Allene Cycloadditions.   Part III.[1]   Synthesis of Alkylidenecyclobutenes
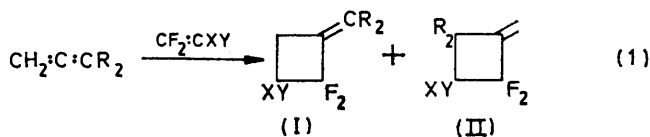
By D. R. Taylor,* M. R. Warburton, and D. B. Wright, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Thermal cycloaddition of chlorotrifluoroethylene and 1,1-dichlorodifluoroethylene to allene gives mixtures of two 1 : 1 adducts, identified as the 1-halogeno-1-chloro-2,2-difluoro-3-methylenecyclobutanes (Ia and b) and the 2-halogeno-2-chloro-1,1-difluoro-3-methylenecyclobutanes (IVa and b) (halogeno = Cl or F). Base-catalysed elimination of hydrogen fluoride from 1-halogeno-1,2,2-trifluoro-3-alkylidenecyclobutanes (Ic—e) and of hydrogen chloride from the related 1-chlorides (Ib, e, and f) affords 1-halogeno-4,4-difluoro-3-alkylidenecyclobutenes (IIIa—c). The n.m.r. and mass spectra of these and related compounds are discussed.

CYCLOADDITIONS [equation (1); R = H or Me, X = Y = F and R = Me, Y = Cl, X = F or Cl] between allene or 1,1-dimethylallene and polyfluoro-olefins provide a general route to alkylidenecyclobutanes (Ic—f) and (IId—f).[1-3] Experimental details are now reported concerning the cycloadditions of chlorotrifluoroethylene and 1,1-dichlorodifluoroethylene to allene, the general features of which were communicated earlier,[4] which yield two further compounds of this type, namely (Ia—b).

Base-catalysed dehydrohalogenation of four of these alkylidenecyclobutanes (I) has been achieved under mild conditions [equation (2)]. The combination of these two steps establishes a general route to alkylidenecyclobutenes (III), a little-known class of 1,3-dienes which are of special interest because of their enforced *trans*-configuration. The route reported is considered a useful alternative to earlier syntheses of such dienes (*e.g.*, base-catalysed rearrangement of 1,3-dimethylenecyclobutane,[5,6] anionotropic isomerisation of the dimer
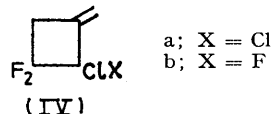
of perfluoroallene,[7] electrocyclic ring-closure of alkenylallenes and related compounds,[8-13] and cycloaddition of

$$CH_2{:}C{:}CR_2 \xrightarrow{CF_2{:}CXY} \quad (I) \quad + \quad (II) \qquad (1)$$

a; R = H, X = Y = Cl
b; R = H, X = F, Y = Cl
c; R = H, X = Y = F
d; R = Me, X = Y = F
e; R = Me, X = F, Y = Cl
f; R = Me, X = Y = Cl

$$\text{(III)} \xleftarrow[\text{10—30 min}]{KOH_{(s)}\,80°} \qquad (2$$
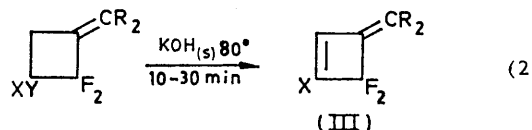
a; R = H, X = F
b; R = Me, X = F
c; R = Me, X = Cl
d; R = H, X = Cl

a; X = Cl
b; X = F

(IV)

[1] Part II, D. R. Taylor and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 391.

[2] D. R. Taylor, M. R. Warburton, and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 385.

[3] D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Amer. Chem. Soc.*, 1949, 71, 490.

[4] D. R. Taylor and M. R. Warburton, *Tetrahedron Letters*, 1967, 3277.

[5] F. F. Caserio, S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, 80, 5507.

[6] J. K. Williams and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1959, 81, 4269.

[7] R. E. Banks, M. G. Barlow, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1966, 981.

[8] E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 1960, 341.

[9] A. V. Federova and A. A. Petrov, *J. Gen. Chem. (U.S.S.R.)*, 1962, 32, 3471.

[10] E. Gil-Av and J. Herling, *Tetrahedron Letters*, 1967, 1.

[11] W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, 1967, 89, 342.

[12] L. Skattebøl, *Tetrahedron*, 1967, 23, 1107.

[13] J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, 1967, 89, 1537.

acetylenes to allenes [14-16]), most of which are of limited applicability. Comparable with the present route are syntheses of the trifluoro-compound (IIIa) [17] and the parent methylenecyclobutene,[18] based on dehydrohalogenation of precursors derived in other ways.

Allene Cycloadditions.—The thermal cycloaddition of chlorotrifluoroethylene or 1,1-dichlorodifluoroethylene to allene proceeds less readily than that of tetrafluoroethylene.[2,3] No attempt was made to establish optimum conditions, and the temperature was kept low (150—180°) to limit the rate of the self-dimerisation of the fluoro-olefins; under such conditions the conversion into cycloadducts was very low, even after 14 days. Nevertheless, the yields of 1 : 1 adducts (based on allene consumed) were high and the desired adducts were readily freed from olefin dimers by preparative g.l.c. Oligomeric adducts corresponding to those obtained [2,3] from allene and tetrafluoroethylene were not detected. However, in both cases the 1 : 1 adduct fractions were mixtures of two isomers, the main constituent (Ia or b) in each case having chlorine remote from the exocyclic double bond, and the minor constituent (IVa or b) having chlorine adjacent to the unsaturated group. Since these constitute the only examples reported hitherto of [2 + 2] cycloadditions to allene, which lack orientational specificity, apart from the thermal dimerisation of allene,[19] the structural evidence will be presented in some detail.

