_2{:}CX{\cdot}CH_2Y$, where X = H or Cl and Y = Et,[14] OMe,[14] NEt_2,[14] NO_2,[14] CN,[7] or CO_2H,[7] in mild conditions at 0—5° in carbon tetrachloride. Compounds having Y = Ph, NO_2, CN, or CO_2H have been found to add chlorine smoothly according to the scheme :

$$CCl_2{:}CX{\cdot}CH_2Y + Cl_2 \longrightarrow CCl_3{\cdot}CXCl{\cdot}CH_2Y$$

But with compounds in which Y = OMe or NEt_2 the reaction is accompanied by an energetic evolution of hydrogen chloride indicating that the saturated part of the molecule is undergoing chlorination.[14] Thus, chlorination in the dark of 1 : 1-dichloro-3-methoxyprop-1-ene under the mildest conditions produces a pentachloro-derivative, b. p. 81–82°/1·5 mm., $n_D^{20} = 1{\cdot}5070$, $d_4^{20} = 1{\cdot}5713$ (Found, MR 46·66 ; calc. for $C_4H_5OCl_5$, MR 46·65). This compound, when heated in methyl alcohol in the presence of hydrochloric acid, gave 2 : 3 : 3 : 3-tetrachloropropan-1-ol in 92% yield, identified by the melting point of its mixture with an authentic sample. Consequently, the structure of the pentachloride obtained can be represented as [18] $CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}CH_2Cl$.

The previously suggested [14] substitution of chlorine for allylic hydrogen does not take place in this case under the conditions studied.

[62] F. W. Kirkbride, U.S.P. 2,292,129 ; G.P. 391,674.

The same 1 : 1 : 1 : 2-tetrachloro-3-chloromethoxypropane has also been obtained according to the scheme : [18]

$$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH \xrightarrow[HCl]{CH_2O} CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}CH_2Cl$$

and then had b.p. 81—82°/1·5 mm., $n_D^{20} = 1{\cdot}5065$, $d_4^{20} = 1{\cdot}5711$.

The reaction between chlorine and 1 : 1 : 5-trichloropent-1-ene, 1 : 1-dichloro-5-cyanopent-1-ene, and 1 : 1-dichloro-7-cyanohept-1-ene at 0—15° in chloroform also proceeds with strong evolution of hydrogen chloride and formation of a mixture of products.[18] In all cases, it has proved possible to suppress chlorination of the saturated part of the molecule by carrying out the chlorination in a mixture of ether and concentrated hydrochloric acid, simultaneously saturated with chlorine and hydrogen chloride.[14, 18] It will be recalled that diallyl ether, allyl alcohol, allyl acetate, and allyl benzoate are already known [63] to add chlorine smoothly in hydrochloric acid.

Chlorination of Compounds containing the 2 : 2-Dichlorovinyl Group in Sulphuric Acid. A New Synthesis of α-Chloro-carboxylic Acids.[17, 18]— Direct chlorination of carboxylic and ω-chloro-carboxylic acids in the presence of catalysts yields a number of corresponding α-chloro- and αω-dichloro-carboxylic acids. The method for obtaining αδ-dichlorovaleric acid by chlorination of δ-chlorovaleric acid has, in particular, been described.[64] But chlorination at the α-position to the carboxy-group necessitates relatively vigorous heating to 120—150°, and often leads to isomeric chloro-acids as well as to formation of by-products. Direct chlorination of dicarboxylic acids usually gives a mixture of products difficult to separate.

One of us and Ye. J. Vasil'eva,[15] using 1 : 1 : 1 : 2 : 5-pentachloropentane, have shown compounds containing the $CCl_3{\cdot}CHCl{\cdot}$ group and not hydrolysed by concentrated sulphuric acid to be smoothly hydrolysed by fuming nitric acid to the corresponding α-chloro-carboxylic acids. The synthesis of αααβ-tetrachloro-derivatives from trichloromethyl derivatives involves a two-step process, the first step consisting of dehydrochlorination of the trichloromethyl derivative to 1 : 1-dichloroalk-1-enes, the second in chlorination of the 1 : 1-dichloroalk-1-enes. Though the simple conditions for carrying out, in a high yield, both the dehydrochlorination [4] and chlorination [17] have been found, we thought it advisable to look for a means of direct conversion of 1 : 1-dichloroalk-1-enes into α-chloro-carboxylic acids.

Two of us and V. N. Kost [17] have worked out a new synthesis of chloro-carboxylic acids by chlorinating 1 : 1-dichloroalk-1-enes in 92—93% sulphuric acid at 0—20°. The reaction is accompanied by evolution of hydrogen chloride. After the reaction mixture has been decomposed by water, α-chloro-carboxylic acids are obtained in high yield. In this way we obtained αγ-dichlorovaleric, α-chlorovaleric, 2 : 7-dichloroheptanoic, and 2-chloroheptanoic acid, starting from 1 : 1 : 5-trichloropent-1-ene, 1 : 1-dichloropent-1-ene, 1 : 1 : 7-trichlorohept-1-ene, and 1 : 1-dichlorohept-1-ene, respectively.[17] For the synthesis of these starting products see ref. 4.

[63] H. Ing, *J.*, 1948, 1393.

[64] R. Gaudry and L. Berlinquet, *Canad. J. Res.*, 1949, **27**, *B*, 282.

In some cases we observed, as side reaction, the addition of chlorine to the double bond, but the separation of α-chloro-carboxylic acids from these neutral products presented no difficulty.

The reaction proved to be applicable to the synthesis of α-chloro-dicarboxylic acids.[17] Thus, from 6 : 6-dichlorohexen-5-oic, 7 : 7-dichloro-hept-6-enoic, and 8 : 8-dichloro-oct-7-enoic acid were obtained in a good yield α-chloroadipic, α-chloropimelic, and α-chlorosuberic acid, respectively. For the syntheses of the initial acids see ref. 12.

It is to be noted that under the conditions of this reaction at 0—20° there is no hydrolysis of the dichlorovinyl group to carboxylic acid.

When the reaction is carried out at a higher temperature or in more dilute sulphuric acid, the yield of α-chloro-carboxylic acid drops. Thus, at 30—40°, hydrolysis of the dichlorovinyl group is rather pronounced whilst when chlorination takes place in 70% sulphuric acid only the product of addition of chlorine to the double bond is formed.[18]

The mild conditions of the reaction enable one to obtain α-chloro-carboxylic acids with a variety of substituents. In particular, under the action of chlorine on 1 : 1 : 5 : 5 : 5-pentachloropent-1-ene in concentrated sulphuric acid at 20—25° the trichloromethyl group is retained, 2 : 5 : 5 : 5-tetrachloropentanoic acid being formed.[18] The reaction is presumed to pass through the intermediate formation of compounds of the type, $R{\cdot}[CH_2]_n{\cdot}CHCl{\cdot}CCl_2{\cdot}O{\cdot}SO_3H$. Reactions of this type are well known.[33, 65]

A. J. Titov and F. L. Maklyayev [33] have recently shown that reaction of chlorine with olefins in concentrated mineral acids produces α-chloro-esters, according to the scheme :

$$R{\cdot}CH{:}CH_2 + Cl_2 + HA \longrightarrow ClCH_2{\cdot}CHRA + HCl$$

where A = SO_3H, H_2PO_3, etc.

The reactions investigated allowed us to show that compounds containing the 2 : 2-dichlorovinyl group are also liable to undergo conjugated addition.

Action of Sodium on Compounds containing the 2 : 2-Dichlorovinyl Group. Synthesis of Monosubstituted Acetylenes.—Pinner [66, 67] was the first to investigate the action of sodium on the unsymmetrical dichlorovinyl group, as exemplified by 1 : 1-dichloroprop-1-ene. He demonstrated that decomposition with water of the product of the reaction of 1 : 1-dichloro-prop-1-ene and sodium gave methylacetylene [67] in low yield, and, under the action of carbon dioxide, propiolic acid.[68] Pinner suggested that the initial product was $C_3H_4Cl_2Na_2$ and that the reaction took the following course :

$$CH_3{\cdot}CH{:}CCl_2 + 2Na \longrightarrow C_3H_4Cl_2Na_2 \xrightarrow{H_2O} CH_3{\cdot}C{\equiv}CH + 2NaCl$$

The reaction has not been further investigated.

It appeared to us of interest to investigate the reaction as a preparative

[65] C. K. Ingold, " Structure and Mechanism in Organic Chemistry ", Cornell, 1953.
[66] A. Pinner, *Annalen*, 1875, **179**, 49.
[67] *Idem*, *Ber.*, 1875, **8**, 1282.
[68] *Idem*, *ibid.*, 1881, **14**, 1081.

route as well as to elucidate the mechanism of the conversion of the dichlorovinyl into the ethynyl group. In accordance with existing data it has been found that, when treated with carbon dioxide, the product of the reaction of 1 : 1-dichloropent-1-ene with sodium results in pentynecarboxylic acid, and the action of benzaldehyde on the product of the reaction of 1 : 1-dichloro-5-diethylaminopent-1-ene and sodium leads to 6-diethylamino-1-hydroxy-1-phenylhex-2-yne. These findings clearly show that the product of the reaction of a dichlorovinyl derivative with sodium contains $RC{\equiv}CNa$ and that the dichlorovinyl group gives up two chlorine atoms and one hydrogen atom. It is quite obvious that chlorine is eliminated as sodium chloride. It was found that in the course of the reaction only a negligible amount of hydrogen is eliminated (2—5%) and that only when the product is decomposed with water is the necessary amount of hydrogen liberated (0·5 mol.). Also, one must use 4 g.-atoms of sodium per mole of dichlorovinyl derivative in contradistinction to the 2 g.-atoms suggested by Pinner. These results can be explained on the assumption that the hydrogen from the dichlorovinyl group is taken up as sodium hydride, and the reaction of the dichlorovinyl derivative with sodium can then be represented by the equation:

$$R{\cdot}CH{:}CCl_2 + 4Na \longrightarrow R{\cdot}C{\equiv}CNa + NaH + 2NaCl$$

Confirmation of this suggestion is seen in the formation of some monosubstituted acetylenes and sodium and lithium hydrides, in some reactions of sodium or lithium with monohalogeno-olefins, $R{\cdot}CH{:}CHX$.[69, 70] The substitution of sodium for chlorine in $R{\cdot}C{\equiv}C{\cdot}Cl$ takes place extremely readily.[71] Investigation of the action of sodium on dichlorovinyl derivatives has shown the reaction to proceed smoothly and in most investigated cases to produce monosubstituted acetylenes in 40—80% yield. Data for monosubstituted acetylenes so produced are listed in Table 9. With *ββ*-dichlorostyrene we have not been able to obtain a good yield of phenylacetylene because of failure to bring the reaction to completion. With dichlorostyrene a mixture of products, consisting mainly of phenylallene, $Ph{\cdot}CH{:}C{:}CH_2$, has been obtained.

1 : 1 : 3-Trichloro-5-diethylaminopent-1-ene being taken as example, the trichlorovinyl group has been converted into the ethynyl group by the action of sodium:

$$Et_2N{\cdot}[CH_2]_3{\cdot}CCl{:}CCl_2 + 4Na \longrightarrow Et_2N{\cdot}[CH_2]_3{\cdot}C{\equiv}CH + 3NaCl$$

The yield of 5-diethylaminopent-1-ene is good. 5-Ethoxypent-1-ene, as the bromomagnesium derivative, and benzaldehyde gave 1-hydroxy-1-phenyl-6-ethoxyhex-2-yne in a good yield.

