

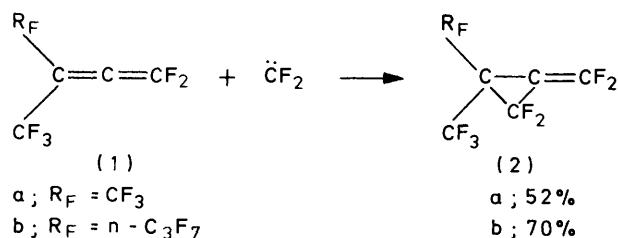
Polyhalogeno-allenes and -acetylenes. Part 14.¹ The Reactions of Perfluoro-1,2-dienes with Dichloro- and Difluoro-carbene, and a New Route to 1,1-Dichloroperfluoro-1,2-dienes †

By Paul W. L. Bosbury, Roy Fields,* Robert N. Haszeldine,* and G. Robert Lomax, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Perfluoro-1,2-dienes $R_F(CF_3)C=C=CF_2$ ($R_F = CF_3$ or $n-C_3F_7$) react in the gas phase with difluoro- and dichloro-carbene to give methylenecyclopropanes $R_F(CF_3)CCF_2C=CF_2$ ($R_F = CF_3, n-C_3F_7$; $X = F, Cl$) in good yield by an addition-rearrangement sequence. Pyrolysis of 1-dichloromethylene-3,3-difluoro-2,2-bis(trifluoromethyl)cyclopropane results in extrusion of difluorocarbene and the formation of 1,1-dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene in high yield. This new allene reacts readily with methanol and undergoes efficient Diels-Alder additions to the perfluoroalkyl-substituted double bond.

EARLIER papers in this series have described a convenient preparation of perfluoro-allenes of the type $R_F(CF_3)C=C=CF_2$ (1; $R_F = CF_3, C_2F_5, n-C_3F_7, (CF_3)_2CF$) and some of their reactions with nucleophilic reagents.² The lower members of the perfluoro-allene series, such as perfluoropropadiene and perfluorobuta-1,2-diene, dimerise rapidly,³ but allenes of type (1) are sufficiently stable to undergo reactions involving elevated temperatures or prolonged reaction times. We report here some reactions with carbenes which lead both to an interesting rearrangement and to the preparation of a new polyhalogeno-allene.

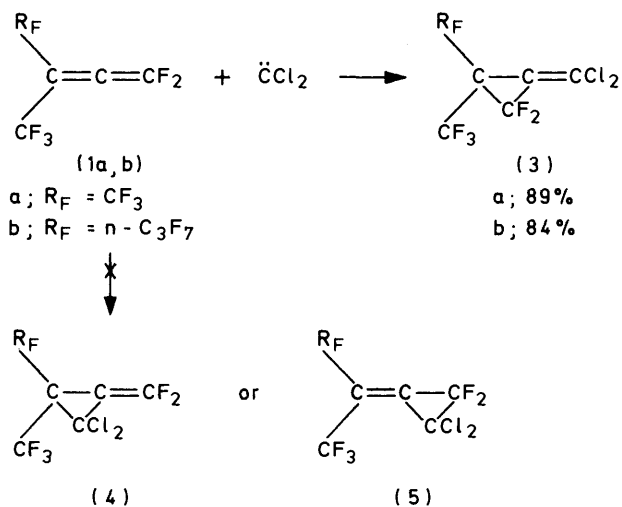
When perfluoro(3-methylbuta-1,2-diene) and perfluoro(3-methylhexa-1,2-diene) were heated with 2,2,3-trifluoro-3-trifluoromethyloxiran, a convenient gas-phase source of difluorocarbene,⁴ the perfluoro(methylenecyclopropanes) (2) were produced. Although under the reaction conditions (175 °C, 5 h) some 40% of compound (1a) was converted into perfluoro(3-isopropylidene-1,1-dimethyl-2-methylenecyclobutane), the known thermal dimer,^{2a} the methylenecyclopropane (2a) was produced in reasonable yield, and the thermally more stable compound (1b) gave the cyclopropane (2b) almost quantitatively (90% by g.l.c. analysis, 70% after separation) (Scheme 1).



