Addition of Carbon Tetrachloride to 3,3,4,4-Tetrafluorohexa-1,5-diene

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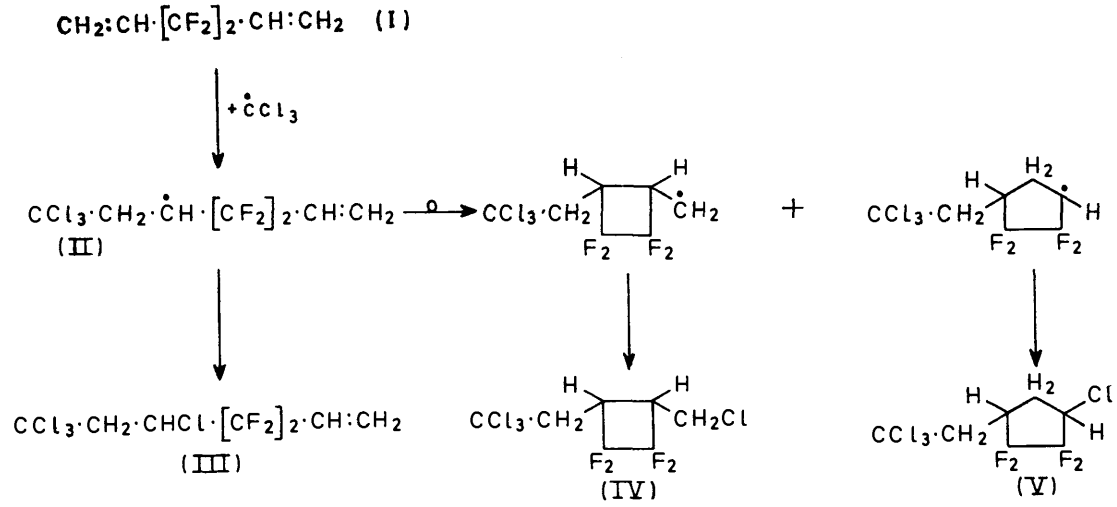
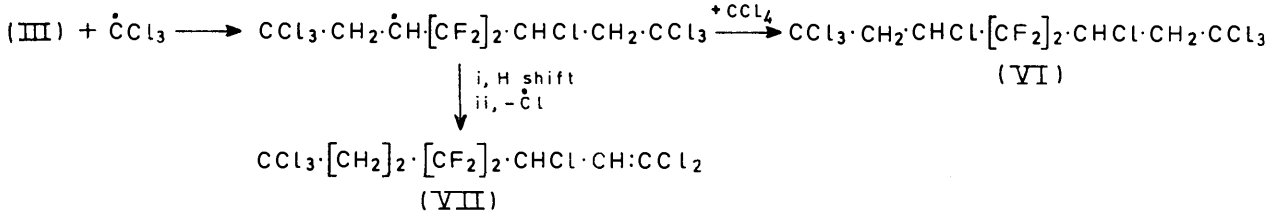
The free-radical reaction of carbon tetrachloride with 3,3,4,4-tetrafluoro-1,5-hexadiene is described. Initiation of the chain process by a variety of redox-transfer systems has been studied. The cyclic isomeric monoadducts have been shown to possess four-, five-, six-, and seven-membered ring structures. The extent of rearrangement observed in the products is greatly influenced by metallic salt additives and by the solvent. However, the solvent effect is not observed in the presence of some copper(II) species.

In this paper we discuss the free-radical addition of carbon tetrachloride to 3,3,4,4-tetrafluorohexa-1,5-diene (I), and the effect on product distribution of initiation by various redox-transfer systems.

As shown elsewhere,[1] the free-radical chain reaction of the diene (I) with iodoperfluoroethane gave, besides an unsaturated monoadduct, two isomeric cyclobutane derivatives and a smaller amount of a cyclopentane derivative. It is interesting that these saturated adducts arise from γ-alkenyl radicals, which are generally thought[2] unable to cyclise. Free-radical addition of carbon tetrachloride to the diene (I) yields the 2,2,3,3-tetrafluoro-1-(2,2,2-trichloroethyl)pent-4-enyl radical (II), which can give by chlorine transfer with CCl_4 the open-chain product 5,7,7,7-tetrachloro-3,3,4,4-tetrafluorohept-1-ene (III) or, by intramolecular addition followed by transfer, the four- and the five-membered ring compounds 3-chloromethyl-1,1,2,2-tetrafluoro-4-(2,2,2-trichloroethyl)cyclobutane (IV) and 3-chloro-1,1,2,2-tetrafluoro-5-(2,2,2-trichloroethyl)cyclopentane (V).

Also the olefin (III) can react with a trichloromethyl radical to give the linear diadduct 1,1,1,3,6,8,8,8-octachloro-4,4,5,5-tetrafluoro-octane (VI). This is often accompanied by the unsaturated compound (VII), which could be formed by an intramolecular hydrogen shift in the initially formed radical followed by chlorine elimination. A large number of very efficient intramolecular 1,5-hydrogen transfer processes are known;[3] such a reaction has also been observed in the thermal addition[1] of pentafluoroethyl iodide to the diene (I). The reaction of the radical (II) with the diene (I) gives the telomeric radical (VIII) which can cyclise yielding 3-chloromethyl-1,1,2,2,5,5,6,6-octafluorodecahydro-7-(2,2,2-trichloroethyl)naphthalene (IX). This reaction is in agreement with the reported ready cyclisation of some hept-6-enyl systems.[4]





The structures of all the products were elucidated by

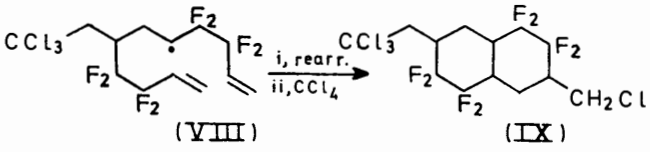
[1] P. Piccardi, M. Modena, and L. Cavalli, *J. Chem. Soc.* (*C*), 1971, 3959.

