Journal of Fluorine Chemistry, 15 (1980) 497–509

Received: October 30, 1979

CARBENE CHEMISTRY. PART 13 [1]. PREPARATION OF SOME FLUOROALLENES BY A CARBENE ROUTE, AND THE REACTION OF ALLENES WITH HALOGENOCARBENES

MICHAEL J. BUNEGAR, ROY FIELDS AND ROBERT N. HASZELDINE

Chemistry Department, The University of Manchester
Institute of Science and Technology, Manchester M60 1QD
(Great Britain)

SUMMARY

Fluoroallene and 1,3-difluoroallene are prepared in good overall yield by the addition of dichlorocarbene to vinyl fluoride and 1,2-difluoroethylene respectively, followed by pyrolysis of the dichlorocyclopropanes and treatment of the resulting dichloropropenes with zinc. Pyrolysis of 1,1-dichloro-2-fluorocyclopropane over zinc gives fluoroallene directly.

The reaction of allene with 2,2,3-trifluoro-3-trifluoromethyloxiran at 180°C as a source of difluorocarbene gives both 1,1-difluoro-2-methylenecyclopropane and its rearrangement product 1-(difluoromethylene)cyclopropane, the latter reacting more readily with a second difluorocarbene to give 2,2,3,3-tetrafluorospiropentane. In an analogous way, fluoroallene reacts with dichlorocarbene, generated from trifluoro(trichloromethyl)silane at 140°C, to give E- and Z-1,1-dichloro-2-(fluoromethylene)cyclopropane, 1-(dichloromethylene)-2-fluorocyclopropane, and 2,2,3,3-tetrachloro-4-fluorospiropentane.

INTRODUCTION

Early routes to tetrafluoroallene had the disadvantage of a low-yield final step, the dehydrobromination with strong base of 1,3-dibromo-1,1,3,3-tetrafluoropropane[2,3];

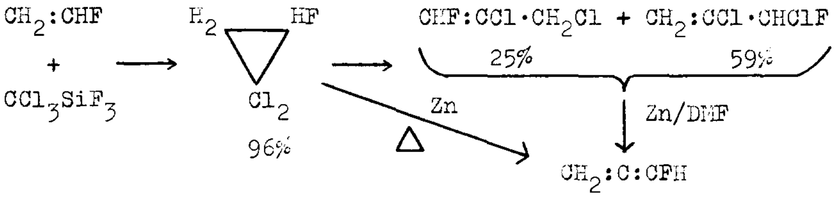
$$CF_2BrCH_2CF_2Br \xrightarrow{-2HBr} CF_2{:}C{:}CF_2$$

Similar routes to fluoroallene, the difluoroallenes and trifluoroallene have recently been used [4]. An improved route to tetrafluoroallene used dehalogenation of 2,3-dibromo-1,1,3,3-tetrafluoropropene under mild conditions as the final step [5], and the pyrolytic dehalogenation of several perfluoroiodo-olefins over copper has also allowed the formation of perfluoroalkylallenes in excellent yield [6]. Dehalogenation of the products of the pyrolysis of silicon-substituted 1,1-dichlorocyclopropanes has been used to prepare silyl-allenes in good yield [7], and we report here the adaptation of these methods to the preparation of fluoroallene and 1,3-difluoroallene, and some reactions of allenes with halogenocarbenes.

RESULTS AND DISCUSSION

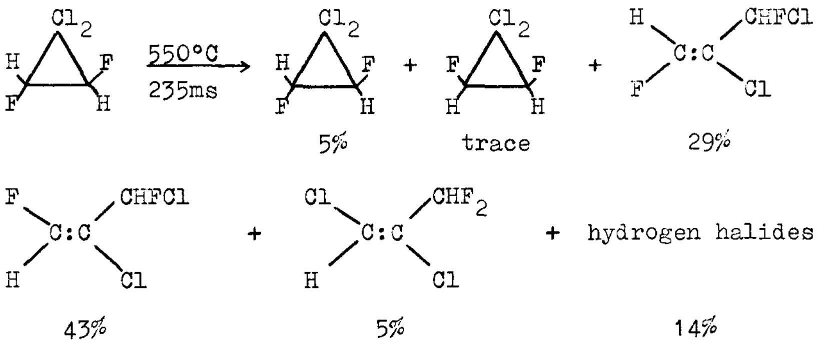
(a) Preparation of mono- and di-fluoroallene