The Action of Alkali on ββ-Dichloroacraldehyde Acetals.[21] Synthesis of Chloropropiolaldehyde Acetals.—3-Alkoxy-1 : 1 : 1 : 3-tetrachloropropanes are easily obtained by the reaction of carbon tetrachloride and alkyl vinyl ethers in the presence of radical initiators. 3-Alkoxy-1 : 1 : 1 : 3-tetrachloropropanes at 130—150° readily lose hydrogen chloride and give in

[69] A. Kirrmann, *Compt. rend.*, 1925, **181**, 671.
[70] E. A. Braude and J. A. Coles, *J.*, 1950, 179.
[71] R. Truchet, *Ann. Chim.*, 1931, **16**, 349.

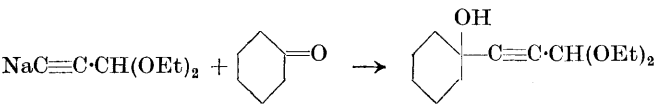
high yield 3-alkoxy-1 : 1 : 3-trichloroprop-1-ene. These with an equivalent amount of the appropriate sodium alkoxide in alcohol in the cold result in $\beta\beta$-dichloroacraldehyde acetals which are converted, without isolation from the reaction mixture, by hot potassium hydroxide into chloropropiolaldehyde acetals, as represented by the scheme :

$$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}OR \longrightarrow CCl_2{:}CH{\cdot}CHCl{\cdot}OR \longrightarrow CCl_2{:}CH{\cdot}CH(OR)_2 \longrightarrow CCl{\equiv}C{\cdot}CH(OR)_2$$

The diethyl and dibutyl acetals of chloropropiolaldehyde are liquids, stable when stored and distilling *in vacuo* without decomposition. Sodium is readily substituted for chlorine in these acetals by the action of sodium in ether, to give sodiopropiolaldehyde acetals.

$$CCl{\equiv}C{\cdot}CH(OR)_2 + 2Na \longrightarrow NaC{\equiv}C{\cdot}CH(OR)_2 + NaCl$$

Sodiopropiolaldehyde acetals enter into the usual reaction with carbonyl compounds, *e.g.*, with *cyclo*hexanone :



and can also be alkylated, *e.g.*, by dimethyl sulphate :

$$NaC{\equiv}C{\cdot}CH(OBu)_2 + (MeO)_2SO_2 \longrightarrow CMe{\cdot}C{\equiv}C{\cdot}CH(OCBu)_2$$

Organomagnesium compounds and diethyl and dibutyl acetals of chloropropiolaldehyde do not react, as one might have expected, at the acetal group but mainly at the chlorine atom to form the acetals of substituted propiolaldehydes :

$$ClC{\equiv}C{\cdot}CH(OR)_2 + R'MgX \longrightarrow R'C{\equiv}C{\cdot}CH(OR)_2$$

This reaction takes place with both aliphatic and aromatic organomagnesium compounds ; we have studied the action of organomagnesium compounds of the following bromine derivatives : n-C_3H_7Br, i-C_3H_7Br, n-C_4H_9Br, i-C_4H_9Br, n-$C_6H_{13}Br$, n-$C_9H_{19}Br$, PhBr, and α-$C_{10}H_7Br$. The reaction was carried out by adding the organometallic compound to an ethereal solution of chloropropiolaldehyde acetal, the heat of reaction being sufficient to maintain boiling.

The yields in the cases investigated were 50—70% of theory. Data concerning the products are summarised in Table 9. Proof of the structure of the products is exemplified by butylpropiolaldehyde diethyl acetal, which was hydrogenated to heptanal diethyl acetal, the latter being identified as heptanal 2 : 4-dinitrophenylhydrazone.

Allylic Rearrangements in the Series of Polychlorobutyl Acids and some Mistakes made by Auwers and Wissebach [72, 52]

In collaboration with V. N. Kost [8] we have examined the relationship of the acids $CHCl_2{\cdot}CH{:}CH{\cdot}CO_2H$ and $CCl_2{:}CH{\cdot}CH_2{\cdot}CO_2H$ and that of their derivatives ; *i.e.* the relationship of the prototropic allylic rearrangement.

[72] K. Auwers and H. Wissebach, *Ber.*, 1923, **56**, *B*, 715.

There are two $\gamma\gamma$-dichlorocrotonic acids described in the literature, one, m.p. 42—43°, obtained by Auwers and Wissebach [72, 52] by the reduction of $\gamma\gamma\gamma$-trichlorocrotonic acid (see also ref. 73) and the other, m.p. 101—102°, obtained from dichloroacetaldehyde and malonic acid.[74]

It was decided to prepare the hitherto unknown 4 : 4-dichlorobut-3-enoic acid by mildly hydrolysing its nitrile, obtained by action of cuprous cyanide on 1 : 1 : 3-trichloroprop-1-ene :

$$CCl_2{:}CH{\cdot}CH_2Cl + CuCN \longrightarrow CCl_2{:}CH{\cdot}CH_2{\cdot}CN \longrightarrow CCl_2{:}CH{\cdot}CH_2{\cdot}CO_2H$$

Both 3 : 3 : 3- and 1 : 1 : 3-trichloroprop-1-ene give the same 1 : 1-dichloro-3-cyanoprop-1-ene when treated with cuprous cyanide,[7] the yields being high. The identity of both products has been proved by their yielding the same crystalline tetrachloride (mixed melting point) on addition of chlorine. The unsaturated nitrile is proved to be 1 : 1-dichloro-3-cyanoprop-1-ene by hydrolysing it to succinic acid. The crystalline tetrachloride was proved to be $\beta\gamma\gamma\gamma$-tetrachlorobutyronitrile by obtaining trichlorocrotononitrile when it was dehydrochlorinated with alcoholic alkali.[7]

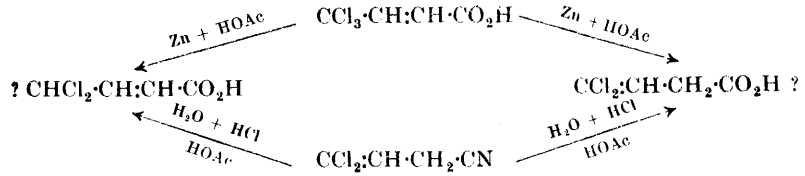
The nitrile [8] was hydrolysed to dichlorobut-3-enoic acid by heating it with a 2 : 1 : 1 mixture of acetic acid, concentrated hydrochloric acid, and water.

The 4 : 4-dichlorobutenoic acid obtained melts at 42—43°, just as does the acid described by Auwers and Wissebach as $\gamma\gamma$-dichlorocrotonic. A mixture of our acid and that obtained by following Auwers and Wissebach's method had the same melting point. The products of chlorine and bromine addition to acids which had been synthesised following both methods also proved identical, as shown by the absence of depression of the melting point of mixtures. As evidence that the acid that has been obtained by both routes has the 4 : 4-dichlorobut-3-enoic acid structure is the fact that, according to Auwers and Wissebach, its esters do not exhibit any exaltation of the molecular refraction, and its hydrolysis in the presence of concentrated sulphuric acid gives succinic acid. On the other hand, the suggestion is opposed by the reduction of the acid with sodium amalgam to crotonic acid, which was effected by Auwers and Wissebach.[52] The point at issue is the more entangled by Auwers and Wissebach's having also obtained from their acid through the acid chloride an amide and a nitrile with constants differing from those of 4 : 4-dichlorobut-3-enonitrile and exhibiting an exaltation of the molecular refraction. The repetition of the syntheses of these derivatives according to the procedure of these authors, starting from the acids obtained in both ways, gave the same acid chloride, amide, and nitrile, notwithstanding the origin of the parent acid ; but only the constants for the acid chloride agreed fully with those given by Auwers and Wissebach, those of the amide and nitrile being different.

As the structure of the starting materials for the syntheses of the unsaturated dichloro-acid by both methods has been proved (the structure of $\gamma\gamma\gamma$-trichlorocrotonic acid by its acid hydrolysis to furmaric acid, that

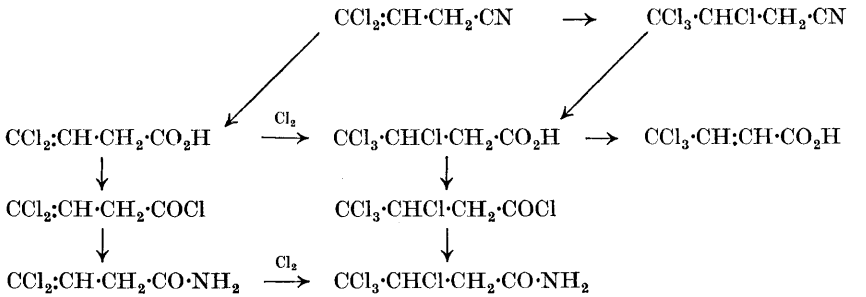
[73] G. Braun, *J. Amer. Chem. Soc.*, 1930, **52**, 3172.
[74] G. W. Deodhar, *J. Indian Chem. Soc.*, 1934, **11**, 83.

of 4 : 4-dichlorobut-3-enonitrile by its acid hydrolysis to succinic acid), one has to assume that one and the same acid could have been obtained only by rearrangement or in the reduction of trichlorocrotonic acid, or in the hydrolysis of the nitrile, as is represented by the following scheme :



The answer has been found in the following correlation. On the one hand, the addition of chlorine to 4 : 4-dichlorobut-3-enonitrile gave $\beta\gamma\gamma\gamma$-tetrachlorobutyronitrile and then, in the usual way, the corresponding acid, acid chloride, and amide. During the first step of these changes isomerisation is hardly likely, in the other ones it is impossible. The structure of tetrachlorobutyric acid has been proved by dechlorination to $\gamma\gamma\gamma$-trichlorocrotonic acid, identical with that described by Auwers and Wissebach and of unambiguous structure, this excluding the possibility of any isomerisation taking place in the first step as well.

On the other hand, the unsaturated dichloro-acid investigated, obtained by acid hydrolysis of the 4 : 4-dichlorobut-3-enonitrile, was converted into acid chloride, amide, and nitrile, the last having been found to be identical with the parent nitrile. The addition of chlorine to this acid, its amide, and nitrile resulted in compounds identical with $\beta\gamma\gamma\gamma$-tetrachlorobutyric acid and its derivatives, described above. The results are correlated as follows :



and show that the above-mentioned acid has the structure 4 : 4-dichlorobut-3-enoic acid, no isomerisation taking place either when it is being produced from nitrile or undergoing other changes indicated in the above scheme.

