

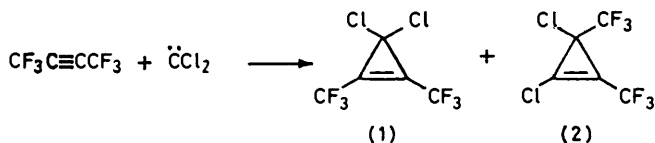
## Cyclopropene Chemistry. Part 1. Preparation and Some Reactions of 3,3-Dichloro-1,2-bistrifluoromethyl- and 1,3-Dichloro-2,3-bistrifluoromethyl-cyclopropene

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Both the title compounds may be obtained from the reaction of dichlorocarbene [generated by thermal decomposition of trifluoro(trichloromethyl)silane] with hexafluorobut-2-yne; the 3,3-dichloro-compound is isomerised to the 1,3-dichloro-isomer by heat, light, or chemical catalysis, but conditions are described for the preparation of either pure cyclopropene. Treatment of either isomer with antimony pentafluoride gives solutions containing the chlorobistrifluoromethylcyclopropenium ion. Both isomers undergo free-radical addition of halogens, but the slow reaction of the 1,3-dichloro-compound with trifluoromethyl radicals gives a mixture of products. Diels-Alder reactions of both cyclopropenes with cyclopentadiene or with furan are described, and the 3,3-dichloro-compound gives a high yield of 'ene'-reaction products with (*E*)-but-2-ene.

ALTHOUGH the literature abounds with examples of the synthesis of *gem*-dihalogeno-cyclopropanes *via* the addition of carbenes to olefinic systems, relatively few examples have emerged of the corresponding synthesis of cyclopropenes by the direct addition of carbenes to acetylenes. Difluorocarbene, generated either from difluorotriethylphosphorane at 100 °C<sup>1</sup> or from epoxyhexafluoropropene at 185 °C,<sup>2</sup> adds to hexafluorobut-2-yne to give 3,3-difluoro-1,2-bistrifluoromethylcyclopropene in low yield, and low yields of 3,3-difluoro-1-perfluoroalkylcyclopropenes have been obtained by the thermolysis of trimethyltrifluoromethyltin at 150 °C in the presence of (perfluoroalkyl)acetylenes.<sup>3</sup> Traditional routes to dichlorocarbene have also usually given poor results with acetylenes,<sup>4</sup> but the development of trifluoro(trichloromethyl)silane as a convenient gas-phase source of this carbene<sup>5</sup> suggested that better results could be achieved in this area.

*Preparation of the Cyclopropenes.*—Reaction of trifluoro(trichloromethyl)silane with a six-fold excess of hexafluorobut-2-yne (total pressure *ca.* 2 atm) at 180 °C during 24 h gives two products, identified as 3,3-dichloro-1,2-bistrifluoromethylcyclopropene (1) (40% yield after purification) and its 1,3-dichloro-isomer (2) (9%). Both products show distinctive cyclopropene double-bond



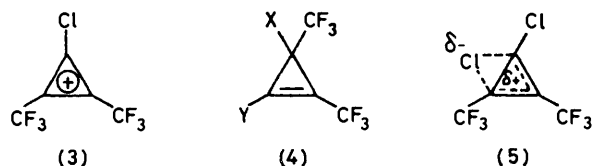
absorption in the 5.3 μm region [(1), 5.27; (2), 5.37 μm; *cf.* 3,3-difluoro-1,2-bistrifluoromethylcyclopropene,<sup>1</sup> 5.49; 3-chlorotriethylphosphorane,<sup>6</sup> 5.29 μm] and the expected parent ions in their mass spectra; the base peak in both cases arises from loss of a chlorine atom (presumably from the allylic position in the unsymmetrical isomer (2)). The <sup>19</sup>F n.m.r. spectrum of the *gem*-dichloro-compound (1) shows only a singlet at δ<sub>F</sub> 14.8 whereas the isomer (2) shows quartets at δ<sub>F</sub> 16.0 ('vinylic' CF<sub>3</sub>) and 4.8 ('allylic' CF<sub>3</sub>), with *J ca.* 0.8 Hz.

The unsymmetrical dichloro-compound (2) is produced under a variety of conditions by rearrangement of the symmetrical isomer (1) (see below), and its formation during the reaction of hexafluorobut-2-yne with dichlorocarbene is probably facilitated by the initial formation of the expected adduct (1) in a 'chemically activated' condition. The effect of 'chemical activation' may be controlled, as in the reaction of dichlorocarbene with tetrafluoroethylene,<sup>7</sup> by the use of increased reaction pressure and lower temperatures, and at *ca.* 6.5 atm and 140 °C reaction between the butyne and the silane yields only the symmetrical cyclopropene (1) in excellent yield (93%). Although the two cyclopropenes are separable by careful fractionation or by preparative g.l.c., both these procedures are inefficient, and control of the reaction to give a single product is therefore highly desirable. The pure unsymmetrical isomer (2) may be obtained quantitatively from the symmetrical compound (1) either by the action of heat (250 °C for 24 h) or by catalysis with aluminium chloride or antimony pentachloride at room temperature or below; irradiation with ultraviolet light appears to lead to only partial conversion of (1) into (2).

*The Cyclopropenium Ion.*—No evidence for the formation of a cyclopropenium ion<sup>8,9</sup> was obtained when either of the cyclopropenes was treated with aluminium chloride or antimony pentachloride in liquid sulphur dioxide under conditions which result in the formation of trichlorocyclopropenium ion from tetrachlorocyclopropene.<sup>8</sup> Attempts to 'trap' the cation by treatment of the symmetrical cyclopropene (1) with aluminium chloride in benzene led only to isomerisation to (2), and a slower isomerisation occurred in the presence of boron trichloride or boron trifluoride in sulphur dioxide. An excess of aluminium bromide also catalyses the rearrangement of (1) but results in some bromine-chlorine exchange; traces of the bromochloro-compounds (4a and b) are probably formed.