Elemental analysis and mass spectrometry (Found: M, 156) showed the chlorotrifluoroethylene-adduct fraction to contain only 1 : 1 adducts, and the i.r. spectra indicated the presence of the exocyclic methylene group [$\nu_{max.}$ 5·91 (C:C stretch) and 11·61 μm (out-of-plane def. for :CH$_2$)]. The structure of the major component (Ib) was deduced from (i) a comparison of the mass spectrum of the mixture with that of the tetrafluoroethylene adduct (Ic) (see later) and (ii) the n.m.r. data (see Figure 1 and Tables 1 and 2). In the ¹H n.m.r. spectrum, which is dominated by the major isomer, the signal for ring methylene protons appears as a doublet (J ca. 13 Hz) of multiplets centred at δ 3·08 p.p.m. [cf. the corresponding band in compound (Ie); also a doublet (J ca. 13 Hz) at δ 3·08 p.p.m.]. In this type of molecule the geminal proton–proton coupling is known to be ca. 13 Hz,[20-22] and the average of vicinal *cis*- and *trans*-coupling between a fluorine atom and adjacent non-equivalent protons in cyclobutanones is of similar magnitude; [21] a first-order interpretation is therefore impossible. However, had the reverse orientation predominated, the signal for the ring methylene protons would be a triplet, as it is in the C$_2$F$_4$ adducts (Ic and d). The ¹H n.m.r. spectrum also excludes the possibility that the adduct is formed by cycloaddition to propyne formed by rearrangement of allene, because there are two vinyl protons.

The ¹⁹F n.m.r. spectrum of the mixture of the chlorotrifluoro-compounds (Ib) and (IVb) is shown in Figure 1. It consists of a doublet of doublets (A$_1$A$_2$B$_1$B$_2$, J_{AB} 210 Hz), accompanied by a high-field triplet (X, $|J_{HF}|$ ca. 13 Hz), all assigned to isomer (Ib), overlapping a weaker pattern due to (IVb) which consists of a doublet of doublets of multiplets (A′$_1$A′$_2$B′$_1$B′$_2$, $J_{A'B'}$ 195 Hz) and a
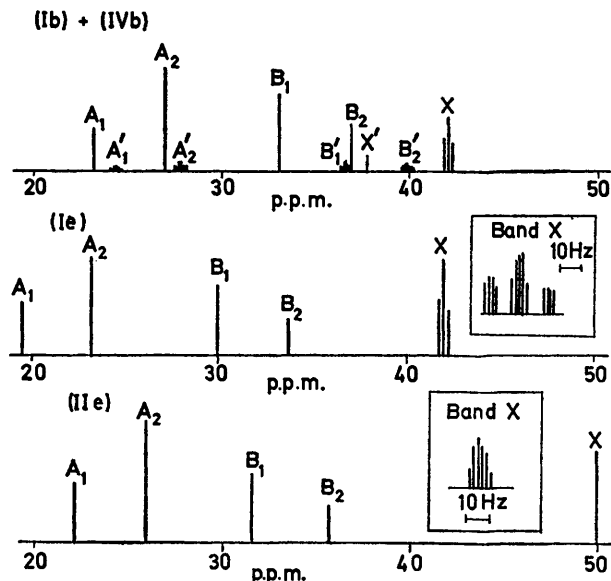

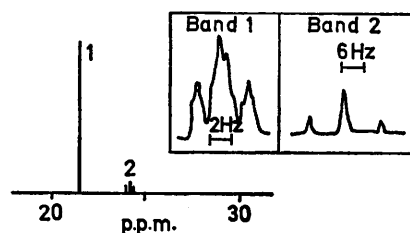
FIGURE 1   ¹⁹F N.m.r. spectra of CF$_2$:CFCl adducts

FIGURE 2   ¹⁹F N.m.r. spectrum of a mixture of the dichlorodifluoro-compounds (Ia) and (IVa)

broad singlet (X′). Careful integration indicated that the ratio of (Ib) to (IVb) is 85 : 15. The small multiplets of the A′B′ pattern of (IVb) are apparent triplets, due to the averaging of J_{HF}(*cis*) and J_{HF}(*trans*) to ca. 13 Hz; the X-band of (Ib) presents a similar appearance. For comparison purposes; the ¹⁹F n.m.r. spectra of the related adducts (Ie) and (IIe) [1] are also shown in Figure 1; in that of (Ie), the X-band triplet is further resolved and appears as a doublet of doublets of doublets of doublets, as expected for an ABXYZ system.

Similar arguments lead to the conclusion that the adduct fraction obtained from CF$_2$:CCl$_2$ and allene con-

14 J. D. Roberts and D. E. Applequist, *J. Amer. Chem. Soc.*, 1956, **78**, 4012.

15 R. E. Banks, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1966, 2051.

16 B. E. Kirk and D. R. Taylor, unpublished results.

17 J. M. Birchall, R. Fields, R. N. Haszeldine, and R. McLean, personal communication.

18 E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 784.

19 D. R. Taylor, *Chem. Rev.*, 1967, **67**, 319, and references cited therein.

20 M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 2935.

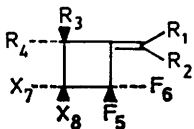21 J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3891.

22 I. Fleming and D. H. Williams, *Tetrahedron*, 1967, **23**, 2747.

sists of a 95 : 5 mixture of the isomers (Ia) and (IVa). In this case, the n.m.r. spectra (Tables 1 and 2, and Figure 2) are considerably simplified by the absence of an asymmetric centre.