Hence, the reduction of $\gamma\gamma\gamma$-trichlorocrotonic acid by zinc and glacial acetic acid in ethyl alcohol does not lead to $\gamma\gamma$-dichlorocrotonic acid as has been presumed by Auwers and Wissebach, but results in 4 : 4-dichlorobut-3-enoic acid, that is, the reduction takes place with rearrangement :

$$CCl_3{\cdot}CH{:}CH{\cdot}CO_2H \xrightarrow{Zn-HOAc} CCl_2{:}CH{\cdot}CH_2{\cdot}CO_2H$$

Dichlorobutenoic acid does not undergo further reduction under the same conditions.[72]

It has also proved possible to elucidate the reason for this, at first sight, obscure point in the reduction of the 4 : 4-dichlorobut-3-enoic acid to the crotonic acid with sodium amalgam. We have found that 4 : 4-dichlorobut-3-enoic acid, its amide, and nitrile are readily isomerised by a base (*e.g.*, triethylamine) to $\gamma\gamma$-dichlorocrotonic acid and its derivatives. The resulting $\gamma\gamma$-dichlorocrotonic acid was identical with the acid synthesised from dichloroacetaldehyde and malonic acid,[74] its structure being thereby ascertained. As the reduction of 4 : 4-dichlorobut-3-enoic acid had been effected by Auwers and Wissebach by the action of sodium amalgam, it provided conditions for isomerisation to $\gamma\gamma$-dichlorocrotonic acid and its further reduction to crotonic acid.

The conversion of $\gamma\gamma\gamma$-trichlorocrotonic acid, on one hand, by hydrolysis to fumaric acid and, on the other hand, by reduction to crotonic acid is taken in the current reviews and textbooks as rigid proof of the *trans*-configuration of the crotonic acid and as an example of the determination of geometrical configuration by conversion into a derivative of known configuration by reactions without effect on the olefinic bond.

Now we are, however, able to see that the two-step reduction, effected by Auwers and Wissebach, of the $\gamma\gamma\gamma$-trichlorocrotonic acid to crotonic acid proceeds with twofold isomerisation, which they had failed to notice, that it cannot therefore serve to determine the configuration of the crotonic acid, and that allylic rearrangement substantially restricts the method of determining configuration by conversion into a derivative of known steric configuration. That we obtained acid chlorides, amides, and nitriles of both 4 : 4-dichlorobut-3-enoic acid and $\gamma\gamma$-dichlorocrotonic acid enabled us to determine that the acid chloride described by Auwers and Wissebach is the 4 : 4-dichlorobut-3-enoyl chloride, their amide and nitrile being, on the other hand, $\gamma\gamma$-dichlorocrotonic acid derivatives. It is evident that the conversion of the 4 : 4-dichlorobut-3-enoyl chloride into the amide was accompanied by isomerisation to give the amide of $\gamma\gamma$-dichlorocrotonic acid which had passed unnoticed by them.

It is to be pointed out that both series of derivatives, $CCl_2{:}CH{\cdot}CH_2X$ and $CHCl_2{\cdot}CH{:}CHX$, fail to isomerise in acids. Thus, hydrolysis of 4 : 4-dichlorobut-3-enonitrile in hydrochloric and acetic acid gave 4 : 4-dichlorobut-3-enoic acid, and that of $\gamma\gamma$-dichlorocrotononitrile under the same conditions gave $\gamma\gamma$-dichlorocrotonic acid. The same is true of $\gamma\gamma\gamma$-trichlorocrotonic acid, which in strong acid hydrolyses, without isomerisation, to yield fumaric acid. It follows, then, that the production by Auwers and Wissebach of 4 : 4-dichlorobut-3-enoic acid by reducing $\gamma\gamma\gamma$-trichlorocrotonic acid in acid cannot be explained either by the preliminary isomerisation of the parent acid or by intermediate formation of $\gamma\gamma$-dichlorocrotonic acid followed by isomerisation.

Rearrangement seems to be taking place in the very process of reduction. We believe this reaction also to follow the " transfer of reaction centre " mechanism.

Allylic Rearrangements in the Substituted Polyhalogenoallyl Alcohol Series [23]

Allylic anionotropic rearrangements of substituted allyl alcohols involving a halogen atom at the double bond have been investigated in detail only in the case of monochloro-derivatives HO·CRR′·CH:CHCl producing in the course of rearrangement unsaturated aldehydes.[75–77]

As far as dichloro-derivatives of allyl alcohols are concerned it has been noted that, for example, 1 : 1-dichloro-3-hydroxy-3-methylnon-1-ene-4-yne fails to rearrange to the corresponding unsaturated acid.[76] 1 : 1 : 3-Trichloroprop-1-ene [1, 3] and 1 : 1 : 3-trichloro-2-methylprop-1-ene,[78] involving the $\rangle CCl\cdot\dot{C}:CCl_2$ system, also did not undergo allylic rearrangement. It seemed of interest to investigate in detail the possibility of allylic rearrangement of polyhalogenoallyl alcohols (or their ethers), according to the following scheme:

$$\underset{\text{(I)}}{HO\cdot CRR'\cdot CH:CX_2} \longrightarrow (CRR':CH\cdot CX_2\cdot OH) \longrightarrow CRR':CH\cdot CO_2H$$

$$\underset{\text{(II)}}{HO\cdot CRR'\cdot CX:CHX} \longrightarrow (CRR':CX\cdot CHX\cdot OH) \longrightarrow CRR':CX\cdot CHO$$

$$\underset{\text{(III)}}{HO\cdot CRR'\cdot CX:CX_2} \longrightarrow (CRR':CX\cdot CX_2\cdot OH) \longrightarrow CRR':CX\cdot CO_2H$$

Compounds (I), containing alkyl groups as substituents, did not rearrange even under vigorous conditions: neither 1 : 1-dichloro-3-hydroxyhept-1-ene after prolonged heating with 10% sulphuric acid in aqueous alcohol or aqueous dioxan nor 1 : 1-dichloro-3-ethoxyhept-1-ene when heated in acetic acid in the presence of sulphuric acid was changed. 1 : 1-Dichloro-3-hydroxy-3-methylbut-1-ene in acid medium easily loses water, giving 1 : 1-dichloro-3-methylbuta-1 : 3-diene, and 1 : 1-dichloro-3-methoxy-3-methylbut-1-ene when heated with 10% sulphuric acid in aqueous alcohol remains intact. Compounds (I), where R = aryl and R′ = hydrogen, readily rearrange in acid to arylacrylic acids: [11]

$$ArCH(OH)\cdot CH:CCl_2 \xrightarrow[H_2O]{H^+} ArCH:CH\cdot CO_2H$$

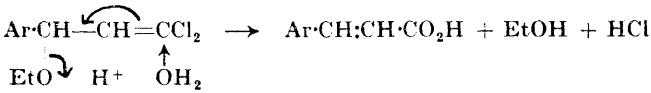
The reaction is carried out by heating the aryl derivative in acetic acid in the presence of hydrochloric acid. As aryl substituents we used phenyl, *p*-tolyl, α-naphthyl, and *p*-chlorophenyl. 1 : 1-Dichloro-3-hydroxy-3-phenylbut-1-ene does not, however, rearrange under these conditions or with 10% sulphuric acid in aqueous alcohol, only losing water to give 1 : 1-dichloro-3-phenylbuta-1 : 3-diene:

$$HO\cdot CPhMe\cdot CH:CCl_2 \xrightarrow{H^+} CH_2:CPh\cdot CH:CCl_2$$

The latter, when heated, dimerises with loss of a hydrogen chloride

[75] E. R. H. Jones and B. C. L. Weedon, *J.*, 1946, 937.
[76] I. M. Heilbron, E. R. H. Jones, and M. Julia, *J.*, 1949, 1430.
[77] M. Julia, *Ann. Chim.*, 1950, **5**, 595.
[78] A. Kirrmann and R. Jacob, *Bull. Soc. chim. France* 1940 **7** 586.

molecule to yield a product of the composition $C_{20}H_{17}Cl_3$. 3-Alkoxy-3-aryl-1 : 1-dichloroprop-1-enes when heated in acetic acid in the presence of hydrochloric acid are smoothly converted into arylacrylic acids, possibly with no migration of the ethoxy-group taking place, the reaction proceeding by the "transfer of reaction centre" mechanism:



1 : 1-Dichloro-3-phenylprop-1-ene, however, remains unaltered when heated with acetic acid in the presence of hydrochloric acid.

The presence of an electron-accepting substituent in compounds (I) hinders anionotropic rearrangement even if, owing to double-bond transfer, there is the possibility of a conjugated system's being formed. Thus, 1 : 1-dichloro-3-cyano-3-ethoxy(or hydroxy)prop-1-ene when heated in acid does not undergo anionotropic allylic rearrangement, which would have produced fumaric acid, only hydrolysis of the nitrile group to carboxyl taking place.

The prototropic allylic rearrangement of 1 : 1-dichloro-3-cyano-3-ethoxyprop-1-ene takes place readily however with triethylamine (to be compared with ref. 8). The product when heated with dilute hydrochloric acid undergoes an interesting conversion into chloroacrylic acid:

$$CCl_2{:}CH{\cdot}CH(OEt){\cdot}CN \longrightarrow CHCl_2{\cdot}CH{:}C(OEt){\cdot}CN \xrightarrow[H_2O]{H^+} (CHCl_2{\cdot}CH_2{\cdot}CO{\cdot}CN) \longrightarrow CHCl{:}CH{\cdot}CO_2H$$

Synthesis of compounds (I) was carried out by the following routes: [2, 3] 1 : 1-dichloro-3-hydroxy-3-methylbut-1-ene by the action of methylmagnesium iodide on 4 : 4-dichlorobut-3-en-2-one; and 1 : 1-dichloro-3-hydroxyhept-1-ene, 1 : 1-dichloro-3-ethoxyhept-1-ene, 3-aryl-1 : 1-dichloro-3-hydroxyprop-1-ene, and 1 : 1-dichloro-3-ethoxy-3-phenylprop-1-ene by the action of the corresponding organomagnesium derivative on $\beta\beta$-dichloroacraldehyde or 1 : 1 : 3-trichloro-3-ethoxyprop-1-ene:

$$CCl_2{:}CH{\cdot}CHCl{\cdot}OEt + RMgX \longrightarrow CCl_2{:}CH{\cdot}CHR{\cdot}OEt$$

1 : 1-Dichloro-3-*p*-chlorophenyl-3-hydroxyprop-1-ene was produced in the following way:

$$C_6H_5Cl + CCl_2{:}CH{\cdot}COCl \xrightarrow{AlCl_3} Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CCl_2 \xrightarrow{Al(OPr^i)_3} Cl{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH{:}CCl_2$$

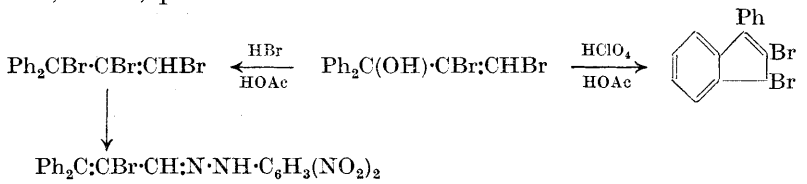
We prepared $\beta\beta$-dichloroacrylic acid, needed for this reaction, by oxidising $\beta\beta$-dichloroacraldehyde with chromic anhydride in acetone. 1 : 1-Dichloro-3-cyano-3-ethoxybut-1-ene was obtained by the action of cuprous cyanide on 1 : 1 : 3-trichloro-3-ethoxyprop-1-ene. As far as allylic rearrangements are concerned, compounds (II) behave as do compounds (I). With alkyl substituents rearrangement does not occur even under vigorous conditions.

With 10% sulphuric acid in aqueous alcohol, 1 : 2-dibromo-3-hydroxyhex-1-ene, 1 : 2-dibromo(and 1 : 2-dichloro)-3-hydroxy-3-methyl-pent-1-ene, and 1-(1 : 2-dibromovinyl)-1-hydroxy*cyclo*hexane are recovered unchanged at room temperature and when heated lose water or form a slurry.