[2] C. Walling and M. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262; N. O. Brace, *J. Org. Chem.*, 1966, **31**, 2879.

[3] E. S. Huyser, 'Free-Radical Chain Reactions,' Wiley-Interscience, New York, 1970, p. 189.

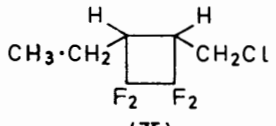
[4] M. Pines, N. C. Sih, and D. B. Rosenfield, *J. Org. Chem.*, 1966, **31**, 2255.

mass and n.m.r. spectroscopy; chemical shifts of the protons in the $-CH_2Cl$, $-CHCl-$, and $CCl_3 \cdot CH_2-$ groups



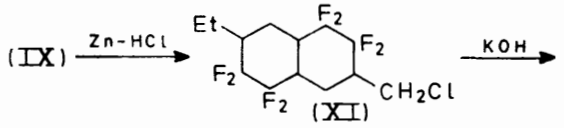
(VIII) (IX)

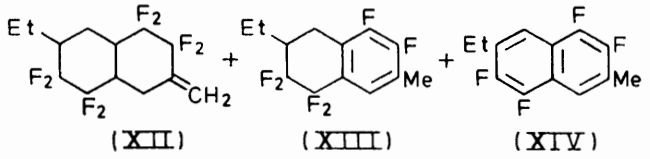
were as anticipated.[5] The four-membered ring structure of compound (IV) was also established by selective [6]



(X)

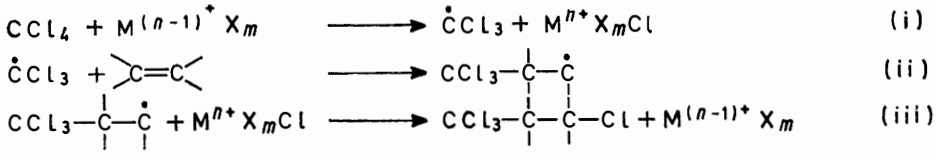
reduction of the CCl_3 group with zinc to give 3-chloromethyl-4-ethyl-1,1,2,2-tetrafluorocyclobutane (X) in the





(XII) (XIII) (XIV)

n.m.r. spectrum of which the methyl group resonance appears as a triplet (J 7 Hz) at τ 8·98.



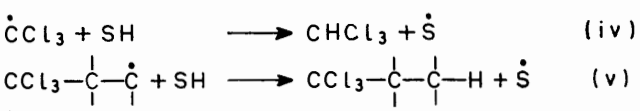
The structure of compound (IX) was also fully established by chemical means. Hydrogenation of the trichloromethyl group gave the ethyl compound (XI), which, on treatment with potassium hydroxide, yielded a mixture of dehydrohalogenation products in which (XIII) and (XIV) predominated.

The reaction between the diene (I) and carbon tetrachloride in the presence of di-t-butyl peroxide gave only a small amount of the described monoaddition products and a much higher yield of higher telomers, the formation of which could not be suppressed even by increasing the ratio of CCl_4 to diene (I). The amount of telomers was greatly decreased when the initiating systems developed by Asscher and Vofsi [7] were used. This reaction provides an excellent method for comparing the properties of these initiating systems based on salts of transition metals: one would expect [8] that the transfer with a metal halide would result in altered proportions of olefinic and cyclic adducts.

The catalytic behaviour of the metal ions can be summarised as in equations (i)—(iii), where M = Cu or Fe and X collects all the metal complexing species. In this scheme, if a hydrogen donor substrate (SH) is present the radical reactions (iv)—(vi) are induced. Results of the reactions initiated by $CuCl_2,2H_2O$ and amines in acetonitrile are given in the Table. The mechanism of initiation for these systems has been widely studied.[9] In step (iii) copper(II) ions are very efficient [10] and completely suppress telomerisation, (II) does not rearrange to (IV) or (V) and only small amounts of (VII) are formed. The product (III) reacts with the very active Cu^I–n-butylamine system to give an unsaturated radical, which can cyclise * to 4,4,6-trichloro-3-chloromethyl-1,1,2,2-tetrafluorocyclohexane (XV), 3,5,5,7-tetrachloro-1,1,2,2-tetrafluorocycloheptane (XVI) and 1,5-dichloro-2-chloromethyl-3,3,4,4-tetrafluorocyclohexene (XVII). The last named should arise from dehydrochlorination of (XV). Evidence for the cyclisation mechanism has been obtained from the isomerisation of compound (III) with copper salts and amines.

It is significant that the high reactivity of amine-coordinated copper(II) ions as chlorine-transfer agents is also responsible for the relevant amount of the linear di-adducts (VI). Without amine higher temperatures or longer induction periods are required (see Table, no. 10).

The structure of the oxidant is presumably important in the chlorine-transfer reaction; therefore variation of the ligands around copper could be responsible for the



differences in products observed. To test this hypothesis a number of copper chloride–amine complexes were studied. The more significant results are reported in the Table. When amines with two functional groups such as 2-aminoethanol or ethylenediamine are used, copper(II) ions appear to be less reactive as ligand-transfer

* Our results parallel the free-radical-induced cyclisation of 7-phenylhept-1-ene, which is reported [4] to give six-membered rings and traces of seven-membered rings.

[5] B. A. Englin, T. A. Onishenko, V. A. Valovoi, T. A. Babushkina, T. K. Semin, L. G. Zelenskaya, and R. Kh. Freidlina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 332.

[6] N. O. Brace, *J. Org. Chem.*, 1969, **34**, 2441.

[7] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1963, 1887, p. 3921.

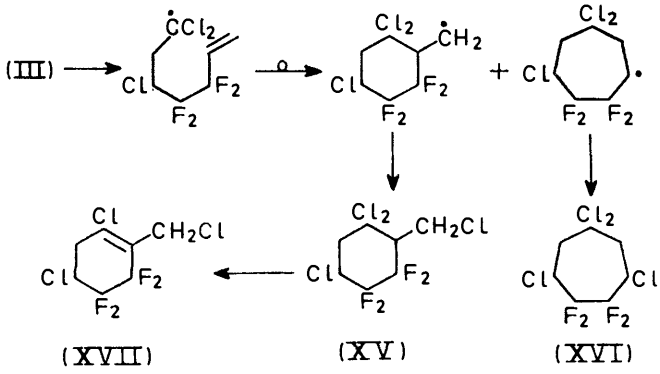
[8] H. G. Kuivila, *Accounts Chem. Res.*, 1968, **1**, 299.