The fact that the presence of trifluoromethyl groups discourages cyclopropenium ion formation is not surprising, and the successful isolation of such ions as stable

salts is known to depend heavily on the nature of the counter ion.<sup>8</sup> The powerful Lewis acid, antimony pentafluoride in sulphur dioxide, does convert both cyclopropenes [(1) and (2)] virtually quantitatively into chlorobistrifluoromethylcyclopropenium salts, although with the unsymmetrical isomer (2) some evidence for equilibration and/or fluorine-chlorine exchange was also apparent in the <sup>19</sup>F n.m.r. spectrum. Solid salts of the cyclopropenium ion (3) have not been obtained in an



a; X = Br, Y = Cl  
b; X = Cl, Y = Br

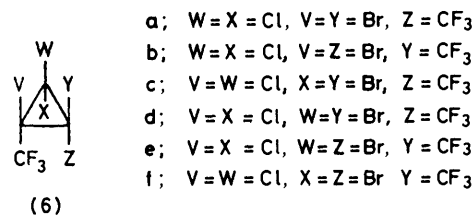
analytically pure condition, but the <sup>19</sup>F n.m.r. spectrum of the cyclopropene (1) in sulphur dioxide containing antimony pentafluoride shows only a sharp singlet at  $\delta_F$  18.0, assigned to the trifluoromethyl groups in the ion (3), and a broad band centred on  $\delta_F$  -34.0, attributed to SbF<sub>5</sub> and SbF<sub>5</sub>Cl<sup>-</sup> absorptions. The relatively small downfield shift of the CF<sub>3</sub> groups is consistent with indirect attachment of the fluorine atoms to the three-membered ring. Further support for the formation of the cation comes from its i.r. spectrum in antimony pentafluoride, which shows characteristic bands at 5.42 and 7.02  $\mu\text{m}$  (cf. ref. 8). The unsymmetrical cyclopropene (2) gives solutions of the ion (3) which show broad absorption in the  $\delta_F$  18 region of the <sup>19</sup>F spectrum, possibly reflecting the lower reactivity of the unsymmetrical compound (2) relative to its isomer (1) (see below).

Attempts to obtain chemical evidence for the presence of the ion (3) have been unsuccessful. In each case, the ion (3) was obtained from the symmetrical cyclopropene (1) and antimony pentafluoride, but reaction of the solution (in SO<sub>2</sub>) with water gave only an unidentified mixture; none of the anticipated bistrifluoromethylcyclopropenone was found. Reactions with aromatic substrates (benzene, anisole, or *p*-xylene)<sup>10</sup> also failed to give significant yields of tractable products and it appeared that the main reactions occurring in these systems involved polymerisation of the arene under the influence of the Lewis acid.

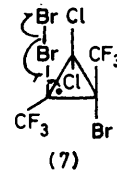
It is tempting to suggest that rearrangement of the symmetrical (1) to the unsymmetrical (2) cyclopropene, particularly when it is catalysed by Lewis acids, does proceed through the cyclopropenium ion (3) as an intermediate. However, it seems unlikely that the ion (3) is formed during thermal (vapour phase) or photochemical isomerisation of the cyclopropene. Furthermore, the symmetrical cyclopropene (1) is slowly isomerised to (2) when it is kept in contact with pure water at room temperature (slow hydrolysis also occurs) and, rather surprisingly, at a greater rate in contact with ethereal solvents.<sup>11</sup> The most attractive mechanism

for all these reactions involves a transition state of type (5), in which the negative charge on the migrating chlorine may be stabilised by co-ordination to a Lewis acid, or the positive character of the ring may be reduced by co-ordination to a saturated oxygen atom. The driving force for the rearrangement must be the greater thermodynamic stability of the unsymmetrical isomer (2) (now known to be less reactive than the symmetrical compound towards a wide variety of reagents), but only tentative explanations for this could be advanced at present.

**Addition Reactions.**—Despite the apparent steric congestion of the products, the 3,3-dichlorocyclopropene (1) reacts with bromine in the dark, giving both the *cis*- and the *trans*-adduct [(6a): (6b) = 1.0 : 4.6 at room



temperature, 1.0 : 3.0 at 70 °C]. This result is consistent with a free-radical mechanism, in which the preferred, less congested product (6b) is formed by approach of the bromine molecule from the more hindered side of the intermediate (7). Reaction of the unsymmetrical cyclo-

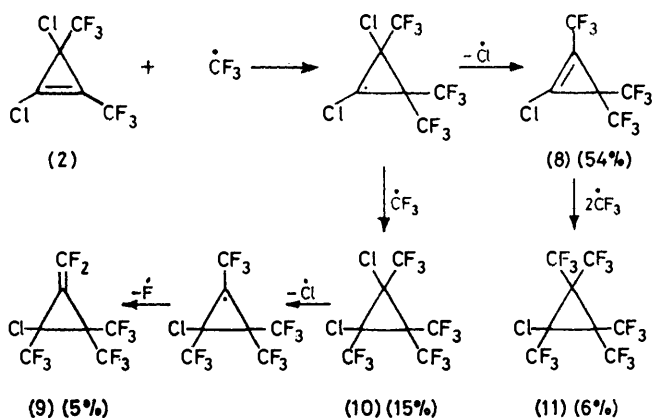
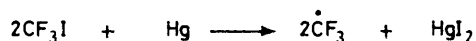


propene (2) with bromine at 70 °C is more complicated and leads to a mixture of four dibromo-compounds (6c—f); only the stereochemical relationships between the trifluoromethyl groups are clear from the <sup>19</sup>F n.m.r. spectrum of the mixture ( $J_{cis-CF_3,CF_3}$  ca. 14.3;  $J_{trans-CF_3,CF_3}$  0 Hz), but these together with steric arguments give a product ratio of (6) c : d : e : f = 4.0 : 2.2 : 1.1 : 1.0 (initial attack by a bromine atom at the end of the double bond which carries the CF<sub>3</sub> group is assumed).<sup>12</sup>

Because of the tendency of the symmetrical cyclopropene (1) to rearrange under the anticipated conditions, the susceptibility of the cyclopropene system to attack by trifluoromethyl radicals was investigated with the unsymmetrical isomer (2). However, no significant reaction occurred when this compound was heated with a three-fold excess of trifluoroiodomethane at 240 °C for 40 h. Repetition of this experiment in the presence of mercury (to absorb the iodine atoms) led to 33% conversion into a complex mixture, the main components of which were identified by i.r.—mass spectrometry as compounds (8)—(11) (Scheme 1) [yields based on cyclopropene (2) transformed]; the scheme provides a reasonable rationalisation of the main reaction pathways involved.