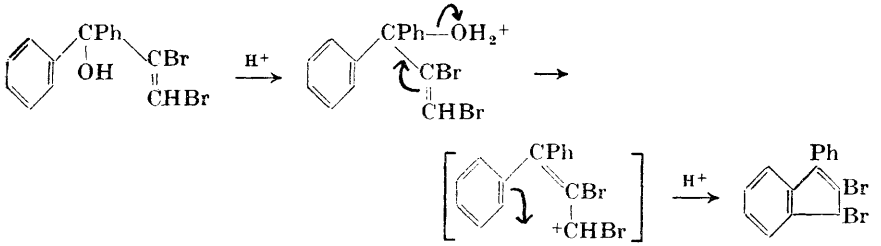
1 : 2-Dibromo-3-hydroxy-3-phenylprop-1-ene and 3-acetoxy-1 : 2-dichloro-3-phenylprop-1-ene readily rearrange to the corresponding α-halogenocinnamaldehyde when heated in acetic acid containing hydrochloric acid :

$$Ph{\cdot}CH(OH){\cdot}CBr{:}CHBr \xrightarrow[H_2O]{H^+} Ph{\cdot}CH{:}CBr{\cdot}CHO$$

1 : 2-Dibromo-3-hydroxy-3-phenylbut-1-ene, like 1 : 1-dichloro-3-hydroxy-3-phenylbut-1-ene, does not rearrange in acid medium but loses water. It is noteworthy that 1-chloro-3-hydroxy-3-phenylbut-1-ene rearranges to the aldehyde. The behaviour of 1 : 2-dibromo-3-hydroxy-3 : 3-diphenylprop-1-ene in acid medium presents some peculiarities. With hydrochloric or hydrobromic acid in acetic acid it yields first 1 : 2-dibromo-3-chloro- and 1 : 2 : 3-tribromo-3 : 3-diphenylprop-1-ene, respectively, which, when heated in 90% acetic acid, produce 1 : 2-dibromo-3-phenylindene rather than α-bromo-β-phenylcinnamaldehyde, though the two trihalogeno-derivatives and 1 : 2-dibromo-3-hydroxy-3 : 3-diphenylprop-1-ene with 2 : 4-dinitrophenylhydrazine in alcohol–sulphuric acid yield the 2 : 4-dinitrophenylhydrazone of α-bromo-β-phenylcinnamaldehyde. 1 : 2-Dibromo-3-phenylindene is produced immediately from 1 : 2-dibromo-3-hydroxy-3 : 3-diphenylprop-1-ene when its acetic acid solution is treated with sulphuric acid or, better, perchloric acid.



The formation of 1 : 2-dibromo-3-phenylindene can be best represented as follows :



The structure of 1 : 2-dibromo-3-phenylindene follows from the *o*-carboxybenzophenone obtained by oxidation with potassium permanganate. Compounds (II) were produced by adding bromine to the corresponding acetylenic alcohols.

The possibility of rearrangement in the system $HO{\cdot}CRR'{\cdot}CX{:}CX_2$ has been investigated in the case of 1 : 1 : 2-trichloro-3-hydroxy-3-phenylprop-1-ene. When heated in acetic acid in the presence of hydrochloric acid it was converted into α-chlorocinnamic acid,[23] rearrangement taking place much less readily than with 1 : 1-dichloro-3-hydroxy-3-phenylprop-1-ene:

$$HO{\cdot}CHPh{\cdot}CCl{:}CCl_2 \xrightarrow[H_2O]{H^+} PhCH{:}CCl{\cdot}CO_2H$$

To obtain a 75% conversion of the trichloro-compound into α-chlorocinnamic acid the former has to be heated for 25 hours whilst the 1 : 1-dichloro-derivative is converted into cinnamic acid in 30—35 minutes. 1 : 1 : 2-Trichloro-3-hydroxy-3-phenylprop-1-ene was obtained by reduction of the phenyl αββ-trichlorovinyl ketone with aluminium *iso*propoxide.

$$C_6H_6 + CCl_2{:}CCl{\cdot}COCl \xrightarrow{AlCl_3} C_6H_5{\cdot}CO{\cdot}CCl{:}CCl_2 \xrightarrow{Al(OPr^i)_3} C_6H_5{\cdot}CH(OH){\cdot}CCl{:}CCl_2$$

It will be noted that 3 : 3-dialkoxy-1 : 1-dichloroprop-1-enes are converted into ββ-dialkoxypropionic esters by simply boiling them with alcohols.[10] This change seems to be due to allylic isomerisation, according to the scheme:

$$CCl_2{:}CH{\cdot}CH(OR)_2 \longrightarrow (RO{\cdot}CH{:}CH{\cdot}CCl_2{\cdot}OR) \longrightarrow RO{\cdot}CH{:}CH{\cdot}COCl + RCl \xrightarrow{ROH} (RO)_2CH{\cdot}CH_2{\cdot}CO_2R$$

or through addition of alcohol to the dichlorovinyl group:

$$CCl_2{:}CH{\cdot}CH(OR)_2 + ROH \longrightarrow [(RO)_2CH{\cdot}CH_2{\cdot}CCl_2{\cdot}OR] \longrightarrow (RO)_2CH{\cdot}CH_2{\cdot}CO_2R$$

ββ-Dialkoxypropionic esters can also be produced by boiling 3-alkoxy-1 : 1 : 1 : 3-tetrachloropropane or 3-alkoxy-1 : 1 : 3-trichloroprop-1-ene in alcohol.[10]

Supplement

Synthesis of Higher αααω-Tetrachloroalkanes and ααα-Trichloroalkanes by the Telomerisation Reaction.—Joyce and Hanford,[28–30] who discovered the telomerisation reaction of ethylene and carbon tetrachloride and of ethylene and chloroform, have shown that a mixture of αααω-tetrachloroalkanes and ααα-trichloroalkanes are formed, and have isolated the corresponding individual compounds containing 3—9 carbon atoms in the former and 3—11 carbon atoms in the latter.

As it is most difficult to synthesise organic molecules of an average molecular weight and more than about 10 carbon atoms, it seems worthwhile to determine the conditions for the telomerisation reaction which would provide for higher tetra- and tri-chloroalkanes and for their isolation as pure substances.

Two of us and Sh. A. Karapetyan[24] have shown that higher tetra- and tri-chloroalkanes can be obtained by the reaction of ethylene with carbon tetrachloride and chloroform under comparatively low pressures, from 100

to 150 atmospheres. The yield of higher polychloroalkanes is about equally dependent on the initial pressure at which the reaction is being run and on the initial molar ratio of ethylene to halogenomethane. The higher these two parameters are, the higher is the yield of polychloralkanes.

This relation is due to the fact, found by G. D. Yefremova and G. G. Leont'eva,[79] that at 100° and pressures above 105 atmospheres the ethylene–carbon tetrachloride system is homogeneous whatever its composition.

Thus, the reaction between ethylene and carbon tetrachloride, taken at 20 : 1 mole ratio, at 150 atmospheres and 90°, in the presence of azobis*iso*butyronitrile, produced a mixture of αααω-tetrachloroalkanes consisting of tetrachloropentane (9%), tetrachloroheptane (12%), a fraction (24%) of tetrachloroalkanes with 9—15 carbon atoms, a paraffin-like fraction (44%) of tetrachloroalkanes soluble in acetone with an average molecular weight of 420, and a tetrachloroalkane fraction (11%) insoluble in acetone with an average molecular weight 720.

The molecular weight of the fractions was ascertained by chlorine determination. Increase of the molar ratio of ethylene to carbon tetrachloride, other things being equal, is accompanied by the increase in yield of higher tetrachloroalkanes as well as by increase in the average molecular weight of the higher fractions.

The same is observed in the reaction with chloroform, this leading to the suggestion that in the ethylene–chloroform system critical phenomena also take place under the indicated conditions.

From the mixtures obtained by telomerisation we have isolated higher tetrachloroalkanes with 13 and 15 carbon atoms [13] and trichloroalkanes with 13, 15, and 17 carbon atoms,[24] their constants being given in Table 3.

Synthesis of Compounds containing Two and Three Functional Groups, starting with αααω-Tetrachloroalkanes.—αααω-Tetrachloroalkanes have already been shown to undergo chemical changes by the action of nucleophilic, electrophilic, and radical reagents, reaction taking place selectively, either at the chloromethyl or at the trichloromethyl group. By combining successively reactions of the two types it is possible to effect the synthesis of various compounds involving two functional groups.

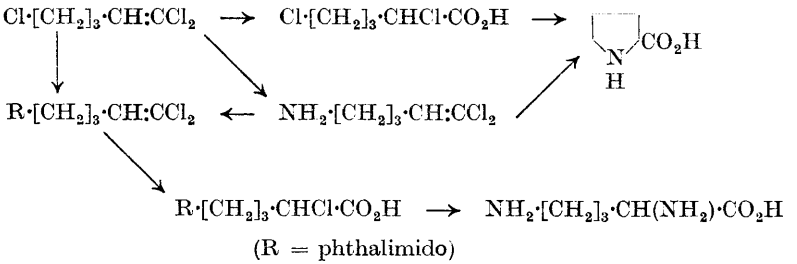
Thus, reaction of αααω-tetrachloroalkanes and the readily available αααω-trichloroalk-1-enes with ammonia [5] resulted in aminotrichloroalkanes $CCl_3{\cdot}[CH_2]_n{\cdot}NH_2$ and aminodichloroalkenes $CCl_2{:}CH{\cdot}[CH_2]_n{\cdot}NH_2$. Hydrogenation of the polychloro-nitriles $CCl_3{\cdot}[CH_2]_4{\cdot}CN$ and $CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}CN$ with hydrogen under pressure in the presence of Raney nickel produced the amines $CHCl_2{\cdot}[CH_2]_5{\cdot}NH_2$ and $CCl_2{:}CH{\cdot}[CH_2]_4{\cdot}NH_2$. Tetrachloroalkanes and trichloroalkenes reacting with sodium sulphide gave $(CCl_3{\cdot}[CH_2]_n)_2S$ and $(CCl_2{:}CH{\cdot}[CH_2]_n)_2S$, which, on being hydrolysed, gave di-(ω-carboxyalkyl sulphides [6] (see Table 5).

Another route for obtaining compounds with two functional groups consists in the hydrolysis of αααω-tetrachloroalkanes to ω-chloro-carboxylic acids followed by chlorine substitution under the action of nucleophilic reagents. This procedure resulted in ω-amino-carboxylic acids [25c] with

[79] G. D. Yefremova and G. G. Leont'eva, *Trudy G.I.A.P., Sh.*, 1954, 5.

7, 9, and 11 carbon atoms in a molecule, di-(ω-carboxyalkyl) sulphides,[6] ω-hydroxy-carboxylic acids, and many other compounds some of which are listed in Tables 5, 7, and 8.

The conjugated addition of chlorine to the dichlorovinyl group in concentrated sulphuric acid, leading to α-chloro-carboxylic acids,[17] reveals new possibilities for the synthesis of compounds involving three functional groups. Thus, two of us and R. G. Petrova,[26] starting with 1 : 1 : 5-trichloropent-1-ene, have obtained DL-proline and DL-ornithine according to the scheme:



(R = phthalimido)

The conversion of 1 : 1 : 5-trichloropent-1-ene into 2 : 5-dichloropentanoic acid and that of 1 : 1-dichloro-5-phthalimidopent-1-ene into 2-chloro-5-phthalimidopentanoic acid was achieved by chlorine addition in sulphuric acid at 0—5°, the reaction giving good yields (cf. ref. 17).

