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FREE RADICAL ADDITION REACTIONS—I

THE REACTION OF TRI-, DI- AND MONO-CHLOROMETHANESULPHONYL CHLORIDES WITH ALKENES[1]

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Abstract—Trichloromethanesulphonyl chloride reacts with hept-1-ene, with propene, and with 1,1,1,3-tetrachloro-cyclohexene to give octane, 1,1,1,3-tetrachlorobutane, and 1-chloro-2-trichloromethylcyclohexane respectively, together with sulphur dioxide and small amounts of chloroform and carbon tetrachloride. Dichloromethanesulphonyl chloride, for which a new synthesis is described, and chloromethanesulphonyl chloride react with hept-1-ene in the presence of benzoyl peroxide to give 1,1,3-trichlorooctane and 1,3-dichlorooctane respectively. A general mechanism is proposed for these reactions, which are free radical in type.

Reductive cyclisation of 1,3-dichlorooctane with zinc gives n-pentylcyclopropane, providing a new route from alkenes to alkylcyclopropanes. In agreement with structural assignments, reduction of each of 1,1,1,3-tetrachlorooctane, 1,1,3-trichlorooctane, and 1,3-dichlorooctane with $LiAlH_4$ gives n-octane, with lesser amounts of n-pentylcyclopropane.

RECENT investigations have shown that the thermal decomposition of alkanesulphonyl chlorides, essentially according to the equation

$$R—SO_2Cl \rightarrow R^-Cl + SO_2,$$

proceeds by a free radical mechanism,[3] but only in isolated cases have attempts been made to trap or utilise the radical intermediates involved. Trichloromethanesulphonyl chloride reacts[4] with terminal alkenes, e.g. oct-1-ene, in the absence of free radical initiators to give tetrachloroalkanes and sulphur dioxide:

$$C_6H_{13}—CH{=}CH_2 + CCl_3—SO_2Cl \rightarrow C_9H_{16}Cl_4 + SO_2.$$

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

[2] Present address: C. Harris, Department of Chemistry, Texas Technological College, Lubbock, Texas, U.S.A.

[3] G. Geiseler and H. Reinhardt, *Z. Phys. Chem.* (*N. F.*) **28**, 24 (1961); G. Geiseler and R. Kuschmiers, *Z. Phys. Chem.* (*N. F.*) **28**, 33 (1961); cf. earlier data of A. Rieche and E. Naumann, *J. Prakt. Chem.* **9**, 108 (1959); H. F. Herbrandson, W. S. Kelly and J. Versnel, *J. Amer. Chem. Soc.* **80**, 3301 (1958). Alkanesulphonyl chlorides substituted by groups, e.g. phenyl, acetyl, allowing electron delocalisation in the resulting radical are particularly prone to decomposition; cf. H. Limpricht, *Ber. Dtsch. Chem. Ges.* **6**, 532 (1873); W. E. Truce and C. W. Vriessen, *J. Amer. Chem. Soc.* **75**, 2525 (1953).

[4] *British Patent* 649,555 (1951) to U.S. Rubber Co.; alkenylaromatics (e.g., styrene) are included in *U.S. Patent* 2,606,213 (1952), E. C. Ladd and L. Y. Kiley to U.S. Rubber Co.

The products, for which no evidence of homogeneity was adduced, were superficially identified with those of the corresponding initiated carbon tetrachloride–olefine reactions,[5] and so formulated as 1,1,1,3-tetrachloroalkanes, e.g.,

$$C_6H_{13}—CH{=}CH_2 + CCl_4 \rightarrow C_6H_{13}—CHCl—CH_2—CCl_3.$$

Even for the latter reactions, however, the chemical methods used to establish the homogeneity of the tetrachloroalkanes have not, in general, been sufficiently precise[6] to exclude the possibility of some transverse addition of radicals to the double bond to give the isomeric tetrachloroalkane. The present work, undertaken initially to settle the free radical nature of the trichloromethanesulphonyl chloride–olefine reaction and to establish the structure and homogeneity of the resulting adducts,[7] forms part of a more general investigation of the reactions of substituted alkanesulphonyl chlorides with olefines.

Preliminary experiments with trichloromethanesulphonyl chloride and hept-1-ene revealed that the quoted conditions were not ideal. Specifically, an excess of trichloromethanesulphonyl chloride complicated the working-up of reaction mixtures by sublimation during the distillation of the adduct, and the reaction times were excessively long; also, the use of benzene as solvent was unneccessary.[4] It was found that, using a small excess of hept-1-ene, reaction took place smoothly at reflux temperature with elimination of sulphur dioxide and gave 85–95% yields of adduct after only two to three hours.

The possibility that trichloromethanesulphonyl chloride might undergo thermal decomposition under the reaction conditions was discounted by showing that no observable decomposition occurred in toluene at 120° in the absence of initiators.[8] In the presence of benzoyl peroxide, and again in decalin exposed to the atmosphere, brisk evolution of sulphur dioxide took place on heating, and chlorination of the hydrocarbon was noted. The reaction between trichloromethanesulphonyl chloride and hept-1-ene would thus appear to be an induced one. Experiments were accordingly carried out with carefully purified reactants in sealed tubes, with degassing prior to reaction; virtually complete inhibition was observed. Under these conditions, 'pure' commercial trichloromethanesulphonyl chloride (cf. Experimental) reacted fully with pure hept-1-ene in the normal way. Further, the carefully purified compounds reacted fully when air and moisture were not rigorously excluded from the mixture. Traces of adventitious initiator in the sulphonyl chloride are apparently sufficient to bring about reaction. Samples of trichloromethanesulphonyl chloride liberate iodine from acidified potassium iodide solution, and it seems likely that the reaction under discussion is initiated by reactive hydroperoxides[9] present in the olefine or generated in the olefine *via* the sample of the sulphonyl chloride used.