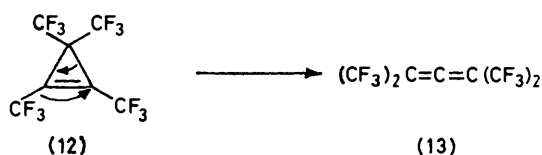
Under photochemical conditions, this reaction takes a

rather different route. In the absence of mercury, irradiation of the cyclopropene (2) and trifluoroiodomethane results in slow conversion into the symmetrical cyclopropene (1), almost all the iodo-compound being



SCHEME 1

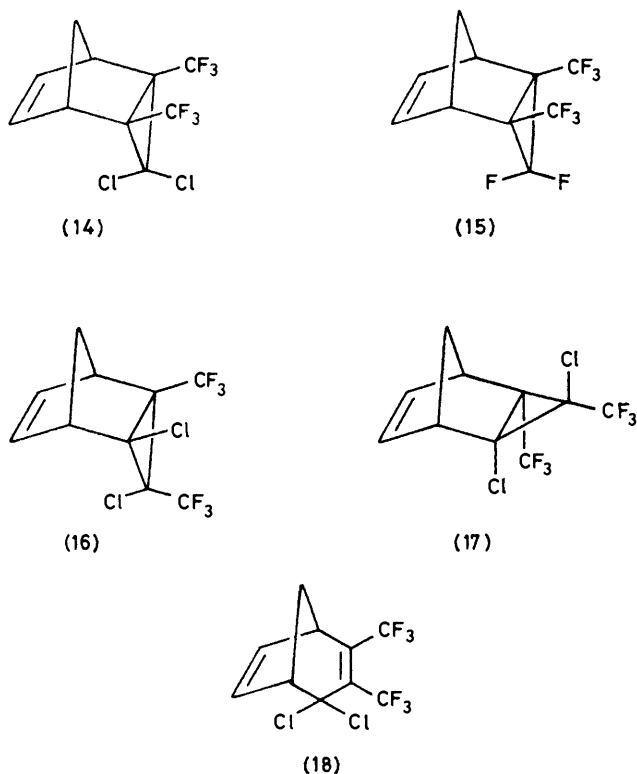
recovered. In the presence of mercury, the main products are hexakistrifluoromethylcyclopropane, 1-chlorotrifluoromethylcyclopropene (8), and tetrakistrifluoromethylallene (13), in ratios which depend upon the period of the irradiation; the allene may be formed by isomerisation (not necessarily by a concerted mechanism) of tetrakistrifluoromethylcyclopropene (12), none of which was detected among the products. Attempts to produce a cleaner reaction by irradiation of a mixture of



the cyclopropene (2) and hexafluoroacetone have been unsuccessful; little of the hexafluoroacetone decomposed during 96 h, but most of the cyclopropene was converted into involatile products and the only tractable product identified was a trace of the allene (13).

The strained, electron-deficient, double bonds in both the dichlorocyclopropenes [(1) and (2)] are dienophilic (*cf.* refs. 2 and 13), and both isomers react with cyclopentadiene or with furan at room temperature. Reaction of the symmetrical compound (1) with cyclopentadiene gives only one product (95% yield), unlike the related reaction of 3,3-difluorobistrifluoromethylcyclopropene.<sup>2</sup> The assignment of definite geometries to the products from the reaction of the 3,3-difluoro-compound with cyclopentadiene proved difficult, even with additional help from the <sup>19</sup>F n.m.r. absorption of the *gem*-difluoro-group,<sup>2,14</sup> and in the present case, identification of the product as the *endo*-isomer (14) is only tentative;

the *endo*-isomer seems more probable on steric grounds and the <sup>1</sup>H n.m.r. bands fit more closely with the necessary revised assignments for the *endo-gem*-difluoro-compound (15).<sup>2,14</sup> The unsymmetrical dichlorocyclopropene (2) gives three adducts with cyclopentadiene at room temperature, and the i.r., n.m.r., and mass spectra of the mixture are consistent with the presence of compounds (16)—(18); all the trifluoromethyl groups show distinct quartets in the n.m.r. spectrum (*J ca.* 15 Hz), indicating that only isomers with these groups *cis* to one another are formed.<sup>15</sup> Formation of the bicyclo-compound (18) by concerted rearrangement of either of

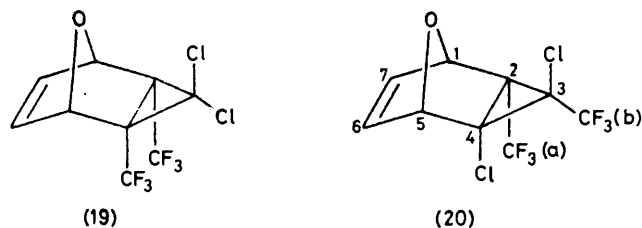


the initial adducts [(16) or (17)] is allowed by the Woodward-Hoffmann rules, but adducts with *trans*-trifluoromethyl groups could give the rearranged compound (18) only by a stepwise or symmetry-forbidden process; it therefore seems improbable that such adducts are formed at all during the reaction.

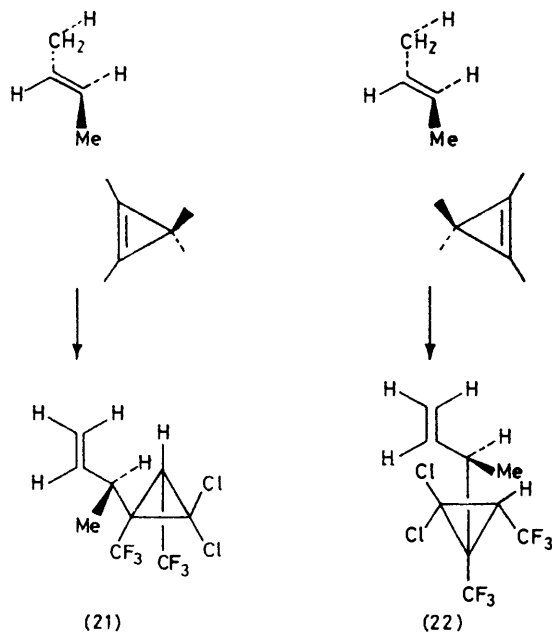
Although it is usually assumed, largely on steric grounds, that cyclopropenes react with furan to give *endo*-adducts,<sup>2,13</sup> the n.m.r. spectra of the products from both the cyclopropenes used here [(1) and (2)] and furan seem to favour *exo*-stereochemistry. Each reaction gives only one product at room temperature [78% yield from (1) or 28% in a more sluggish reaction from (2)]. The singlet olefinic proton absorption ( $\delta_{\text{H}}$  6.92) in the n.m.r. spectrum of the product (19) from the symmetrical cyclopropene (1) has a width at half-height of 6.5 Hz, whilst for the bridgehead protons ( $\delta_{\text{H}}$  5.25) the value is only 4.2 Hz. The most likely explanation for this lies in a weak long-range coupling between *endo*-trifluoromethyl

groups and the olefinic protons; *exo*-trifluoromethyl groups would be expected to couple more strongly to the bridgehead protons.