[9] M. Asscher and D. Vofsi, *J. Chem. Soc.* (*B*), 1968, 847 and references cited therein.

[10] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1961, 2261.

agents, with formation of compounds (X), (IV), (V), and solid telomers (see Table, nos. **7** and **9**). Pyridine gives a lower yield of adducts but retains high efficiency in step (iii).

The reaction catalysed by complexes of copper and n-butylamine proceeds along the same path in isopropyl



(XVIII) (XV) (XVI)

alcohol. However formation of chloroform, acetone, isopropyl chloride, di-isopropyl ether, water, and hydrogen chloride indicates that the solvent is concurrently chlorinated as shown in steps (iv) and (vi), giving 2-chloropropan-2-ol which immediately decomposes.[11]

of products (IV) and (V), the presence of (X), and the formation of telomers, observed when iron chlorides are used. With isopropyl alcohol as solvent, step (iv) becomes important and the alcohol participates to a high degree in the chain transfer. Thus, three new products are present in the reaction mixture: 7,7,7-trichloro-3,3,4,4-tetrafluorohept-1-ene (XX), 1,1,1,8,8,8-hexachloro-4,4,5,5-tetrafluoro-octane (XXI), and 1,1,1,3,8,8,8-heptachloro-4,4,5,5-tetrafluoro-octane (XXII). These products help to confirm the earlier observation that ligand-transfer reactions to alkyl radicals by Fe^{III} complexes are more difficult than those by Cu^{II} complexes. High participation of the isopropyl alcohol in the transfer step, by analogy with other results,[7] should depend on the different radical structures. In our case the intermediate radicals with structure $-CH_2\cdot\dot{C}H\cdot CF_2-$ are more electrophilic than the radicals $-CH_2\cdot\dot{C}H\cdot CH_2-$ formed, for instance, from the addition of carbon tetrachloride to α-olefins. Therefore the nucleophilic solvent should participate to a substantially greater degree in step (iv), in agreement with other results.[12]

An interesting question is why step (iii) occurs more readily with n-butylamine–copper salt than the corresponding reaction with iron salt or 2-aminoethanol– and *p*-phenylenediamine–copper salt initiating systems. Re-

$$(III) \xrightarrow{-HCl} \underset{(XVIII)}{CCl_3\cdot CH{:}CH\cdot[CF_2]_2\cdot CH{:}CH_2} + \underset{(XIX)}{CCl_2{:}CH\cdot CHCl\cdot[CF_2]_2\cdot CH{:}CH_2}$$

Isopropyl chloride, di-isopropyl ether, 7,7,7-trichloro-3,3,4,4-tetrafluorohepta-1,5-diene (XVIII) and 1,1,3-trichloro-4,4,5,5-tetrafluorohepta-1,6-diene (XIX) could be formed by non-radical mechanisms. We have varied the amine in copper complexes in isopropyl alcohol and have found that a large amount of chain-transfer goes through the alcohol [step (iv)] when 2-aminoethanol or *p*-phenylenediamine is used; thus the specificity previously described for step (iii) shown by copper complexes with monofunctional amines is destroyed.

Results of the reaction initiated by $FeCl_3,6H_2O$ and n-butylamine in acetonitrile and isopropyl alcohol are given in the Table. In the initiation mechanism of this system, the amine in the presence of CCl_4 should act only as a reducing agent for the metal ion of higher valency, since iron(II) chloride is effective in step (i), giving comparable yield and distribution of the products.

cent work [13] has shown that copper(II) ions with coordinated amines are effective chlorine-transfer agents,

$$\underset{(XX)}{CCl_3\cdot[CH_2]_2\cdot[CF_2]_2\cdot CH{:}CH_2}$$

$$\underset{(XXI)}{CCl_3\cdot[CH_2]_2\cdot[CF_2]_2\cdot[CH_2]_2\cdot CCl_3}$$

$$\underset{(XXII)}{CCl_3\cdot CH_2\cdot CHCl\cdot[CF_2]_2\cdot[CH_2]_2\cdot CCl_3}$$

and quantitative analysis of experimental results has been given in terms of a transfer step in cages stabilised by amines. The reaction scheme was written [13] as:

$$[M^{n+}Cl\ldots CCl_3](RNH_2)_m + \rangle C{=}C\langle \longrightarrow CCl_3{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl + M^{(n-1)+}(RNH_2)_m \qquad (vii)$$

Higher conversions of the diene (I) are achieved with iron chloride–benzoin catalyst; when this initiation is provided the ligand transfer from metal chloride also appears more pronounced.

The most important difference between iron and copper salts is the lower reactivity of the former in step (iii). This is in agreement with the considerably higher yield

Increasing basicity of the amines enhances the stabilisation of these cage complexes and decreases the activation energy for the insertion reaction. Difunctional amines, possessing strong chelating ability for Cu^{II} ions, make the decomposition of cage complexes feasible.

[11] G. A. Razuvaev, B. N. Moryganov, and A. S. Volkova, *Zhur. obshchei Khim.*, 1955, **25**, 495.

[12] I. A. Shvarts, M. Ya. Khorlina, and R. Kh. Freidlina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 2018.

[13] T. Asahara, M. Seno, and C. Wu, *Buil. Chem. Soc. Japan*, 1970, **43**, 1127.