SCHEME 1

Dichlorocarbene, produced at a somewhat lower temperature in the gas phase from trifluorotrichloromethylsilane,⁵ also reacted efficiently with the two allenes (Scheme 2). The product from compound (1a) showed only a triplet (9.6 Hz) at $\delta +13.8$ and a septet

(9.6 Hz) at $\delta -52.7$, in the ratio 3 : 1, as expected for the symmetrical structure (3a); the strong coupling between the geminal fluorines results in a deceptively simple, apparently first-order pattern, as has been observed in other symmetrically substituted difluorocyclopropanes.⁶



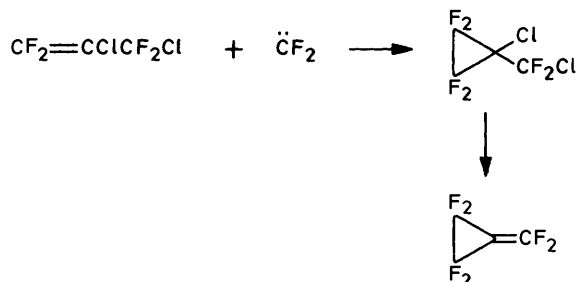
SCHEME 2

The absence of low-field signals for vinylic fluorines clearly rules out the possible isomer (4a), and the two CF_3 groups would have different chemical shifts and be differently coupled to the ring CF_2 group if the structure were (5a). The i.r. C=C stretching absorption at $5.74 \mu m$ provides further evidence against the exocyclic difluoromethylene compound (4a), for which absorption at or below $5.5 \mu m$ would be expected by comparison with compounds (2a and b) and also with perfluoromethylenecyclopropane itself ($5.50 \mu m$); the preparation of this last-named compound by the indirect route shown in Scheme 3 was reported whilst the present work was in progress.⁷ The product from the reaction of compound (1b) with dichlorocarbene was similarly assigned structure (3b).

Mechanism of the Reaction.—Carbene addition to the alkyl-substituted double bond of compounds (1a and b), apparently required for the formation of the exocyclic

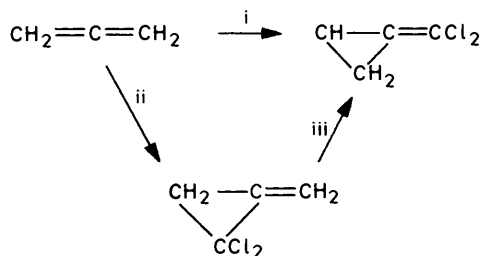
† Presented in part at the 5th European Fluorine Symposium, Aviemore, Scotland, September 1974.

difluoromethylene compounds (2a and b), is unexpected on both steric and electronic grounds. Vinylic fluorine is mildly activating towards carbene attack, but the fluoroalkyl groups are entirely deactivating. However,



SCHEME 3

the products (3a and b) cannot be formed by a single-step reaction of the allene with dichlorocarbene, which could give only compound (4) or its isomer (5); rearrangement of the initially formed adduct is clearly required. Rearrangements in the course of similar gas-phase additions of dichlorocarbene to allenes have been observed previously.⁵ Liquid-phase reactions of alkyl allenes at lower temperatures give the expected adducts, which can be rearranged to exocyclic dichloromethylene cyclopropanes at higher temperatures (Scheme 4).

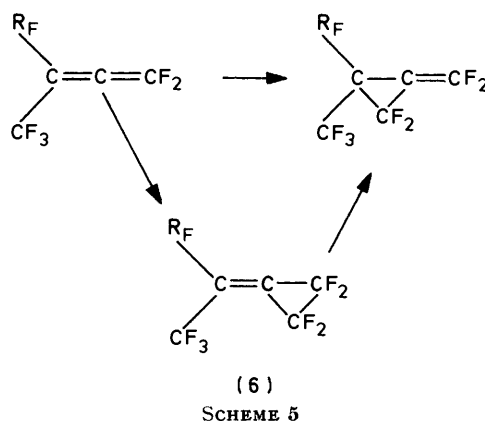


SCHEME 4 Reagents: i, CCl_2SiF_3 at 140°C , ref. 5; ii, $\text{PhHgCCl}_3\text{-NaI-C}_6\text{H}_6$ at 80°C , ref. 8; iii, ref. 9

Although the initial adducts were not observable in the present work, it is clear that either compound (4) or its isomer (5) could rearrange to give the observed product (3). Similarly, the product (2) obtained in the reaction of difluorocarbene with the allenes (1a and b) may have resulted from an addition-rearrangement sequence via the unobserved intermediate (6) rather than by a single-step addition (Scheme 5).