The mixture of 2,3-dichloro-3-fluoropropene and E- and Z-2,3-dichloro-1-fluoropropenes obtained by flow pyrolysis of 1,1-dichloro-2-fluorocyclopropane [8] was unchanged after two hours at reflux with activated zinc dust in anhydrous dioxan, but after six hours in refluxing dimethylformamide gave an 84% yield of 1-fluoroallene. Pyrolysis of the cyclopropane at 400°C over zinc wool also gave the allene (80% yield) but with the pyrolysis system in use, 70% of the cyclopropane was recovered, and attempts to increase the conversion by use of longer contact times resulted only in extensive charring. It is clear, however, that either the one-step or the two-step conversion of 1,1-dichloro-2-fluorocyclopropane into fluoroallene represents an improvement over the literature preparation [4], since the cyclopropane is itself readily prepared in high yield.



cis- And trans-1,2-difluoroethylene reacted in the gas phase at 140°C with trifluoro(trichloromethyl)silane to give the corresponding dichlorocyclopropanes in good yield [10]. Flow pyrolysis of the individual dichlorocyclopropanes resulted in some geometric isomerisation and the formation of three isomeric olefins in each case. The minor component clearly contained the CHF_2 group (55Hz triplet and doublet in the ^1H and ^{19}F n.m.r. spectra), and was identified spectroscopically as trans-1,2-dichloro-3,3-difluoropropene. Its boiling point agreed with that reported by Whaley and Davis for the product obtained by the reaction of 1,2,3,3-tetrachloropropene with antimony trifluoride and stated to be 'probably the trans-isomer', but no other parameters were reported [11].

The other two isomers were identified spectroscopically as 2,3-dichloro-1,3-difluoropropenes, the higher boiling isomer being assigned the E-structure on the basis of estimated dipole moments. The results of the pyrolyses are shown in



the Table. Woodward-Hoffman rules predict the predominant formation of the Z-isomer from the cis-difluorocyclopropane (H-H interaction preferred to F-F interaction in the transition state), but the choice is less clear-cut for the trans-difluorocyclopropane; if the migrating chlorine remains on the same side of the molecule, as shown by Fleming and Thomas for the 6,6-dichloro-3-methoxybicyclo[3,1,0]hexanes [12], it must approach either a hydrogen at the migration terminus to form the E-isomer or a fluorine to form the Z- isomer. On steric and electronic grounds, therefore, preferential formation of

TABLE

Flow pyrolysis of the 1,1-dichloro-2,3-difluorocyclopropanes at 500°C

Starting Material	trans		cis	
Contact time (ms)	196	235	196	265
Mole % recovered as:				
trans-isomer*	9	5	15	14
Z-2,3-Dichloro-1,3-difluoropropene	24	29	39	21
E-2,3-Dichloro-1,3-difluoropropene	53	43	34	11
trans-1,2-Dichloro-3,3-difluoropropene	<1	5	5	41
Hydrogen halides	4	14	9	6
Unknown+	(2)	(4)	(5)	(8)

*Containing a trace of the cis-isomer in each case.

+Weight %

the E-isomer would be expected, and, as shown in the Table, is found experimentally. However, since the cyclopropanes are undergoing geometric isomerisation, and since we were unable to isolate sufficient of the pure *E*- and *Z*-olefins to test for their geometric isomerisation under the reaction conditions, further speculation is unjustified. The formation of the 1,2-dichloro-3,3-difluoropropene requires either a simultaneous migration of chlorine and fluorine, or a two-step reaction, the *Z*- and *E*-2,3-dichloropropenes being formed and then undergoing a fluorine shift. Such a thermal migration of chlorine has been observed previously in similar pyrolyses [13],

$$\mathrm{CHClF{\cdot}CCl{=}CHF} \xrightleftharpoons[+F^-]{-F^-} \left[\mathrm{CHCl}\cdots\mathrm{CCl}\cdots\mathrm{CHF}\right]^+ \xrightleftharpoons[-F^-]{+F^-} \mathrm{CHCl{=}CCl{\cdot}CHF_2}$$