When chlorine was added under the same conditions to 5-amino-1 : 1-dichloropent-1-ene and the mixture neutralised with 5% ammonia, the main product was DL-proline along with a small amount of 5-amino-1 : 1 : 1 : 2-tetrachloropentane and 5-amino-2-chloropentanoic acid. The formation of proline seems to indicate that the intermediate 5-amino-2-chloropentanoic acid readily cyclises in weakly alkaline solutions.

The literature describes the preparation of DL-proline by ammonolysis of 2 : 5-dichloropentanoic acid with 25% aqueous ammonia for one hour at 130°, the yield of proline being 25%.[80] It has now been found [26] that 50—55% yields are obtained when the ammonolysis of 2 : 5-dichloropentanoic acid with 25% ammonia solution is carried out at room temperature for 14 hours.

The isolation of DL-proline was as follows: After removal of ammonia the aqueous solution was passed through S.D.V. cation-exchange resin to liberate chloride ion (cf. ref. 27). Proline was eluted from the resin with 5% aqueous ammonia. After removal of ammonia, the residue was dissolved in alcohol and precipitated with dioxan. The resulting proline was purified by recrystallisation from alcohol. Taking into account the exceedingly ready availability of 1 : 1 : 1 : 5-tetrachloropentane and the high yields obtained when synthesising the intermediate products—1 : 1 : 5-trichloropent-1-ene and 2 : 5-dichloropentanoic acid—this synthesis is to be considered the easiest and the most convenient one at present available.

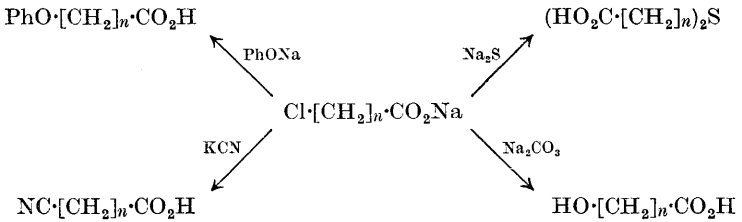
[80] R. Gaudry and L. Berlinquet, *Canad. J. Res.*, 1949, **27**, *B*, 282.

DL-Ornithine was obtained by the ammonolysis of 2-chloro-5-phthalimidopentanoic acid with 25% aqueous ammonia in the presence of ammonium carbonate, and was isolated as its monohydrochloride after refluxing the product with concentrated hydrochloric acid. Ornithine was identified as ornithuric acid or picrate. The yield of ornithine was 30%. Along with ornithine there was formed proline, whose yield (30%) was determined by isolation of the product of condensation with isatin.[26]

The instances shown undoubtedly do not cover all the possibilities of synthesis of natural and other α-amino-acids from αααω-tetrachloroalkanes and ααα-trichloroalkanes.

ω-Chloro-carboxylic Acids and some of their Reactions.[13]—The higher ω-bromo-carboxylic acids, $Br\cdot[CH_2]_n\cdot CO_2H$, have been investigated in detail and are widely used in various syntheses. This is not true of the corresponding ω-chloro-carboxylic acids, which have received comparatively little attention, presumably because the chlorine atom was thought to be fairly unreactive and because of the difficulty of production. We have now investigated some reactions of ω-chloro-carboxylic acids and found that they can be successfully used in place of the corresponding bromo-acids. The corresponding alkoxy-derivatives are smoothly formed from the reaction of sodium alkoxide and ethyl δ-chlorovalerate and ethyl 7-chloroheptanoate. The reaction of ethyl δ-chlorovalerate and ethyl 7-chloroheptanoate with diethyl sodiomalonate in the presence of sodium iodide gives 1 : 1 : 5-triethoxycarbonylpentane and 1 : 1 : 7-triethoxycarbonylheptane in a good yield ; these are hydrolysed with dilute hydrochloric acid to pimelic and azelaic acid, respectively.

Salts of 7-chloroheptanoic and 9-chlorononanoic acid readily react in aqueous solutions with sodium phenoxide, or sodium cyanide, or are hydrolysed by alkali to ω-hydroxy-carboxylic acids. Both these chloro-acids, with sodium sulphide in aqueous solution, readily yield the corresponding di-(ω-carboxyalkyl) sulphide:



Oxidation of 7-hydroxyheptanoic acid with concentrated nitric acid gives pimelic acid in good yield ; hydrogenation of 7-cyanoheptanoic acid in ammonia solution with nickel catalyst leads to 8-amino-octanoic acid.

The action of sodium phenoxide or sodium cyanide in aqueous solution on salts of δ-chlorovaleric acid does not give the corresponding derivatives but leads to δ-valerolactone (or δ-hydroxyvaleric acid) which under these conditions does not react further. On the other hand, sodium thiophenoxide with δ-chlorovaleric acid gives δ-(phenylthio)valeric acid in high yield.

Phenoxyvaleric acid may be obtained from δ-chlorovaleric acid only through δ-valerolactone, which is heated with anhydrous sodium phenoxide at a high temperature, just as γ-phenoxybutyric acid is obtained *via* γ-butyrolactone.[81]

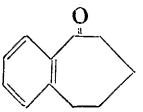
Heating δ-chlorovaleric acid with anhydrous ammonia at 230—250° or its ethyl ester with alcoholic ammonia at 120—140° gave α-piperidone in good yield.

7-Chloroheptanoic acid was converted into hept-6-enoic acid through 7-trimethylaminoheptanoic acid betaine, the betaine being split by alkali:

$$Cl\cdot[CH_2]_6\cdot CO_2H \longrightarrow Me_3\overset{+}{N}\cdot[CH_2]_6\cdot CO_2^- \longrightarrow CH_2{:}CH\cdot[CH_2]_4\cdot CO_2H + Me_3N$$

We have investigated the reaction of ω-chloro-carboxylic acids with benzene in the presence of aluminium chloride; it has been previously shown that γ-chlorobutyric acid with benzene gives γ-phenylbutyric acid.[82]

Similarly, δ-chlorovaleric acid gives δ-phenylvaleric acid in a high yield when aluminium chloride is used in the molar ratio 1 : 1. The amount of aluminium chloride being increased, in addition to phenylvaleric acid one obtains α-benzosuberone.[13]

$$C_6H_6 + Cl\cdot[CH_2]_4\cdot CO_2H \xrightarrow{AlCl_3} C_6H_5\cdot[CH_2]_4\cdot CO_2H + \text{  }$$

The yield of δ-phenylvaleric acid obtained from δ-chlorovaleric acid is higher than stated to be obtainable from reaction with δ-valerolactone.[83] Unlike the lower acids, 7-chloroheptanoic, 9-chlorononanoic, and 11-chloroundecanoic acids react with benzene in the presence of aluminium chloride, undergoing isomerisation; the phenylheptanoic, phenylnonanoic, and phenylundecanoic acids obtained have been proved to be different from the known 7-phenylheptanoic,[84] 9-phenylnonanoic,[85] and 11-phenylundecanoic acids.[86] Oxidation of phenylnonanoic and phenylheptanoic acids with chromic anhydride in acetic acid led to the isolation of acetophenone,* which suggests the presence in the acids of the $C_6H_5\cdot CHMe$ grouping.

Condensation of δ-chlorovaleroyl and 7-chloroheptanoyl chlorides with benzene in the presence of aluminium chloride proceeds as usual and gives the corresponding ω-chloroalkyl phenyl ketones:

$$C_6H_6 + Cl\cdot CO\cdot[CH_2]_n\cdot Cl \xrightarrow{AlCl_3} C_6H_5\cdot CO\cdot[CH_2]_n\cdot Cl$$

where $n = 4$ or 6.

[81] G.P. 741,687 (*Zent.*, 1944, **1**, 907).
[82] I. Eykmann, *Chem. Weekblad*, 1907, **4**, 727.
[83] R. Christian, *J. Amer. Chem. Soc.*, 1952, **74**, 1591.
[84] J. von Braun, *Ber.*, 1911, **44**, 2878.
[85] H. G. Raper and E. J. Wayne, *Biochem. J.*, 1928, **22**, 194.
[86] E. Fourneau and P. Baranger, *Bull. Soc. chim. France*, 1931, **49**, 1161.
* Similar oxidation of δ-phenylvaleric acid gives γ-benzoylbutyric acid.