In a reaction in which the buta-1,2-diene (1a) competed with ethylene for a deficiency of dichlorocarbene, compound (3a) was formed in 88% yield, and no product with g.l.c. retention corresponding to that of a reference sample of 1,1-dichlorocyclopropane could be detected. The initial attack by the carbene is thus clearly on an activated rather than on a deactivated site, favouring the initial formation of compound (5).

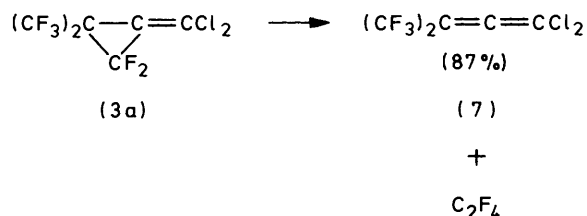
Preparation and Reactions of 1,1-Dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene (7).—Pyrolysis of cyclopropanes containing a ring CF_2 group frequently results in expulsion of difluorocarbene and the formation



SCHEME 5

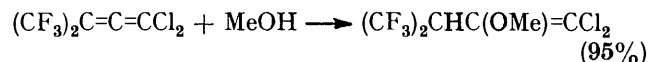
of an olefin.¹⁰ The dichloromethylenecyclopropane (3a) was therefore pyrolysed in a flow system and gave tetrafluoroethylene and 1,1-dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene (7) in good yield (Scheme 6).

This new allene was quantitatively recovered after several weeks at room temperature or three days at 100°C *in vacuo*. The thermal stability contrasted with the ready dimerisation of the perfluoro-analogue (1a) under these conditions. The dichloroallene (7) was fully characterised spectroscopically, analytically, and by its reactions with methanol, furan, and cyclopentadiene. The n.m.r. spectrum showed only a singlet at



SCHEME 6

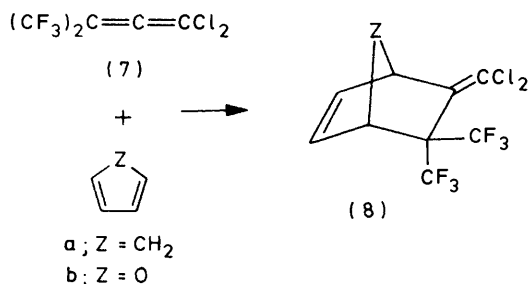
+14.2 p.p.m., the i.r. spectrum was very similar to that of compound (1a), with the exception that the characteristic allenic $\text{C}=\text{C}=\text{C}$ stretching band ($5.0\ \mu\text{m}$) was much weaker than that of the perfluoro-compound, and the mass spectrum showed a parent-ion cluster at m/e 244. As with compound (1a),^{3b} methanol added readily and exclusively across the alkyl-substituted double bond.



Furan and cyclopentadiene gave the Diels-Alder adducts (8), the exothermic reaction again taking place exclusively at the perfluoroalkyl-substituted double bond (Scheme 7). The adduct (8b) was identical with that obtained by D'yatkin *et al.*¹¹ when they carried out the reaction of perfluoroisobutene and caesium fluoride with chloroform in the presence of furan and confirms their suggestion that compound (7) is an intermediate in this complicated reaction sequence.

