744. *Chlorine-activation by Redox-transfer. Part III.[1] The "Abnormal" Addition of Chloroform to Olefins.*
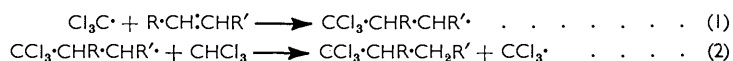
By M. Asscher and D. Vofsi.

Chloroform is added to olefins under the catalytic influence of copper(I or II) or iron(II or III) chloride, the latter being much more effective. The adducts are 1,1,3-trichloroalkanes, as distinguished from 1,1,1-trichloro-alkanes which are the products of peroxide-catalysed reactions.

A free-radical chain mechanism is suggested, in which metal chloride participates in the propagation as a chlorine-atom transfer agent ("redox-transfer"), leading to specific chlorine activation and, as a consequence, to addition of chloroform in the sense $CHCl_2$–Cl across the double bond. The initiation mechanism is discussed.
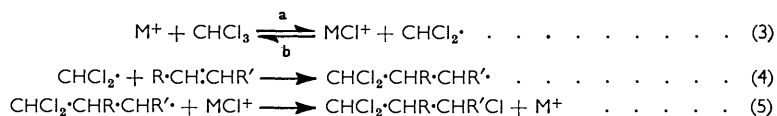
Peroxide-catalysed additions of chloroform to olefins at 140° yield, in addition to 1,1,1-trichloroalkanes, also 1,1-dichloro-, 1,1,3-trichloro-, and 1,1,1,3-tetrachloro-alkanes, indicating that at this temperature the intermediate radicals abstract chlorine as well as hydrogen from chloroform.

IN Part II[1] of this series it was shown that the apparent reactivity of carbon tetrachloride can be greatly enhanced by redox-transfer * leading to the formation of 1:1 adducts, *e.g.*, with vinylic monomers of the electron-acceptor type such as acrylonitrile or acrylic esters, which in peroxide-induced reactions give high telomers even with the much more reactive bromotrichloromethane. Non-polymerisable olefins yield 1:1 adducts with carbon tetrachloride, both in peroxide-induced and redox-transfer reactions.

For chloroform the case is different. Ordinary sources of free radicals induce addition across the double bond in the sense CCl_3–H, as the radical formed in step (1) abstracts hydrogen from chloroform:[2,3]

$$Cl_3C\cdot + R\cdot CH\dot{\cdot}CHR' \longrightarrow CCl_3\cdot CHR\cdot CHR'\cdot \qquad \dots \dots \quad (1)$$

$$CCl_3\cdot CHR\cdot CHR'\cdot + CHCl_3 \longrightarrow CCl_3\cdot CHR\cdot CH_2R' + CCl_3\cdot \qquad \dots \dots \quad (2)$$

Redox-transfer, however, leads to specific chlorine-activation by the propagating sequence (3)—(5) [M^+ denoting Cu(I) or Fe(II) ion, and MCl^+ Cu(II) or Fe(III) ion with at least one chloride ion bound in the co-ordination shell], that results in addition of chloroform in the sense $CHCl_2$–Cl:

$$M^+ + CHCl_3 \overset{a}{\underset{b}{\rightleftharpoons}} MCl^+ + CHCl_2\cdot \qquad \dots \dots \dots \quad (3)$$

$$CHCl_2\cdot + R\cdot CH\dot{\cdot}CHR' \longrightarrow CHCl_2\cdot CHR\cdot CHR'\cdot \qquad \dots \dots \quad (4)$$

$$CHCl_2\cdot CHR\cdot CHR'\cdot + MCl^+ \longrightarrow CHCl_2\cdot CHR\cdot CHR'Cl + M^+ \qquad \dots \dots \quad (5)$$

(Bromodichloromethane is added in this fashion in peroxide-induced reactions.[4])

The interesting situation would thus arise that isomeric adducts can be formed selectively by mechanisms which are both of the radical-chain type. This has now been verified[5] for iron and copper chloride-catalysed addition of chloroform to but-1-ene, but-2-ene, oct-1-ene, styrene, and butadiene.

The reactions are carried out at 100—145°, in methanol, propan-2-ol, or acetonitrile (see Table 1). Iron chloride is a much more efficient catalyst than copper chloride and

* For the meaning of redox-transfer see Parts I and II[1] of this series.