TABLE 3. *Polychloro-hydrocarbons.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$Me{\cdot}CH{:}CCl_2$		77—78	1·4450	1·1687	4
2	$CH_2{:}CH{\cdot}CCl_3$		101—102	1·4680	1·3292	1, 3
3	$CCl_2{:}CH{\cdot}CH_2Cl$		131—132	1·4938	1·3940	3
4	$CH_2{:}CCl{\cdot}CHCl_2$		126—127	1·4840	1·3843	2
5	$CH_2{:}CCl{\cdot}CCl_3$		54—55/30	1·5000	1·5099	1, 3
6	$CH_2Cl{\cdot}CCl{:}CCl_2$		68—69/30	1·5160	1·5409	1, 3
7	$CHCl{:}CCl{\cdot}CCl_3$		59—60/6	1·5282	1·6449	1, 3
8	$CH_2Cl{\cdot}CHCl{\cdot}CCl_3$		64—65/8	1·5105	1·6117	1, 3
9	$CH_2Cl{\cdot}CCl_2{\cdot}CCl_3$		101—102/15	1·5282	1·7187	1, 3
10	$CH_2{:}CBr{\cdot}CCl_3$		54—55/10	1·5327	1·8442	1, 3
11	$CH_2Br{\cdot}CHCl{\cdot}CHCl_2$		92—93/24	1·5290	1·8322	1, 2
12	$CH_2Br{\cdot}CHBr{\cdot}CCl_3$		76—77/3	1·5640	2·1712	1, 3
13	$CCl_3{\cdot}CH{:}CHMe$		57—57·5/49	1·4810	1·2972	22
14	$CCl_2{:}CH{\cdot}CHMeCl$		68/52	1·4815	1·3026	22
15	$CCl_3{\cdot}CH_2{\cdot}CH{:}CCl_2$		44·5—45/3	1·5172	1·5607	2
16	$CCl_2{:}CH{\cdot}CCl{:}CCl_2$		54—55/3·5	1·5620	1·6142	2
17	$CBrCl_2{\cdot}CHCl{\cdot}CH_2{\cdot}CCl_3$		93—94/3	1·5478	1·8859	2
18	$CBrCl_2{\cdot}CHBr{\cdot}CHMeCl$		87/1	1·5590	2·0466	22
19	$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CCl_2$		127—128	1·4548	1·0899	4
20	$CCl_2{:}CH{\cdot}CMe{:}CH_2$		30—31/8	1·5027	1·1537	22, 23
21	$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CCl_2$		68—69/7	1·4892	1·2724	4, 16
22	$CCl_3{\cdot}CH{:}CMe_2$		45—46/8	1·4822	1·2497	22
23	$CCl_2{:}CH{\cdot}CMe_2Cl$		58—58·5/15	1·4847	1·2527	22
24	$CHCl_2{\cdot}[CH_2]_3{\cdot}CH_2Cl$		84/8	1·4788	1·2438	16
25	$CCl_3{\cdot}CHCl{\cdot}[CH_2]_2{\cdot}Me$		72—73/8	1·4825	1·3339	9
26	$CCl_2{:}CCl{\cdot}[CH_2]_2{\cdot}CH_2Cl$		92—93/8	1·5113	1·4121	9
27	$CCl_2{:}CH{\cdot}CH_2{\cdot}CH{:}CCl_2$		57/1·5	1·5197	1·4307	18
28	$CCl_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CCl_3$		101—104/12	1·5125	1·4707	7
29	$CCl_2{:}CH{\cdot}CH_2{\cdot}CHCl{\cdot}CHCl_2$		106—107/7	1·5225	1·5077	7
30	$CCl_3{\cdot}CHCl{\cdot}[CH_2]_2{\cdot}CH_2Cl$		121—122/12	1·5135	1·4807	9, 17
31	$CCl_2{:}CH{\cdot}CH_2{\cdot}CHCl{\cdot}CCl_3$		119—120/10	1·5291	1·5817	7
32	$CBr_3{\cdot}[CH_2]_3{\cdot}CH_2Cl$		101—102/2	1·5655	2·0902	9
33	$CBr_3{\cdot}[CH_2]_3{\cdot}Me$		85—86/8	1·5390	1·9882	9
34	$CCl_3{\cdot}[CH_2]_3{\cdot}CH_2I$		78—79/1·5	1·5480	1·8086	9
35	$Me{\cdot}[CH_2]_4{\cdot}CH{:}CCl_2$		68—69/14	1·4589	1·0430	4
36	$CCl_2{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CCl_2$		98—100/8	1·5149	1·3628	7
37	$CH_2Cl{\cdot}[CH_2]_4{\cdot}CH{:}CCl_2$		66—67/1	1·4850	1·1902	4
38	$CHCl_2{\cdot}[CH_2]_5{\cdot}CH_2Cl$		74—75/1·5	1·4776	1·1744	16
39	$CCl_3{\cdot}CH{:}CH{\cdot}CMe_3$		64—65/10	1·4725	1·1403	22
40	$CCl_3{\cdot}CH_2{\cdot}CHBr{\cdot}CMe_3$		90/5	1·5030	1·4792	22
41	$CCl_2{:}CH{\cdot}[CH_2]_6{\cdot}Me$		85—86/7	1·4597	1·0106	19
42	$CH_2Cl{\cdot}[CH_2]_6{\cdot}CH{:}CCl_2$		91—92/1·5	1·4834	1·7342	4
43	$CH_2Cl{\cdot}[CH_2]_8{\cdot}CH_2Cl$		105—106/1·5	1·4620	0·9992	16
44	$(CH_2Cl{\cdot}[CH_2]_3{\cdot}CCl{:})_2$		152—154/3	1·5055	1·2202	16
45	$Cl{\cdot}[CH_2]_4{\cdot}[CCl_2]_2{\cdot}[CH_2]_4{\cdot}Cl$	84—85				16
46	$H{\cdot}[CH_2]_{12}{\cdot}CCl_3$		103—108/0·3	1·4649	1·0339	24
47	$Cl{\cdot}[CH_2]_{12}{\cdot}CCl_3$		152—153/1·5	1·4842	1·1290	13
48	$CCl_3{\cdot}[CH_2]_{10}{\cdot}Cl$		141—142/5	1·4822	1·1558	13
49	$CH_2Cl{\cdot}[CH_2]_{12}{\cdot}CH_2Cl$	38—39	143—144/1·5			16
50	$(CH_2Cl{\cdot}[CH_2]_5{\cdot}CCl{:})_2$		178—180/2	1·4980	1·1393	16
51	$(CH_2Cl{\cdot}[CH_2]_5{\cdot}CCl_2{\cdot})_2$	57—58				16
52	$H{\cdot}[CH_2]_{14}{\cdot}CCl_3$		123—125/0·3	1·4658	1·0142	24
53	$H{\cdot}[CH_2]_{16}{\cdot}CCl_3$		138—143/0·3	1·4663	0·9992	24
54	$Ph{\cdot}CH_2{\cdot}CH{:}CCl_2$		93—94/6	1·5490	1·2032	1, 3
55	$CCl_3{\cdot}CH{:}CHPh$		91—92/1	1·5710	1·9217	22
56	$Ph{\cdot}CH_2{\cdot}CCl{:}CCl_2$		121—122/8	1·5630	1·3232	1, 3, 14

TABLE 3.—*continued.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
57	*p*-Cl·C_6H_4·CH_2·CH:CCl_2		115—116/6	1·5630	1·3208	20
58	CCl_3·CHCl·CH_2Ph		111—112/2	1·5535	1·3867	14
59	CCl_3·CCl_2·CH_2Ph	76—77				14
60	CCl_3·CHCl·CH_2·C_6H_4Cl-*p*	90	142—143/5			20
61	CCl_2:CH·CPh:CH_2		86—87/1·5	1·5829	1·2048	23
62	CCl_2:CH·CHPhMe		73—74/1·5	1·5423	1·1702	22
63	CCl_2·CHCl·CHPhMe		107—108/1·5	1·5568	1·3634	22
64	CCl_2:CH·$CPhMe_2$		80—81/1	1·1540	1·5411	22
65	CCl_2:CH·$CHPh_2$		142—143/1	1·5951	1·2180	22
66	*p*-Br·C_6H_4·CH_2·CH:CCl_2		117·5—118/5	1·5830	1·5532	20
67	*p*-Br·C_6H_4·CH_2·CHCl·CCl_3	89				20
68	CHBr:CBr·CPh_2Cl	137—138				23
69	CHBr:CBr·CPh_2Br	152—153				23
70	1:2-Dibromo-3-phenylindene	82—83				23

TABLE 4. *Chloro-derivatives containing nitro-, hydroxy-, or oxo-groups; chloro-esters*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	CCl_2:CH·CH_2·NO_2		47—48/2	1·4879	1·4494	14
2	CCl_3·CHCl·CH_2·NO_2		73—74/15	1·5005	1·6355	14
3	CCl_2:CH·CH_2·OH		56—57/4	1·4945	1·3763	18
4	CCl_2:CH·CH_2·OMe		131—132	1·4558	1·2112	7
5	PhO·CH_2·CH:CCl_2		103—104/7	1·5534	1·2718	20
6	CCl_2:CH·CH_2·OAc		71—72/14	1·4650	1·2846	18
7	CCl_2:CCl·CH_2·OMe		53—54/10	1·4871	1·3782	14
8	CCl_2:CH·CHCl·OEt		76—77/14	1·4797	1·2866	10, 21
9	CCl_3·CHCl·CH_2·OH	39—40				18
10	CCl_3·CHCl·CH_2·OMe		58·5—59/4	1·4868	1·4568	14
11	CCl_3·CH_2·CHCl·OAc		70—71/2	1·4721	1·4455	10
12	CCl_3·CHCl·CH_2·OAc		81—82/2	1·4848	1·4905	18
13	$(CCl_3$·CHCl·$CH_2)_2SO_4$	46—47	189—190/2			18
14	CCl_3·CCl_2·CH_2·OMe		63—64/2	1·5085	1·5765	7, 14
14*a*	CCl_3·CHCl·CH_2·O·CH_2Cl		81—82/1·5	1·5070	1·5713	18
15	CCl_2:CH·CHO		124—125	1·5067		11
16	CCl_2:CH_2·CH$(OEt)_2$		83—84/15	1·4478	1·1293	10, 21
17	CCl_2:CH·CH$(OBu)_2$		124—125/9	1·4530	1·0495	10, 19
18	CCl_2:CH·CHMe·OH		72/10	1·4792	1·2745	22
19	CCl_2:CH·CHMe·OMe		64/57	1·1722	1·4580	22
20	CCl_2:CH·CHMe·OAc		83—84/26	1·4590	1·2234	22
21	Bz·$[CH_2]_4$·Cl	49—50				13
22	CCl_2:CH·$[CH_2]_3$·OH		56—60/2·5	1·4923	1·2452	12
23	CCl_2:CH·$[CH_2]_3$·OEt		79—81/11	1·4642	1·1101	19
24	CCl_2:CH·$[CH_2]_3$·OPh		112—113/2	1·5375	1·1914	19
25	CCl_2:CH·$[CH_2]_3$·OAc		58/1·5	1·4690	1·2095	12
26	CCl_2:CH·CMe_2·OH		60—61/20	1·4780	1·2220	23
27	CCl_2:CH·CMe_2·OMe		51—52/10	1·4628	1·1418	22
28	CCl_2:CH·CMe_2OEt		72—73/24	1·4616	1·1101	22
29	CCl_3·$[CH_2]_4$·OH		112—113/10	1·4897	1·3431	12
30	CCl_3·$[CH_2]_4$·OAc		99—100/3·5	1·4700	1·2859	12

continued on next page.

TABLE 4.—*continued.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
31	$CCl_3{\cdot}[CH_2]_3{\cdot}CHO$		103—104/8	1·4890	1·3662	12
32	$CHBr{:}CBr{\cdot}CHPr{\cdot}OH$		78—79/1	1·5380	1·7414	23
33	$CHBr{:}CBr{\cdot}CMeEt{\cdot}OH$		98—99/7	1·5380	1·7417	23
34	$CCl_2{:}CH{\cdot}CH(OH){\cdot}[CH_2]_3{\cdot}Me$		103—104/8	1·4791	1·1431	23
35	$CCl_2{:}CH{\cdot}[CH_2]_4{\cdot}CH_2{\cdot}OEt$		114—116/15	1·4622	1·0603	19
36	$CCl_2{:}CH{\cdot}CH(OEt){\cdot}[CH_2]_3{\cdot}Me$		84—85/9	1·4530	1·0408	19
37	$CCl_2{:}CH{\cdot}CH(OMe){\cdot}CMe_3$		60—61/9	1·4620	1·0755	22
38	$Cl{\cdot}[CH_2]_6{\cdot}COPh$	34—35	147—148/1·5			13
39	$Cl{\cdot}[CH_2]_6{\cdot}CPh{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	110—111				13
40	$CCl_2{:}CH{\cdot}[CH_2]_7{\cdot}OEt$		88—89/1	1·4669	1·1054	19
41	$[CH_2]_5 > C(OH){\cdot}CBr{:}CHBr$	73—74	128—129/5			23
42	$PhCH{:}CCl{\cdot}CHO$	158—159	132—133/9			23
43	$CHCl{:}CCl{\cdot}CHPh{\cdot}OH$		105—106/2	1·5733	1·3238	23
44	$CCl_2{:}CH{\cdot}CHPh{\cdot}OH$	57—58				11
45	$CCl_2{:}CH{\cdot}CHPh{\cdot}OEt$		90—91/1	1·5308	1·1822	11, 22
46	$CCl_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OH\text{-}p$	40·5—41	130—131/3	1·5732	1·3057	20
47	$CCl_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OH\text{-}o$		116—117/3	1·5727	1·3050	20
48	$CCl_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe\text{-}p$		118—119/5	1·5486	1·2307	20
49	$CCl_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe\text{-}o$		109/4·5	1·5525	1·2372	20
50	$CCl_2{:}CCl{\cdot}CHPh{\cdot}OH$		112—113/1·5	1·5820	1·4225	23
51	$p\text{-}Cl{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH{:}CCl_2$		142—143/3	1·5730	1·3999	23
52	$p\text{-}Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CCl_2$	51—52	168—169/8			23
53	$Ph{\cdot}CBr{:}CH{\cdot}CHO$	70—71				23
54	$CHBr{:}CBr{\cdot}CHPh{\cdot}OAc$		139—140/1·5	1·5752	1·6705	23
55	$CCl_2{:}CH{\cdot}CPhMe{\cdot}OH$		106—107/2	1·5574	1·2567	23
56	$CHBr{:}CBr{\cdot}CPhMe{\cdot}OH$		134—135/2	1·6061	1·7217	23
57	$CCl_2{:}CH{\cdot}CH(OEt){\cdot}C_6H_4Me\text{-}p$		106—107/1·5	1·5310	1·1663	11
58	$CPh_2{:}CBr{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	245—246				23
59	$CHBr{:}CBr{\cdot}CPh_2{\cdot}OH$	112—113				23
60	$CCl_2{:}CH{\cdot}CH(OEt){\cdot}C_{10}H_7\text{-}\alpha$		159—160/4	1·5987	1·2299	11
61	α-Suberone		124—125/7	1·5618	1·0780	13