Further evidence of the free radical nature of the trichloromethanesulphonyl chloride–hept-1-ene reaction came from inhibition experiments. The reaction was

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

[6] cf. G. Dupont, R. Dulou and C. Pigerol, *C.R. Acad. Sci., Paris* **240**, 628 (1955); and Refs there cited.

[7] The term 'adduct' is here used to describe the product(s) of addition of the radicals $CCl_3\cdot$ and $Cl\cdot$ to the double bond with no qualification as to the direction of addition.

[8] cf. E. S. Huyser and B. Giddings, *J. Org. Chem.* **27**, 3391 (1962).

[9] K. U. Ingold, *Chem. Rev.* **61**, 563 (1961).

found to be severely inhibited by *p*-benzoquinone, moderately by nitrobenzene, but imperceptibly by nitromethane. This is the same order, qualitatively, as that observed in the inhibition of vinyl polymerisation.[10]

Attention was next focussed on the by-products which accompanied the adduct. Gas-chromatographic analysis of the volatile fractions from the reaction showed the presence of small amounts (<3%) of chloroform and carbon tetrachloride. The same by-products were detected in the tetrachlorobutane (crude adduct) formed in the reaction of trichloromethanesulphonyl chloride with propene. Carbon tetrachloride is apparently derived from the sulphonyl chloride by abstraction of a chlorine atom by trichloromethyl radicals. Chloroform may be derived from the substrate through hydrogen abstraction by either trichloromethyl or trichloromethanesulphonyl radicals. Hydrogen abstraction by the latter species may play some part, since the selectivity of trichloromethanesulphonyl chloride as a chlorinating agent cannot be ascribed solely to hydrogen abstraction by trichloromethyl radicals.[8]

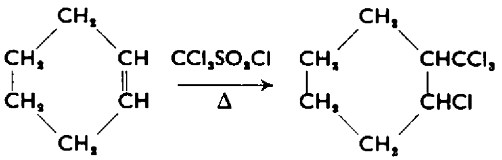
$$\text{(i)} \qquad \mathrm{CCl_3SO_2Cl + CCl_3\cdot \rightarrow CCl_3SO_2\cdot + CCl_4}$$

$$\mathrm{CCl_3SO_2\cdot \rightleftharpoons CCl_3\cdot + SO_2}$$

$$\text{(ii)} \qquad \mathrm{R'H + CCl_3\cdot \rightarrow R'\cdot + CHCl_3}$$

$$\mathrm{R'H + CCl_3SO_2\cdot \rightarrow R'\cdot + CCl_3SO_2H \rightarrow CHCl_3 + SO_2}$$

In the reaction of trichloromethanesulphonyl chloride with cyclohexene, the corresponding adduct was formed in 50–55% yield. The symmetry of the olefine in this case permits immediate formulation of the adduct as 1-chloro-2-trichloromethylcyclohexane, though whether the adduct contained both *cis*- and *trans*- forms was not established. Chloroform was isolated from this reaction in approximately 30% yield, demonstrating unequivocally the intermediacy of either trichloromethyl or trichloromethanesulphonyl radicals.



At this stage, the reactions leading to adduct may be summarised as follows:

$$\text{(1)} \qquad \mathrm{X\cdot + CCl_3SO_2Cl \rightarrow CCl_3SO_2\cdot + XCl}$$

$$\text{(2)} \qquad \mathrm{CCl_3SO_2\cdot \rightleftharpoons CCl_3\cdot + SO_2}$$

$$\text{(3)} \qquad \mathrm{CCl_3\cdot + {>}C{=}C{<} \rightarrow {>}C(CCl_3){-}C\cdot{<}}$$

$$\text{(4)} \qquad \mathrm{{>}C(CCl_3){-}C\cdot{<} + CCl_3SO_2Cl \rightarrow {>}C(CCl_3){-}CCl{<} + CCl_3SO_2\cdot}$$

where X· is the initiating species. Before considering whether radical addition in step (3) is specific, and hence whether one or both tetrachloroalkanes are formed, it is

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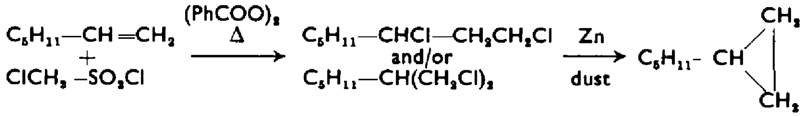
[10] F. A. Bovey and I. M. Kolthoff, *Chem. Rev.* **42**, 491 (1948).

convenient to refer to analogous reactions of hept-1-ene with related sulphonyl halides.

It has been noted that the reaction of trichloromethanesulphonyl chloride with normally purified olefines occurs when the reactants are merely heated together. By contrast, chloromethanesulphonyl chloride and hept-1-ene (present in small excess as before) display little tendency to react at reflux temperature unless an initiator, e.g. benzoyl peroxide, is added. Then, however, sulphur dioxide is briskly evolved and an adduct $C_8H_{16}Cl_2$ is formed in 70–75% yield; small amounts of benzoic acid and an olefinic impurity, presumably derived from abstraction by benzoyloxy radicals, are also formed. The reactions leading to this adduct are clearly of the same type as those in the previous case. A chloromethyl radical, generated in the step corresponding to (2) above, adds to the double bond, and chain transfer then leads to one or both of the possible dichloroalkanes. The two chlorine atoms stand in the 1,3-relationship in the adduct regardless of the precise formulation. This was confirmed experimentally by cyclisation of the adduct with zinc dust in ethanol to give n-pentylcyclopropane. The two reactions together provide a convenient route to alkylcyclopropanes from alkenes.