[1] Asscher and Vofsi, *J.*, 1963, 1887.
[2] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.
[3] (a) Harmon, Ford, Hanford, and Joyce, *J. Amer. Chem. Soc.*, 1950, **72**, 2213; (b) De Tar and Wells, *ibid.*, 1960, **82**, 5839; (c) Fox, Evans, and Szwarc, *Trans. Faraday Soc.*, 1961, **57**, 1927.
[4] Kharasch, Kuderna, and Urry, *J. Org. Chem.*, 1948, **13**, 898.
[5] Asscher and Vofsi, *Chem. and Ind.*, 1962, 209.

affords good yields of 1,1,3-trichloroalkanes. Styrene gives 1′,3′,3′-trichloropropyl-benzene; in alcohol, this adduct is solvolysed. Products of acid-catalysed side-reactions of styrene with itself and with solvent are also obtained. Butadiene gives 1,1,5-tri-chloropent-3-ene (according to the infrared absorption spectrum) and a mixture of isomeric trichlorononadienes; in methanol the adduct is solvolysed. Under the prevailing conditions 1,1,1-trichloroalkanes (the product of peroxide-induced reactions between chloroform and olefins) are not isomerised to 1,1,3-trichloroalkanes and therefore cannot be their precursors.
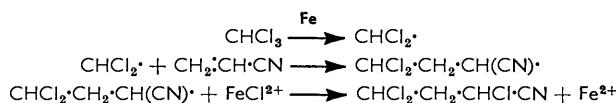
TABLE 1.

Reaction of olefins (0·1 mole) with chloroform (0·3 mole) in solvent (0·2 mole) with catalyst (2 mmoles).

Run No.	Solvent	Catalyst	NH²Et²Cl (3 mmoles)	Benzoin (2 mmoles)	Temp.	Hr.	Product	Yield (%)	Residue (g.)	Note
					But-1-ene					
1	MeOH	$FeCl_3,6H_2O$	+	−	145°	15	$CHCl_2 \cdot CH_2 \cdot CHEtCl$	83	0·6	
2	,,	,,	−	−	130	15	,,	trace	—	
3	,,	,,	+	−	130	15	,,	4	0·6	
4	,,	,,	+	−	130	45	,,	71	1·5	
5	,,	,,	−	+	130	15	,,	45	1·4	
6	,,	,,	+	+	130	15	,,	60	1·9	
7	,,	$FeCl_2,4H_2O$	−	−	130	15	,,	51	1·2	
8	,,	,,	+	−	130	15	,,	65	1·0	
9	MeCN	$FeCl_3,6H_2O$	+	−	130	15	,,	1·5	0·2	
10	,,	,,	−	+	130	15	,,	52	1·5	
11	,,	,,	+	+	130	15	,,	53	1·7	
12	,,	$FeCl_2,4H_2O$	−	−	130	15	,,	28	1·2	
13	,,	,,	+	−	130	15	,,	43	0·9	
					cis-But-2-ene					
14	MeOH	$FeCl_3,6H_2O$	+	−	140	27	$CHCl_2 \cdot CHMe \cdot CHMeCl$	60	0·2	1, 2
15	PrⁱOH	,,	−	+	126	15	,,	23	0·3	1, 2
16	,,	,,	−	+	101	20	,,	10	0·3	1, 2
17	MeCN	,,	+	+	101	20	,,	26	0·4	1, 2
18	,,	$CuCl_2,2H_2O$	+	+	143	23	,,	3·5	0·6	1, 2
					trans-But-2-ene					
19	,,	$FeCl_3,6H_2O$	+	+	143	23	,,	68	0·9	1, 2
					Oct-1-ene					
20	MeOH	,,	−	−	140	17	$CHCl_2 \cdot CH_2 \cdot CHCl \cdot C_6H_{13}$	47	2·0	
21	,,	,,	−	−	140	22	,,	71	2·0	
22	,,	,,	+	−	140	22	,,	80	1·9	
23	,,	,,	+	+	130	15	,,	84	2·5	
24	,,	,,	+	−	130	15	,,	4	—	
25	,,	$FeCl_2,4H_2O$	−	−	140	22	,,	69	1·8	
					Styrene					
26	,,	$FeCl_3,6H_2O$	−	−	140	19	$CHPhCl \cdot CH_2 \cdot CHCl_2$ + $MeO \cdot CHPh \cdot CH_2 \cdot CHCl_2$ (95%)	35	4·1	3
27	MeCN	,,	+	+	126	15	$CHPhCl \cdot CH_2 \cdot CHCl_2$	38	6·8	
					Butadiene					
28	,,	,,	+	+	130	16	$CHCl_2 \cdot CH_2 \cdot CH\vdots CH \cdot CH_2Cl$	32	6·6	3
29	MeOH	,,	+	−	140	22	$CHCl_2 \cdot CH_2 \cdot CH\vdots CH \cdot CH_2OMe$	52	6·0	

Notes: (1) Unisomerised but-2-ene remained after reaction. (2) The product is a mixture of diastereoisomers. (3) See Experimental.