Reactions of the diene (I) (20 mmol) with carbon tetrachloride (100 mmol) in solvent (100 mmol) with catalyst (0·75 mmol) at 120°

Run no.	Solvent	Catalyst	Amine † (mmol)	Time (h)	Conversion of (I) (%)	Yield ‡ (%)	Composition (molar %) of recovered products														Note
							(XXIII) §	(XVIII)	(XIX)	(XX)	(III)	(IV) ¶	(XVII)	(V) **	(XV)	(XVI)	(XXI)	(VII)	(XXII)	(IX)	(VI)	Telomers	
1	None	But_2O_2	None	5	100	90					1·3	11·1		9·1				5·0		21·3		52·2	*a, b*
2	MeCN	$CuCl_2,2H_2O$	A (1·5)	2	31	98			0·5		93·3		0·3		0·3			0·1			5·5		
3	MeCN	$CuCl_2,2H_2O$	A (3·0)	2	39	96			0·9		90·0		0·3		0·3			0·5			8·0		
4	MeCN	$CuCl_2,2H_2O$	A (3·0)	10	68	96			0·1		67·8		0·8		2·9	0·6		3·1			24·7		
5	MeCN	$CuCl_2,2H_2O$	A (6·0)	2	52	96			0·9		85·4		0·9		0·9	0·3		1·6			10·0		
6	MeCN	$CuCl_2,2H_2O$	A (12)	2	59	93			1·0		80·1		1·1		1·7	0·5		3·1			12·5		
7	MeCN	$CuCl_2,2H_2O$	B (3·0)	2	55	34			6·6		72·9	3·9		3·5				2·1		11·0		+	*c*
8	MeCN	$CuCl_2,2H_2O$	C (3·0)	2	15	89					99·2		0·7		0·1								
9	MeCN	$CuCl_2,2H_2O$	D (3·0)	2	60	26			7·2		65·6	4·9		4·3				2·0		14·4	1·6	+	
10	MeCN	CuCl	None	2	8·3	91					98										2		
11	PrⁱOH	$CuCl_2,2H_2O$	A (3·0)	2	27	82	1·1		1·4		93·5		0·2		0·4						3·4		
12	PrⁱOH	$CuCl_2,2H_2O$	A (3·0)	10	63	88	2·2	0·6	1·6		73·6		0·8		2·7	0·5		2·9			15·1		
13	PrⁱOH	$CuCl_2,2H_2O$	A (6·0)	2	36	86	1·1		1·4		91·9		0·4		1·4	0·3		0·3			3·2		
14	PrⁱOH	$CuCl_2,2H_2O$	B (3·0)	2	24	51	2·5			41·3	49·9	0·8		0·4			1·0	0·8		3·3		+	*c*
15	PrⁱOH	$CuCl_2,2H_2O$	C (3·0)	2	9	91			3·7		95·7		0·6										
16	PrⁱOH	$CuCl_2,2H_2O$	E (3·0)	2	17	45				83·2	15·9	0·9										+	*c*
17	MeCN	$FeCl_3,6H_2O$	A (3·0)	2	75	35			10·0		50·3	11·4		6·6				4·8		15·8	1·1	+	*c*
18	MeCN	$FeCl_3,6H_2O$	A (3·0)	10	86	53	0·2		4·9		51·6	11·3		6·1				11·7		12·6	1·6	+	*c*
19	MeCN	$FeCl_3,2H_2O$	None	2	97	44			3·2		30·7	11·3		6·9				27·7		11·7	8·5	+	*c—e*
20	PrⁱOH	$FeCl_3,6H_2O$	A (3·0)	2	36	67	3·9			43·9	35·8	3·9		0·8			1·8	1·3	2·9	5·3	0·4	+	*c*
21	PrⁱOH	$FeCl_3,6H_2O$	A (3·0)	10	68	78	5·7			28·3	39·1	5·1		1·1			2·5	5·1	6·5	4·7	1·9	+	*c*
22	PrⁱOH	$FeCl_3,6H_2O$	None	2	79	64	0·5	2·5		19·8	36·6	5·0		1·9			2·7	9·3	11·1	5·8	4·8	+	*c—e*
23	MeCN	$FeCl_3,4H_2O$	None	2	45	57	0·2		2·4		64·9	9·3		4·5				2·9		15·0	0·8	+	*c*
24	MeCN	$FeCl_3,4H_2O$	None	10	69	71	0·7		1·9		59·3	9·6		4·6				8·6		12·5	2·8	+	*c*
25	PrⁱOH	$FeCl_3,4H_2O$	None	2	36	70	4·2			34·0	45·8	4·9		1·1			1·0	1·3	2·7	4·4	0·6	+	*c*
26	PrⁱOH	$FeCl_3,4H_2O$	None	10	49	78	3·8			30·9	44·5	4·8		0·9			1·3	2·9	4·3	5·5	1·1	+	*c*

† A = n-butylamine, B = 2-aminoethanol, C = pyridine, D = ethylenediamine, E = *p*-phenylenediamine. ‡ Yield of the listed products, based on diene (I) reacted. § 6-Chloro-3,3,4,4-tetrafluorohex-1-ene (see Experimental section). ¶ Single *cis*- or *trans*-isomer. ** Mixture (*ca.* 1 : 1) of *cis*- and *trans*-isomers.

a Reaction conditions: (I) 20 mmol, CCl_4 100 mmol, But_2O_2 1 mmol, 135°. *b* Average molecular weight of the telomers = 1184. *c* Telomers were present but not recovered. *d* 1·5 mmol of LiCl added. 0·75 mmol of benzoin added.

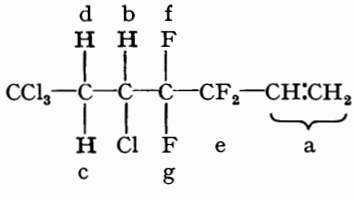
However we think that this mechanism is not sufficient to explain our results, since copper(I) chloride alone has high specificity (see Table, no 10). In addition the formation of products (VII), (XV), and (XVI) suggests a radical feature of the reaction.