It was desirable to examine the corresponding reaction of hept-1-ene with dichloromethanesulphonyl chloride, but few convenient methods exist for the preparation of the latter compound. A recent prescription[11] involves the reaction of sodium dichloromethanesulphonate with phosphorus pentachloride; the required sodium salt was prepared, though in poor yield, from chloroform and aqueous sodium sulphite at elevated temperature and pressure. An attractive alternative was suggested by an older report[12] which stated that bromination of sodium acetonesulphonate gave sodium *sym*-tetrabromoacetonesulphonate, and that subsequent hydrolysis afforded sodium dibromomethanesulphonate.

$$CH_3COCH_2SO_3Na + 4Br_2 \rightarrow CHBr_2COCBr_2SO_3Na$$

$$CHBr_2COCBr_2SO_3Na + H_2O \rightarrow CHBr_2CO_2H + CHBr_2SO_3Na$$

Accordingly, an aqueous solution of sodium acetonesulphonate was exhaustively chlorinated at 60–70°, and the resulting solution then neutralised and evaporated; extraction with ethanol then gave sodium dichloromethanesulphonate directly in 40–50% yield. Evidently hydrolysis occurs under the strongly acidic conditions prevailing in the reaction. Dichloromethanesulphonyl chloride and hept-1-ene do not react appreciably at reflux temperature. When, however, benzoyl peroxide is added, sulphur dioxide is briskly evolved and an adduct $C_8H_{15}Cl_3$ is formed in 70–75% yield, together with small amounts of benzoic acid and an olefinic impurity. Again,

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[11] W. V. Farrar, *J. Chem. Soc.* 3058 (1960).

[12] D. R. P. 575,678 (1931), H. G. Allardt to Schering-Kahlbaum A. G.; cf. J. Houben and Th. Weyl, *Methoden der Organischen Chemie* (Edited by E. Müller), 4th Edition, Vol. 9, p. 373. Thieme, Stuttgart (1955).

a reaction sequence of the type (1)–(4) is indicated, a dichloromethyl radical being generated in the second step.

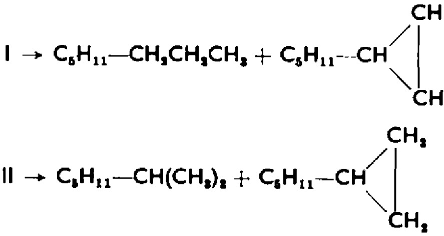
*Structures of the hept-*1*-ene adducts*

In each of the reactions described, two isomeric compounds might be formed, e.g. I and II in the reaction of trichloromethanesulphonyl chloride with hept-1-ene:

$$C_5H_{11}\text{—}CHCl\text{—}CH_2CCl_3 \qquad\qquad C_5H_{11}\text{—}CH(CCl_3)\text{—}CH_2Cl$$

I II

The adduct $C_8H_{14}Cl_4$ is apparently homogeneous on gas–liquid chromatography, but in the absence of reference samples of I and II it is clearly desirable to have available a chemical means of distinguishing between the two isomers. Valuable information has come from studying the behaviour of the adduct on reduction with lithium aluminium hydride. Applied to simple polyhaloalkanes, this leads to alkanes,[13] and, *prima facie*, compounds I and II should yield n-octane and 2-methylheptane respectively. Complete reduction of the adduct $C_8H_{14}Cl_4$ gave high yields (86%) of "C_8 hydrocarbon", closely resembling n-octane but seen from the IR spectrum to contain n-pentylcyclopropane as a minor product. The latter hydrocarbon arises because of the 1,3-arrangement of chlorine atoms in the adduct (cf. reductive cyclisation of the adduct $C_8H_{16}Cl_2$ with zinc), and shows that the decision between I and II rests upon more complex reduction products:



Gas–liquid chromatography of the "C_8 hydrocarbon" showed it to consist of n-octane and n-pentylcyclopropane only, the former predominating; no 2-methylheptane was found. A separate and important experiment showed that n-pentylcyclopropane is stable under the reaction conditions, and not therefore an intermediate in the formation of n-octane. The adduct is thus essentially homogeneous, and can be formulated as 1,1,1,3-tetrachlorooctane (I). Similar reduction of the adducts $C_8H_{15}Cl_3$ and $C_8H_{16}Cl_2$ gave high yields of n-octane, together with small amounts of n-pentylcyclopropane, but no 2-methylheptane; these adducts can thus be formulated as 1,1,3-trichlorooctane and 1,3-dichlorooctane respectively.

Support for these structures is forthcoming from a study of the ^1H NMR spectra of the adducts (see Table).

1,3-*Dichlorooctane*, $CH_2Cl\text{—}CH_2\text{—}CHCl(CH_2)_4CH_3$. The spectrum is in complete agreement with the proposed structure and rules out the possibility of the presence of any substantial amount of the alternative $(CH_2Cl)_2CH\text{—}(CH_2)_4CH_3$. In particular, the presence of a triplet, centred at $\tau = 6{\cdot}33$, which is attributed to the

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[13] V. H. Dibeler, *J. Research Natl. Bur. Standards* **44**, 363 (1950).

TABLE. ^{1}H NMR SPECTRA OF ADDUCTS*

Compound	Group	Chemical shift of peak centre τ	Nature of peak
$CH_2ClCH_2CHCl(CH_2)_4CH_3$	CH_2Cl	6·33	Triplet
	CH_2 at C-2	7·90	Multiplet
	CHCl	5·93	Multiplet
	$(CH_2)_4CH_3$	8–9·2	Broad
$CHCl_2CH_2CHCl(CH_2)_4CH_3$	$CHCl_2$	4·03	Multiplet
	CH_2 at C-2	7·50	Multiplet
	CHCl	5·93	Multiplet
	$(CH_2)_4CH_3$	8–9·2	Broad
$CCl_3CH_2CHCl(CH_2)_4CH_3$	CH_2 at C-2	6·82	Octet
	CHCl	5·70	Multiplet
	$(CH_2)_4CH_3$	8–9·2	Broad
$CCl_3CH_2CHClCH_3$	CH_2	6·80	Octet
	CHCl	5·60	Multiplet
	CH	8·28	Doublet

* Determined at 60 Mc/s in CCl_4 solution with $(CH_3)_4Si$ as internal standard.