de Maldè *et al.*[6a] have obtained an " abnormal " adduct, $CHCl_2 \cdot CH_2 \cdot CHCl \cdot CN$, by heating chloroform and acrylonitrile in a steel autoclave at 190°. This school assumes [6b] that the product is formed as a result of a non-chain reaction involving metallic iron and ferric chloride:
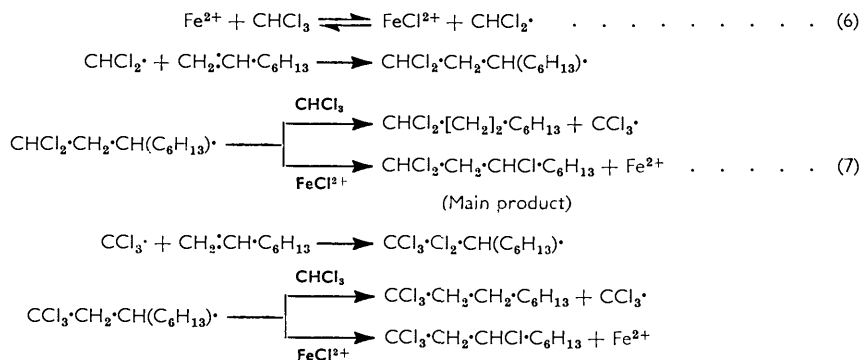
$$CHCl_3 \xrightarrow{\text{Fe}} CHCl_2 \cdot$$
$$CHCl_2 \cdot + CH_2 \vdots CH \cdot CN \longrightarrow CHCl_2 \cdot CH_2 \cdot CH(CN) \cdot$$
$$CHCl_2 \cdot CH_2 \cdot CH(CN) \cdot + FeCl^{2+} \longrightarrow CHCl_2 \cdot CH_2 \cdot CHCl \cdot CN + Fe^{2+}$$

⁶ (*a*) de Maldè, Minisci, Pallini, Volterra, and Quilico, *Chimica é Industria*, 1956, **38**, 371; (*b*) Minisci and Galli, *Tetrahedron Letters*, 1962, 533.

Whereas the last step of this sequence is identical with that postulated by us for redox-transfer,[5] these workers do not consider the possibility of oxidation of ferrous ion by chloroform (step 3a), which gives the overall reaction its chain-character (see below).

As in additions of carbon tetrachloride,[1] solvolysis by alcohol (if used as solvent) is encountered only where the chloroform-adduct is a reactive allylic or benzylic chloride (Table 1, nos. 26 and 29). In additions to aliphatic olefins there is complete absence of solvolysis of the adduct. This shows that a carbonium ion cannot be a precursor of the resulting trichloride, and that therefore step (5) proceeds by ligand- and not by one-electron-transfer.[7] The absence of solvolysis also rules out a mechanism in which a dichloromethyl cation, formed from chloroform, is initially added to olefin. Such a Friedel–Crafts type mechanism is *a priori* highly unlikely, in view of the solvent (alcohol) and hydrated catalyst used. Further, if ferric chloride were required to produce dichloromethyl cations by abstraction of a chloride ion from chloroform, the latter should be more reactive than carbon tetrachloride. The contrary is found to be true (see below). Finally, at 130° and lower, ferric chloride induces a reaction only after a very long induction period (compare nos. 3 and 4 in Table 1), which is much shortened by the presence of a reducing agent (benzoin: Table 1, nos. 5 and 6) or the use of ferrous chloride as the catalyst (Table 1, nos. 7, 8, 12, and 13). In the conditions adopted, ferrous chloride thus appears to be superior to ferric chloride, the supposed Friedel–Crafts catalyst.

Chloroform is much less reactive than carbon tetrachloride. Under identical conditions [iron chloride-catalysis, benzoin as initiator (see below), reaction temperature 101°], 95% of the *cis*-but-2-ene initially present reacts with the excess of carbon tetrachloride in 4 hours,[1] against 10% with chloroform in 20 hours (Table 1, no. 16). This large difference must be due to a much slower reaction of ferrous ion with chloroform (step 3a); this is compatible with the weaker electron-acceptor properties of the latter.[8] With cuprous ion, the difference is still much more pronounced (Table 1, nos. 18). [We have no direct evidence for step (3). Reactions in the presence of labelled chloride ion are being carried out in order to settle this point. At present, we prefer to write this step as an equilibrium, which actually may be displaced far to the left.]