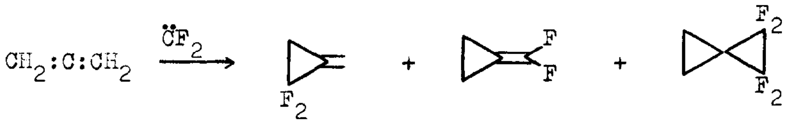
but fluorine migration usually requires a Lewis acid catalyst. However, it is possible that decomposition products accumulating on the wall of the silica pyrolysis tube provide such a catalytic surface. When the mixed *E*- and *Z*-2,3-dichloro-1,3-difluoropropenes were refluxed with activated zinc dust in dimethylformamide, 1,3-difluoroallene was obtained in 73% yield, 37% of the olefins being consumed during a 6-hour reaction. Pyrolysis of the *trans*-dichlorodifluorocyclopropane over zinc at 400°C, however, failed to give the allene. The cyclopropane was recovered (91%), and the dechlorinated product (99% yield based on unrecovered cyclopropane) was shown to be 3,3-difluoropropyne, presumably arising by isomerisation of the 1,3-difluoroallene.

Although the dichlorocyclopropane route to fluoroallene is a considerable improvement over the previous method, particularly for the preparation of small samples of the allene, the corresponding route to 1,3-difluoroallene is less attractive, simply because the 1,2-difluoroethylenes, which need not, of course be separated if the preparation of the allene is the major interest, are less readily available than vinyl fluoride. The 1,1-difluoroethylene, which frequently arises as an impurity in 1,2-difluoroethylene preparation, presents no problem so far as allene preparation is concerned.

The 1,1-dichloro-2,2-difluorocyclopropene formed by the reaction with dichlorocarbene does not isomerise to a potential allene precursor, but loses difluorocarbene to form 1,1-dichloroethylene and tetrafluoroethylene [13], which are readily separated from the dichlorodifluoropropenes.

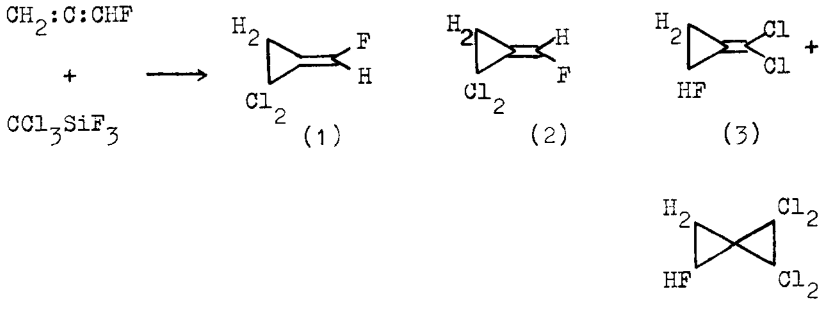
(b) Reactions of allenes with difluoro- and dichloro-carbene

The reaction of allene with difluorocarbene, generated by vapour-phase thermolysis of 2,2,3-trifluoro-3-trifluoromethyloxiran at 180°C, gave a mixture of 1,1-difluoro-2-methylenecyclopropane (47% yield), difluoromethylenecyclopropane (11% yield), and 2,2,3,3-tetrafluorospiro-(2,2)-pentane (11% yield). Separate experiments showed that the difluoromethylenecyclopropane is formed from 1,1-difluoro-2-methylenecyclopropane under these conditions; after 3 hours at 200°C, 1,1-difluoro-2-methylenecyclopropane gave a 1:1 mixture of starting material and difluoromethylenecyclopropane. This is in accord with previous work in which a higher temperature was used to generate difluorocarbene from perfluorocyclopropane, when difluoromethylenecyclopropane was the only C_4 product detectable [14] and with the recent report by Dolbier and Fielder [15].