CH_2Cl group, indicates that this group is adjacent to a —CH_2— group and not to a $\rangle$—CH group.

1,1,3-*Trichlorooctane*, $CHCl_2$—CH_2—$CHCl(CH_2)_4CH_3$. The spectrum is again fully confirmatory, and rules out the possibility of substantial amounts of the alternative $CHCl_2$—$CH(CH_2Cl)$—$(CH_2)_4CH_3$ being present. The hydrogen atom of the —$CHCl_2$ group, being on the same carbon atom as two strongly electronegative chlorine atoms, is expected to give rise to the signal observed at lowest field. This is a multiplet (at least four lines) centred at $\tau = 4{\cdot}03$. The complexity of this signal rules out the branched-chain structure which would lead to a doublet for the —$CHCl_2$ group adjacent to $\rangle$—CH.

The multiplet signal observed strongly suggests that the spectrum is of the ABX type[14] with the two hydrogen atoms of the methylene group at C-2 being magnetically non-equivalent, presumably because they are adjacent to the asymmetric carbon atom at C-3.

1,1,1,3-*Tetrachlorooctane*, CCl_3—CH_2—$CHCl(CH_2)_4CH_3$. In this case the spin–spin splitting pattern does not distinguish between the possible structures. However the chemical shift for the hydrogen atoms of the methylene group at C-2 suggests that this group is adjacent to the highly electronegative trichloromethyl group. It is interesting to note the steady downfield progression of the signal for the C-2 methylene

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[14] K. B. Wiberg and B. J. Nist, *Interpretation of* NMR *Spectra* p. 21. W. A. Benjamin, New York (1962).

group in the series of adducts as C-1 becomes more highly chlorinated, and consequently more electron withdrawing, thus deshielding the hydrogen nuclei attached to C-2.

CHEMICAL SHIFT FOR UNDERLINED ATOMS IN COMPOUNDS $\mathrm{RC\underline{H_2}CHCl(CH_2)_4CH_3}$

R	CH_2Cl	$CHCl_2$	CCl_3
τ	7·90	7·50	6·82

The signal for the $—CH_2—$ group at C-2 in 1,1,1,3-tetrachlorooctane is an eight-line multiplet, typical of the AB portion of an ABX spectrum, which again indicates the magnetic non-equivalence of the two hydrogen atoms, which are adjacent to the asymmetric carbon atom at C-3.

The mechanism of the addition reactions

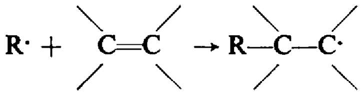
It is clear from the reaction conditions and the effects of initiators and inhibitors that a free radical addition reaction leads to the observed products. A general mechanism for the reactions, embodying (1)–(4) above, may be written as follows:
Initiation

$$RSO_2Cl + X\cdot \rightarrow RSO_2\cdot + XCl \tag{1a}$$

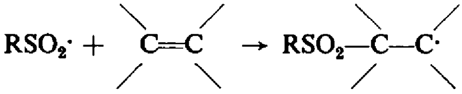
Dissociation of intermediate radical

$$RSO_2\cdot \rightleftharpoons R\cdot + SO_2 \tag{2a}$$

Addition reactions

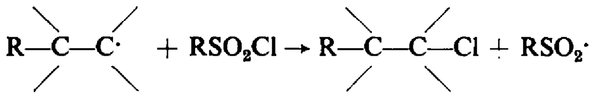


$$R\cdot + \mathrm{C{=}C} \rightarrow \mathrm{R{-}C{-}C}\cdot \tag{3a}$$

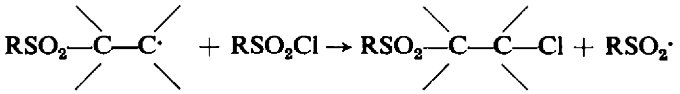


$$RSO_2\cdot + \mathrm{C{=}C} \rightarrow \mathrm{RSO_2{-}C{-}C}\cdot \tag{3b}$$

Propagation

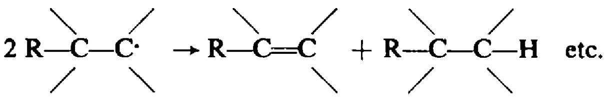


$$\mathrm{R{-}C{-}C}\cdot + RSO_2Cl \rightarrow \mathrm{R{-}C{-}C{-}Cl} + RSO_2\cdot \tag{4a}$$



$$\mathrm{RSO_2{-}C{-}C}\cdot + RSO_2Cl \rightarrow \mathrm{RSO_2{-}C{-}C{-}Cl} + RSO_2\cdot \tag{4b}$$

Termination



$$2\,\mathrm{R{-}C{-}C}\cdot \rightarrow \mathrm{R{-}C{=}C} + \mathrm{R{-}C{-}C{-}H} \quad \text{etc.} \tag{5}$$

With methanesulphonyl chloride, the bond dissociation energy for the process $CH_3SO_2\cdot \rightarrow CH_3\cdot + SO_2$ is 21·5 kcal/mole, and the activation energy for this reaction is at least this much.[15] Consequently, the equilibrium concentration of free methyl radicals is very low. Under the conditions used in the present work, methanesulphonyl chloride does not add to olefines.[16]

The bond dissociation energies[17] for reactions of the type $R—Y \rightarrow R\cdot + Y\cdot$, where R is CH_3, CH_2Cl, $CHCl_2$, and CCl_3, and Y is H, Br, Cl etc., suggest that chlorinated methyl radicals are resonance stabilised with respect to the methyl radical. A rough estimate of the amounts of resonance stabilisation leads to about 6 kcal/mole for chloromethyl radicals; about 13 kcal/mole for dichloromethyl radicals; and perhaps as much as 18 kcal/mole for trichloromethyl radicals. If it is assumed that the activation energies for the dissociations $RSO_2\cdot \rightarrow R\cdot + SO_2$ are diminished by these amounts from that observed for the methanesulphonyl radical, then it is at least qualitatively clear that the equilibrium concentrations of the chlorinated methyl radicals from the respective alkanesulphonyl radicals will be very much greater than that of methyl radicals from methanesulphonyl radicals.