The iron chloride-catalysed addition of chloroform to oct-1-ene gives minor amounts of several by-products, of which 1,1-dichloro-, 1,1,1-trichloro- (traces), and 1,1,1,3-tetra-chloro-nonane have been identified by gas chromatography. Similar products are formed from but-1-ene. The formation of these compounds, which amount to about 3% of total product, can be accounted for by the following equations for the case of oct-1-ene:

$$Fe^{2+} + CHCl_3 \rightleftharpoons FeCl^{2+} + CHCl_2\cdot \qquad \qquad (6)$$

$$CHCl_2\cdot + CH_2{:}CH\cdot C_6H_{13} \longrightarrow CHCl_2\cdot CH_2\cdot CH(C_6H_{13})\cdot$$

$$CHCl_2\cdot CH_2\cdot CH(C_6H_{13})\cdot \begin{cases} \xrightarrow{\ CHCl_3\ } CHCl_2\cdot[CH_2]_2\cdot C_6H_{13} + CCl_3\cdot \\ \xrightarrow[FeCl^{2+}]{} CHCl_2\cdot CH_2\cdot CHCl\cdot C_6H_{13} + Fe^{2+} \quad \dots \quad (7) \\ \text{(Main product)} \end{cases}$$

$$CCl_3\cdot + CH_2{:}CH\cdot C_6H_{13} \longrightarrow CCl_3\cdot Cl_2\cdot CH(C_6H_{13})\cdot$$

$$CCl_3\cdot CH_2\cdot CH(C_6H_{13})\cdot \begin{cases} \xrightarrow{\ CHCl_3\ } CCl_3\cdot CH_2\cdot CH_2\cdot C_6H_{13} + CCl_3\cdot \\ \xrightarrow[FeCl^{2+}]{} CCl_3\cdot CH_2\cdot CHCl\cdot C_6H_{13} + Fe^{2+} \end{cases}$$

[7] Nonhebel and Waters, *Proc. Roy. Soc.*, 1957, *A*, **242**, 26; Kochi, *Tetrahedron*, 1962, **18**, 483; *J. Amer. Chem. Soc.*, 1962, **84**, 774, 2785; Kochi and Rust, *ibid.*, p. 3946; Kumamoto, de la Mare, and Rust, *ibid.*, 1960, **82**, 1935.

[8] Sharpe and Walker, *J.*, 1962, 160; Stevenson and Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 140; Kuivila, Menapace, and Warner, *ibid.*, p. 3584; Lorenz and Becker, *J. Org. Chem.*, 1962, **27**, 3370.

The relative unimportance of these side reactions is a direct outcome of the efficiency of ferric chloride in step (7). Formation of dichloromethyl radicals (step 6) is then the only possible course.
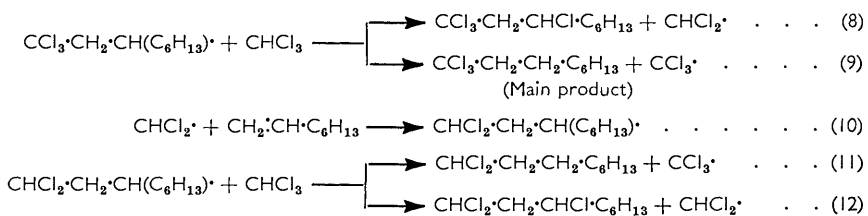
It was found that, in methanol, the presence of a soluble chloride (diethylammonium chloride) somewhat enhances the yields (cf. nos. 5 and 21 with 6 and 22 of Table 1). This is probably due to the suppression of hydrolysis of ferric chloride. In the absence of added chloride, ferric oxide hydrate was precipitated in the initial stages of the reaction.

The propagation step (3) can, of course, also initiate the reaction, provided that ferrous ions are present from the start. If there are initially only ferric ions, any reduction of them, *e.g.*, by the solvent or the olefin, can be regarded as an initiation (see also ref. 1). When this reduction is very slow, as it apparently is at $\gg 130°$, there is a long induction period (cf. in Table 1, nos. 3 and 4). Faster initiation, and thereby a shorter induction period, can be brought about by the use of a reducing agent (benzoin: Table 1, nos. 5, 6, 10, and 11), of ferrous chloride as catalyst (Table 1, nos. 7, 8, 12, and 13), or by a higher temperature (Table 1, no. 1). These observations strongly indicate a free-radical chain mechanism in which the initiation step involves formation of ferrous ion.

The structures assigned to the adducts of chloroform to oct-1-ene, but-1-ene, the but-2-enes, and styrene are supported by their conversion into non-2-enal, pent-2-enal, 2-methylbut-2-enal, and cinnamaldehyde, respectively (cf. ref. 4). Both 1′,3′,3′, trichloropropylbenzene (the styrene–chloroform adduct) and 1,1,5-trichloropent-3-ene (the butadiene–chloroform adduct) react with thiourea, giving an isothiouronium chloride in which chloride ion amounts to one-third of the total chlorine (Table 2, nos. 11 and 12). This shows the presence of one reactive (allylic or benzylic) and two inert chlorine atoms in the parent trichloro-hydrocarbons.