The mechanism of cycloadditions to allenes is an area of current interest and since this work was completed diradical may be supposed to be (V), in which the allene transforms into a planar allylic radical, and the olefin to a RCF_2·CClX· radical. The other intermediate, required to explain the formation of the minor adducts (IVa and b), is more likely to be (VI), in which the olefin still places the lone electron at its chlorine-bearing
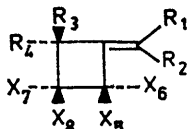
TABLE 1

^{1}H N.m.r. data for polyfluoroalkylidenecyclobutanes

Compound				Chemical shift (p.p.m.)			Ref.	Multiplicities ^{a}		
R_1R_2	R_3R_4	X_7	X_8	δ_1	δ_2	$\delta_3\delta_4$	cpd.	H_1	H_2	H_3H_4
(Ia)	H	H	Cl	Cl	5·68	5·97	3·50	b	dm	dm	bm
(Ib)	H	H	F	Cl	5·36	5·64	3·08	b	dtt	dm	dm ^{c}
(Ic)	H	H	F	F	5·30	5·57	2·86	b	dtt	dm	tddt ^{c}
(Id)	Me	H	F	F	1·69	1·87	2·90	d	tt	quin	tm ^{c}
(Ie)	Me	H	F	Cl	1·68	1·89	3·08	d	tt	quin	dm ^{c}
(If)	Me	H	Cl	Cl	1·68	1·88	3·19	e	tt	quin	bm
(IId)	H	Me	F	F	5·40	5·65	1·28	d	dt	dt	bm
(IIe)	H	Me	F	Cl	5·42	5·65	1·34	d	dt	dt	bm
(IIf)	H	Me	Cl	Cl	5·32	5·60	1·40	e	dt	dt	t

^{a} b = Broad; d = doublet; t = triplet; quin = quintet; m = multiplet. ^{b} Neat benzene interchange, assigned a δ-value of 6·70 p.p.m. ^{c} Deceptively simple pattern, not first-order. ^{d} Internal tetramethylsilane. ^{e} Sample analysed as 50% CCl$_4$ solution, with tetramethylsilane as standard.

TABLE 2

^{19}F N.m.r. data for polyfluoroalkylidenecyclobutanes

Compound						Chemical shift (p.p.m.) ^{a}				Multiplicities			
R_1R_2	R_3R_4	X_5	X_6	X_7	X_8	ϕ_5	ϕ_6	ϕ_7	ϕ_8	F_5	F_6	F_7	F_8
(Ia)	H	H	F	F	Cl	Cl	21·6				ddm			
(Ib)	H	H	F	F	F	Cl	25·3 ^{a}	34·4	42·2		dd ^{f}	t ^{d}		
(Ic)	H	H	F	F	F	F		38·7		40·3	m ^{g}		tm ^{d}	
(Id)	Me	H	F	F	F	F		35·3		38·5	bm		tm ^{d}	
(Ie)	Me	H	F	F	F	Cl	21·7 ^{e}	31·5	42·1		dd ^{f}	dddd		
(If)	Me	H	F	F	Cl	Cl	17·1 ^{e}				qq			
(IId)	H	Me	F	F	F	F		36·5		49·9	bm		sep	
(IIe)	H	Me	F	F	F	Cl	24·6 ^{e}	33·4	50·1		dd ^{f}	s ^{d}		
(IIf)	H	Me	F	F	Cl	Cl	31·0 ^{e}				bm			
(IVa)	H	H	Cl	Cl	F	F			24·2				t ^{d}	
(IVb)	H	H	F	Cl	F	F	37·7		26·2	37·8	bm		ddt ^{d,f}	

^{a} For convenience, ϕ (rel. to external CF$_3$·CO$_2$H) is positive for an *upfield* shift; no solvent unless indicated. ^{b} b = Broad; d = doublet; t = triplet; q = quartet; s = sextet; sep = septet; m = multiplet. ^{c} The lowfield doublet is assumed to be due to the F-nucleus *cis* to Cl (see text). ^{d} Deceptively simple, not first-order. ^{e} 50% solution in CCl$_4$. ^{f} AB spectrum. ^{g} 12-line multiplet.

much new information has emerged.[23] It is now widely accepted that, according to the new terminology, these cycloadditions are *energetically non-concerted*, *i.e.*, an intermediate diradical is formed, but *orbitally concerted*, a term used to convey that the intermediate forms and collapses in accordance with orbital symmetry requirements. The preferential formation of (Ia and b) is in agreement with these conclusions, but provides no further test for them. The structure of the intermediate terminus, than (VII) (see Scheme 1). Allene shows a tendency to undergo free-radical additions *via* intermediate vinyl radicals,[19] whereas these fluoro-olefins rarely experience radical attack except at the difluoromethylene group.[24]

Attempts to achieve comparable cycloadditions between allene and vinylidene fluoride or perfluoropropene were unsuccessful, and 1 : 1 adducts were not isolated.

Dehydrohalogenations.—The elimination of hydrogen

[23] J. E. Baldwin and R. H. Fleming, *Fortschr. chem. Forsch.*, 1970, **15**, 281.

[24] C. Walling and E. S. Huyser, *Org. Reactions.* 1963, **13**, 91; F. W. Stacey and J. F. Harris, *ibid.*, p. 150.

fluoride from the tetrafluoromethylenecyclobutane (Ic) takes place smoothly over dry finely-divided potassium hydroxide. The reaction is conveniently performed in

SCHEME 1
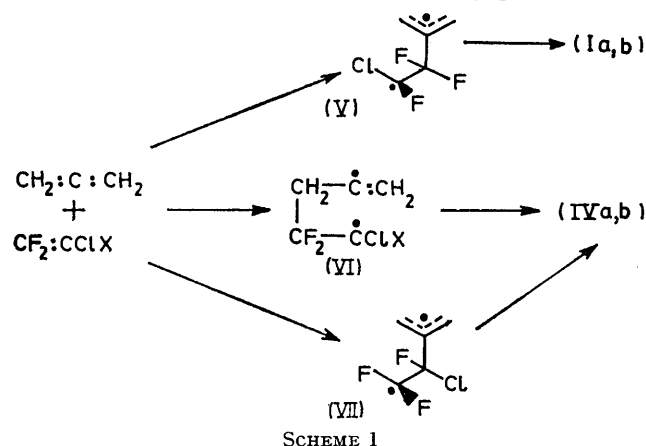
an evacuated Pyrex flask; after 30 min at 80°, no starting material remains, and the product (30%) is the diene (IIIa), b.p. 64—66°. The diene displays i.r. absorptions at 5·89 (C:CH₂ stretch) and 11·50 μm (:CH₂ def.) characteristic of an exocyclic methylene group, and a further

spectrum of the diene prepared from the mixture of the monochlorides (Ib) and (IVb) suggested that a small percentage of a substance of a molecular weight 136, either (IIId) or (VIII), was formed by simultaneous elimination of hydrogen fluoride from either (Ib) or (IVb), respectively.
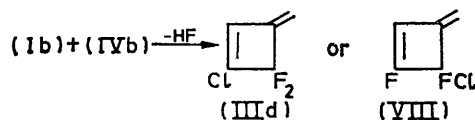