As in the reaction of allene with perfluorocyclopropane, [14] the formation of 2,2,3,3-tetrafluorospiropentane rather than the 2,2,4,4-isomer parallels the reaction of trifluoro-(trichloromethyl)silane with allene [8]. Addition of $:CX_2$ to the exocyclic dihalogenomethylene group is markedly faster than to the exocyclic methylene in both cases. 1,1-Dichloro- and 1,1-difluoroethylene are known [16] to be more reactive towards dichlorocarbene and, to a lesser extent, difluorocarbene, than ethylene itself, but the complete absence of the 2,2,4,4-tetrahalogenospiropentane suggests additional deactivation of the exocyclic methylene by the ring dihalogenomethylene group. Seyferth has reported the formation of the 2,2,4,4-tetrachloro-compound when allene reacted with phenyltrichloromethylmercury in refluxing benzene [17]; the parameters reported clearly distinguish this from our tetrachlorospiropentane. Presumably at 80°C the only compounds competing for dichlorocarbene are 1,1-dichloro-2-methylenecyclopropane and allene itself, no isomerisation taking place at this temperature.

The reaction of fluoroallene with an equimolar amount of trifluoro(trichloromethyl)silane gave as major product a 2:1 adduct of dichlorocarbene and the allene, identified unambiguously as 2,2,3,3-tetrachloro-4-fluorospiro(2,2)pentane (4) in 66% yield. The minor products comprised the two dichlorocarbene adducts to the unsubstituted double bond of the allene (1 and 2), together with the rearrangement product containing the exocyclic dichloromethylene group (3), which were identified by their n.m.r. spectra and g.l.c. mass spectra,

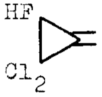


(1) (2) (3)

(4)

each showing the expected molecular ion cluster. The n.m.r. spectra of (1) and (2) were very similar, and their mass spectra were, as expected for geometric isomers, identical. The assignment of *E*- and *Z*- configuration as shown rests mainly on the correlation of g.l.c. retention time with the calculated dipole moments of the two isomers, but is supported by the low field shift of the olefinic hydrogen in (1), *cis* to the CCl_2 group (cf. the 1,2-dichloro-2-butenes [18]). The n.m.r. spectrum of (3) was a close-coupled ABPX pattern, and overlap prevented full analysis. The geminal HH and HF couplings (8.5 and 68.5 Hz), however, were similar to those previously found for 1,1-dichloro-2-fluorocyclopropane (9.8 and 68.5 Hz respectively [8]).

Although (3) could be formed by rearrangement of (1) and (2), its formation from the undetected isomer (5), which



(5)

would be formed by addition of dichlorocarbene to the substituted double bond of fluoroallene, cannot be ruled out. It is clear, however, that as in the reactions of allene with dichloro- and difluoro-carbene, the rearranged compound with the exocyclic dihalogenomethylene group is considerably more reactive towards the carbene than the original adducts.

EXPERIMENTAL

Pyrolyses were carried out at low pressure through a silica tube (i.d. 12 mm, either empty or packed as appropriate) heated over 50 cm by a Wild-Barfield electric furnace. The sample was contained in a stainless steel autoclave (16 cm^3) kept at ca. 100 °C and connected via a needle valve and flow meter to the pyrolysis tube, at the entrance to which was a manometer. The exit vapours were condensed at −196 °C. G.l.c. analysis was carried out on a Pye 104 chromatograph with flame ionisation detector, using 2 m columns for analysis and 4 m or 10 m for preparative-scale separations. I.r. spectra were recorded on Perkin-Elmer Model 257 or 621 instruments, n.m.r. spectra on either a Perkin-Elmer R10 or Perkin-Elmer Hitachi R20A (^1H at 60.0 MHz, ^{19}F at 56.46 MHz) or a Varian HA100 (^1H at 100.0 MHz, ^{19}F at 94.1 MHz) spectrometer; chemical shifts are reported with positive values to low field of the reference material (^{1}H, tetramethylsilane, ^{19}F, trifluoroacetic acid), and mass spectra on a A.E.I. MS/902 mass spectrometer.