RAMAN SPECTRAL DATA FOR RSO_2Cl

R	CH_3	CH_2Cl	$CHCl_2$	CCl_3
S—Cl (cm^{-1})	379	385	385	384
C—S (cm^{-1})	751	727	690	—

The Raman spectra of the various sulphonyl chlorides add weight to this argument. While the S—Cl stretching frequency is constant for this series, the C—S stretching frequency falls steadily with increasing chlorine substitution in the methyl group, suggesting a steadily weakening C—S bond.

With the chlorinated methanesulphonyl chlorides, the factors which control product formation are the position of equilibrium in (2a), which favours chloroalkyl radicals more than it would alkyl radicals, and the relative energetics of reactions (3a) and (3b). Since the formation of a new C—C bond is more exothermic than the formation of a new $C—SO_2$ bond by approximately 20 kcal/mole,[17] the formation of polychloroalkanes rather than polychloroalkyl sulphones is also reasonable on this basis. Further, it is the more stable of the isomeric radicals produced in step (3a) which determines the orientation of addition.

The free radical addition reactions described open up attractive possibilities for the synthesis of polychloroalkanes and derived products, e.g. alkanes and alkylcyclopropanes, and may well prove useful in other connections.

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin.

IR spectra were measured for liquid films.

Reagents. Trichloromethanesulphonyl chloride (Eastman Kodak) had m.p. 140–141° (Found: Cl, 64·95. Calc. for CCl_4O_2S: Cl, 65·1%), not raised by crystallization, and was used without purification for most experiments. Pure samples, when required, were prepared by sublimation

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[15] W. K. Busfield, K. J. Ivin, H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.* **57**, 1064 (1961).

[16] It is possible by using photochemical initiation to add methanesulphonyl chloride to an olefine; the product is a β-chloroalkyl methyl sulphone. Details will be reported in a later communication.

[17] T. L. Cottrell, *The Strengths of Chemical Bonds.* Butterworths, London (1958).

in vacuo (10^{-4} mm) and had m.p. 141–141·5° (lit[18] 140–140·5°), λ_{max} (EtOH) 204 mμ (ε 3100). Hept-1-ene was purified by fractional distillation, and the purity estimated by gas-liquid chromatography (2 metres squalene at 95°) and by determination of refractive index (n_D^{20} 1·3999 for pure hept-1-ene[19]). Benzoyl peroxide was purified by precipitation, and then dried.[20]

Other commercial products were distilled or crystallized before use, as necessary.

Thermal stability of trichloromethanesulphonyl chloride. Toluene (5g, 0·054 mole, n_D^{25} 1·4939) and trichloromethanesulphonyl chloride (3·5 g, 0·016 mole, m.p. 140–141°) were heated for 5 hr at 118–120° under N_2. No SO_2 was evolved, and practically all of the trichloromethanesulphonyl chloride (3·3 g) was recovered.

When this experiment was repeated in the presence of benzoyl peroxide, sulphur dioxide was evolved, and benzyl chloride identified in the reaction products.[8]

The reaction of trichloromethanesulphonyl chloride with hept-1-ene

(a) *Preparation of 1,1,1,3-tetrachlorooctane.* Hept-1-ene (14·7 g, 0·15 mole, n_D^{20} 1·4000) and trichloromethanesulphonyl chloride (21·8 g, 0·1 mole, m.p. 140–141°) were placed in a flask fitted with reflux condenser; the apparatus was flushed with N_2, and the mixture brought to reflux (94°) during 15 min. The temp was allowed to rise to 133° during 3 hr, and the reaction then concluded. Evolution of SO_2 virtually ceased after the first 2 hr. Hept-1-ene was removed *in vacuo*, and the residual oil distilled giving 1,1,1,3-tetrachlorooctane (23·5 g), b.p. 112·5–113·5°/10 mm, n_D^{20} 1·4772 (lit[21] b.p. 130°/19 mm, n_D^{20} 1·4772 for the 1:1-adduct from CCl_4 and hept-1-ene).

Redistillation afforded an analytical sample (Found: C, 38·2; H, 5·6; Cl, 56·1. Calc. for $C_8H_{14}Cl_4$: C, 38·1; H, 5·6; Cl, 56·3%); ν_{max} 2924(s), 2865, 1460, 1416, 1374, 1208, 1117, 1047, 1029, 980, 938, 800(s) and 705(s) cm^{-1}.

Similar results were obtained when trichloromethanesulphonyl chloride purified by sublimation was used, or when greater care was taken to exclude air and moisture from the reaction mixture.