The addition of chloroform to but-2-ene gives a mixture of the two diastereoisomers expected for the structure $CH_3 \cdot CH(CHCl_2) \cdot CHCl \cdot CH_2$ (Table 2, no. 2), whereas only one adduct of the structure $CH_3 \cdot CH_2 \cdot CH(CCl_3) \cdot CH_3$ is obtained in a peroxide-catalysed reaction (Table 2, no. 4). Nuclear magnetic resonance further support the structures assigned. The composition of the diastereoisomeric mixture is 59—41% for iron chloride-catalysis at 101°, 126°, and 143°, for both *cis*- and *trans*-but-2-ene; this ratio is not affected by solvent or an excess of chloride ion (Table 1, nos. 14—17 and 19). Copper chloride-catalysis at 143° gives a ratio of 56—44% (Table 1, no. 18) (cf. similar additions of carbon tetrachloride [1]).

Peroxide-induced reactions between chloroform and oct-1-ene have been carried out at 140°, in order to allow a comparison with reactions catalysed by iron chloride at that temperature. Here, in addition to 1,1,1-trichlorononane (the main product), there are formed 14% of 1,1-dichloro-, 5% of 1,1,3-trichloro-, and 5% of 1,1,1,3-tetrachloro-nonane (identified by gas chromatography). Similar products are formed from but-1-ene. Their formation can be understood by assuming that, at 140°, intermediate radicals abstract, not only hydrogen, but also chlorine from chloroform, according to the following equations for the case of oct-1-ene:

$$CCl_3 \cdot CH_2 \cdot CH(C_6H_{13}) \cdot + CHCl_3 \longrightarrow \begin{cases} CCl_3 \cdot CH_2 \cdot CHCl \cdot C_6H_{13} + CHCl_2 \cdot & \cdots \quad (8) \\ CCl_3 \cdot CH_2 \cdot CH_2 \cdot C_6H_{13} + CCl_3 \cdot & \cdots \quad (9) \\ \text{(Main product)} \end{cases}$$

$$CHCl_2 \cdot + CH_2 \colon CH \cdot C_6H_{13} \longrightarrow CHCl_2 \cdot CH_2 \cdot CH(C_6H_{13}) \cdot \quad \cdots \cdots \quad (10)$$

$$CHCl_2 \cdot CH_2 \cdot CH(C_6H_{13}) \cdot + CHCl_3 \longrightarrow \begin{cases} CHCl_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_{13} + CCl_3 \cdot & \cdots \quad (11) \\ CHCl_2 \cdot CH_2 \cdot CHCl \cdot C_6H_{13} + CHCl_2 \cdot & \cdots \quad (12) \end{cases}$$

The product of step (12) is identical with that of step (7), the main product of a redox-transfer reaction. Hydrogen abstraction apparently still greatly predominates. As a consequence, much more 1,1-dichlorononane is formed (step 11) than 1,1,3-trichloro- or

1,1,1,3-tetrachloro-nonane (steps 12 and 8, respectively). Concurrent hydrogen- and chlorine-abstraction is in accord with the results of Stacey and Walling,[9] who observed the related phenomenon with deuteriochloroform.

EXPERIMENTAL

Materials.—Chloroform, methanol, propan-2-ol, acetonitrile, ferrous and ferric chloride hydrate, and diethylammonium chloride were B.D.H. products. Benzoin was once recrystallised from carbon tetrachloride and had m. p. 137°.

But-1-ene, *cis*- and *trans*-but-2-ene, and butadiene were Matheson C.P. products, of >99% purity. Styrene was of commercial polymerisation-grade, used as supplied, without removal of inhibitor. Oct-1-ene was freshly distilled and subsequently freed from peroxide by percolation through acid-washed alumina.

The physical constants and analyses of the products recorded in Table 2 were measured after fractionation of the crude products through a column of 50 cm. length, packed with glass helices. The purity of products was assessed by gas chromatography.

TABLE 2.

Chloroform adducts and their derivatives.