TABLE 5. *Compounds containing sulphur.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$(CCl_2{:}CH{\cdot}CH_2)_2S$		92—94/1	1·5630	1·4481	6, 7
2	$(CCl_2{:}CH{\cdot}CH_2)_2SO_2$	114—115				6, 7
3	$(CCl_2{:}CH{\cdot}CHMe)_2S$		104/5	1·5345	1·3156	22
4	$(CCl_2{:}CH{\cdot}[CH_2]_3)_2S$		147/1	1·5368	1·2818	6
5	$(CCl_3{\cdot}CH_2{\cdot}[CH_2]_3)_2S$	35—36	203—205/5			6
6	$(CCl_3{\cdot}CH_2{\cdot}[CH_2]_3)_2SO$	67—68				6
7	$(CCl_3{\cdot}CH_2{\cdot}[CH_2]_3)_2SO_2$	114—115				6
8	$(CCl_2{:}CH{\cdot}[CH_2]_5)_2S$		186—187/1·5	1·5214	1·1853	6
9	$CCl_2{:}CH{\cdot}[CH_2]_6{\cdot}CH_2{\cdot}SEt$		120—121/1	1·4991	1·0672	19
10	$CCl_2{:}CH{\cdot}CMe_2{\cdot}SPh$		102—103/1·5	1·5705	1·1988	22
11	$(HO_2C{\cdot}[CH_2]_6)_2S$	96—97				6
12	$(EtO_2C{\cdot}[CH_2]_6)_2S$		183—184/1·5	1·4660	1·9951	6
13	$(BuO_2C{\cdot}[CH_2]_6)_2S$		214—215/1·5	1·4641	0·9678	6
14	$(HO_2C{\cdot}[CH_2]_6)_2SO_2$	156—157				6
15	$(HO_2C{\cdot}[CH_2]_8)_2S$	98—99				6
16	$(EtO_2C{\cdot}[CH_2]_8)_2S$	37	219—220/2			6
17	$(BuO_2C{\cdot}[CH_2]_8)_2S$	22—23	239—241/1·5	1·4660		6
18	$(HO_2C{\cdot}[CH_2]_8)_2SO_2$	148—149				6

TABLE 6. *Chloro-compounds containing the amino-group.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$CCl_2{:}CH{\cdot}CH_2{\cdot}NEt_2$		65—66/7	1·4708	1·0693	7
2	$CCl_2{:}CH{\cdot}CH_2{\cdot}NEt_2$,HCl	139—140				7
3	$CCl_2{:}CCl{\cdot}CH_2{\cdot}NEt_2$		81—82/4	1·4894	1·1942	14
4	$CCl_2{:}CCl{\cdot}CH_2{\cdot}NEt_2$,HCl	168—169				14
5	$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}NEt_2$	108·5—109·5				14
6	$CCl_2{:}CH{\cdot}CHMe{\cdot}NEt_2$		79·5—80/14	1·4690	1·0470	22
7	$CCl_2{:}CH{\cdot}CHMe{\cdot}NEt_2$,HCl	167·5				22
8	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}NH_2$		68—69/7	1·4899	1·1736	5
9	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}NHBz$	55—56				5
10	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}NEt_2$		63—64/2	1·4719	1·0349	19
11	$CCl_2{:}CH{\cdot}CMe_2{\cdot}NH_2$,HCl	180—181				22
12	$CCl_2{:}CH{\cdot}CMe_2{\cdot}NH_2$		64—65/12	1·4785	1·1488	22
13	$CCl_2{:}CH{\cdot}CMe_2{\cdot}NC_5H_{10}$,HCl	248—249				22
14	$CCl_3{\cdot}[CH_2]_4{\cdot}NH_2$		69—70/1·2	1·4862	1·2619	5
15	$CCl_3{\cdot}[CH_2]_4{\cdot}NH_2$,HCl	229—230				5
16	$CCl_3{\cdot}[CH_2]_4{\cdot}NHBz$	95—96				5
17	$CCl_2{:}CCl{\cdot}[CH_2]_3{\cdot}NEt_2$		84—85/2	1·4886	1·1378	19
18	$CCl_2{:}CH{\cdot}[CH_2]_4{\cdot}NH_2$		83—84	1·4865	1·1331	5
19	$CCl_2{:}CH{\cdot}[CH_2]_4{\cdot}NHBz$	36·5—37				5
20	$CHCl_2{\cdot}[CH_2]_5{\cdot}NH_2$		93—94/7	1·4730	1·1088	5
21	$CHCl_2{\cdot}[CH_2]_5{\cdot}NHBz$	56—57				5
22	$CCl_3{\cdot}[CH_2]_5{\cdot}NH_2$		78—79/1·2	1·4843	1·2192	5
23	$CCl_3{\cdot}[CH_2]_5{\cdot}NHBz$	70·5—71·5				5
24	$CCl_2{:}CH{\cdot}[CH_2]_5{\cdot}NH_2$		102—103/7	1·4842	1·1039	5
25	$CCl_2{:}CH{\cdot}[CH_2]_5{\cdot}NHBz$	36·5—37·5				5
26	$CCl_2{:}CH{\cdot}[CH_2]_5{\cdot}NEt_2$		89—90/1·5	1·4730	1·0097	19
27	$CCl_3{\cdot}[CH_2]_6{\cdot}NH_2$		95—96/1·5	1·4828	1·1857	5
28	$CCl_3{\cdot}[CH_2]_6{\cdot}NHBz$	91—92				5
29	$CCl_2{:}CH{\cdot}[CH_2]_7{\cdot}NH_2$		100—101/3	1·4822	1·0599	5
30	$CCl_2{:}CH{\cdot}[CH_2]_7{\cdot}NHBz$	44·5—45·5				5
31	$CCl_2{:}CH{\cdot}CHPh{\cdot}NEt_2$		98—99/1	1·5335	1·1116	22
32	$CCl_2{:}CH{\cdot}CHPh{\cdot}NEt_2$,HCl	149—150				22
33	$CCl_2{:}CCl{\cdot}[CH_2]_3{\cdot}NEt_2$, $C_2H_2O_4$	125—126				19

TABLE 7. *Monocarboxylic acids and derivatives.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$CHCl{:}CH{\cdot}CO_2H$	85—86				23
2	$CCl_2{:}CH{\cdot}CO_2H$	76—77				23
3	$(EtO)_2CH{\cdot}CH_2{\cdot}CO_2Et$		95—96/12	1·4170	0·9779	10
4	$(BuO)_2CH{\cdot}CH_2{\cdot}CO_2Bu$		112—114/1	1·4280	0·9239	10
5	$CCl_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$	159—160				12
6	$CH_2Cl{\cdot}[CH_2]_3{\cdot}CO{\cdot}NH_2$	78—79				13
7	$CH_2Cl{\cdot}[CH_2]_3{\cdot}CO{\cdot}NHPh$	108—109				13
8	$CHCl_2{\cdot}CH{:}CH{\cdot}CO_2H$	99—100	101—102/4			8
9	$CHCl_2{\cdot}CH{:}CH{\cdot}CO{\cdot}NH_2$	81—82				8
10	$CHCl_2{\cdot}CH{:}CH{\cdot}CN$		90—91/8	1·4970	1·3055	8
11	$CHCl_2{\cdot}CH{:}C(OEt){\cdot}CN$		86/10	1·4797	1·2074	23
12	$CHCl_2{\cdot}CH{:}C(OBu){\cdot}CN$		96—97/4	1·4760	1·1347	23
13	$CCl_2{:}CH{\cdot}CH_2{\cdot}CO_2H$	42—43	111—112/7			8, 12
14	$CCl_2{:}CH{\cdot}CH_2{\cdot}COCl$		67—68/13			8
15	$CCl_2{:}CH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$	93—94				8
16	$CCl_2{:}CH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$	82—83				12
17	$CCl_2{:}CH{\cdot}CH_2{\cdot}CN$		77—78/11	1·4831	1·3122	7
18	$CCl_2{:}CH{\cdot}CH(OEt){\cdot}CO_2H$		114—115/2	1·4889	1·3445	23
19	$CCl_2{:}CH{\cdot}CH(OEt){\cdot}CN$		84—85/8	1·4642	1·2160	23
20	$CCl_2{:}CH{\cdot}CH(OBu){\cdot}CN$		102—103/5	1·4635	1·1443	23
21	$CCl_3{\cdot}CH{:}CH{\cdot}CN$		68—69/7	1·5082	1·4237	7
22	$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$	108—109				8
23	$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}COCl$		69—70/2·5	1·5130	1·6129	8
24	$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO{\cdot}NH_2$	138—138·5				8
25	$CCl_3{\cdot}CHCl{\cdot}CH_2{\cdot}CN$	43·5—44	105—107/6·5			7, 8
26	$CCl_3{\cdot}CH(OMe){\cdot}CH_2{\cdot}CN$		99·5/6·5	1·4820	1·3879	7
27	$CCl_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H$	121—122				8
28	$HO_2C{\cdot}[CH_2]_4{\cdot}NH_2$	155—156				5
29	$Me{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}CO_2H$		93—94/5	1·4442	1·1445	17
30	$Me{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}COCl$		61—62/28	1·4465	1·1765	17
31	$Me{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}CO{\cdot}NHPh$	63—64				17
32	$PhO{\cdot}[CH_2]_4{\cdot}CO_2H$	65—66				13
33	$PhS{\cdot}[CH_2]_4{\cdot}CO_2H$	63—64				13
34	$CH_2Cl{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}CO_2H$		129—131/5	1·4835	1·3421	15, 1
35	$CH_2Cl{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}COCl$		80/5	1·4840	1·3513	17
36	$CH_2Cl{\cdot}[CH_2]_2{\cdot}CHCl{\cdot}CO{\cdot}NHPh$	58—59				17
37	$CCl_2{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$		93—94/1	1·4898	1·3546	12
38	$CCl_2{:}CH{\cdot}[CH_2]_2{\cdot}CO{\cdot}NHPh$	72—73				12
39	$CCl_3{\cdot}[CH_2]_3{\cdot}CO_2H$	65—66				12
40	$CCl_3{\cdot}[CH_2]_3{\cdot}CO{\cdot}NHPh$	117—118				12
41	$CCl_3{\cdot}[CH_2]_3{\cdot}CO_2{\cdot}[CH_2]_4{\cdot}CCl_3$		164—165/1·5	1·5000	1·4060	12
42	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}CO_2H$		139—140/8	1·4895	1·2967	12
43	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}CO{\cdot}NHPh$	63—64				12
44	$CCl_2{:}CH{\cdot}[CH_2]_3{\cdot}CN$		80—81/3	1·4815	1·2018	5
45	$CCl_3{\cdot}[CH_2]_4{\cdot}CO_2H$	50—51	114—115/1			12
46	$CCl_3{\cdot}[CH_2]_4{\cdot}CO{\cdot}NHPh$	109—110				12
47	$CCl_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$		102/1	1·4800	1·2739	22
48	$CCl_3{\cdot}CHCl{\cdot}[CH_2]_3{\cdot}CO_2H$	47—48				18
49	$CH_2{:}CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$	60—61				13
50	$CH_2{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H$		118—120/14	1·4400	0·9500	13
51	$CH_2Cl{\cdot}[CH_2]_5{\cdot}CO_2H$		122—123/11	1·4392	1·0110	13
52	$CH_2Cl{\cdot}[CH_2]_5{\cdot}CO{\cdot}NH_2$	82—83				13
53	$CH_2Cl{\cdot}[CH_2]_5{\cdot}CO{\cdot}NHPh$	85—86				13
54	$EtO{\cdot}[CH_2]_6{\cdot}CO_2Et$		77—78/1·5	1·4292	0·9290	13
55	$PhO{\cdot}[CH_2]_6{\cdot}CO_2H$	56—57				13