Stronger evidence exists for the structure (20) of the product from the unsymmetrical cyclopropene (2) and furan.  $^1\text{H}$  Double-resonance experiments suggest that one of the olefinic protons (H-7) and a bridgehead proton (H-1) are coupled to the tertiary trifluoromethyl group



(a). Furthermore, this coupling is *ca.* 2.4 Hz for the olefinic proton and only *ca.* 1.0 Hz for the bridgehead proton; only an *exo*-configuration, with the trifluoromethyl group (a) in the *endo*-position can lead to such an observation. Molecular models suggest that in the *endo*-isomer, the trifluoromethyl-group (a) is very much closer to the bridgehead proton (H-1) than to the olefinic proton (H-7). Further support for the *exo*-configuration comes from the  $^{19}\text{F}$  spectrum, which shows the quartet absorption of the tertiary trifluoromethyl group (a) to be further coupled.



SCHEME 2

In comparison with the Diels–Alder reaction of cyclopropenes, the related ‘ene’ reaction appears to have been rather neglected although cyclopropene itself apparently dimerises *via* a reaction of this type.<sup>16</sup> During the present work, the reaction of equimolar proportions of 3,3-dichloro-1,2-bistrifluoromethylcyclopropene (1) and

(*E*)-but-2-ene at 80 °C for 110 h gave a high yield of two products, which showed remarkably similar spectroscopic properties following separation by preparative g.l.c. The expected ‘ene’ reaction produces a product with three new chiral centres, although the relationship between the two produced in the three-membered ring is fixed by the *cis*-nature of the addition.<sup>17</sup> The isolated products are therefore believed to be diastereoisomers (11) and (12) resulting from the two possible stereochemical approaches of the enophilic cyclopropene; the major product (56% yield) would be expected to be the result of the ‘pseudo-*exo*’ approach (21) since the bulky chlorine atoms seem likely to interfere with the ‘pseudo-*endo*’ approach necessary for the formation of the other isomer (22) (30%). The spectra of the two adducts are consistent with the structures proposed but do not clarify the stereoisomerism. Further work on reactions in this category is in progress.

#### EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 257 or 621 grating spectrometer, fitted with sodium chloride optics. N.m.r. spectra were recorded on a Perkin-Elmer model R10 or Varian HA-100 high resolution spectrometer; the former instrument operated at 60 MHz for  $^1\text{H}$  or at 56.46 MHz for  $^{19}\text{F}$  spectra and the latter at 100 MHz or 94.1 MHz, respectively. Chemical shifts ( $\delta$ ) are quoted relative to external tetramethylsilane for  $^1\text{H}$  or external trifluoroacetic acid for  $^{19}\text{F}$  nuclei and are positive to low field of the reference in each case; the solvent for solid specimens was carbon tetrachloride. Mass spectra were recorded on an A.E.I. model MS 902 instrument.

G.l.c. columns were of 0.4-cm i.d. stainless steel or copper tubing, packed with Celite (Johns–Manville 545) coated with 30% w/w of the stationary phase; the carrier gas was nitrogen. Molecular weights were determined by Regnault’s method unless otherwise stated.

**Preparation of 3,3-Dichloro-1,2-bistrifluoromethylcyclopropene.**—(a) *At ca. 2 atm.* Hexafluorobut-2-yne (40.0 g, 247 mmol) and trifluoro(trichloromethyl)silane (7.25 g, 35.6 mmol)<sup>5</sup> were sealed *in vacuo* in a 5-l flask and kept at 180 °C for 24 h. The volatile products were distilled *in vacuo*, and the fraction condensing at  $-78$  °C (4.90 g;  $M$  241) was separated by g.l.c. (7 m Silicone MS 550; room temperature) (distillation through a spinning-band column was also effective) to give 3,3-dichloro-1,2-bistrifluoromethylcyclopropene (3.51 g, 40%) (Found: C, 24.5.  $\text{C}_5\text{Cl}_2\text{F}_6$  requires C, 24.5%),  $M$  245, b.p. (isoteniscope) 52.7 °C at 760 mmHg,  $L_v$  31.49 kJ mol $^{-1}$ , and 1,3-dichloro-2,3-bistrifluoromethylcyclopropene (0.80 g, 9%). The fraction condensing at  $-196$  °C from the reaction was shown (i.r.) to consist of hexafluorobutyne and the usual mixture of silanes produced by decomposition of the carbene precursor.<sup>5</sup> Both dichloro-cyclopropenes were shown to contain two chlorine atoms by mass spectrometry [Found:  $M$  ( $^{35}\text{Cl}$ ) 244] and showed major fragmentation patterns dominated by loss of an allylic chlorine atom. The 3,3-dichloro-compound showed  $\lambda_{\text{max}}$  (vapour) 5.27, 7.64, 7.82, 8.07, 8.38, 8.62, 9.26, 9.51, 9.73, 11.05, 11.90, 12.30, 12.60, 12.96, and 14.22  $\mu\text{m}$ .

(b) *At ca. 6.5 atm.* Hexafluorobut-2-yne (6.32 g, 39.0 mmol) and trifluoro(trichloromethyl)silane (1.83 g, 8.90 mmol), sealed *in vacuo* in a 250-cm $^3$  Pyrex tube for 12 h at

140 °C, gave a fraction condensing at  $-78$  °C consisting of pure (g.l.c., n.m.r.) 3,3-dichloro-1,2-bistrifluoromethylcyclopropene (2.04 g, 93%), *M* 244.

*Rearrangement of the 3,3-Dichlorocyclopropene.*—(a) *Thermal.* 3,3-Dichloro-1,2-bistrifluoromethylcyclopropene (0.72 g), heated *in vacuo* in a sealed 30-cm<sup>3</sup> tube at 250 °C for 24 h, gave a  $-78$  °C fraction consisting of pure (g.l.c.) 1,3-dichloro-2,3-bistrifluoromethylcyclopropene (0.71 g, 99%) (Found: C, 24.4%); *M* 243, b.p. (isoteniscope) 61.4 °C at 760 mmHg,  $L_v$  31.52 kJ mol<sup>-1</sup>,  $\lambda_{\text{max}}$  5.37, 7.63, 7.82, 8.26, 8.30, 8.45, 9.60, 11.04, 12.61, 12.98, 13.25, 13.90, and 14.24  $\mu\text{m}$ .