(b) *Inhibition of the reaction by purification of reactants.* A Carius tube (100 ml) was cleaned with chromic acid, washed well with distilled water, dried overnight at 120°, and then degassed at 10^{-4} mm for 20 min. Freshly sublimed trichloromethanesulphonyl chloride (2·0 g, m.p. 141–141·5°) was introduced, and the tube again degassed at 10^{-4}–10^{-6} mm for 20 min. Meanwhile, freshly distilled hept-1-ene (1·8 g, n_D^{20} 1·4004) in a distillation tube cooled in liquid nitrogen was degassed for 20 min; the tube was then allowed to warm to room temp, and hept-1-ene collected in a second distillation tube cooled in liquid N_2. The process was repeated, and the hept-1-ene collected in the Carius tube; undistilled hept-1-ene from the two operations totalled ca. 0·2 ml. The Carius tube was sealed, heated at 90–115° for 3½ hr, chilled and opened. Trichloromethanesulphonyl chloride was removed by filtration, and the filtrate distilled *in vacuo* (10 mm) using a trap cooled in liquid N_2 as receiver. Hept-1-ene (1·1 g, n_D^{20} 1·4049, smelling strongly of trichloromethanesulphonyl chloride) was thus recovered; the undistilled residue (0·3 g) commenced to boil at 112°/10 mm, and possessed the odour of the tetrachlorooctane. A sublimate of trichloromethanesulphonyl chloride in the distillation apparatus was dissolved in ethanol, precipitated with water and dried. The recovered sulphonyl chloride (totalling 1·2 g) had m.p. 138–140°.

Reaction occurred under identical conditions between hept-1-ene (1·7 g) and unpurified trichloromethanesulphonyl chloride (3·1 g, m.p. 140–141°) to give the tetrachlorooctane (2·5 g, n_D^{20} 1·4770).

(c) *Inhibition of the reaction by addition of inhibitors.* A mixture of trichloromethanesulphonyl chloride (10·9 g, 0·05 mole, m.p. 140–141°), hept-1-ene (6 g, 0·06 mole, n_D^{20} 1·4010) and *p*-benzoquinone (0·35 g, 0·0032 mole) was refluxed for 2 hr (internal temp. 98–118°) and then allowed to cool. The trichloromethanesulphonyl chloride (5 g, m.p. 134–136°) that separated was collected, and the filtrate chilled providing a further crop (2 g, m.p. 140–141·5°). The filtrate, after concentration *in vacuo* (10 mm), gave a sublimate of sulphonyl chloride (2 g, m.p. 140–141°), and the dark brown residual oil (ca. 1 ml) commenced to boil at 112°/10 mm.

When nitrobenzene (0·7 g, 0·0057 mole) replaced *p*-benzoquinone in the above reaction, the internal temperature rose from 95° to 132° and evolution of SO_2 was noted. Distillation gave a

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[21] E. C. Kooyman and E. Farenhorst, *Rec. Trav. Chim.* **70**, 867 (1951).

forerun, b.p. <120°/25 mm and the tetrachlorooctane (n_D^{20} 1·4919, estimated yield 40–60%) as fractions (i) 2·5 g, b.p. 120–130°/25 mm and (ii) 5 g, b.p. 134°/25 mm, all contaminated with the sulphonyl chloride.

When nitromethane (0·7 g, 0·011 mole) replaced *p*-benzoquinone in the above reaction, complete consumption of the sulphonyl chloride was noted and the tetrachlorooctane (n_D^{20} 1·4774) obtained in 90% yield.

(d) *Identification of by-products.* Trichloromethanesulphonyl chloride (21·8 g, 0·1 mole, m.p. 140–141°) and hept-1-ene (14·7 g, 0·15 mole, n_D^{20} 1·4000; chromatographically pure) were reacted in the normal way, and on distillation *in vacuo* (12 mm) the volatile forerun was collected in a trap cooled in liquid N_2. This fraction separated into three well-defined components (retention times 10·5, 26 and 57; peak area ratio, 24:3:73) on chromatography on 2 metres squalene at 101°; the second and third components were identified as chloroform and hept-1-ene by comparison with authentic samples. The suspected presence of a fourth component (retention time 43, peak area <10% that of chloroform peak area) was confirmed by chromatography of the forerun (1 ml) from redistillation of the reaction volatiles (3·8 g) on squalene at 101°; this was identified as CCl_4.

The reaction of trichloromethanesulphonyl chloride with propene

Trichloromethanesulphonyl chloride (21·8 g, 0·1 mole, m.p. 140–141°) and propene (6·4 g, 0·15 mole) were placed in a 300 ml stainless steel autoclave and heated from 0° to 110° over 3 hr, then at 110–120° for a further 4 hr, with gentle rocking. When cool, the autoclave was opened and liquid products (20 g), smelling strongly of HCl, collected. Distillation gave a forerun, b.p. < 64°/18 mm, followed by slightly impure 1,1,1,3-tetrachlorobutane (9 g), b.p. 64°/18 mm.

GLC of the crude reaction product (2 metres tricresyl phosphate at 131°) showed the presence of four components (retention times 6·5, 11·5, 16·5 and 48; peak area ratio 2:6:2:90), the second and third being identified as chloroform and CCl_4 respectively; no allyl chloride was detected. These compounds were also present in the distilled tetrachlorobutane.

For the 1:1-adduct from CCl_4 and propene the following data are quoted:[22] (a) b.p. 65–69°/20 mm, n_D^{20} 1·4852, and (b) b.p. 60·5°/15 mm, n_D^{20} 1·4794.

The reaction of trichloromethanesulphonyl chloride with cyclohexene

Trichloromethanesulphonyl chloride (43·6 g, 0·2 mole, m.p. 140–141°) and cyclohexene (24 g, 0·3 mole, b.p. 83°) were placed in a flask fitted with reflux condenser; the apparatus was flushed with N_2, and the mixture brought to reflux (90°), when evolution of SO_2 was noticed. The temp was raised to 98° over 5 hr, and the reaction terminated. Volatile material (b.p. < 100°/13 mm), including some unreacted trichloromethanesulphonyl chloride, was removed and the residue distilled giving a small forerun, b.p. 121–125°/12 mm, followed by 1-chloro-2-trichloromethylcyclohexane (24 g), collected as two fractions, b.p. 125–129°/12 mm (n_D^{20} 1·5263) and b.p. 129–130°/12 mm (n_D^{20} 1·5274). The two fractions were combined, redistilled, and the heart fraction (5 g, b.p. 127°/12 mm) collected for analysis (Found: C, 35·8; H, 4·2. Calc. for $C_7H_{10}Cl_4$: C, 35·6; H, 4·2%); ν_{max} 2874(s), 2793, 1433(s), 1285, 1266, 1239, 1190, 1114, 1099, 1075, 1050, 1020, 951(s), 922, 908, 860, 841, 822, 790(s), 775(s), 756(s), 728 and 690 cm^{-1}.

