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Hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (Hexafluoro-Dewar-benzene Oxide) from the Photochemical Oxidation of Hexafluorobenzene

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Summary Photochemical oxidation of hexafluorobenzene in the vapour phase yields the title compound, which undergoes thermal rearrangement into hexafluorocyclohexa-2,4-dienone and two acid fluorides, attack by diethyl ether at the oxiran ring, and cycloaddition to its C=C double bond.

ULTRAVIOLET irradiation ($\lambda > 200$ nm) of a gaseous mixture of hexafluorobenzene, nitrogen (300 mmHg), and oxygen (200 mmHg), leads rapidly to the formation of hexafluoro-Dewar-benzene (1),¹ and more slowly (7% yield after 72 h) to hexafluoro-3-oxatricyclo[3.2.0.0²,⁴]hept-6-ene (2) together with much polymeric material.



The oxide (2), which is conveniently separated from its presumed precursor (1) by reaction of the latter with bromine in the dark,² has v_{max} . 1755 cm⁻¹ (C=C stretch), m/e 202 (M^{+} , 60·8), 174 (C_5F_6 , 40·9), 155 (C_5F_5 , 39·7), and

124 (C₄F₄, 100%), and $\delta_{\rm F}$ (positive to low field of external CF₃CO₂H) -43·3 (=CF), -97·0 (CFO), and -119·0 p.p.m. (CCFC), and is a potential source of hexafluorobenzene oxide (3) or its valence-bond isomer, the oxepin (4);³ however, at 50 °C during 7 days, only hexafluorocyclohexa-2,4-dienone (5) was obtained as a volatile product, and flow thermolysis (at 275 °C and 1 mmHg) yielded the dienone (5) (72%),⁴ together with small amounts of the isomeric acid fluorides (6) (7%) and (7) (12%), which were identified spectroscopically.⁵ If the dipolar intermediate (8) is involved, it could undergo fluorine or carbon migration to give (5) and (6), respectively, and (7) is the product of the allowed suprafacial [1,5] shift of fluorine in (6). A dipolar intermediate may well be involved also in the slow reaction of (2) with diethyl ether, where ethyl fluoride (100%) and the cyclohexa-2,5-dienone (9) (75%) are formed after 90 days at room temperature.

The oxiran (2) shows the expected reactivity at the C=C double bond in comparison to compound (1),^{2,6} adding photochemically chlorine or bromine in carbon tetrachloride to give (10) (70%) or (11) (75%) (mainly the *cis-exo*isomers), forming the adduct (12) with benzonitrile oxide, and Diels-Alder adducts, for example (13), with furan (42%) after 30 h at room temperature in n-pentane).



Despite the failure to obtain the oxepin (4), the derivatives (14) (60%) and (15) (39%) were obtained by flow thermolysis of the compounds (10) (at 400 $^{\circ}\mathrm{C}$ and $<\!1$ mmHg) and (12) (at 440 $^{\circ}C$ and <1 mmHg), but attempts to dechlorinate (14) have so far proved unsuccessful.⁷

If (8) is an intermediate in the rearrangement of (3), then

the formation of (5) has an interesting analogy in the aromatisation of arene oxides to phenols via the NIH shift 8

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¹G Camaggi, F Gozzo, and G Cevidalli, Chem Comm, 1966, 313, I Haller, J Amer Chem Soc, 1966, 88, 2070 ²M G Barlow, R N Haszeldine, W D Morton, and D R Woodward, J C S Perkin I, 1972, 2170 ³Cf, the hydrocarbon analogue E E van Tamelen and D Carty, J Amer Chem Soc, 1971, 93, 6102 ⁴With m/e 202 (M^+ , 47 0) and 124 (C_4F_4 , 100%), and δ_F -35 9 (F-6), -55 4 (F-3), -77 3 (F-5) -78 3 (F-4), and -84 9 p p m (F-2), and the expected resemblance to the spectra of the 6-chloro- and 6-bromo-compounds N E Akhmetova, N V Kostina, V J Mamatyuk, A A Shtark, and V D Shteingarts, *Izvest sibirsk Otdel Akad Nauk*, Ser khim Nauk, 1973, 86 (Chem Abs, 1974, 80, 107493) 107493s)

⁵ Compound (6) has $\delta_{\rm F}$ 954 (COF), -715 (F-2,3), -886 (F-1,4), and -1176 p pm (\geqslant CF), and (7) has 1099 (COF), -166 (F-2), -575 (CF₂) -709 (F-4), and *ca* -785 [F-3, largely masked by an absorption of (5)] *cf*, the chemical shifts of 1- and 5-chloropentafluorocyclopentadiene R E Banks, M Bridge, R N Haszeldine, D W Roberts, and N I Tucker, *J Chem Soc* (*C*), 1970, 2531

⁶ M G Barlow, R N Haszeldine, and R Hubbard, J Chem Soc (C) 1971, 90, M G Barlow, R N Haszeldine, W D Morton, and D R Woodward, J C S Perkin I, 1973, 1798

⁷ The preparation and thermal isomerisation of the diffuoroanalogue of (10) has recently been described M S Foy and R S Stringham, J Fluorine Chem, 1978, 12, 23, J Org Chem, 1979, 44, 2813 *G Guroff, J W Daley, D M Jerina, J Renson, B Witkop, and S Udenfriend Science, 1967, 158, 1524