No.	Compound	B. p./mm.	M. p.	n_D^{25}	Remarks
1	$CHCl_2 \cdot CH_2 \cdot CHEtCl$	75°/25		1·4641	
2	$CHCl_2 \cdot CHMe \cdot CHMeCl$	76°/25		1·4683	Mixture of diastereoisomers
3	$CCl_3 \cdot (CH_2)_3 \cdot CH_3$	61°/25		1·4513	Ref. 3a: n_D^{25} 1·4530
4	$CCl_3 \cdot CH(CH_3) \cdot Et$	59°/25		1·4590	
5	$CHCl_2 \cdot CH_2 \cdot CH{:}CH \cdot CH_2Cl$ ...	99°/25		1·4969	
6	$CHCl_2 \cdot CH_2 \cdot CHCl \cdot C_6H_{13}$	90°/0·5		1·4653	
7	$CCl_3 \cdot (CH_2)_7 \cdot CH_3$	85°/0·5		1·4580	Ref. 2: n_D^{25} 1·4620. Ref. 3a: 1·4582
8	$CHPhCl \cdot CH_2CHCl_2$	62°/0·1		1·5477	
9	$CHO \cdot CH{:}CH \cdot Et$ D.N.P.*		162—163°		Ref. 13: m. p. 160°
10	$CHO \cdot CH{:}CH \cdot C_6H_{13}$ D.N.P.*		124—125		Ref. 5: m. p. 124—125°
11	$CHPh(R) \cdot CH_2 \cdot CHCl_2$ *		211—213 (dec.)		Cl⁻: found, 11·7; calc., 11·8%
12	$CHCl_2 \cdot CH_2 \cdot CH{:}CH \cdot CH_2R$ * ...		98—99		Cl⁻: found, 14·3; calc., 14·2%
13	$CHCl_2 \cdot (CH_2)_7 \cdot CH_3$	60°/0·3		1·4458	
14	$CHCl_2 \cdot CH_2 \cdot CHPh \cdot OMe$	67°/0·3		1·5192	O-Me: found, 6·7; calc., 6·85%
15	$CHCl_2 \cdot CH_2 \cdot CH{:}CH \cdot CH_2OMe$	105°/25		1·4710	O-Me: found, 7·9; calc., 8·9%

* $R = S \cdot C(NH_2)_2Cl$.   D.N.P. = 2,4-Dinitrophenylhydrazone.

No.	Found (%)					Formula	Required (%)				
	C	H	N	Cl	S		C	H	N	Cl	S
1	34·2	5·1		60·2			34·2	5·2		60·6	
2	34·1	5·4		60·5		$C_5H_9Cl_3$					
3	35·5	5·2		59·15							
4	34·4	5·3		60·8							
5	35·8	4·1		59·8		$C_5H_7Cl_3$	34·6	4·1		61·3	
6	47·0	7·4		44·9		$C_9H_{17}Cl_3$	46·7	7·4		46·0	
7				44·5							
8	49·1	4·1		45·5		$C_9H_9Cl_3$	48·35	4·1		47·5	
9	50·0	4·7	20·9			$C_{11}H_{12}N_4O_4$	50·0	4·6	21·2		
10	56·4	6·3	17·4			$C_{15}H_{20}N_4O_4$	56·2	6·3	17·5		
11				9·6	35·3	10·7	$C_{10}H_{13}Cl_3N_2S$			9·35	35·5	10·7
12				11·2	42·6	12·9	$C_6H_{11}Cl_3N_2S$			11·2	42·6	12·8
13				36·2		$C_9H_{18}Cl_2$				36·0	
14	55·1	5·6		31·5		$C_{10}H_{12}Cl_2O$	54·8	5·5		32·4	
15	39·9	5·3		42·2		$C_6H_{10}Cl_2O$	42·6	5·95		41·9	

Gas Chromatography.—The distillates of products of reaction between chloroform and olefin were analysed by gas chromatography through a column of 1·5 m. length, packed with 25% of diethylene glycol polyadipate (LAC2-R-446, Cambridge Industries Co., Inc., Cambridge, Mass., U.S.A.), 10% of tri-*o*-tolyl phosphate, or 5% of Silicone grease on Chromosorb W. For adducts of chloroform to butadiene, but-1-ene, and the but-2-enes, the column temperature was 105°, for those of oct-1-ene and styrene 160°. Helium-flow was 80 ml. per min.

[9] Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 256.

Of the impurities which accompany 1-1-3-trichloroalkanes (1,1-dichloro-, 1,1,1-trichloro-, and 1,1,1,3-tetrachloro-alkanes), the first two were not resolved on polyadipate as the stationary phase. They were separated on Silicone grease, but on this phase resolution between 1,1,1- and 1,1,3-trichloroalkane was poor. Best results were obtained with tri-*o*-tolyl phosphate.

The diastereoisomeric adducts of chloroform to the but-2-enes were nearly completely resolved on polyadipate, less on tritolyl phosphate, and not at all on Silicone grease. Resolution was much poorer than for the corresponding carbon tetrachloride adducts. Unconverted but-2-ene was analysed as described in ref. 1, Table 2, footnote 1. Good separation between 1′,3′,3′-trichloropropyl- and 1′-methoxy-3′,3′-dichloropropyl-benzene was achieved on polyadipate.

1,1-Dichloro-, 1,1,1-trichloro-, and 1,1,1,3-tetrachloro-alkanes were identified by addition of authentic samples, and subsequent chromatography on two different stationary phases.