The above experiment was repeated, but the temperature was raised to 105° over 1 hr and to 111° over the following 4 hr, all of the sulphonyl chloride being consumed. Distillation of the mixture then gave fraction (A) (12·5 ml), b.p. 71–74°/700 mm, fraction (B) (1·2 ml), b.p. < 44°/16 mm, and the residue afforded 1-chloro-2-trichloromethylcyclohexane (26·5 g) b.p. 124–127°/12 mm. Chromatography of fraction (A) on 2 metres squalene at 97° showed the presence of chloroform and cyclohexene, and traces (< 3%) of CCl_4; fraction (B) was similarly shown to contain a small amount (< 5%) of chloroform. By comparison with a series of prepared mixtures of chloroform and cyclohexene, fraction (A) was shown to contain approximately 27% of chloroform by volume (i.e. 3·4 ml, or 5·1 g).

For the 1:1-adduct from CCl_4 and cyclohexene the following data are given: (a) b.p. 148–150°/30 mm, n_D^{20} 1·5251,[21] and (b) b.p. 98–100°/10 mm, n_D^{20} 1·5232.[23]

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[22] [a] M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Amer. Chem. Soc.* **69**, 1100 (1947); [b] E. C. Kooyman, *Rec. Trav. Chim.* **70**, 684 (1951).

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*The reaction of chloromethanesulphonyl with hept-*1*-ene*

Chloromethanesulphonyl chloride[11] (14·3 g, 0·096 mole, b.p. 71°/13 mm, n_{D}^{20} 1·4858), hept-1-ene (15 g, 0·15 mole, n_{D}^{20} 1·4000) and benzoyl peroxide were placed in a flask fitted with reflux condenser; the apparatus was flushed with nitrogen, and the mixture brought to reflux (95°). The temp was raised to 110° over 5½ hr, benzoyl peroxide (0·2 g) being added after 1, 2½, 3¾ and 4¾ hr respectively. Hept-1-ene was removed *in vacuo*, and the residue distilled giving fractions (i) 1 g, b.p. 90–100°/14 mm, n_{D}^{20} 1·4520, (ii) 11·5 g, b.p. 100–101°/14 mm, n_{D}^{20} 1·4554, (iii) 0·5 g, b.p. 101–102°/14 mm, n_{D}^{20} 1·4560, and a residue, b.p. 101–102°/14 mm, from which benzoic acid, m.p. and mixed m.p. 121°, slowly sublimed. Redistillation of fraction (ii) gave 1,3-*dichlorooctane* (9 g), b.p. 100°/14 mm, n_{D}^{20} 1·4554 (Found: Cl, 38·5. $C_8H_{16}Cl_2$ requires: Cl, 38·8%); $\nu_{\max}$ 2890(s), 2841, 1686(w), 1441(s), 1408, 1370, 1312, 1279(s), 1250, 1235, 1200, 1149, 1112, 1029, 966, 929, 850, 812, 778 and 727(s) cm⁻¹.

Preparation of n-pentylcyclopropane. A mixture of 1,3-dichlorooctane (40 g, 0·22 mole, n_{D}^{20} 1·4537), anhydrous Na_2CO_3 (42 g), NaI (10 g), Zn dust (104 g) and 75% w/w ethanol (160 ml) was refluxed for 14 hr with vigorous stirring. The solid was then removed, and the filtrate diluted with water. The oil that separated was washed with water, dried ($MgSO_4$) and distilled giving a small forerun, b.p. 125°, followed by *n*-pentylcyclopropane (9·5 g) collected as two fractions, b.p. 125–126°, n_{D}^{20} 1·4105 and b.p. 126–127°, n_{D}^{20} 1·4105 (lit[24] b.p. 128–129°, n_{D}^{25} 1·4105). The hydrocarbon was chromatographically pure (2 metres dinonyl phthalate at 127°) and showed $\nu_{\max}$ 3106(w), 3030, 2960, 2940(s), 2865, 1456, 1372, 1252, 1163, 1098, 1037, 1010, 947, 895, 820, 797 and 723 cm⁻¹.

Preparation of dichloromethanesulphonyl chloride

ω-Chloroacetone (277·5 g, 3·0 mole) was added dropwise to a stirred solution of anhydrous Na_2SO_3 (416 g, 3·3 mole) in water (384 ml) over 3 hr at 55–65°, the temp being maintained by the heat of reaction. Stirring was continued for 1 hr at 55–60°, and then for ½ hr at 90–92°. Insoluble material was removed, and the filtrate stirred for 5 hr at 70–75°. Water (100 ml) was then added and the solution of sodium acetonesulphonate was chlorinated at 60–70° until no further absorption of chlorine took place. The resulting solution was made just alkaline to Congo Red by the addition of 30% NaOH aq, then evaporated to dryness *in vacuo*, and the residual solid extracted with boiling 95% ethanol. The ethanolic extracts deposited crude sodium dichloromethanesulphonate (215 g) as lustrous plates; the salt was dried at 100° for 12 hr, and used without further purification.