Elimination of hydrogen chloride occurs quite readily when either of the isopropylidenecyclobutanes (Ie or f) is treated with base. The dichloride (If) affords a chloro-difluoro-diene (55% yield), identified by mass spectrometry and n.m.r. analysis (see Table 3) as the 1-chloro-diene (IIIc). This diene also polymerises very rapidly, despite the terminal alkylation of the diene system. When the monochloride (Ie) was treated with dry KOH, a 1 : 3 mixture of two dienes was obtained. N.m.r. analysis of the mixture showed that the minor component (22% yield) is the chloro-diene (IIIc), identical to that obtained from the dichloride (If). The major product, b.p. 107°, was isolated on a scale sufficient only for

TABLE 3

¹H and ¹⁹F N.m.r. data for alkylidenecyclobutenes

| Compound		Chemical shift(p.p.m.) [a]					Multiplicities [b]				
R_1R_2	X_7	δ_1	δ_2	δ_3	ϕ_5, ϕ_6	ϕ_7	H_1	H_2	H_3	F_5F_6	F_7
(IIIb) Me	F	1·64	1·75	6·05	37·8	34·0	u	u	td	dd	dt
(IIIc) Me	Cl	1·65	1·74	6·84	36·5		u	u	t	d	

[a] ¹H Shifts measured with internal tetramethylsilane, ¹⁹F shifts (φ positive for an *upfield* shift) measured from external CF₃·CO₂H; no solvent. [b] u = Not resolved; d = doublet; t = triplet.

strong C:C band at 6·11 μm. It readily polymerises to a rubbery solid, as reported for the parent hydrocarbon.[14]
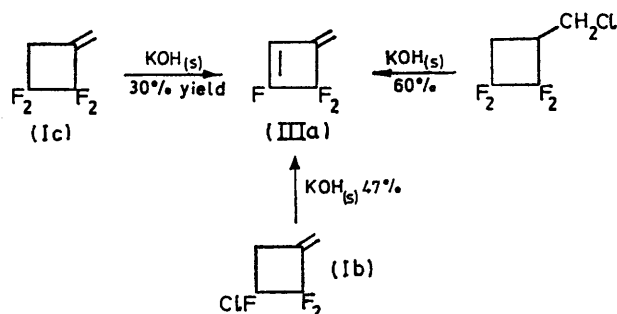

The diene (IIIa) so prepared was spectroscopically identical with material prepared (i) by base-catalysed dehydrohalogenation of 3-chloromethyl-1,1,2,2-tetra-fluorocyclobutane,[17] and (ii) by dehydrochlorination of the allene–chlorotrifluoroethylene adducts, of which (Ib) must therefore be the main component. The mass

spectroscopic investigation. Its n.m.r. data (see Table 3) and mass spectrum are wholly consistent with its formulation as the trifluoro-diene (IIIb). These reactions completely confirm the structures of these two 1,1-di-methylallene adducts (Ie and f), which previously relied on spectroscopic data alone.[1]
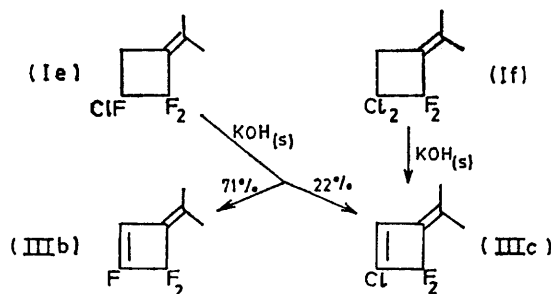
Mass Spectra of Alkylidenecyclobutanes.—The methyl-enecyclobutanes (Ia—c) were examined by low resolution

mass spectrometry. When chlorine is present, the main breakdown pathway is loss of Cl· followed by elimination of HF from (Ib) or HCl from (Ia); metastable ions corresponding to these fragmentations were observed. The
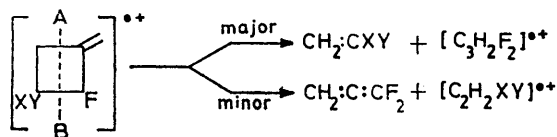
SCHEME 2

base peak in the spectrum of the tetrafluoride (Ic) is at m/e 83, corresponding to either $(M - F_3)$ or more probably $(M - C_3H_2F)$. In spite of this difference, all

TABLE 4

Mass spectral data for methylenecyclobutanes

Ion [a]	Relative intensity (% of base peak) in compound		
	(Ic)	(Ia)—(IVa)	(Ib)—(IVb)
$[C_3H_2F_2]^{\cdot+}$	50	49	74
$[C_3H_2ClX]^{\cdot+}$		6	16
$[C_2H_2F_2]^{\cdot+}$	14		
$[C_2H_2ClX]^{\cdot+}$		29	16

[a] X may be F or Cl.

three compounds display peaks of moderate intensity corresponding to ring fission across A–B (see Scheme 2). Although metastable ions to support this mode of

rived from 1,1-dimethylallene [1,2] also show significant amounts of ions due to ring fragmentation of this type. Both tetrafluoroethylene adducts (Id) and (IId) also display a common tendency to eliminate Me· followed by HF (metastables at 139·4 and 115·5), and intense peaks corresponding to loss of CF_3·. All the chlorine-containing adducts show a principal breakdown via loss of Cl· followed by elimination of either HF or HCl.

The mass spectra of the three alkylidenecyclobutenes (IIIa—c) did not show clearly defined ring cleavage. In the trifluorides (IIa and b) the parent ions are strong, and loss of F·, H·, and in (IIIb) Me· followed by HF, are observed. The chloride (IIIc) fragments by loss of Cl· or Me·.