(b) *Photochemical.* The 3,3-dichlorocyclopropene (1.50 g, 6.13 mmol), sealed *in vacuo* in a 30-cm<sup>3</sup> silica tube, was shaken and irradiated with light from a Hanovia U.V.S. 500-W lamp (12 cm distant) for 48 h. Fractionation *in vacuo* gave a fraction condensing at  $-78$  °C, shown (g.l.c., i.r., n.m.r.) to consist of starting material (0.93 g, 62%) and

sulphur dioxide (5 vol.) were sealed *in vacuo* in a thick-walled n.m.r. tube. Some precipitate appeared when the mixture was allowed to warm to room temperature, but it dissolved on shaking (**CARE!**). The resulting red-brown solution was shown by its <sup>19</sup>F n.m.r. spectrum (see above) to contain chlorobistrifluoromethylcyclopropenium chloropentafluoroantimonate as the only organic compound.

(ii) The cyclopropene (1) (0.865 g, 3.53 mmol) was slowly introduced, *via* a syringe, into a flask equipped with a serum cap and containing freshly distilled antimony pentafluoride (1.585 g, 7.34 mmol). The resulting exothermic reaction gave a red-brown solution, a drop of which was placed between two sodium chloride plates and protected from moisture by a film of Silicone grease. The i.r. spectrum thus obtained showed the disappearance of the absorption at 5.27  $\mu\text{m}$  (C=C stretching) and the appearance of characteristic cyclopropenium bands <sup>8</sup> at 5.42 and 7.02  $\mu\text{m}$ .

(b) *From the 1,3-dichlorocyclopropene.* Freshly distilled

Rearrangement of the 3,3-dichlorocyclopropene (1)

Starting materials			Time/ h	Products		
(1) (mmol)	Lewis acid (mmol)	Others (mmol)		(1) (mmol)	(2) (mmol)	Others (mmol)
5.27	BF <sub>3</sub> (5.24)	SO <sub>2</sub> (24.2)	120	4.53	0.37	
1.00	BCl <sub>3</sub> (1.00)	SO <sub>2</sub> (4.00)	24	0.92 <sup>a</sup>	0.08 <sup>a</sup>	
4.53	AlCl <sub>3</sub> (7.26)		48		4.45	
4.08	AlCl <sub>3</sub> (3.80)	SO <sub>2</sub> (16.10)	60		3.88	
2.70	AlCl <sub>3</sub> (2.55)	C <sub>6</sub> H <sub>6</sub> (6.41)	48		2.65 <sup>b</sup>	C <sub>6</sub> H <sub>6</sub> (6.28)
2.43	SbCl <sub>5</sub> (3.33)		48		2.37	
0.50	SbCl <sub>5</sub> (1.00)	SO <sub>2</sub> (5.00)	<i>c</i>		<i>c</i>	
4.00	SbCl <sub>5</sub> (3.20)	C <sub>6</sub> H <sub>6</sub> (9.36)	76		3.92 <sup>b</sup>	C <sub>6</sub> H <sub>6</sub> (8.98)
12.78	SbF <sub>5</sub> (6.95) <sup>d</sup>	SO <sub>2</sub> (4.53)	1		6.98	Involatile <sup>e</sup>

<sup>a</sup> Carried out in standard n.m.r. tube; analysis only by n.m.r. <sup>b</sup> Contaminated with some benzene; amounts estimated by g.l.c.

<sup>c</sup> In n.m.r. tube; reactants kept initially at  $-78$  °C for 30 min then examined by variable-temperature <sup>19</sup>F n.m.r., starting at  $-70$  °C; reaction began at  $-40$  °C and was complete at  $-30$  °C, no components other than cyclopropenes being detected. <sup>d</sup> Freshly distilled in Pyrex under nitrogen. <sup>e</sup> A brown liquid, probably impure cyclopropenium salt (*ca.* 2.9 g), which failed to crystallise when kept.

its unsymmetrical isomer (0.37 g, 25% conversion). The involatile residue (0.16 g) (Found: C, 22.5; F, 43.9%) was unidentified.

(c) *With Lewis acids.* These experiments (Table) were conducted, except where otherwise stated, *in vacuo* in sealed tubes (25–30 cm<sup>3</sup>) kept at room temperature (15–20 °C). The products were distilled *in vacuo* and the  $-78$  °C fraction, which contained the cyclopropenes, was analysed by g.l.c., i.r. and <sup>19</sup>F n.m.r. spectroscopy, and molecular-weight determination.

*Reaction of the 3,3-Dichlorocyclopropene with Aluminium Bromide.*—The cyclopropene (0.65 g, 2.65 mmol) and anhydrous aluminium bromide (0.96 g, 3.60 mmol) were sealed *in vacuo* in a 10-cm<sup>3</sup> tube and shaken at room temperature for 110 h. The resulting  $-78$  °C fraction was shown by <sup>19</sup>F n.m.r. to contain four components, identified by their chemical shifts as starting material (0.20 g, 31% recovery), the unsymmetrical cyclopropene (2) [0.40 g, 89% based on (1) transformed], 3-bromo-2-chloro-1,3-bistrifluoromethylcyclopropene (0.04 g, 9%), showing poorly resolved quartets at  $\delta_F$  5.4 and 15.7 (*J ca.* 0.8 Hz), and 2-bromo-3-chloro-1,3-bistrifluoromethylcyclopropene (0.007 g, 2%), having absorption at  $\delta_F$  3.14 and 16.6. The i.r. spectrum of the mixture showed C–Br stretching bands at 15.55 and 17.10  $\mu\text{m}$ , and the presence of the bromochloro-compounds was also confirmed by a parent peak at *m/e* 288 in the mass spectrum (C<sub>5</sub>BrClF<sub>6</sub> requires *M*, 288).

*The Cyclopropenium Ion (3).*—(a) *From the 3,3-dichlorocyclopropene.* (i) Freshly distilled antimony pentafluoride (1 vol., *ca.* 0.1 cm<sup>3</sup>), the cyclopropene (1) (0.5 vol.), and

antimony pentafluoride (1 vol., *ca.* 0.1 cm<sup>3</sup>), the cyclopropene (2) (0.5 vol.), and sulphur dioxide (5 vol.), sealed in a thick-walled n.m.r. tube, gave a <sup>19</sup>F spectrum which showed chlorobistrifluoromethylcyclopropenium chloropentafluoroantimonate to be the major organic component (see above). The other components (total *ca.* 5%) gave absorption at  $\delta_F$  17.0 and 17.7.