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
56	$Me\cdot[CH_2]_4\cdot CHCl\cdot CO_2H$		92—93/1	1·4485	1·0830	17
57	$Me\cdot[CH_2]_4\cdot CHCl\cdot COCl$		76—77/13	1·4498	1·1006	17
58	$CCl_2{:}CH\cdot[CH_2]_4\cdot CO_2H$		120—121/1	1·4872	1·2479	12
59	$CCl_2{:}CH\cdot[CH_2]_4\cdot CO\cdot NHPh$	68—69				12
60	$CH_2Cl\cdot[CH_2]_4\cdot CHCl\cdot CO_2H$	22—24	128—130/1	1·4804	1·2441	17
61	$CH_2Cl\cdot[CH_2]_4\cdot CHCl\cdot CO\cdot NHPh$	42—43				17
62	$CH_2Cl\cdot[CH_2]_4\cdot CHCl\cdot COCl$		104/2	1·4817	1·2557	17
63	$CCl_3\cdot[CH_2]_5\cdot CO_2H$	36—37	120—121/0·5			5, 12
64	$CCl_3\cdot[CH_2]_5\cdot COCl$		91—92/1			5
65	$CCl_3\cdot[CH_2]_5\cdot CO\cdot NH_2$	78—79				5
66	$CCl_3\cdot[CH_2]_5\cdot CO\cdot NHPh$	98—99				12
67	$CCl_2{:}CH\cdot[CH_2]_5\cdot CO_2H$		128—129/1	1·4859	1·2120	12
68	$CCl_2{:}CH\cdot[CH_2]_5\cdot CO\cdot NHPh$	62—63				12
69	$CCl_2{:}CH\cdot[CH_2]_5\cdot CN$		99—100/1·5	1·4840	1·1410	12
70	$CCl_3\cdot[CH_2]_6\cdot CO_2H$	38—39	139—140/1			12
71	$CCl_3\cdot[CH_2]_6\cdot CO\cdot NHPh$	108—109				12
72	$CCl_3\cdot[CH_2]_6\cdot CN$		123—125/2·5	1·4787	1·2097	12
73	$CH_2Cl\cdot[CH_2]_7\cdot CO_2H$	29—30				13
74	$CH_2Cl\cdot[CH_2]_7\cdot CO_2Et$		136—137/8	1·4434	0·9854	13
75	$CH_2Cl\cdot[CH_2]_7\cdot COCl$		100—101/3			13
76	$CH_2Cl\cdot[CH_2]_7\cdot CO\cdot NH_2$	76—77				13
77	$CH_2Cl\cdot[CH_2]_7\cdot CO\cdot NHPh$	95—96				13
78	$CCl_3\cdot CHCl\cdot[CH_2]_5\cdot CO_2H$		158—160/1	1·5018		18
79	$NH_2\cdot[CH_2]_7\cdot CO_2H$	187—188				13
80	$PhO\cdot[CH_2]_8\cdot CO_2H$	69—70				13
81	$CCl_2{:}CH\cdot[CH_2]_6\cdot CO_2H$		132—133/1	1·4848	1·1806	12
82	$CCl_2{:}CH\cdot[CH_2]_6\cdot CO\cdot NHPh$	54—55				12
83	$Ph\cdot CH{:}CCl\cdot CO_2H$	139—140				23
84	$p\text{-}Cl\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$	122·5—123				20
85	$p\text{-}Cl\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$	244—245				23
86	$p\text{-}Br\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$	135				20
87	$p\text{-}Me\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$	195—196				11
88	$Ph\cdot[CH_2]_4\cdot CO_2H$	59—60	132—133/1·5			13
89	$\alpha\text{-}C_{10}H_7\cdot CH{:}CH\cdot CO_2H$	205—206				11

TABLE 8. *Other carboxylic acids and derivatives.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$HO_2C\cdot[CH_2]_3\cdot CHCl\cdot CO_2H$	104—105				17
2	$CCl_2{:}CH\cdot CH_2\cdot CH(CO_2Et)_2$		102—103/1·5	1·4633	1·2135	7
3	$HO_2C\cdot[CH_2]_4\cdot CHCl\cdot CO_2H$	88—89				17
4	$CCl_2{:}CH\cdot CHMe\cdot CH(CO_2Et)_2$		107/1	1·4605	1·1829	22
5	$NC\cdot CH_2\cdot[CH_2]_5\cdot CO_2H$		145—147/1·5			13
6	$HO_2C\cdot[CH_2]_5\cdot CHCl\cdot CO_2H$	98—99				17
7	$CCl_2{:}CH\cdot[CH_2]_3\cdot CH(CO_2Et)_2$		122—123/1·5	1·4650	1·1693	12
8	$CCl_3\cdot[CH_2]_4\cdot CH(CO_2Et)_2$		141—142·5/2·5	1·4624	1·2130	5
9	$(CCl_2{:}CH\cdot CH_2)_2C(CO_2Et)_2$	39—40	138—140/1·5			7
10	$CCl_2{:}CH\cdot[CH_2]_5\cdot CH(CO_2Et)_2$		142—143/1	1·4663	1·1341	12
11	$(HO_2C\cdot[CH_2]_3\cdot CCl_2)_2$	223				16
12	$NC\cdot[CH_2]_{10}\cdot CN$		156—167/2			16
13	$(HO_2C\cdot[CH_2]_4\cdot CCl{:})_2$	108·5—109·5				16
14	$(NC\cdot[CH_2]_4\cdot CCl{:})_2$		212—214/45	1·4943	1·1295	16
15	$NC\cdot[CH_2]_{14}\cdot CN$	48—49				16
16	$(HO_2C\cdot[CH_2]_6\cdot CCl{:})_2$	95—96				16
17	$(NC\cdot[CH_2]_6\cdot CCl{:})_2$		212—213/1	1·4895	1·0704	16
18	$EtO_2C\cdot[CH_2]_4\cdot CH(CO_2Et)_2$		147—149/2	1·4389	1·0568	13
19	$EtO_2C\cdot[CH_2]_6\cdot CH(CO_2Et)_2$		169—170/1·5	1·4419	1·0316	13

TABLE 9. *Acetylenic compounds.*

No.	Compound	M.p.°	B.p.°/mm.	n_D^{20}	d_4^{20}	Ref.
1	$ClC{:}C{\cdot}CH(OEt)_2$		55—56/10	1·4307	1·0300	21
2	$ClC{:}C{\cdot}CH(OBu)_2$		109·5—110·5/8	1·4450	0·9820	21
3	$CH{:}C{\cdot}CH(OBu)_2$		118—120/27	1·4280	0·8752	19
4	$CH{:}C{\cdot}[CH_2]_3{\cdot}OEt$		126—127	1·4204	0·8268	19
5	$CH{:}C{\cdot}[CH_2]_3{\cdot}OPh$		108—109/9	1·5210	0·9848	19
6	$CH{:}C{\cdot}[CH_2]_3{\cdot}NEt_2$		54/10	1·4412	0·8061	19
7	$CH{:}C{\cdot}[CH_2]_5{\cdot}OEt$		63—64/10	1·4289	0·8318	19
8	$CH{:}C{\cdot}[CH_2]_5{\cdot}NEt_2$		84—85/10	1·4460	0·8128	19
9	$CH{:}C{\cdot}[CH_2]_7{\cdot}OEt$		94—95/10	1·4350	0·8336	19
10	$CH{:}C{\cdot}[CH_2]_7{\cdot}SEt$		129—130/12	1·4771	0·8854	19
11	$CH{:}C{\cdot}CHBu^n{\cdot}OEt$		45—46/9	1·4206	0·8229	19
12	$[CH_2]_5{>}C(OH){\cdot}C{:}C{\cdot}CHO$		117·5—118·5/1·5	1·4741	1·0047	21
13	$[CH_2]_5{>}C(OH){\cdot}C{:}C{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	136—137				21
14	$Ph{\cdot}CH(OH){\cdot}C{:}C{\cdot}[CH_2]_2{\cdot}CH_2{\cdot}OEt$		185—186/3	1·5265	1·0284	19
15	$Ph{\cdot}CH(OH){\cdot}C{:}C{\cdot}[CH_2]_2{\cdot}CH_2{\cdot}NEt_2$		172—173/2	1·5327	1·006	19
16	$Me{\cdot}C{:}C{\cdot}CH(OBu)_2$		109·5—111/8	1·4380	0·8820	21
17	$Pr^n{\cdot}C{:}C{\cdot}CH(OEt)_2$		79—80/8	1·4338	0·8898	21
18	$Pr^i{\cdot}C{:}C{\cdot}CH(OEt)_2$		73—75/8	1·4321	0·8902	21
19	$Pr^i{\cdot}C{:}C{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	119—120				21
20	$Bu^n{\cdot}C{:}C{\cdot}CH(OEt)_2$		99—100/10	1·4328	0·8771	21
21	$Bu^n{\cdot}C{:}C{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	71—72				21
22	$Bu^i{\cdot}C{:}C{\cdot}CH(OEt)_2$		91—92/8	1·4397	0·8768	21
23	$Bu^i{\cdot}C{:}C{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$	55—55·5				21
24	$n\text{-}C_6H_{13}{\cdot}C{:}C{\cdot}CH(OEt)_2$		123—124/8	1·4395	0·8760	21
25	$n\text{-}C_6H_{13}{\cdot}C{:}C{\cdot}CH(OBu)_2$		156—158/8	1·4453	0·8653	21
26	$n\text{-}C_9H_{19}{\cdot}C{:}C{\cdot}CH(OEt)_2$		158—160/9	1·4419	0·8669	21
27	$Ph{\cdot}C{:}C{\cdot}CH(OEt)_2$		136—137/8	1·5219	0·9956	21
28	$Ph{\cdot}C{:}C{\cdot}CH(OBu)_2$		128—129/2	1·5058	0·9540	21
29	$\alpha\text{-}C_{10}H_7{\cdot}C{:}C{\cdot}CH(OBu)_2$		178—179/2	1·5610	1·0108	21