Reaction of Chloroform with Olefins (Table 1).—Olefin (0·1 mole) was passed into, or mixed with, ice-cooled chloroform (0·3 mole). The solution was introduced into a precooled Carius tube. Catalyst and diethylammonium chloride (if used) were dissolved in solvent and likewise introduced. After cooling in liquid air, the tube was evacuated to 0·05 mm., sealed, and heated to the indicated temperature. After the reaction, the contents were washed with 0·1n-aqueous hydrochloric acid (30 ml.) and freed from solvent, chloroform, and unconverted olefin by distillation at 1 atm. in a bath up to 140°. In the case of the butenes and butadiene, distillation was continued at 25 mm. in a bath up to 180°. Unconverted octene or styrene was distilled off at 25 mm. and a bath temperature up to 120°. Distillation at 0·1 mm. up to 180° (bath) gave the product. The distillate was analysed by gas chromatography as described and the residue weighed. The amount of residue gave a rough indication of the extent of telomer formation. The yields were calculated on olefin, and on the content of pure product in crude distillate.

For physical constants and analyses of purified reaction products, see Table 2.

Reaction of Butadiene with Chloroform.—Treatment as indicated above and in Table 1, no. 28, gave a fraction of b. p. 100—140°/25 mm. (6·2 g.) containing, according to gas chromatography, 90% of 1,1,5-trichloropent-3-ene (yield, 32% calc. on butadiene). For characteristics of purified product, see Table 2, no. 5. Continued distillation gave a fraction of b. p. 85—135°/0·06 mm. (4·6 g., 40%) (Found: Cl, 46·8. Calc. for ·2 : 1 adduct, $C_9H_{13}Cl_3$: Cl, 46·7%). It consisted of at least four components (gas chromatography on Silicone grease–Chromosorb W at 160°), probably isomeric trichlorononadienes. A dark, viscous oil (2·0 g.) remained.

Reaction of 1,1,5-Trichloropent-3-ene with Thiourea.—1,1,5-Trichloropent-3-ene (3·5 g., 0·02 mole) was refluxed with thiourea (1·52 g., 0·02 mole) in acetonitrile (5 g.) for 3 hr. The mixture, which on cooling separated into two layers, was kept in ice–salt for 1 hr. The solid formed was filtered off, washed with methylene chloride, and dried overnight *in vacuo* over calcium chloride (yield, 4·0 g.; m. p. 97—98%). After recrystallisation from acetonitrile and drying over phosphorus pentoxide at 0·1 mm. for 6 hr., the m. p. was 98—99°. For analysis see Table 2, no. 12.

Reaction of Styrene with Chloroform in Methanol.—After reaction as indicated in Table 1, no. 26, the product was cautiously washed with 0·1n-hydrochloric acid. [A very volatile compound formed during reaction (methyl chloride or dimethyl ether) may cause sudden foaming.] After separation and heating at 1 atm. (bath-temperature up to 140°), distillation was continued *in vacuo*, giving a fraction, b. p. 40—110°/25 mm. (bath-temp. up to 185°) (2 g.), which consisted mainly of 1′-methoxyethylbenzene and some unconverted styrene. The former was identified by gas chromatography, by admixture with an authentic sample [10] (this ether was also formed, together with " distyrene," when styrene and methanol were heated with ferric chloride hydrate in the absence of chloroform).

A second fraction, b. p. 80—100°/0·3 mm. (8 g.), was obtained, containing 3′,3′-dichloropropyl-1′-methoxybenzene, ∼3% of 1′,3′,3′-trichloropropylbenzene, and ∼1% of cinnamaldehyde (isolated as dinitrophenylhydrazone, m. p. and mixed m. p. 255°).

On chromatography over acid-washed alumina, only the trichloride was eluted by pentane; methylene chloride eluted the methoxy-dichloride (see Table 2, no. 14).

A third fraction had b. p. 100—130°/0·3 mm. (bath-temp. up to 170°) (3·1 g.). A dark tacky resin remained (2 g.). The third fraction contained 80% of " distyrene," identified by gas

[10] Miller, *J. Org. Chem.*, 1956, **21**, 247; Nezhuta and Savitskii, *Zhur. obschei Khim.*, 1957, **27**, 1079.

chromatography (Silicone grease at 200°) by admixture with an authentic sample.[11] Fractionation afforded a fraction, b. p. 107—109°/0·3 mm., n_D^{25} 1·5820 (lit.,[11] for " distyrene," 1·590) chlorine-free and reacting with bromine–water.