*Bromination of the Cyclopropenes.*—(a) *The 3,3-dichloro-compound.* The cyclopropene (1) (0.73 g, 2.98 mmol) and bromine (0.74 g, 4.63 mmol) were sealed *in vacuo* in a 60-cm<sup>3</sup> tube and kept at 70 °C for 16 h. Removal of the volatile materials *in vacuo* then left a white crystalline residue, which sublimed to give *cis/trans*-1,2-dibromo-3,3-dichloro-1,2-bistrifluoromethylcyclopropane (Found: C, 14.9. C<sub>5</sub>Br<sub>2</sub>Cl<sub>2</sub>F<sub>6</sub> requires C, 14.8%), *m.p.* 49–52 °C; attempts to separate the isomers by g.l.c. (10 m Polyethyleneglycol adipate, 100 °C) were unsuccessful. The i.r. spectrum showed the disappearance of the C=C absorption at 5.27  $\mu\text{m}$ , and the <sup>19</sup>F n.m.r. spectrum showed only two singlets (intensity ratio 1.0:3.0) at  $\delta_F$  22.7 and 20.0, assigned to CF<sub>3</sub> absorption in the *cis*- and *trans*-isomers, respectively. The mass spectrum showed no parent ion, but the breakdown pattern was in agreement with the structure proposed; peaks at *m/e* 323, 325, 327, and 329 in the correct isotopic ratio of 3:7:5:1 indicated the presence of the ion C<sub>5</sub>BrClF<sub>6</sub><sup>+</sup>, and the base peak at *m/e* 209 was assigned to the cyclopropenium ion, C<sub>3</sub>ClF<sub>6</sub><sup>+</sup>. Repetition of the experiment at room temperature for 48 h gave the same products in a *cis:trans* ratio of 1.0:4.6.

(b) *The 1,3-dichloro-compound.* The cyclopropene (2)

(0.31 g, 1.27 mmol) and bromine (0.35 g, 2.19 mmol) were heated in a sealed tube *in vacuo* at 70 °C for 16 h. Removal of volatile material left a white crystalline residue, sublimation of which yielded a mixture of 1,3-dibromo-2,3-dichloro-1,2-bistrifluoromethylcyclopropanes (0.25 g, 49%) (Found: C, 14.5%), m.p. 42–44 °C. The i.r. spectrum showed no unsaturation and the mass spectrum was similar to that of the products from the 3,3-dichlorocyclopropene; the  $^{19}\text{F}$  n.m.r. spectrum showed bands at  $\delta_{\text{F}}$  22.6 and 19.9 (q,  $J$  14.3 Hz) (6d), 21.8 and 19.2 (q,  $J$  14.3 Hz) (6c), 20.9 and 16.5 (s) (6e), and 20.4 and 17.4 (s) (6f) with relative intensities 2.2 : 4.0 : 1.1 : 1.0, respectively.

**Reaction of the 1,3-Dichlorocyclopropene with Trifluoroiodomethane.**—(a) *Thermally, with mercury.* The cyclopropene (2) (1.86 g, 7.59 mmol), trifluoroiodomethane (4.31 g, 22.0 mmol), and mercury (3 cm<sup>3</sup>), sealed *in vacuo* in a 250-cm<sup>3</sup> tube, were kept at 240 °C for 40 h. The resulting –78 °C fraction (1.91 g) showed ten peaks on g.l.c. (2 m Silicone SE-30, 60 °C), and further examination by i.r.–g.l.c. (10 m Silicone SE-30, 100 °C) and mass spectrometry–g.l.c. (4.5 m Silicone SE-30, 60 °C) resulted in the identification of: (i) 2-chloro-1,3,3-tristrifluoromethylcyclopropene (8) [0.38 g, 54% based on (2) consumed]; (ii) 2-chloro-3-(difluoromethylene)-1,1,2-tristrifluoromethylcyclopropane (9) (0.04 g, 5%); (iii) starting material (2) (1.24 g, 67% recovery); (iv) chloropentakistrifluoromethylcyclopropane (11) (0.05 g, 6%); and (v) 1,2-dichlorotetrakistrifluoromethylcyclopropane (10) (stereochemistry unknown) (0.13 g, 15%). The fraction condensing at –196 °C (2.61 g) was shown by i.r. spectroscopy to be mainly trifluoroiodomethane containing a trace of hexafluoroethane. Compound (8) showed  $\lambda_{\text{max}}$  5.30  $\mu\text{m}$  (C=C stretching) and a strong absorption region at 7.60–8.50  $\mu\text{m}$  (C–F stretching);  $m/e$  278 ( $M^+$ , 100%), 259 ( $M^+ - \text{F}$ , 95), 243 ( $M^+ - \text{Cl}$ , 50), and 69 ( $\text{CF}_3$ , 69). Compound (9) showed  $\lambda_{\text{max}}$  5.70 (C=C str) and 7.30–8.60  $\mu\text{m}$  (C–F str);  $m/e$  328 ( $M^+$ , 90%), 309 ( $M^+ - \text{F}$ , 95), 293 ( $M^+ - \text{Cl}$ , 95), 259 ( $M^+ - \text{CF}_3$ , 100), and 69 ( $\text{CF}_3$ , 30). Compound (11) showed  $\lambda_{\text{max}}$  7.60–8.70  $\mu\text{m}$  (C–F str);  $m/e$  (416 ( $M^+$ , 20%), 397 ( $M^+ - \text{F}$ , 10), 381 ( $M^+ - \text{Cl}$ , 2), 347 ( $M^+ - \text{CF}_3$ , 50), and 69 ( $\text{CF}_3$ , 100). Compound (10) showed  $\lambda_{\text{max}}$  7.70–8.60  $\mu\text{m}$  (C–F str);  $m/e$  382 ( $M^+$ , 25%), 363 ( $M^+ - \text{F}$ , 25), 347 ( $M^+ - \text{Cl}$ , 12), 313 ( $M^+ - \text{CF}_3$ , 100), and 69 ( $\text{CF}_3$ , 100).