N.m.r. Spectra.—Altogether, eleven structurally related alkylidenecyclobutanes (Ia—f), (IId—f), and (IVa and b) have now been examined by n.m.r. spectroscopy.[1,2] In spite of the complexity of many of the spectra, which defy first-order treatment, certain generalisations may usefully be made. Approximate coupling constants are shown in Table 5.

(1) The ^{19}F resonance of a difluoromethylene group undergoes a very regular lowfield shift as the neighbouring group is changed from CF_2 to $CFCl$ to CCl_2 (the average value of ϕ is used when the two fluorines are non-equivalent). This change is proportional to the total electronegativity ($\Sigma\chi$) of neighbouring halogen

TABLE 5

Spin–spin coupling constants for alkylidenecyclobutanes (IX) and alkylidenecyclobutenes (X)
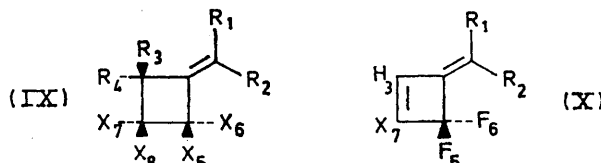
Compound	$J_{1.2}$	$J_{1.3}$	$J_{1.5}$	$J_{2.3}$	$J_{2.5}$	$J_{3.7}$	$J_{4.7}$	$J_{3.5}$	$J_{3.6}$	$J_{5.6}$	$J_{5.7}$	$J_{6.7}$	$J_{7.8}$
(Ia)	2		2·4		2·8								
(Ib)	1·8	2·5	2·5			12·5—13·0 [a]				210			
(Ic)	1·8	3	3	3·2	3	11·6—12·2 [a]		ca. 1 [a]					
(Id)		2	3·5	2·5	2·5	11·5—11·8 [a]							
(Ie)		1·5	3	2	2	12·7—13·9 [b]				215	2 [b]	4	
(If)		1·8	3·5	2·5	2·5								
(IId)	1·8		2·5		3·0	1—2							
(IIe)	1·8		2·3		2·8					219			
(IIf)	1·8		2·2		2·8			ca. 0·5					
(IIIb)						7·0			11·6		5·6	5·6	
(IIIc)									12·0				
(IVa)				12 [a]									
(IVb)				13 [a]									195

[a] Value shown is the average of *cis* and *trans* coupling. [b] It is assumed that $J_{cis} > J_{trans}$ (see ref. 25).

cleavage were not detected, the relative intensities of this type of fragment support the n.m.r. analysis of the adduct mixtures of dichlorides (Ia)—(IVa) and trifluorides (Ib)—(IVb). The ion current borne by the $[C_3H_2F_2]^{\cdot+}$ and $[C_2H_2ClX]^{\cdot+}$ ions greatly exceeds that carried by the $[C_3H_2ClX]^{\cdot+}$ and $[C_2H_2F_2]^{\cdot+}$ ions (where X = F or Cl), confirming that in both mixtures the major component has a difluoromethylene group adjacent to the exocyclic double bond (see Table 4).

The alkylidenecyclobutanes (Id—f) and (IId—f) de-

atoms, in all four of the series of compounds studied (see Figure 3), the shift increment for each replacement of fluorine by chlorine being 7—8 p.p.m., much greater than the corresponding change of δ_{CH_2} (0·1—0·4 p.p.m.). Similar instances of increased deshielding by neighbours of lower electronegativity are known.[25]

(2) The geminal proton coupling in the exocyclic methylene group is consistently 1·8 Hz. The shift

[25] R. Fields, ' Annual Reports on N.M.R. Spectroscopy.' vol. 5, ed. E. F. Mooney, Academic Press, London, in the press.

assignments for these protons and for the methyl groups in compounds (IId—f) were made on the assumption that the proton resonance at lower field is that due to the group *cis* to the ring difluoromethylene group. This follows from reported assignments for acyclic fluoro-olefins.[25]

(3) Cross-ring H–F coupling, negligible in alkylidenecyclobutanes, rises to 11—12 Hz in the alkylidenecyclobutenes (IIIb and c).
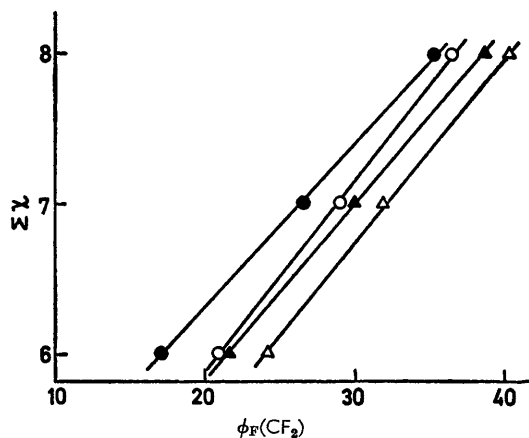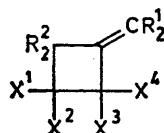

FIGURE 3 Variation of ϕ_F for alkylidenecyclobutanes with total halogen electronegativity ($\Sigma\chi$) at neighbouring carbon atom

●, $R^1 = Me$, $R^2 = H$, $X^3 = X^4 = F$, $CX^1X^2 = CF_2$, CFCl, or CCl_2; ○, $R^1 = H$, $R^2 = Me$, $X^3 = X^4 = F$, $CX^1X^2 = CF_2$, CFCl, or CCl_2; ▲, $R^1 = R^2 = H$, $X^3 = X^4 = F$, $CX^1X^2 = CF_2$, CFCl, or CCl_2; △, $R^1 = R^2 = H$, $X^1 = X^2 = F$, $CX^3X^4 = CF_2$, CFCl, or CCl_2

(4) The average value for $^3J_{HF}$ (measured as the average of J_{cis} and J_{trans}) in these alkylidenecyclobutanes is 12·5 Hz, in agreement with accurate data for a difluorocyclobutanone,[21] indicating that the ring is planar.