The carbene addition-rearrangement-difluorocarbene extrusion sequence suggests a route to other allenes of the

type $(CF_3)_R C=C=CXY$, provided that the carbene $:CXY$ can be produced in a manner which avoids nucleophilic attack on the perfluoroalkylallene. 1,2,2-Trifluoroethylidene is formed at 175 °C under conditions



SCHEME 7

similar to those for the formation of dichloro- and difluoro-carbene.¹² However it failed to react with either compound (1a), which dimerised quantitatively, or with the more thermally stable diene (1b), which was recovered in 76% yield together with a liquid product (21%), identical with that formed from the thermal reaction of compound (1b) alone. Trifluoroethylene and silicon tetrafluoride accounted for at least 90% of the trifluorotetrafluoroethylsilane consumed, and a small amount of 3-difluoromethyl-1,1,2,3-tetrafluorocyclopropane was formed by addition of the carbene to trifluoroethylene.¹² It is thus clear from the experimental evidence that the alternative pathways open to 1,1,2-trifluoroethylidene are preferred to reaction with the allenes (1a and 1b). The precise reasons for this are not clear, however, since 1,1,2-trifluoroethylidene reacts readily with ethylene, which (see above) is much less reactive towards dichlorocarbene than compound (1a).

EXPERIMENTAL

The perfluoro-1,2-dienes were prepared as described previously.^{2a} I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer, n.m.r. spectra on a Perkin-Elmer R 10 (60.0 MHz for ¹H, 56.46 MHz for ¹⁹F) or a Varian HA 100 (100.0 MHz for ¹H, 94.1 MHz for ¹⁹F) spectrometer, with positive shifts to low field of tetramethylsilane or trifluoroacetic acid respectively, and mass spectra on an A.E.I. MS 902 spectrometer.

Reaction of Perfluoro(3-methylbuta-1,2-diene) (1a) with 2,2,3-Trifluoro-3-trifluoromethyloxiran.—Perfluoro(3-methylbuta-1,2-diene) (1.27 g, 6.0 mmol) and 2,2,3-trifluoro-3-trifluoromethyloxiran (1.01 g, 6.0 mmol) were kept *in vacuo* in a Pyrex reaction bulb (5.5 l) at 175 °C (5 h). The following compounds were obtained: a mixture of trifluoroacetyl fluoride, silicon tetrafluoride, and tetrafluoroethylene (0.4 g), perfluoro(3-isopropylidene-1,1-dimethyl-2-methylenecyclobutane) (0.51 g, 40%) and perfluoro(1-methylene-2,2-dimethylcyclopropane) (2a) (0.81 g, 52%) (Found: C, 26.9; F, 71.6%; *M*⁺, 262. C₆F₁₀ requires C, 27.5; F, 72.5%; *M*, 262), b.p. 40 °C; i.r. 5.46 μm (C=C); δ(¹⁹F) +17.0 (d, 7.3 Hz; t, 6.7 Hz; sept., 2.1 Hz; =CF), +12.1 [t, 9.4 Hz; d, 2.3 Hz; d, 2.1 Hz; (CF₃)₂C], +8.7 (d,

7.3 Hz; t, 5.6 Hz; sept., 2.3 Hz; =CF), and -51.8 p.p.m. (sept., 9.4 Hz; d, 6.7 Hz; d, 5.6 Hz; CF₃).

Reaction of Perfluoro(3-methylhexa-1,2-diene) (1b) with 2,2,3-Trifluoro-3-trifluoromethyloxiran.—Perfluoro(3-methylhexa-1,2-diene) (1.87 g, 6.0 mmol) and 2,2,3-trifluoro-3-trifluoromethyloxiran (1.01 g, 6.0 mmol) were kept *in vacuo* in a Pyrex bulb (5.5 l) at 180 °C (5 h). Fractionation *in vacuo* and g.l.c. separation gave recovered diene (0.07 g, 4%), trifluoroacetyl fluoride (0.4 g), and perfluoro(1-methylene-2-methyl-2-propylcyclopropane) (2b) (1.52 g, 70%) (Found: C, 26.8; F, 73.7%; *M*⁺, 362. C₈F₁₄ requires C, 26.5; F, 73.5%; *M*, 362), b.p. 86 °C, i.r. 5.44 μm (C=C); δ(¹⁹F) +17.4 (t, 6.3 Hz; d, 6.3 Hz; q, 2.1 Hz; t, 2.1 Hz, =CF), +14.6 (t, 19.0 Hz; t, 9.5 Hz with further splitting, ring CF₃), +8.8 (unresolved m, =CF), -5.2 (d, 11.5 Hz; d, *J* 9.5 Hz, CF₃CF₂), -35.0 (AB pattern, *J*_{AB} 300 Hz, Δ_{AB} 3.4 p.p.m., C₂F₅CF_AF_B), -48.5 (complex, CF₃CF₂), and -49.7 (complex, ring CF₃).

