

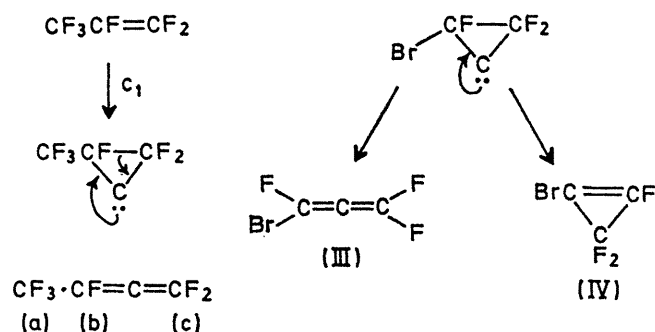
Synthesis of Fluorinated Allenes using Atomic Carbon

By M. J. MCGLINCHY, T. REYNOLDS, and F. G. A. STONE*

(Department of Inorganic Chemistry, The University, Bristol BS8 1TS)

Summary Carbon vapour generated with a carbon arc reacts with $\text{CF}_2:\text{CFX}$ ($\text{X} = \text{CF}_3$, Cl, or Br) to give the fluoro-allenes $(\text{X})(\text{F})\text{C}:\text{C}:\text{CF}_2$. The products are rationalised in terms of cyclopropylcarbene intermediates.

PREVIOUS routes to fluorinated allenes involve multi-stage syntheses.¹⁻⁴ We now report that perfluoropropene reacts with carbon vapour generated in an arc^{5,6} to give perfluorobuta-1,2-diene (I) (b.p. -5°) in yields of 20%. In a



single arcing experiment⁶ it is possible to prepare a gram of (I). The nature of (I) was established by its mass spectrum,

and i.r. and ^{19}F n.m.r. spectra. The mass spectrum showed a molecular ion at m/e 162, and major ions corresponding to C_4F_5^+ , C_4F_4^+ , C_3F_3^+ , C_3F_2^+ , CF_3^+ , C_3F^+ , and CF^+ . The i.r. spectrum had an allene band at 2056 cm^{-1} , together with C-F stretching vibrations similar to those observed in the spectra of fluoro-allenes.^{2-4,7} The ^{19}F n.m.r. spectrum showed signals (relative to CCl_3F) at 72.2 (3F, d of t), 73.5 (2F, d of q) and 103.2 (1F, t of q) p.p.m., with $|J_{ab}| = 15.0$, $|J_{ac}| = 4.3$, and $|J_{bc}| = 36.4$ Hz. Similarly, chlorotrifluoroethylene reacted with carbon vapour to give $\text{ClFC}:\text{C}:\text{CF}_2$ (II) (b.p. 12.6°) in yields of 10–15%. The i.r. spectrum of (II) showed bands at 2044 and 2016 cm^{-1} , and the ^{19}F n.m.r. spectrum had signals at 48.2 (1F, t, $|J_{FF}| 30.2$ Hz) and 75.0 (2F, d) p.p.m.

Products from bromotrifluoroethylene and carbon vapour are obtained in low yield (ca. 5%), but besides $\text{BrFC}:\text{C}:\text{CF}_2$ (III) [ν_{max} 2030 cm^{-1}] include 1-bromo-2,3,3-trifluorocyclopropene (IV) [b.p. 44° ; ν_{max} 1844 cm^{-1}]. The ^{19}F n.m.r. spectrum of (IV) showed peaks at 97.9 (2F, d, $|J_{FF}| 40.7$ Hz) and 126.0 (1F, t) p.p.m., and is consistent with a cyclopropene having a CF_2 bridge.⁸ The two major peaks in the mass spectrum are the parent ion and C_3F_3^+ . Formation of (III) and (IV) may be visualised as involving an intermediate cyclopropylcarbene which either rearranges to an allene, or stabilises itself by bromine migration.

We thank the S.R.C. for a research studentship (T.R.).

(Received, July 20th, 1970; Com. 1166.)

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

² W. T. Miller, W. Frass, and P. R. Resnick, *J. Amer. Chem. Soc.*, 1961, **83**, 1767.

³ D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 5582.

⁴ R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1968, 2593.

⁵ P. S. Skell, L. D. Wescott, J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 1965, **87**, 2829.

⁶ J. E. Dobson, P. M. Tucker, F. G. A. Stone, and R. Schaeffer, *J. Amer. Chem. Soc. (A)*, 1969, 1882.

⁷ T. L. Jacobs and R. S. Bauer, *J. Amer. Chem. Soc.*, 1959, **81**, 606.

⁸ W. R. Cullen and M. C. Waldman, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 205.