Photochemical Isomerization of Octafluorocyclohexa-1,3-diene

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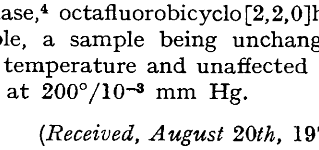
Summary Octafluorocyclohexa-1,3-diene (**1**) is isomerized to octafluorobicyclo[2,2,0]hex-2-ene (**2**) on direct irradiation in the vapour phase; the reverse isomerization occurs thermally.

THE photochemical conversion of hexafluorobenzene into hexafluorobicyclo[2,2,0]hexa-2,5-diene has received considerable attention.[1] Also, decafluorocyclohexene has been shown to undergo photochemical isomerization.[2] 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**) (λ_{max} 256 nm, ϵ 3·2 × 10^3)[3] 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^{-1} (–CF=CF–) and the ^{19}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$_3$ (4F, –CF$_2$–CF$_2$–). Pyrolysis of olefin (**2**) in a flow system at 300°/10^{-3} mm Hg gave diene (**1**) quantitatively.



(1) (2)

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