(b) *Photochemically, without mercury.* The cyclopropene (2) (1.20 g, 4.90 mmol) and trifluoroiodomethane (2.61 g, 13.25 mmol), sealed *in vacuo* in a 60-cm<sup>3</sup> silica tube, were irradiated with a Hanovia U.V.S. 500-W lamp (10 cm distant) for 135 h. The fraction condensing at –78 °C (1.20 g) contained two components, identified by i.r.–g.l.c. (3 m Silicone SE-30, 70 °C) as the 3,3-dichlorocyclopropene (1) (0.12 g, 10%) and starting material (1.08 g, 90%). The fraction condensing at –196 °C (2.51 g) was trifluoroiodomethane with a trace of hexafluoroethane.

(c) *Photochemically, with mercury.* The cyclopropene (2) (1.16 g, 4.74 mmol), trifluoroiodomethane (2.88 g, 14.70 mmol), and mercury (5 cm<sup>3</sup>), irradiated as above for 175 h, gave a fraction condensing at –78 °C (1.22 g). Analysis of this by i.r.–g.l.c. and mass spectrometry–g.l.c. showed the four major components to be (i) tetrakistrifluoromethylallene [0.09 g, 17% based on (2) transformed],<sup>18</sup> (ii) hexakistrifluoromethylcyclopropane (0.41 g, 53%), (iii) 2-chlorotrifluoromethylcyclopropene (0.085 g, 18%), and (iv) starting material (2) (0.75 g, 65%). The hexakistrifluoromethylcyclopropane showed  $\lambda_{\text{max}}$  7.70–9.00  $\mu\text{m}$  (C–F str);  $m/e$  450 ( $M^+$ , small), 381 ( $M^+ - \text{CF}_3$ , 20%), 343 ( $M^+ -$

$\text{C}_3\text{F}_5$ , 32), 293 ( $M^+ - \text{C}_4\text{F}_5$ , 27), and 69 ( $\text{CF}_3$ , 100). Repetition of this reaction for 42.5 and for 116 h gave the same products in the molar ratios (i) : (ii) : (iii) : (iv) of 4 : 5 : 7 : 84 and 14 : 11 : 12 : 63, respectively.

**Diels–Alder Reactions.**—(a) *With cyclopentadiene.* (i) The 3,3-dichlorocyclopropene (1) (0.79 g, 3.22 mmol) and freshly distilled cyclopentadiene (0.24 g, 3.63 mmol) were sealed *in vacuo* in a 10-cm<sup>3</sup> tube and kept at room temperature for 16 h. Removal of the volatile materials *in vacuo* left a white crystalline solid, which on sublimation gave endo-3,3-dichloro-2,4-bistrifluoromethyltricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (14) (0.95 g, 95%) (Found: C, 38.9; H, 2.2.  $\text{C}_{10}\text{H}_6\text{Cl}_2\text{F}_6$  requires C, 38.6; H, 1.9%), m.p. 78 °C,  $\delta_{\text{H}}$  6.23br (H-6 and -7), 3.66br (H-1 and -5), 2.26 (*syn*-H-8), and 1.86 (AB system,  $J_{\text{AB}}$  8.0 Hz, bridge protons) [cf. the gem-difluoro-compound (15), which shows bands at  $\delta_{\text{H}}$  6.27, 3.57, 2.36, and 1.84; its *exo*-isomer absorbs at  $\delta_{\text{H}}$  6.72, 3.57, 2.01, and 1.15];  $^{2,14}\delta_{\text{F}}$  20.43 (s),  $\lambda_{\text{max}}$  7.22, 7.45, 7.66, 7.80, 7.91, 7.97, 8.20, 8.44, 8.64, 8.73, and 14.70  $\mu\text{m}$ ,  $m/e$  310 ( $M^+$ ) with appropriate ( $M^+ + 2$ ) and ( $M^+ + 4$ ) peaks for two chlorine atoms. No structural change was detected when the adduct was kept at room temperature for 3 months.

(ii) The 1,3-dichlorocyclopropene (2) (0.81 g, 3.27 mmol) and cyclopentadiene (0.25 g, 3.79 mmol) were kept in a sealed tube at room temperature for 20 h. Removal of the volatile products left a liquid, shown by g.l.c. (2 m Silicone SE-30, 140 °C) and n.m.r. spectroscopy to consist of endo-2,3-dichloro-3,4-bistrifluoromethyltricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (16) (0.65 g, 65%), the *exo*-isomer (17) (0.095 g, 9%), and 4,4-dichloro-2,3-bistrifluoromethylbicyclo[3.2.1]octa-2,6-diene (18) (0.10 g, 10%) (Found: C, 38.9; H, 2.0%). The *endo*-structure is assigned to the major product mainly by analogy with the reaction of the symmetrical cyclopropene [paragraph (i)]; its  $^{19}\text{F}$  spectrum showed  $\delta_{\text{F}}$  23.70 and 14.70 (each q,  $J$  15.7 Hz). The *exo*-isomer showed  $\delta_{\text{F}}$  20.20 and 10.35 (each q,  $J$  14.9 Hz), and the diene (18) showed  $\delta_{\text{F}}$  21.20 and 20.20 (each q,  $J$  14.9 Hz). The i.r.,  $^1\text{H}$  n.m.r., and mass spectra were consistent with the presence of this mixture of isomers, but the assignment of bands to particular structures was not possible.

(b) *With furan.* (i) The 3,3-dichlorocyclopropene (0.40 g, 1.63 mmol) and furan (0.12 g, 1.77 mmol), kept in a sealed tube at room temperature for 16 h, yielded a white crystalline residue which sublimed to give *exo*-3,3-dichloro-2,4-bistrifluoromethyl-8-oxatri-cyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (19) (0.40 g, 78%) (Found: C, 34.2; H, 1.4.  $\text{C}_9\text{H}_4\text{Cl}_2\text{F}_6\text{O}$  requires C, 34.5; H, 1.3%), m.p. 60 °C,  $\delta_{\text{H}}$  6.92 ( $W_{\frac{1}{2}}$  6.5 Hz, H-6 and -7) and 5.25 ( $W_{\frac{1}{2}}$  4.2 Hz, H-1 and -5),  $\delta_{\text{F}}$  22.70 (s,  $W_{\frac{1}{2}}$  3.6 Hz),  $\lambda_{\text{max}}$  7.16, 7.66, 7.73, 7.96, 8.08, 8.47, 8.73, 9.02, 9.80, 9.94, 10.56, 10.96, 11.09, 12.50, 13.55, 13.75, 14.53, and 15.80  $\mu\text{m}$ ; the mass spectrum showed no parent ion, but there was a weak ( $M^+ - \text{H}$ ) peak at  $m/e$  311, and the spectrum was fully consistent with the proposed structure.