EXPERIMENTAL

General experimental procedures and spectroscopic techniques have been described previously.[2] Allene was obtained from Cambrian Chemicals, chlorotrifluoroethylene from Société d'Electrochimie d'Ugine, and hexafluoropropene and 1,1-difluoroethylene from Pennwalt Chemical Corporation. 1,1-Dichlorodifluoroethylene was a gift from Professor R. N. Haszeldine. 1,1,2,2-Tetrafluoro-3-methylenecyclobutane,[2] 1-chloro-1,2,2-trifluoro-3-isopropylidenecyclobutane,[1] and 1,1-dichloro-2,2-difluoro-3-isopropylidenecyclobutane[1] were prepared as described previously. Temperatures are given in degrees Celsius.

Reaction of Allene with Chlorotrifluoroethylene.—Allene (13·4 g, 0·335 mol), chlorotrifluoroethylene (44·6 g, 0·383 mol), and Terpene B polymerisation inhibitor[2] (0·5 ml) were

kept at 150° in a Langalloy-lined autoclave (300 ml) for 60 h. Gaseous products were transferred to the vacuum manifold and separated by trapwise fractional condensation *in vacuo* to give a mixture of allene (12·9 g, 96% recovery) and chlorotrifluoroethylene (40·4 g, 91% recovery), which was analysed by Regnault molecular weight determination and i.r. spectroscopy. Products condensing *in vacuo* at −78° and above (4·25 g) were analysed collectively by g.l.c. (4 m Kel-F 10 Oil, 100°) and consisted of *cis*-1,2-dichlorohexafluorocyclobutane (62%, 2·6 g, 11·2 mmol; 62% yield on olefin consumed), identified by comparison with an authentic sample prepared by dimerisation of chlorotrifluoroethylene,[26] and an unknown (38%, 1·7 g). The unknown was collected by autopreparative g.l.c. (3 m Carbowax 1000 + 2 m diethylene glycol succinate, 75°) and identified as an 85 : 15 mixture [Found: C, 38·2; H, 2·7%; M, 156. $C_5H_4ClF_3$ requires C, 38·4; H, 2·6%; M, (for ^{35}Cl), 156] of 1-*chloro*-1,2,2-*trifluoro*-3-*methylenecyclobutane* (Ib) (74% yield based on C_3H_4 consumed) and 2-*chloro*-1,1,2-*trifluoro*-3-*methylenecyclobutane* (IVb) (13% yield based on C_3H_4 consumed). The mixture of isomers, b.p. 90—92°, displayed the following spectroscopic properties: $\lambda_{max.}$ (EtOH) 205 nm, $\nu_{max.}$ (film) 3·34m, 3·41w, 5·36w, 5·91m (C:C str.), 7·01s, 7·08s, 7·71vs, 7·95s, 8·19s, 8·6—8·8s,br, 9·00s, 9·46s, 9·85s, 10·5—10·7s, 11·61s (:CH$_2$), 12·23s, and 14·28s µm, m/e 158 (5%, $C_5H_4{}^{37}ClF_3$), 156 (13%, $C_5H_4{}^{35}ClF_3$), *121* (100%, $C_5H_4F_3$), 120 (7%, $C_5H_3F_3$), 101 (41%, $C_5H_3F_2$), 95 (9%, $C_3H_2F_3$), 94 (4%, $C_3H_2{}^{37}ClF$), 92 (12%, $C_3H_2{}^{35}ClF$), 87 (10%), 85 (12%), 83 (13%), 82 (5%, $C_2H_2{}^{37}ClF$), 80 (11%, $C_2H_2{}^{35}ClF$), 78 (33%, $C_2{}^{35}ClF$ or $C_3H_4F_2$), 77 (46%, $C_3H_3F_2$), 76 (74%, $C_3H_2F_2$), 75 (30%, C_3HF_2), 71 (7%, C_4H_4F), 70 (5%, CHF_3 or C_4H_3F), 69 (16%, CF_3 or C_4H_2F), 57 (13%, C_3H_2F), 51 (6%, CHF_2), 50 (6%, CF_2), 45 (6%, C_2H_2F), 40 (17%, C_3H_4), 39 (23%, C_3H_3), 38 (6%, C_3H_2), and 31 (11%, CF), metastable ion at 85 (121 ⟶ 101). The components were identified, and the composition determined, by ^1H and ^{19}F n.m.r. analysis (see Tables 1, 2, and 5).

Reaction of Allene with 1,1-Dichlorodifluoroethylene.—Allene (2·00 g, 50 mmol), 1,1-dichlorodifluoroethylene (6·65 g, 50 mmol), and Terpene B (0·5 ml) were kept at 180° for 14 days in a Pyrex pressure tube (400 ml). Gaseous products were transferred to the vacuum manifold and shown by Regnault's molecular weight determination and i.r. spectroscopy to consist of a mixture of allene (40·8 mmol, 82% recovery) and dichlorodifluoroethylene (36·8 mmol, 74% recovery). A liquid product (2·13 g) condensing *in vacuo* at −23° and above was shown by g.l.c. (2 m polyethyleneglycol adipate, 100°) to consist of a 1 : 2 mixture of two components, which were collected by autopreparative g.l.c. (5 m Carbowax 1000, 160°) and identified spectroscopically as 1,1,2,2-tetrachlorotetrafluorocyclobutane (0·71 g, 2·7 mmol, 41% yield based on olefin consumed), and a 95 : 5 mixture (1·42 g) [Found: C, 34·7; H, 3·1%; M, 172. $C_5H_4Cl_2F_2$ requires C, 34·7; H, 2·3%; M (for ^{35}Cl), 172] of 1,1-*dichloro*-2,2-*difluoro*-3-*methylenecyclobutane* (Ia) (7·8 mmol, 85% yield based on C_3H_4 consumed) and 2,2-*dichloro*-1,1-*difluoro*-3-*methylenecyclobutane* (IVa) (0·4 mmol, 4% yield). The mixture showed $\nu_{max.}$ (film) 3·33w, 3·40w, 5·02w, 5·37w, 5·90m (C:C str.), 7·02s, 7·09s, 7·24m, 7·42m, 7·76vs, 8·16vs, 8·79vs, 8·97vs, 9·32s, 10·00vs, 10·24vs, 10·77s, 10·96vs, 12·04vs, 12·62s, 13·03vs, and 14·31s µm, m/e (bands of less than 5% base peak omitted) 172 (6%,

[26] J. D. Park, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, 1960, **25**, 990.