Preparation of fluoroallene

(a) Via the dichlorofluoropropenes

In a typical experiment, 1,1-dichloro-2-fluorocyclopropane [8] (0.24 g, 1.9 mmol) was passed through a silica pyrolysis tube at 650 °C, with a contact time of 133 ms, to give a mixture of 2,3-dichloro-3-fluoropropene (0.14 g, 59%) and E- and Z-2,3-dichloro-1-fluoropropene (0.06 g, 25%), identified as described previously [8], together with hydrogen chloride (0.01 g) and unidentified material (0.02 g).

The mixed dichlorofluoropropenes (0.32 g, 2.5 mmol) were refluxed (6 h) with activated zinc dust (0.65 g) in dry dimethylformamide (2 cm^{3}), and the products were collected at -78 °C, then distilled in vacuo to give fluoroallene (0.13 g, 84%), identified by its i.r. [4], n.m.r. (^{1}H, d 86 Hz of d 6 Hz at +7.0; d 6 Hz of d 2.8 Hz at +5.7 p.p.m., intensity ratio 1:2; ^{19}F, d 86 Hz of d 2.8 Hz at -97.8 p.p.m.) and mass spectra [M^{+}, 58], and mixed dichlorofluoropropenes (0.05 g, 14%) with the same isomeric composition as the starting material.

(b) By pyrolysis of 1,1-dichloro-2-fluorocyclopropane over metal

(i) Over zinc

1,1-Dichloro-2-fluorocyclopropane (0.12 g, 0.9 mmol) was passed at 0.4 mm Hg through a silica tube packed with zinc wool kept at 395 °C; the contact time was 2.37 s. The products were separated in vacuo to give fluoroallene (0.010 g, 24%) and the cyclopropane (0.08 g, 70%). In a control experiment, the cyclopropane was recovered unchanged after passage through an unpacked silica tube at 0.3 mm Hg and 400 °C with a contact time of 2.90 sec.

(ii) Over copper

1,1-Dichloro-2-fluorocyclopropane (0.73 g, 5.7 mmol) was passed at 2.0 mm Hg and 500 °C through a silica tube packed with activated copper powder [cf. ref 6], with a contact time of 219 ms. Considerable charring was evident, and volatile products were distilled *in vacuo* to give hydrogen chloride (0.06 g, 28%) fluoroallene (0.09 g, 27%), and a mixture (0.30 g, 41%) of dichlorofluoropropenes similar to that obtained by pyrolysis of the cyclopropane through an unpacked silica tube. In trial pyrolyses the cyclopropane was completely recovered after passage over copper at temperatures up to 400 °C and contact times up to 2.63 s.

Preparation of 1,3-Difluoroallene

In a typical pyrolysis, 1,1-dichloro-*trans*-2,3-difluorocyclopropane (0.72 g, 4.9 mmol), prepared by the reaction of *trans*-1,2-difluoroethylene with trifluoro(trichloromethyl)-silane [10], was passed at 500 °C and 3.5 mm Hg through a silica tube with contact time 235 ms to give hydrogen halides (0.03 g), recovered 1,1-dichloro-*trans*-2,3-difluorocyclopropane (0.03 g, 5%) and the *cis*-isomer (trace), and, separated by preparative g.l.c., (4 m, S.E. 30, 20 °C); (i) *Z*-2,3-dichloro-1,3-difluoropropene (nc) (0.21 g, 29%), b.p. 86 °C/760 mm Hg, ^{1}H n.m.r., d 48 Hz of d 1.6 Hz at +7.2, d 77.6 Hz at +6.8 p.p.m., equal intensities; ^{19}F n.m.r., d 48 Hz of d 2.3 Hz at -58.3, d 77.6 Hz of d 2.3 Hz of d 1.6 Hz at -43.8 p.p.m., equal intensities; Analysis: Found: C 24.2; H, 1.5; Cl, 48.6; F, 25.0%; *M*$^+$, 146. $C_3H_2F_2Cl_2$ requires C, 24.4; H, 1.4; Cl, 48.3; F, 25.8%; *M*, 146; (ii) *E*-2,3-dichloro-1,3-difluoropropene (nc) (0.31 g, 43%), b.p. 96 °C/760 mm Hg, ^{1}H n.m.r., d 48 Hz of d 0.9 Hz at +6.7, d 76 Hz of d 3 Hz at +7.4, equal intensities; ^{19}F n.m.r., d 48 Hz of d 5.9 Hz of d 3 Hz at -52.2, d 77.6 Hz of d 5.9 Hz of d 0.9 Hz at -46.0, equal intensities; Analysis: Found: C, 24.2; H, 1.5%; *M*$^+$ 146; and (iii) *trans*-1,2-dichloro-3,3-difluoropropene