EXPERIMENTAL

Techniques.—Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer 225 grating spectrophotometer), ^1H and ^{19}F n.m.r. spectroscopy [Varian HA100 instrument; the ^{19}F figures quoted are chemical shifts in p.p.m. from internal trichlorofluoromethane and ^1H figures are τ values (internal tetramethylsilane standard)], and mass spectrometry (Hitachi–Perkin-Elmer RMU/6E instrument). Analytical g.l.c. was carried out with a column (2·5 m × 4 mm) packed (20%) with high vacuum silicone grease on Chromosorb or a column (6 m × 4 mm) packed (20%) with Carbowax 20M on Chromosorb; temperatures were 80—200 °C (2·5° min^{-1}).

General Procedure for the Metal Salt-catalysed Additions.—The reactions were carried out in 28 ml ampoules by agitating for the time reported in the Table at 120 °C. The reagents were charged as follows. The ampoule, containing a weighed amount of metal salts, was evacuated and cooled to −50 °C. The appropriate solution of a standard mixture of the diene (I) and CCl_4 in acetonitrile or propan-2-ol was injected into the ampoule, which was then sealed and placed in the thermostatted bath. After the reaction the ampoule was broken and the contents filtered through a glass sinter into a test tube with a well fitting ground-glass stopper. The solution was analysed by g.l.c. in a Carlo Erba Model G.T. dual column instrument, using for a quantitative determination n-pentadecane as internal reference. In all the cases after the g.l.c. analysis the mixture was washed with dilute hydrochloric acid and water, and dried ($MgSO_4$). Unchanged diene (I), carbon tetrachloride, and the volatile products were removed by distillation. The telomeric residue, if present, was dissolved in acetone, precipitated from ethanol, and dried, at room temperature, under vacuum.

Identification of Products.—5,7,7,7-*Tetrachloro*-3,3,4,4-*tetrafluorohept*-1-*ene* (III) was obtained from a preparative scale run by fractional distillation (Found: C, 27·5; H, 1·8. $C_7H_6Cl_4F_4$ requires C, 27·3; H, 1·95%), b.p. 216—217° at 752 mmHg; $\nu_{max.}$ 1650 cm^{-1} (C=C); *m/e* 306, 308, 310, and 312 (M^+); n.m.r. chemical shifts and coupling constants (Hz) are shown below formula (A).



(A)

τ_a 3·7—4·4 τ_b 5·43 τ_c 6·39 τ_d 6·81

$\phi_e^* = 111{\cdot}62$ $\phi_f^* = 114{\cdot}84$ $\phi_g^* = 118{\cdot}00$

$|J_{b,c}|$ 1·8 $|J_{b,d}|$ 7·6 $|J_{b,f}|$ 10·4

$|J_{b,g}|$ 13·5 $|J_{c,d}|$ 16·0 $|J_{f,g}|$ 273

3-*Chloromethyl*-1,1,2,2-*tetrafluoro*-4-(2,2,2-*trichloroethyl*)-*cyclobutane* (IV) was obtained by preparative g.l.c. The collected product was isomerically pure (Found: C, 27·4; H, 2·0. $C_7H_6Cl_4F_4$ requires C, 27·3; H, 1·95%), b.p. 233° at 750 mmHg; τ (CCl_4) 6·25 (2H, d, J 7 Hz, CH_2Cl) and 6·6—7·3 (4H, m); ϕ^* 109·50 and 134·47 (2F, AB, J 214 Hz, CF_2), and 108·89 and 130·79 (2F, AB, J 210 Hz, CF_2); *m/e* 306/308/310/312 (M^+, <0·1%), 271/273/275/277 (M^+ — Cl, 8·5/8·0/2·3/0·2%), 96/98/100 ($C_2H_2Cl_2^+$, 34·0/23·5/4·1%) and 77 ($C_3H_3F_2^+$, 100%).

3-Chloro-1,1,2,2-tetrafluoro-5-(2,2,2-trichloroethyl)cyclopentane (V) was isolated by g.l.c. and was a mixture (*ca.* 1 : 1) of *cis*- and *trans*-isomers; τ (CCl_4) 5·7 (1H, m, CHCl), 6·6—7·3 (2H, m, $CH_2{\cdot}CCl_3$), and 7·5br (2H, CH_2); ϕ^* (*cis*-isomer) 113·7 and 125·4 [2F, AB, J 242 Hz, C(2)F] and 118·0 and 127·1 [2F, AB, J 241 Hz, C(1)F], (*trans*-isomer) 121·0 and 128·1 [2F, AB, J 243 Hz, C(2)F] and 123·7 [2F, m, C(1)F]; *m/e* 306/308/310 (M^+, 1·4/1·8/0·9%), 271/273/275 (M^+ — Cl, 35/34/11%), 235/237/239 (M^+ — Cl — HCl, 25/17/2·5%), 143/145/147 ($C_3H_2Cl_3^+$, 29/28/8·5%), 117/119/121 (CCl_3^+, 25/24/7·5%), 96/98/100 ($C_2H_2Cl_2^+$, 66·5/45/7·5%), and 77 ($C_3H_3F_2^+$, 100%).

1,1,1,3,6,8,8,8-*Octachloro*-4,4,5,5-*tetrafluoro-octane* (VI) was obtained from a preparative scale run (Found: C, 20·9; H, 1·1. $C_8H_6Cl_8F_4$ requires C, 20·8; H, 1·3%), m.p. (ethanol) 56°; the ^1H n.m.r. spectrum showed the resonance of the $CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CF_2$ part of (III).

1,1,3,8,8,8-Hexachloro-4,4,5,5-tetrafluoro-oct-1-ene (VII) was obtained by preparative g.l.c.; $\lambda_{max.}$ 6·17 μm (C=C); τ (CCl_4) 3·96 (1H, d, $J_{2,3}$ 10 Hz, $CCl_2{=}CH$), 4·92 [1H, d ($J_{3,4}$ 16 Hz) of d ($J_{3,4}$ 6 Hz) of d ($J_{3,2}$ 10 Hz), CHCl], 6·9—7·2 (2H, complex, $CH_2{\cdot}CCl_3$), and 7·3—7·8 (2H, complex, $CH_2{\cdot}CF_2$); *m/e* 388/390/392/394/396/398 (M^+, 1·8/3·4/2·7/1·2/0·3%), 353/355/357/359 (M^+ — Cl, 1·9/2·9/1·9/0·6%), 317/319/321/323 (M^+ — Cl — HCl, 2·5/3·3/1·6/0·4%), 281/283/285 (M^+ — Cl — 2HCl, 3·0/3·0/1·1%),and 143/145/147/149 ($C_3H_2Cl_3^+$, 100/95/31/3·3%).