Reaction of Perfluoro(3-methylbuta-1,2-diene) (1a) with Trifluorotrichloromethylsilane.—Perfluoro(3-methylbuta-1,2-diene) (1.11 g, 5.0 mmol) and trifluorotrichloromethylsilane (1.01 g, 5.0 mmol) were kept *in vacuo* in a Pyrex reaction bulb (5.5 l) at 140 °C (5 h). The following compounds resulted: a mixture of silicon halides (0.31 g), recovered perfluoro(3-methylbuta-1,2-diene) (0.09 g, 8%), and 1-dichloromethylene-2,2-difluoro-3,3-bis(trifluoromethyl)cyclopropane (3a) (1.23 g, 84%) (Found: C, 23.9; Cl, 24.5; F, 50.8%; *M*⁺, 294. C₆Cl₂F₈ requires C, 24.4; Cl, 24.1; F, 51.5%; *M*, 294), b.p. 101 °C, i.r. 5.74 μm (C=C).

Reaction of Perfluoro(3-methylhexa-1,2-diene) (1b) with Trifluorotrichloromethylsilane.—Perfluoro(3-methylhexa-1,2-diene) (1.87 g, 6.0 mmol) and trifluorotrichloromethylsilane (1.20 g, 6.0 mmol) were kept *in vacuo* in a Pyrex bulb (5.5 l) at 140 °C (4 h). The following compounds were obtained: a mixture of silicon halides (0.41 g), recovered diene (0.06 g, 3%), and 1-dichloromethylene-3,3-difluoro-2-heptafluoro-propyl-2-trifluoromethylcyclopropane (3b) (1.98 g, 84%) (Found: C, 24.2; Cl, 18.0; F, 57.7%; *M*⁺, 394. C₉Cl₂F₁₂ requires C, 24.3; Cl, 18.0; F, 57.7%; *M*, 394), b.p. 144 °C, i.r. 5.74 μm (C=C); δ(¹⁹F) +17.1 (t, 20 Hz; t, 10 Hz with further unresolved coupling, ring CF₃), -4.5 (d, 12.6 Hz; d, 9.8 Hz, CF₂CF₂), -38.5 (AB pattern, *J*_{AB} 298 Hz, Δ_{AB} 4.8 p.p.m., C₂F₅CF_AF_B), -49.0 (complex m, CF₃CF₂), -52.2 p.p.m. (complex m, ring CF₃).

Reaction of Trifluorotrichloromethylsilane with a mixture of Ethylene and Perfluoro(3-methylbuta-1,2-diene) (1a).—Ethylene (0.18 g, 7.1 mmol), perfluoro(3-methylbuta-1,2-diene) (1.50 g, 7.1 mmol), and trifluorotrichloromethylsilane (0.29 g, 1.4 mmol) were kept *in vacuo* in a Pyrex bulb (5 l) at 160 °C (10 h). The following compounds resulted: a mixture of silicon halides and ethylene (8.2 mmol), recovered perfluoro(3-methylbuta-1,2-diene) (1.08 g, 72% recovery), dimers of the perfluorodiene (0.14 g, 8%), 1-dichloromethylene-2,2-difluoro-3,3-bis(trifluoromethyl)cyclopropane (3a) (0.38 g, 88% based on trifluorosilane consumed) and three unidentified compounds (0.04 g, total). No g.l.c. peak corresponding to that of a known sample of 1,1-dichlorocyclopropane could be detected (1% yield would have been readily observed).

Preparation of 1,1-Dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene (7).—1-Dichloromethylene-2,2-difluoro-3,3-bis(trifluoromethyl)cyclopropane (3a) (1.02 g, 3.5 mmol) was passed *in vacuo* through a silica tube (1.0 cm int. diam., heated zone 50 cm) at 550 °C/2 mmHg, to give tetrafluoroethylene (0.17 g, 96%), starting material (0.12 g, 12%),

and 1,1-dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene (0.65 g, 87%) (Found: C, 24.7; Cl, 29.4; F, 46.3%; M^+ , 244. $C_5Cl_2F_6$ requires C, 24.5; Cl, 29.0; F, 46.5%; M , 244), b.p. 88 °C, i.r. 5.00 μm (C=C); δ (^{19}F) +14.2 (s).