(0.03 g, 5%), b.p. 89 °C/760 mm Hg (lit. [11] b.p. 89 °C/760 mm Hg), ^{1}H n.m.r. t 55 Hz at +6.2, t 2 Hz at +6.5 p.p.m., equal intensities, ^{19}F n.m.r. d 55 Hz of d 2 Hz at -38.3 p.p.m.

The dichlorodifluoropropenes (0.58 g, 4.0 mmol) were refluxed (6 h) with dry dimethylformamide (2 cm^3) and zinc dust to give 1,3-difluoroallene (0.080 g, 27%), identified by its i.r. [4] and mass spectra, and a mixture (0.37 g, 63%) of dichlorodifluoropropenes with the same isomeric composition as the starting material.

Pyrolysis of 1,1-Dichloro-trans-2,3-difluorocyclopropane over zinc

1,1-Dichloro-*trans*-2,3-difluorocyclopropane (0.21 g, 1.4 mmol) was pyrolysed over zinc wool at 400 °C and 0.3 mm Hg pressure with contact time 1.94 s, to give 3,3-difluoropropyne (0.01 g, 8%), identified by its i.r. spectrum [19], and starting material (0.19 g, 91%).

Reaction of allene with 2,2,3-trifluoro-3-trifluoromethyloxiran

Allene (4.6 g, 115 mmol) and 2,2,3-trifluoro-3-trifluoromethyloxiran (6.3 g, 38 mmol) were kept *in vacuo* in a 5 litre Pyrex bulb at 180 °C (6 h) to give a mixture (8.8 g) of allene and trifluoroacetyl fluoride, 1,1-difluoro-2-methylenecyclopropane (1.63 g, 47%), 1-(difluoromethylene)cyclopropane (0.20 g, 11%), and 2,2,3,3-tetrafluorospiropentane (0.28 g, 11%), identified by comparison with authentic samples [14].

1,1-Difluoro-2-methylenecyclopropane (0.31 g, 3.4 mmol), after 3 h *in vacuo* at 200 °C in a 15 cm^3 Pyrex tube, gave starting material (0.15 g, 48%) and 1-(difluoromethylene)-cyclopropane (0.15 g, 48%). A second sample (0.43 g, 4.8 mmol) in a 6 cm^3 Pyrex tube was extensively charred after 6 h at 200 °C, and gave silicon tetrafluoride (0.18 g, 35%), starting material (0.03 g, 6%), and 1-(difluoromethylene)cyclopropane (0.17 g, 40%).

Reaction of fluoroallene with trifluoro(trichloromethyl)silane

Trifluoro(trichloromethyl)silane (4.67 g, 23.0 mmol) and fluoroallene (1.34 g, 23.0 mmol) were kept in vacuo in a 3 litre Pyrex bulb at 140 °C (12 h) to give a mixture (2.81 g) of silicon halides and fluoroallene, a mixture of E-1,1-dichloro-2-(fluoromethylene)cyclopropane (1) (0.39 g, 12%), Z-1,1-dichloro-2-(fluoromethylene)cyclopropane (2) (0.20 g, 6%), and 1-fluoro-2-(dichloromethylene)cyclopropane (3) (0.25 g, 8%), identified by their n.m.r. and mass spectra, and 2,2,3,3-tetrachloro-4-fluorospiropentane (nc) (4) (1.70 g, 66%), b.p. 67 °C/9 mm Hg, m.p. 20 °C; identified by its n.m.r. and mass spectra. Analysis: Found: C, 26.8; H, 1.4; F, 8.2; Cl, 63.6%. $C_5H_3FCl_4$ requires C 26.8; H, 1.3; F, 8.5; Cl. 63.4%).