(ii) The 1,3-dichlorocyclopropene (0.82 g, 3.35 mmol) and furan (0.204 g, 3.00 mmol), kept for 50 h at room temperature, gave *exo*-3,4-dichloro-2,3-bistrifluoromethyl-8-oxatri-cyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (20) (0.26 g, 28%) (Found: C, 34.5; H, 1.4; F, 36.4.  $\text{C}_9\text{H}_4\text{Cl}_2\text{F}_6\text{O}$  requires C, 34.5; H, 1.3; F, 36.4%), m.p. 46 °C (sublimation). The olefinic  $^1\text{H}$  n.m.r. absorption was an AB system with further splitting;  $\delta_{\text{H}}$  7.11 (dd,  $J_{6,7}$  5.0,  $J_{6,5}$  1.7 Hz, H-6), 6.94 (ddq,  $J_{7,6}$  5.0,  $J_{7,1}$  1.7,  $J_{7,(a)}$  2.4 Hz, H-7), 5.26 (m, H-5), and 5.15 [m, shown by double resonance to be coupling to the  $\text{CF}_3$  group (a) with  $J$  ca. 1.0 Hz, H-1];  $\delta_{\text{F}}$  23.8 (q, a- $\text{CF}_3$ ) and 12.5 (q, b- $\text{CF}_3$ ) ( $J_{(a),(b)}$  11.3 Hz);  $m/e$  311 ( $M^+ - \text{H}$ );  $\lambda_{\text{max}}$  7.34, 7.40,

7.53, 7.62, 7.74, 7.85, 8.03, 8.24, 8.33, 8.51, 8.62, 8.70, 9.01, 9.51, 9.59, 9.76, 9.97, 10.55, 10.92, 11.29, 12.28, 13.15, 13.63, 13.92, 14.19, 14.59, and 14.91  $\mu\text{m}$ .

*Ene Reaction.*—The 3,3-dichlorocyclopropene (0.946 g, 3.86 mmol) and (*E*)-butene (0.216 g, 3.86 mmol) were kept at 80 °C in a sealed tube for 110 h. The resulting high-boiling products (1.00 g) were separated by g.l.c. (2 m Silicone SE-30, 100 °C) into 3,3-dichloro-1-(1-methylprop-2-enyl)-1,2-bistrifluoromethylcyclopropane (22) (0.35 g, 30%) (Found: C, 35.6; H, 3.0.  $\text{C}_9\text{H}_8\text{Cl}_2\text{F}_6$  requires C, 35.9; H, 2.7%), b.p. 170 °C, and its isomer (21) (0.65 g, 56%) (Found: C, 36.0; H, 2.7%), b.p. 178 °C. The minor product (22) showed  $\delta_{\text{H}}$  5.56(m), 4.70(m), 2.00(m), 1.78(m), and 0.95(d, *J* 5.7 Hz),  $\delta_{\text{F}}$  22.50(m) and 20.45(m); the isomer (21) gave  $\delta_{\text{H}}$  5.50, 4.76, 2.10, 1.72, and 0.90 (d, *J* 5.7 Hz),  $\delta_{\text{F}}$  22.53 and 20.25. Isomer (22) showed  $\lambda_{\text{max}}$  7.05, 7.24, 7.66, 7.73, 7.89, 8.08, 8.54, 8.66, 8.81, and 6.11  $\mu\text{m}$  (weak, C=C str); isomer (21) showed  $\lambda_{\text{max}}$  7.05, 7.26, 7.70, 7.90, 8.08, 8.55, 8.81 and 6.10  $\mu\text{m}$  (C=C str). Neither isomer gave a parent ion in the mass spectrum, but the breakdown patterns were consistent with the proposed structures. No products arising from behaviour of the cyclopropene as a vinyl carbene were detected.<sup>19</sup>

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#### REFERENCES

- <sup>1</sup> W. Mahler, *J. Am. Chem. Soc.*, 1962, **84**, 4600.
- <sup>2</sup> P. B. Sargeant, *J. Am. Chem. Soc.*, 1969, **91**, 3061.
- <sup>3</sup> W. R. Cullen and M. C. Waldman, *Can. J. Chem.*, 1969, **47**, 3093; see also *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 205, and *Can. J. Chem.*, 1970, **48**, 1885.
- <sup>4</sup> W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 2nd edn., 1971, p. 367.
- <sup>5</sup> J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2530; F. Anderson, J. M. Birchall, R. N. Haszeldine, and B. J. Tyler, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1051.
- <sup>6</sup> M. W. Grayston and D. M. Lemal, *J. Am. Chem. Soc.*, 1976, **98**, 1278.
- <sup>7</sup> J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1071.
- <sup>8</sup> R. West, A. Sadò, and S. W. Tobey, *J. Am. Chem. Soc.*, 1966, **88**, 2488; D. C. F. Law, S. W. Tobey, and R. West, *J. Org. Chem.*, 1973, **38**, 768.
- <sup>9</sup> P. B. Sargeant and C. G. Krespan, *J. Am. Chem. Soc.*, 1969, **91**, 415; B. E. Smart, *J. Org. Chem.*, 1976, **41**, 2377.
- <sup>10</sup> cf. R. West, D. C. Zecher, and W. Goyert, *J. Am. Chem. Soc.*, 1970, **92**, 149.
- <sup>11</sup> J. M. Birchall, R. N. Haszeldine, and P. D. Morley, unpublished results.
- <sup>12</sup> cf. K. J. Klabunde, *J. Am. Chem. Soc.*, 1970, **92**, 2427.
- <sup>13</sup> D. C. F. Law and S. W. Tobey, *J. Am. Chem. Soc.*, 1968, **90**, 2376.
- <sup>14</sup> C. W. Jefford, J.-C. E. Gehret, J. Mareda, nT. Kabengele, W. D. Graham, and U. Burger, *Tetrahedron Lett.*, 1975, 823.
- <sup>15</sup> cf. S. Ng and C. H. Sederholm, *J. Chem. Phys.*, 1964, **40**, 2090; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, London, 1966, vol. 2, p. 911.
- <sup>16</sup> P. Dowd and V. Gold, *Tetrahedron Lett.*, 1969, 85.
- <sup>17</sup> H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 556.
- <sup>18</sup> D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, 1966, **88**, 5582; provision of a reference spectrum by Dr. Krespan is gratefully acknowledged.
- <sup>19</sup> cf. W. Weber and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 138.