3-*Chloromethyl*-1,1,2,2,5,5,6,6-*octafluorodecahydro*-7-(2,2,2-*trichloromethyl*)*naphthalene* (IX) was obtained from a preparative scale run (Found: C, 33·6; H, 2·6. $C_{13}H_{12}Cl_4F_8$ requires C, 33·8; H, 2·6%), m.p. (ethanol) 122°; n.m.r. spectrum (CCl_4) showed no olefinic proton; the CH_2Cl resonance appeared as part of an ABX pattern (peaks at τ 6·53, 6·44, 6·41, 6·32 and 6·04, 6·00, 5·92, 5·88); *m/e* 460/462/464/466 (M^+, <0·1%), 425/427/429 (M^+ — Cl, 14·5/13·0/0·44%), 96/98/100 ($C_2H_2Cl_2^+$, 100/65·5/10·5%), and 77 ($C_3H_3F_2^+$, 30%). Evidence for the structure was obtained by reduction with zinc and dehydrohalogenation to compound (XIV).

4,4,6-Trichloro-3-chloromethyl-1,1,2,2-tetrafluorocyclohexane (XV), 3,5,5,7-tetrachloro-1,1,2,2-tetrafluorocycloheptane (XVI), and 1,5-dichloro-2-chloromethyl-3,3,4,4-tetrafluorocyclohexane (XVII) were identified by comparing their retention times and mass spectra with those of authentic materials prepared by isomerisation of (III) (see later).

7,7,7-Trichloro-3,3,4,4-tetrafluorohepta-1,5-diene (XVIII) and 1,1,3-trichloro-4,4,5,5-tetrafluorohepta-1,6-diene (XIX) were identified by comparing their retention times and mass spectra with those of authentic materials prepared by treatment of compound (III) with diethylamine (see later).

7,7,7-*Trichloro*-3,3,4,4-*tetrafluorohept*-1-*ene* (XX) was obtained from a preparative scale run by fractional distillation (Found: C, 30·5; H, 2·7. $C_7H_7Cl_3F_4$ requires C, 30·75; H, 1·3%), b.p. 187° at 750 mmHg; $\lambda_{max.}$ 6·05 μm (C=C); τ (CCl_4) 3·7—4·4 (3H, complex, $CH{=}CH_2$), 6·9—7·2 (2H, complex; $CH_2{\cdot}CCl_3$), and 7·3—7·8 (2H, complex, $CH_2{\cdot}CF_2$); ϕ^* 114·88 (2F, complex, $CF_2{\cdot}CH_2$) and 115·36 (2F, complex, $CF_2\,CH{=}CH_2$).

1,1,1,8,8,8-*Hexachloro*-4,4,5,5-*tetrafluoro-octane* (XXI) was obtained from a preparative scale run (Found: C, 24·5, H, 1·8. $C_8H_8Cl_6F_4$ requires C, 24·45; H, 2·05%), m.p. (ethanol) 120°, τ (CCl_4) 6·9—7·2 (2H, complex, $CH_2{\cdot}CF_2$); ϕ^* 14·43 (complex, CF_2); *m/e* 355/357/359/361/363 (M^+ — Cl, 21·5/34·4/20·8/6·6/1·1%), 195/197/199/201 ($C_4H_4Cl_3F_2^+$, 35·4/33·8/10·7/1·2%), 159/161/163 (*m/e* 195 — HCl, 72·4/51·6/8·4%), 117/119/121 (CCl_3^+, 47·8/45·5/13·8%), and 109/111/113 ($C_3H_3Cl_2^+$, 100/68/11·6%).

1,1,1,3,8,8,8-*Heptachloro*-4,4,5,5-*tetrafluoro-octane* (XXII) was obtained by preparative g.l.c. (Found: C, 23·3; H, 1·5. $C_8H_7Cl_7F_4$ requires C, 22·5; H, 1·65%), m.p. (ethanol) 24°; ^{1}H n.m.r. spectrum showed the presence of $CCl_3{\cdot}CH_2{\cdot}$-$CHCl{\cdot}CF_2$ and $CCl_3{\cdot}CH_2{\cdot}CH_2{\cdot}CF_2$ groups; *m/e* 389/391/393/395/397/399 (M^+ — Cl, 25/47/37·5/16/4·0/0·5%), 159/161/163 ($C_4H_3Cl_2F_2^+$, 73/50·5/13·0%), 143/145/147 ($C_3H_2Cl_3^+$, 63/62·5/27·0%), and 109/111/113 ($C_3H_3Cl_2^+$, 100/70/14%).

6-*Chloro*-3,3,4,4-*tetrafluorohex*-1-*ene* (XXIII) was isolated by g.l.c. (Found: C, 37·7; H, 3·8. $C_6H_7ClF_4$ requires C, 37·8; H, 3·7%); τ (CCl_4) 3·7—4·4 (3H, complex, $CH{=}CH_2$), 6·0 (2H, A part of an AA'BB' spin system, CH_2Cl), and 7·4 (2H, complex m, $CH_2{\cdot}CF_2$).

