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## Photochemical Isomerization of Octafluorocyclohexa-1,3-diene

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Summary Octafluorocyclohexa-1,3-diene (1) is isomerized to octafluorobicyclo[2,2,0]hex-2-ene (2) on direct irradiation in the vapour phase; the reverse isomerization occurs thermally.

THE photochemical conversion of hexafluorobenzene into hexafluorobicyclo[2,2,0]hexa-2,5-diene has received considerable attention.<sup>1</sup> Also, decafluorocyclohexene has been shown to undergo photochemical isomerization.<sup>2</sup> We now report that direct isomerization of octafluorocyclohexa-1,3-diene (1) (b.p. 63°) in the vapour phase results in its isomerization to octafluorobicyclo[2,2,0]hex-2-ene (2) (b.p. 47°).

Direct irradiation (253.7 nm, low-pressure mercury lamp) of diene (1) ( $\lambda_{\rm max}$  256 nm,  $\epsilon$  3.2  $\times$  10<sup>3</sup>)<sup>3</sup> in the vapour phase in a quartz ampoule gave olefin (2), in good yield, as the only product. Olefin (2), which was separated from diene (1) by preparative gas-chromatography, was characterized by spectroscopy and its thermal isomerization to diene (1). The mass spectrum of (2) showed the same parent and fragment ions as that of diene (1); however, the relative abundances of ions differed in the two cases. The i.r. spectrum showed a single strong absorption at 1764 cm<sup>-1</sup> (-CF=CF-) and the <sup>19</sup>F n.m.r. spectrum showed a broad resonance at 201.4 p.p.m. (2F, tertiary fluorines), a complex multiplet at 122.0 p.p.m. (2F, vinylic fluorines), and a system of four complex multiplets at 117.0, 121.0, 128.3, and 132.3 p.p.m. w.r.t. external CFCl<sub>3</sub> (4F, -CF<sub>2</sub>-CF<sub>2</sub>-). Pyrolysis of olefin (2) in a flow system at  $300^{\circ}/10^{-3}$ mm Hg gave diene (1) quantitatively.



In contrast to hexafluorobicyclo[2,2,0]hexa-2,5-diene, which is reported to be dangerously explosive in the liquid phase and isomerizes to hexafluorobenzene above 40° in the vapour phase,<sup>4</sup> octafluorobicyclo [2,2,0] hex-2-ene (2) is relatively stable, a sample being unchanged after three years at room temperature and unaffected by pyrolysis in a flow system at 200°/10-3 mm Hg.

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- <sup>1</sup> G. Camaggi and F. Gozzo, J. Chem. Soc. (C), 1969, 489, and reference therein.
  <sup>2</sup> G. Camaggi and F. Gozzo, Chem. Comm., 1967, 236.
  <sup>8</sup> D. E. M. Evans and J. C. Tatlow, J. Chem. Soc., 1954, 3779.
  <sup>4</sup> E. Rajczak and A. F. Trotman-Dickenson, J. Chem. Soc. (A), 1968, 509.