A mixture of sodium dichloromethanesulphonate (94 g), PCl_5 (120 g) and phosphorus oxychloride (30 ml) was heated in an oil bath at 105 ± 5° for 3 hr. Phosphorus oxychloride was removed *in vacuo*, and the residue was taken up in chloroform (100 ml). The solution was washed with water (2 × 25 ml), dried ($MgSO_4$), evaporated, and the residue distilled giving dichloromethanesulphonyl chloride (34 g), b.p. 60–62°/9 mm, n_{D}^{20} 1·4949 (lit[11] b.p. 64°/14 mm).

For characterization, the sulphonyl chloride was converted to dichloromethanesulphonanilide, which crystallized from benzene–light petroleum (b.p. 60–80°) as plates, m.p. 76° (lit[11] m.p. 78°).

*The reaction of dichloromethanesulphonyl chloride with hept-*1*-ene*

Dichloromethanesulphonyl chloride (30 g, 0·16 mole, n_{D}^{20} 1·4949), hept-1-ene (22·5 g, 0·23 mole, n_{D}^{20} 1·4010) and benzoyl peroxide (0·3 g) were placed in a flask fitted with reflux condenser; the apparatus was flushed with N_2 and the mixture brought to reflux (94°). The temperature was raised to 110° over 3 hr. After the reaction had proceeded for ½ hr, another portion of benzoyl peroxide (0·25 g) was added, and another (0·3 g) after 1½ hr. At the end of the reaction period, hept-1-ene was removed *in vacuo* and the residue distilled giving (i) 1 g, b.p. 99·5°/7 mm, free from sulphonyl chloride (ii) 17·5 g, b. p. 99·5-101·5°/7mm, n_{D}^{20} 1·4616, (iii) 8·0 g, b.p. 101·5–103·5°/7 mm, n_{D}^{20} 1·4632, and a residue b.p. 103·5°/7 mm from which benzoic acid, m.p. and mixed m.p. 121°, slowly sublimed. Fractions (ii) and (iii) had virtually identical IR spectra, but the former fraction contained an olefinic impurity ($\nu_{\max}$ 1669 cm⁻¹). These two fractions were combined, added to the corresponding fractions from an identical experiment, and the whole carefully fractionated; 1,1,3-*trichlorooctane* (16 g) was collected as a steadily boiling fraction, b.p. 111°/13 mm, n_{D}^{20} 1·4632 (Found: Cl, 48·4. $C_8H_{15}Cl_3$ requires: Cl, 48·9%); $\nu_{\max}$ 2910(s), 2840, 1451, 1425, 1368, 1307, 1241, 1112, 1078, 1026, 965, 918, 762(s) and 727 cm⁻¹.

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Reduction of the three polychlorooctanes with $LiAlH_4$

A solution of 1,1,1,3-tetrachlorooctane (12·6 g, 0·05 mole, n_D^{20} 1·4771) in dry, peroxide-free dioxan (40 ml, AnalaR grade) was added dropwise during 2½ hr to a mixture of $LiAlH_4$ (12 g, 0·35 mole) and dioxan (150 ml) at reflux under N_2, with stirring. After a further 5½ hr at reflux, the mixture was cooled, and excess $LiAlH_4$ decomposed by the dropwise addition of water. After ¾ hr, the mixture was slowly stirred into 4N H_2SO_4 (200 ml); light petroleum (80 ml, b.p. 40–60°) was added after 10 min, and stirring continued for 1 hr. The organic phase was separated, and the extraction repeated with light petroleum (50 ml, then 40 ml). The combined extracts were washed with 45% H_2SO_4 (4 × 25 ml) to remove dioxan, and then well with water to remove acid. The dried extract was evaporated and the residue distilled, the products being collected as one fraction (4·9 g, 86%), b.p. 120–126°. The IR spectrum of this material was similar to that of n-octane, but showed the presence of n-pentylcyclopropane. The crude hydrocarbon was chromatographed on 2 metres dinonyl phthalate at 127°; two components were observed (retention times 54 and 66) and identified as n-octane (54) and n-pentylcyclopropane (66) by comparison with authentic samples. The introduction of pure 2-methylheptane produced a new peak (retention time 42). The hydrocarbon mixture from the reduction contained approximately 75% octane and 25% n-pentylcyclopropane.

1,1,3-Trichlorooctane (15 g, 0·07 mole, n_D^{20} range 1·4592–1·4632) in dioxan (50 ml) was similarly treated with $LiAlH_4$ (9 g) in dioxan (150 ml), and the products isolated as before. The crude hydrocarbon (6·4 g, 81%, b.p. 120–127°) was shown to contain n-octane and n-pentylcyclopropane only by chromatography on 2 metres dinonyl phthalate at 127° when two peaks were observed (retention times 54 and 66); no 2-methylheptane was detected.

1,3-Dichlorooctane (15 g, 0·082 mole, n_D^{20} 1·4540) in dioxan (50 ml) was also reduced with $LiAlH_4$ (9 g) in dioxan (150 ml). The crude hydrocarbon (8·1 g, 87%, b.p. 121–127°), isolated as previously, was chromatographed on 2 metres dinonyl phthalate at 127° and found to contain n-octane and n-pentylcyclopropane (retention times 54 and 66), but no 2-methylheptane.

Stability of n-pentylcyclopropane to $LiAlH_4$

n-Pentylcyclopropane (2 g, n_D^{20} 1·4105) and $LiAlH_4$ (1·5 g) in dioxan (40 ml) were refluxed for 6½ hr under nitrogen, cooled, and the hydride decomposed by the dropwise addition of water. The mixture was stirred into 4N H_2SO_4 (60 ml) and, after 1 hr, extracted with light petroleum (50 ml, b.p. 0–40°). The extract was washed free from dioxan, dried ($MgSO_4$), and chromatographed directly on 2 metres dinonyl phthalate at 127°. The chromatogram showed one peak (retention time 66); the addition of authentic samples of n-octane and 2-methylheptane produced two peaks (retention times 54 and 42).

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