Synthesis of Fluorinated Allenes using Atomic Carbon

By M. J. MCGLINCHEY, T. REYNOLDSON, and F. G. A. STONE*
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary Carbon vapour generated with a carbon arc reacts with $CF_2{:}CFX$ (X = CF_3, Cl, or Br) to give the fluoro-allenes (X)(F)C:C: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 experiment[6] 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 $|J_{ab}| = 15{\cdot}0$, $|J_{ac}| = 4{\cdot}3$, and $|J_{bc}| = 36.4$ Hz. Similarly, chlorotrifluoroethylene reacted with carbon vapour to give ClFC:C: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 BrFC:C: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.

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