N.m.r. parameters

Compound	δH	δH_2	δF	$^2J(HF)$	$^4J(HH)$	$^4J(HF)$
(1)	+7.56	+2.23	-50.0	87.0	3.3	7.0
(2)	+6.76	+2.25	-36.4	87.0	2.5	7.0
(3)*	+5.33	+1.86	-53.1	68.5	-	-
(4)**	+5.05	+1.92(A) +1.67(B)	-132.0	64.6	-	-

* J(AB) 8.5Hz

**J(AB) 8.0, J(AX) 18.5, J(BX) 10.3, J(AP) 4.1, J(BP) 5.3Hz.

REFERENCES

1 Part 12: R.N. Haszeldine, C. Parkinson, P.J. Robinson and W.J. Williams, J.Chem.Soc.Perkin Trans.II, in the press.

2 T.L. Jacobs and R.S. Bauer, J.Amer.Chem.Soc., 81 (1959) 606.

3 R.E. Banks, R.N. Haszeldine and D.R. Taylor, J.Chem.Soc., (1965) 978.

4 A.P. Zens, P.D. Ellis and R. Ditchfield, J.Amer.Chem.Soc., 96 (1974) 1309.

5 R.E. Banks, M.G. Barlow, W.D. Davies, R.N. Haszeldine and D.R. Taylor, J.Chem.Soc.(C), (1969) 1104.

6 P.W.L. Bosbury, R. Fields, R.N. Haszeldine and D. Moran, J.Chem.Soc.Perkin Trans.I, (1976) 1173; P.W.L. Bosbury, R. Fields and R.N. Haszeldine, J.Chem.Soc.Perkin Trans.I, (1978) 422.

7 R. Fields, R.N. Haszeldine and J.D. Lee, unpublished results.

8 R. Fields, R.N. Haszeldine and D. Peter, J.Chem.Soc.(C), (1969) 165.

9 W. von E. Doering and P.M. La Flamme, Tetrahedron, 2 (1958), 75; L. Skattebøl, Tetrahedron Letters, (1961) 167; W.R. Moore and H.R. Ward, J.Org.Chem., 27 (1962) 4179.

10 M.G. Barlow, B. Coles and R.N. Haszeldine, unpublished results.

11 A.M. Whaley and H.W. Davies, J.Amer.Chem.Soc., 70 (1948) 1026.

12 I. Fleming and E.J. Thomas, Tetrahedron, 28 (1972) 4989.

13 J.M. Birchall, R. Fields, R.N. Haszeldine and N.T. Kendall, J.Chem.Soc. Perkin Trans.I, (1973) 1773.

14 J.M. Birchall, R. Fields, R.N. Haszeldine, and R.J. McLean, J. Fluorine Chem. 15 (1980), 487.

15 W.R. Dolbier and T.H. Fielder, J.Amer.Chem.Soc., 100 (1978) 5577.

16 R.N. Haszeldine, J.M. Birchall, R.A. Burton, S.G. Farrow, R. Fields, G.N. Gilmore, D.W. Roberts, J.G. Speight and P. Tissington, 4th International Symposium on Fluorine Chemistry, Estes Park, 1967.

17 D. Seyferth, J.M. Burlitch, R.J. Minasz, J. Yick-Pui Mui, H.D. Simmons, A.J.H. Treiber, and S.R. Dowd, J.Amer.Chem. Soc., 87 (1965) 4259.

18 D.F. Ewing and K.A.W. Parry, J.Chem.Soc.(B), (1970) 970.

19 A.L. Bel'ferman, V.U. Shevchuk, I.D. Kushina, M.M. Gil'burd and B.G. Syrvatka, J.Org.Chem. U.S.S.R., 37 (1967) 1870.