Synthesis of 3-*Chloromethyl*-4-*ethyl*-1,1,2,2-*tetrafluorocyclobutane* (X).—Compound (IV) (4·0 g, 13·0 mmol), anhydrous ethanol (40 cm^3), and zinc dust (4·0 g, 0·06 g atom) were stirred rapidly while being saturated with gaseous hydrogen chloride at 75—80 °C. After 1 h the liquid was decanted, water was added, and the organic layer was separated and combined with ethereal extracts. The ether solution was dried ($MgSO_4$) and evaporated to yield a residue, which was subjected to semi-preparative g.l.c. to give, besides unchanged (IV), 3-chloromethyl-4-ethyl-1,1,2,2-tetrafluorocyclobutane (X) (1·3 g, 6·3 mmol, 48%), b.p. 148° at 754 mmHg; τ (CCl_4) 6·39 (2H, complex, CH_2Cl), 7·16—8·00 (2H, complex, >CH·CH<), 8·29 (2H, quin, *J* 7 Hz, $CH_2{\cdot}CH_3$), and 8·98 (3H, t, *J* 7 Hz, Me); ϕ^* 109·48 and 133·93 (2F, AB, *J* 211 Hz, CF_2) and 110·34 and 133·93 (2F, AB, *J* 212 Hz, CF_2); *m/e* 169 (M^+ — Cl, 0·6%), 155 (M^+ — CH_2Cl, 0·7%), 92 ($C_4H_6F_2^+$ 100%), 77 ($C_3H_3F_2^+$, 67·5%).

Chemical Identification of 3-*Chloromethyl*-1,1,2,2,5,5,6,6-*octafluorodecahydro*-7-(2,2,2-*trichloroethyl*)*naphthalene* (IX).—To a stirred mixture of compound (IX) (20·5 g, 44·4 mmol), ethanol (30 cm^3), and zinc dust (18·0 g, 0·275 g atom) gaseous hydrogen chloride was added at 72—74°. After 1 h the liquid was decanted, water was added, and the organic layer was separated and combined with ethereal extracts. The ether solution was dried ($MgSO_4$) and distilled to give, besides unchanged (IX), a fraction (b.p. 97—98° at 1 mmHg) shown by g.l.c. to contain only one component. Repeated recrystallisation (ethanol) of this fraction gave 3-chloromethyl-7-ethyl-1,1,2,2,5,5,6,6-octafluorodecahydro-naphthalene (XI) (9·4 g, 26·2 mmol, 59%), m.p. 122°; *m/e* 358/360 (M^+, 2·5/0·7%), 338/340 (M^+ — HF, 13·0/4·2%), 322 (M^+ — HCl, 24·6%), 105 ($C_4H_7^+$, 100%), and 29 ($C_2H_5^+$, 69%); the ^{1}H n.m.r. spectrum showed the CH_3 of ethyl at τ 9·0 and a CH_2Cl signal identical to that of compound (IX). The product (XI) (24·8 mmol) was sealed onto powdered potassium hydroxide (*ca.* 10 g) in a Pyrex tube and warmed to 150° (6 h). The volatile products were removed by heating and pumping through a cold (−190°) trap, and separated by g.l.c. to yield: (i) 3-ethyl-1,1,2,2,5,5,6,6-octafluorodecahydro-8-methylenenaphthalene (XII) (2·0 g, 6·3 mmol, 25%); the mass spectrum showed a strong parent at *m/e* 322 and a consistent fragmentation pattern; the ^{1}H n.m.r. spectrum displayed a clean signal for the $CH_2{=}C<$ group at τ 4·34 (d, *J* 4 Hz) and 4·58 (m); (ii) 3-ethyl-1,1,2,2,5,6-hexafluoro-1,2,3,4-tetrahydro-7-methylnaphthalene (XIII) (1·9 g, 6·7 mmol, 27%); τ (CCl_4) 2·75 (1H, d, *J ca.* 7 Hz, aromatic), 6·9—8·2br (3H, >CH·CH_2), 7·66 (3H, d, *J ca.* 2 Hz, ArMe), 8·4 (2H, m, $CH_2{\cdot}CH_3$), and 8·94 (3H, t, *J* 7 Hz, Me); ϕ^* 89·94 and 125·58 [2F, AB, *J* 276 Hz, tentatively assigned to C(2)F)], 131·28 (2F, m, CF_2), 138·01 [1F, d (*J* 20 Hz) of m, aromatic fluorine], and 141·71 (1F, d, *J* 20 Hz, aromatic fluorine); the mass spectrum showed a strong parent at *m/e* 282 and a consistent fragmentation pattern; (iii) 3-ethyl-1,2,5,6-tetrafluoro-7-methylnaphthalene (XIV) (2·3 g, 9·5 mmol, 38%), τ (CCl_4) 2·51 (2H, d, *J* 6 Hz, aromatic), 7·15 (2H, q, *J* 7 Hz, $CH_2{\cdot}CH_3$), 7·5 (3H, d, *J ca.* 2 Hz, ArMe), and 8·62 (3H, t, *J* 7 Hz, $CH_2{\cdot}CH_3$); ϕ^* 145·25 (1F, d, *J* 16 Hz), 147·05 (1F, dq, *J* 16 and 4·5 Hz), and 149·85 (2F, complex); the mass spectrum showed a strong parent at *m/e* 242 and a consistent fragmentation pattern.