Reaction of 1′,3′,3′-Trichloropropylbenzene with Thiourea.—1′,3′,3′-Trichloropropylbenzene (4·48 g., 0·02 mole) and thiourea (1·52 g., 0·02 mole) were refluxed in propan-2-ol (20 ml.) for 24 hr. After 1 hr. the solution became homogeneous, and after 12 hr. a white precipitate had appeared. After being kept overnight, the precipitate was sucked off, washed with propan-2-ol, and dried in the air (yield, 3·6 g.). After recrystallisation from water acidified with a few drops 0·1N-hydrochloric acid, the m. p. was 211—213° (decomp.) (apparatus preheated to 200°). For analysis of this compound, S-(2′,2′-*dichloroethylbenzyl*)*isothiouronium chloride*, see Table 2, no. 11.

Reaction of 1,1,3-Trichloroalkanes and of 1′,1′,3′-Trichloropropylbenzene with Sodium Ethoxide. Preparation of Pent-2-enal, 2-Methylbut-2-enal, Non-2-enal, and Cinnamaldehyde).— Treatment of 1,1,3-trichloropentane, 1,1,3-trichloro-2-methylbutane, 1,1,3-trichlorononane, and 1′,1′,3′-trichloropropylbenzene with sodium ethoxide as in ref. 5 gave pent-2-enal in 16% yield [dinitrophenylhydrazone (from ethanol); Table 2, no. 9], 2-methylbut-2-enal in 5% [dinitrophenylhydrazone (from butyl acetate), m. p. and mixed m. p.[12] 222°], non-2-enal 20% [dinitrophenylhydrazone (from ethanol); Table 2, no. 10], and cinnamaldehyde 45% [dinitrophenylhydrazone (from butyl acetate), m. p. and mixed m. p. 255—256°].

The yields were calculated from isolated dinitrophenylhydrazone. By-products were not investigated. See, however, ref. 4.

Reaction of But-1-ene with Chloroform, with Di-t-butyl Peroxide as Catalyst.—But-1-ene (8·4 g., 0·15 mole) was dissolved in a cooled solution of di-t-butyl peroxide (1·5 g.) in chloroform (60 g., 0·5 mole) and heated in a Carius tube (sealed after evacuation) at 140° during 24 hr. The excess of chloroform was distilled off at 1 atm. (bath up to 150°). A fraction of b. p. 65—125°/25 mm. (9·1 g.; bath up to 190°) was collected (3·9 g. of residue remains). This fraction contained about 60% of 1,1,1-trichloropentane (for purified product see Table 2, no. 3), 15% of 1,1-dichloropentane (identified with an authentic sample [14] by gas chromatography on Silicone grease or tritolyl phosphate), about 3% of 1,1,3-trichloropentane and 6% of 1,1,1,3-tetrachloropentane (identified in the same way, on tritolyl phosphate or polyadipate), together with heavier, unidentified products.

Reaction of Oct-1-ene with Chloroform, with Di-t-butyl Peroxide as Catalyst.—Treatment of oct-1-ene (11·2 g., 0·1 mole), chloroform (60 g., 0·5 mole), and di-t-butylperoxide (1·5 g.) as above gave a fraction, b. p. 50—70°/25 mm. (0·4 g.), containing mainly unconverted octene and a second fraction, b. p. 75—95°/0·3 mm. (12·2 g.), containing 75% of 1,1,1-trichlorononane (for the purified product see Table 2, no. 7), 14% of 1,1-dichloro-, 5% of 1,1,3-trichloro-, and 5% of 1,1,1,3-tetrachloro-nonane,[1] identified with authentic samples by gas chromatography on tritolyl phosphate or Silicone grease.

Reaction of cis-But-2-ene with Chloroform, with Di-t-butyl Peroxide as Catalyst.—Treatment of cis-but-2-ene (8·4 g., 0·15 mole), chloroform (60 g., 0·5 mole), and di-t-butyl peroxide (1·5 g.) as above gave a fraction, b. p. 60—95°/25 mm. (10·4 g.) (1·8 g. of residue remained). The fraction contained about 85% of 1,1,1-trichloro-2-methylbutane. For the purified product, see Table 2, no. 2. Gas chromatography showed a single peak, both on tritolyl phosphate and on polyadipate, in distinction from 1,1,3-trichloro-2-methylbutane (Table 1, no. 14) which showed a double peak, poorly resolved on tritolyl phosphate and somewhat better on polyadipate.

1,1-Dichlorononane.—This compound (Table 2, no. 13) was prepared (25%) from pelargonaldehyde and phosphorus pentachloride, by Hill and Tyson's method [15] for 1,1-dichloroheptane.

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[12] Doeuvre, *Bull. Soc. chim. France*, 1934, **1**, 204.
[13] Schinz and Rossi, *Helv. Chim. Acta*, 1948, **31**, 1961.
[14] Kohlrausch and Koppel, *Monatsh.*, 1935, **65**, 197.
[15] Hill and Tyson, *J. Amer. Chem. Soc.*, 1928, **50**, 172.