$C_5H_4{}^{35}Cl_2F_2$), 139 (35%, $C_5H_4{}^{37}ClF_2$), *137* (100%, $C_5H_4{}^{35}ClF_2$) 134 (10%, $C_5H_3{}^{37}Cl^{35}Cl$), 132 (14%, $C_5H_2{}^{35}Cl_2$), 108 (6%, $C_3H_2{}^{35}Cl_2$), 101 (16%, $C_5H_3F_2$), 98 (12%, $C_2H_2{}^{35}Cl^{37}Cl$), 96 (17%, $C_2H_2{}^{35}Cl_2$), 89 (6%), 87 (7%), 85 (8%), 76 (49%, $C_3H_2F_2$), 75 (20%, C_3HF_2), 61 (8%, $C_2H_2{}^{35}Cl$), and 57 (6%, C_3H_2F). The isomers were identified, and their proportion determined, by ^1H and ^{19}F n.m.r. analysis (see Tables 1, 2, and 5). A similar reaction conducted at 165° for 72 h gave a lower conversion (5%) of allene, but the same products.

Reaction of Allene with Hexafluoropropene.—Allene (1·98 g, 49·4 mmol), hexafluoropropene (7·67 g, 51·1 mmol), and Terpene B (0·5 ml) were kept at 185° for 60 h in a Pyrex pressure tube (400 ml) to give unchanged allene (47·7 mmol, 96%), hexafluoropropene (50·7 mmol, 99%), and a liquid (0·1 g) condensing *in vacuo* at −78°. Two further reactions provided an additional 0·29 g of this material, and the combined product was shown by g.l.c. (2 m silicone oil, 100°) to contain mainly (*ca.* 80%) one component, a small sample of which was collected by preparative g.l.c. (5 m Carbowax 20M, 180°) and identified as a 2 : 1 adduct (Found: *M*, 230. Calc. for $C_9H_8F_6$: *M*, 230) but not examined further. In a further reaction, allene (96 mmol), hexafluoropropene (92 mmol), and Terpene B (1 ml) were kept at 300—400° in a Langalloy-lined autoclave (50 ml) for 30 h. A mixture of allene (*ca.* 22 mmol) and hexafluoropropene (*ca.* 59 mmol) was recovered, accompanied by (i) a liquid (1·8 g) condensing *in vacuo* at −45° and above, shown to consist of at least five components and not examined further, and (ii) a dark involatile oil (2 g).

Attempted Reaction of Allene with 1,1-Difluoroethylene.—A 99% recovery of 1,1-difluoroethylene was observed in a reaction between allene (0·47 mol), 1,1-difluoroethylene (0·48 mol), and Terpene B (1 ml) at 200° for 5 days in a Langalloy-lined autoclave (300 ml), and the product was a mixture of oligomers of allene accompanied by a rubbery polymer (Found: C, 86·4; H, 9·0. Calc. for C_3H_4: C, 90·0; H, 10·0%).

Dehydrofluorination of 1,1,2,2-Tetrafluoromethylenecyclobutane.—1,1,2,2-Tetrafluoromethylenecyclobutane (2·0 g, 14·3 mmol) was condensed *in vacuo* onto finely powdered anhydrous potassium hydroxide (*ca.* 5 g) in a Pyrex flask attached to the vacuum manifold *via* a short water-cooled condenser. The flask was gently warmed to 80° for 30 min, after which the sole volatile product was identified as 1,4,4-*trifluoro-3-methylenecyclobutene* (IIIa) (0·5 g, 4·2 mmol; 29% yield) (Found: C, 50·0; H, 2·8; *M*, 120. $C_5H_3F_3$ requires C, 50·0; H, 2·5%; *M*, 120), a readily polymerised liquid, ν_{max} (vapour) 3·25w, 3·40m, 4·47w, 5·70w, 5·89m, 6·11vs, 7·02vs, 7·31vs, 7·71m, 8·19vs, 8·76vs, 8·82vs, 9·46m, 10·05vs, 10·11vs, 10·31m, 10·69m, 10·72m, 10·92m, 11·29vs, 11·39vs, 11·50vs, and 13·38s μm, *m/e* (bands below 5% omitted) *120* (100%, $C_5H_3F_3$), 119 (59%, $C_5H_2F_3$), 101 (42%, $C_5H_3F_2$), 100 (5%, $C_5H_2F_2$), 99 (8%, C_5HF_2), 94 (14%, C_3HF_3), 93 (5%, C_3F_3), 76 (22%, $C_3H_2F_2$), 75 (45%, C_3HF_2), 70 (88%, CHF_3 or C_4H_3F), 69 (37%, CF_3 or C_4H_2F), 51 (41%, C_4H_3 or CHF_2), 50 (20%, CF_2 or C_4H_2), 39 (24%, C_3H_5), and 31 (20%, CF). An attempt to dehydrofluorinate the methylenecyclobutane in 20% aqueous potassium hydroxide solution at 30—50° for 30 min gave mainly starting material.

Dehydrochlorination of 1-Chloro-1,2,2-trifluoro-3-methylenecyclobutane.—A sample (0·50 g, 3·2 mmol) of the 85 : 15 mixture of 1-chloro-1,2,2-trifluoro-3-methylenecyclobutane (Ib) and 2-chloro-1,1,2-trifluoro-3-methylenecyclobutane (IVb) was kept at 80° for 10 min over powdered anhydrous

potassium hydroxide as described before. The volatile product (0·3 g) was dried over phosphorus pentoxide *in vacuo* and shown by g.l.c. (2 m Silicone oil, 105°) to consist of recovered methylenecyclobutanes (69 parts, 41% recovery), and 1,4,4-trifluoro-3-methylenecyclobutene (IIIa) (31 parts, 0·09 g, 0·75 mmol; 47% yield based on 1-chlorotrifluoromethylenecyclobutane consumed) which was collected and identified by g.l.c., m.s., and i.r. comparison with authentic material prepared as described above, and shown to contain *ca.* 10% of a compound $C_5H_3ClF_2$ [Found: *M* (by mass spec.), 136 and 138. Calc. for C_5H_3-ClF_2: *M*, 136 and 138].