Reaction of 5,7,7,7-*Tetrachloro*-3,3,4,4-*tetrafluorohept*-1-*ene* (III) *with Diethylamine*.—Compound (III) (10·0 g, 32·5 mmol), diethylamine (2·4 g, 32·8 mmol), and ethanol (8 cm^3) were sealed in a Pyrex tube and heated in an oil-bath at 120° for 2 h with stirring. Water was added to the cooled mixture, which was acidified with hydrochloric acid and extracted twice with ether. Distillation of the dry ($MgSO_4$) organic extract gave, besides unchanged (III), a mixture (5·8 g, 21·4 mmol, 66%) (Found: C, 31·1; H, 1·6. Calc. for $C_7H_5Cl_3F_4$: C, 30·95; H, 1·85%), b.p. 67—69° at 8 mmHg, shown by g.l.c. to contain two components in the ratio 1 : 2 (in order of elution). The mixture was separated by g.l.c. to give (in order of elution): 7,7,7-*trichloro*-3,3,4,4-*tetrafluorohepta*-1,5-*diene* (XVIII), b.p. 178° at 752 mmHg; $\lambda_{max.}$ 6 μm (C=C); τ (CCl_4) 3·27 [1H, d ($J_{6,5}$ 15 Hz) of t ($J_{6,4}$ 2 Hz), $=CH{\cdot}CCl_3$], 3·69 [1H, d ($J_{5,6}$ 15 Hz) of t ($J_{5,4}$ 11 Hz) of t ($J_{5,3}$ 1 Hz), $=CH{\cdot}CF_2$], and 3·7—4·4 (3H, m, $CH{=}CH_2$); *m/e* 270/272/274 (M^+, 0·65/0·6/0·2%), 158/160/162 ($C_4H_2Cl_2F_2^+$, 20·0/12·8/2·0%), and 77 ($C_3H_3F_2^+$, 100%); and 1,1,3-*trichloro*-4,4,5,5-*tetrafluorohepta*-1,6-*diene* (XIX), b.p. 185° at 752 mmHg; $\lambda_{max.}$ 6·17 μm (C=C); τ (CCl_4) 3·96 (1H, d, $J_{2,3}$ 10 Hz, $CH{=}CCl_2$), 3·7—4·4 (3H, m, $CH{=}CH_2$), and 4·92 [1H, d ($J_{3,4}$ 16·5 Hz) of d ($J_{3,4}$ 6 Hz) of d ($J_{3,2}$ 10 Hz), CHCl]; ϕ^* 113·88 and 122·40 (2F, AB, *J* 269 Hz, $CF_2{\cdot}CHCl$) and 113·14 (2F, complex, $CF_2{\cdot}CH{=}CH_2$); *m/e* 270/272/274 (M^+, 1·5/1·4/0·45%), 143/145/147/149 ($C_3H_2Cl_3^+$, 50·0/48·0/15·0/1·5%), and 77 ($C_3H_3F_2^+$, 100%).

Cyclisation of the Olefin (III) *to* 4,4,6-*Trichloro*-3-*chloromethyl*-1,1,2,2-*tetrafluorocyclohexane* (XV) *and* 3,5,5,7-*Tetrachloro*-1,1,2,2-*tetrafluorocycloheptane* (XVI).—Compound (III) (13·4 g, 43·5 mmol), acetonitrile (8·8 g, 215 mmol), copper(II) chloride (0·557 g, 3·2 mmol), and n-butylamine (0·909 g, 12·4 mmol) were heated in a sealed, evacuated glass ampoule at 120° for 23 h. The black semi-solid product was shaken with water and extracted with ether. The dried ($MgSO_4$) ether layer was concentrated and separated by g.l.c. to yield, besides unchanged starting material (III) and product (XIX) (0·98 g, 3·6 mmol, 8·3%), 1,5-*dichloro*-2-*chloromethyl*-3,3,4,4-*tetrafluorocyclohexene* (XVII) (1·40 g, 5·1 mmol, 11·7%) (Found: C, 30·8; H, 1·7. $C_7H_5Cl_3F_4$ requires: C, 30·95; H, 1·85%), 4,4,6-*trichloro*-3-*chloromethyl*-1,1,2,2-*tetrafluorocyclohexane* (XV) (two isomers in the ratio 1·8 : 1) (2·60 g, 8·4 mmol, 19·3%) [Found (for mixture): C, 27·1; H, 1·8. $C_7H_6Cl_4F_4$ requires C, 27·3; H, 1·95%], and 3,5,5,7-*tetrachloro*-1,1,2,2-*tetrafluorocycloheptane* (XVI) (two isomers in the ratio 1 : 1·5) (1·56 g, 5·1

mmol, 11·7%) [Found (for mixture): C, 27·2; H, 1·9. $C_7H_6Cl_4F_4$ requires C, 27·3; H, 1·95%].

Spectra.—Compound (XVII) had $\lambda_{max.}$ 6·05 μm (C=C); τ (CCl_4) 5·6 (1H, complex, CHCl), 5·72 (2H, s, CH_2Cl), and 6·85 (2H, complex, CH_2); ϕ^* 97·76 and 124·42 (2F, AB, J 283 Hz, CF_2·CHCl), and 129·15 and 132·04 (2F, AB, J 248 Hz, CF_2); *m/e* 270/272/274 (M^+ — Cl, 40/25/4%), and 199/201 (M^+ — Cl — HCl, 100/33·3%).

Compound (XV), first isomer (more abundant), had τ (CCl_4) 5·6 (1H, complex, CHCl), 6·0 (2H, complex, CH_2Cl), 6·7—7·3br (3H, CH_2·CCl_2·CH<); ^{19}F n.m.r. spectrum showed two equal resonances at ϕ^* 120·2 and 129·8 (outer bands of the two AB quartets too small for accurate measurement); *m/e* 271/273/275 (M^+ — Cl, 3·5/3·5/1·1%) and 235/237/239 (M^+ — Cl — HCl, 100/63/10%); second isomer had τ (CCl_4) 5·6 (1H, complex, CHCl), 6·1 (2H, complex, CH_2Cl), 6·7br (1H, >CH·CH_2Cl), and 7·0 (2H, complex, CH_2); ϕ^* 56·78 and 118·21 (2F, AB, J 273 Hz, CHCl·CF_2), and 68·07 and 128·21 (2F, AB, J 259 Hz, CF_2); the mass spectrum was similar to that of the first isomer.

For compound (XVI), first isomer (less abundant), the ^1H n.m.r. spectrum (CCl_4) displayed two signals, with intensities in the ratio 1 : 2, at τ 5·83 (CHCl) and 6·86 (CH_2); the ^{19}F n.m.r. spectrum showed a pair of symmetrical absorptions, with equal intensities, centred at ϕ^* 114·23 and 126·45; *m/e* 271/273/275 (M^+ — Cl, 21/21·7%) and 235/237/239 (M^+ — Cl — HCl, 100/63/10%); for the second isomer, the ^1H n.m.r. spectrum (CCl_4) displayed two signals, with intensities in the ratio 1 : 2, at τ 5·63 (CHCl) and 6·80 (CH_2); the ^{19}F n.m.r. spectrum showed a pair of symmetrical absorptions, with equal intensities, centred at ϕ^* 107·73 and 120·43; the mass spectrum was similar to that of the first isomer.

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