Reactions of 1,1-Dichloro-4,4,4-trifluoro-3-trifluoromethylbuta-1,2-diene (7).—(a) With methanol. The diene (0.25 g, 1.0 mmol), methanol (1.0 ml) and sodium methoxide (trace) were kept *in vacuo* at room temperature (15h) to give 1,1-dichloro-4,4,4-trifluoro-2-methoxy-3-trifluoromethylbut-1-ene (0.20g, 72%), δ (^1H) (external benzene in CCl_4) -2.8 (s) and -2.2 (sept. J_{HF} 8 Hz); δ (^{19}F) +12.8 p.p.m. (d, J_{HF} 8 Hz).

(b) With furan. The diene (0.67 g, 2.7 mmol) and furan (0.18 g, 2.7 mmol) were shaken together *in vacuo* at room temperature (0.5 h). The solid product was sublimed *in vacuo* to give 6-dichloromethylene-5,5-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (8b) (0.81 g, 95%) as white crystals (Found: C, 34.2; H, 1.5; Cl, 22.5; F, 36.6%; M^+ , 312. Calc. for $C_9H_4Cl_2F_6O$: C, 34.5; H, 1.3; Cl, 22.6; F, 36.7%; M , 312), m.p. 51–52 °C (lit.,¹¹ m.p. 52–53 °C), i.r. 6.06, 6.36 μm (C=C).

(c) With cyclopentadiene. The dichloro-diene (0.55 g, 2.3 mmol) and cyclopentadiene (0.15 g, 2.3 mmol) were sealed *in vacuo* at -196 °C. As the tube warmed to room temperature an exothermic reaction took place. The contents were shaken (0.5 h) and the solid product was sublimed *in vacuo* to give 6-dichloromethylene-5,5-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (8a) (0.61 g, 87%) (Found: C, 38.3; H, 2.1%; M^+ , 310. $C_{10}H_6Cl_2F_6$ requires C, 38.6; H, 1.9%;

M , 310), m.p. 29–30 °C, i.r. 6.15, 6.37 μm (C=C) as a white wax which decomposed on prolonged exposure to air.

[2/057 Received, 12th January, 1982]

REFERENCES

- ¹ Part 13, R. E. Banks, W. D. Davies, R. N. Haszeldine, G. R. Lomax, and D. R. Taylor, *J. Fluorine Chem.*, 1980, **15**, 79.
- ² (a) P. W. L. Bosbury, R. Fields, R. N. Haszeldine, and D. Moran, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1173; (b) P. W. L. Bosbury, R. Fields, and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. 1*, 1978, 422.
- ³ (a) T. L. Jacobs and R. S. Bauer, *J. Am. Chem. Soc.*, 1959, **81**, 606; (b) R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. C*, 1969, 996.
- ⁴ P. B. Sergeant, *J. Org. Chem.*, 1970, **35**, 678.
- ⁵ R. Fields, R. N. Haszeldine, and D. Peter, *J. Chem. Soc. C*, 1969, 165.
- ⁶ J. M. Birchall, R. Fields, R. N. Haszeldine, and R. J. McLean, *J. Fluorine Chem.*, 1980, **15**, 487.
- ⁷ B. E. Smart, *J. Am. Chem. Soc.*, 1974, **96**, 927.
- ⁸ D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Yick-Pui Mui, H. D. Simmons, A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, 1965, **87**, 4259.
- ⁹ W. R. Dolbier, D. Lomas, T. Garza, C. Harmon, and P. Tarrant, *Tetrahedron*, 1972, **28**, 3185.
- ¹⁰ J. M. Birchall, R. Fields, R. N. Haszeldine, and N. T. Kendall, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1773; J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1071.
- ¹¹ B. L. D'yatkin, N. I. Delyagina, E. I. Mysov, and I. L. Knunyants, *Tetrahedron*, 1974, **30**, 4031.
- ¹² R. N. Haszeldine and J. G. Speight, *J. Chem. Soc., Chem. Commun.*, 1976, 995.