Dehydrohalogenation of 1-Chloro-1,2,2-trifluoro-3-isopropylidenecyclobutane.—Finely powdered potassium hydroxide (6·0 g) and Terpene B polymerisation inhibitor (0·5 ml) were placed in a Pyrex flask (50 ml) attached to the vacuum manifold, and evacuated for 3 h. 1-Chloro-1,2,2-trifluoro-3-isopropylidenecyclobutane (Ie) (1·0 g, 5·5 mmol) was admitted *in vacuo*, and the mixture warmed to 80° for 15 min. The hydroxide rapidly darkened; volatile products were condensed into an adjacent trap and shown by g.l.c. (2 m polyethylene glycol adipate, 75°) to consist of a 1 : 3 mixture (0·77 g) (Found: C, 54·9; H, 4·7. Calc. for a 1 : 3 mixture of $C_7H_7ClF_2$–$C_7H_7F_3$: C, 55·5; H, 4·5%) of 1-chloro-4,4-difluoro-3-isopropylidenecyclobutene (IIIc) (1·2 mmol, 22% yield) (identified by comparison with an authentic sample prepared from 1,1-dichloro-2,2-difluoro-3-isopropylidenecyclobutane) and an unknown substance. Repeated trapwise fractional condensation *in vacuo* gave a small sample of the unknown, identified by m.s. and n.m.r. as 1,4,4-*trifluoro-3-isopropylidenecyclobutene* (IIIb) (Found: *M*, 148. Calc. for $C_7H_7F_3$: *M*, 148), a most readily polymerised liquid, b.p. 107° at 741 mmHg (decomp.), $n_D{}^{18}$ 1·4130 (4·0 mmol by g.l.c., 71% yield), ν_{max} (film) 3·21w, 3·35m, 3·40w, 3·43w, 3·47w, 3·50w, 5·75m, (C:C), 6·12vs (C:C), 6·90s, 7·25s, 7·35vs, 7·60m, 7·67s, 7·72s, 8·03s, 8·48s, 9·17vs, 9·52s, 10·38s, 11·49m, 11·86s, 13·51s, and 15·43m μm, the ^1H and ^{19}F n.m.r. data are shown in Tables 3 and 5, *m/e* (peaks less than 5% base omitted) 148 (59%, *M*), 147 (8%, $C_7H_6F_3$), 133 (48%, $C_6H_4F_3$), 132 (6%, $C_6H_3F_3$), 129 (12%, $C_7H_7F_2$), 127 (18%, $C_7H_5F_2$), 113 (13%, $C_6H_3F_2$), 98 (19%, C_5F_2 or C_6H_7F), 95 (7%, C_6H_4F), 86 (18%), 85 (18%), 83 (35%, C_5H_4F), 79 (11%), 77 (15%), 71 (32%), 70 (15%), 63 (9%, C_5H_3), 57 (60%, C_3H_2F), 56 (45%, C_3HF), 55 (18%, C_3F), 51 (10%), *43* (100%, C_3H_7), 42 (76%, C_3H_6), 41 (60%, C_3H_5), 39 (55%, C_3H_3), 31 (13%, CF), 29 (30%, C_2H_5), and 26 (28%, C_2H_2), and a metastable ion at 96·4 (132 or 133 ⟶ 113).

Dehydrochlorination of 1,1-Dichloro-2,2-difluoro-3-isopropylidenecyclobutane.— 1,1-Dichlorodifluoroisopropylidenecyclobutane (If) 1·0 g, 5·0 mmol) was syringed into an evacuated flask containing anhydrous potassium hydroxide (6·0 g) and Terpene B (0·2 ml) and the mixture was shaken at 80° for 20 min. Volatile products were passed through a trap at 0° *in vacuo* giving a −196° condensate (0·55 g) shown by g.l.c. to consist of a 9 : 1 mixture of 1-*chloro-4,4-difluoro-3-isopropylidenecyclobutene* (IIIc) (0·45 g, 2·5 mmol; 55% yield) and an unknown substance (10%). A small sample of the 3-chloroisopropylidenecyclobutene was collected as a liquid (Found: *M*, 164. Calc. for $C_7H_7{}^{35}ClF_2$: *M*, 164), ν_{max} (film) 3·36m, 3·40m, 3·43m, 3·47w, 3·50w, 5·75w (C:C), 5·81w, (C:C), 6·46s, 6·88w, 6·90s, 7·27s, 7·68vs, 7·73vs, 8·01m, 8·14m, 8·93m, 9·17vs, 9·67m, 10·53m, 11·49m, 12·79s, 12·94m, and 13·66s μm, *m/e* (⩽5% base omitted) 164/166 (87%/24%, *M*), 149/151 (19%/6%, $C_6H_4ClF_2$), *129*

(100%, $C_7H_7F_2$), 127 (33%, $C_7H_5F_2$), 114 (31%, $C_6H_4F_2$), 113 (18%, $C_6H_3F_2$), 109 (25%, C_7H_6F), 101 (8%, $C_5H_3F_2$), 93 (15%, $C_4H_7F_2$), 92 (7%, $C_4H_6F_2$), 91 (8%, $C_4H_5F_2$), 89 (8%, $C_4H_3F_2$), 79 (14%), 77 (15%, C_6H_5), 75 (10%), 65 (8%), 63 (10%, C_5H_3), 51 (10%, C_4H_3), 41 (8%, C_3H_5), and 38 (12%, C_3H_3), m^* 135·2 (164 ⟶ 149), and the ^{1}H and [19]F n.m.r. data are shown in Tables 3 and 5.