

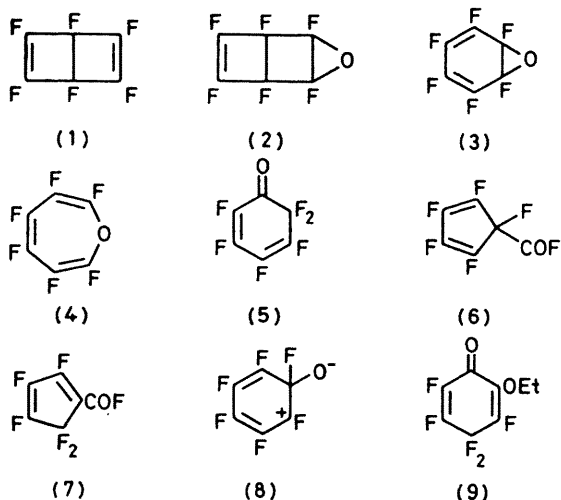
Hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (Hexafluoro-Dewar-benzene Oxide) from the Photochemical Oxidation of Hexafluorobenzene

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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.

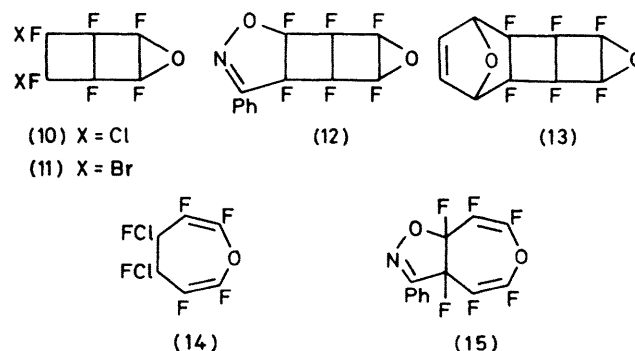
ULTRAVIOLET irradiation ($\lambda > 200$ nm) of a gaseous mixture of hexafluorobenzene, nitrogen (300 mmHg), and oxygen (200 mmHg), leads rapidly to the formation of hexafluoro-Dewar-benzene (1),¹ and more slowly (7% yield after 72 h) to hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (2) together 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 ν_{\max} 1755 cm^{-1} (C=C stretch), m/e 202 (M^+ , 60.8), 174 (C_6F_6 , 40.9), 155 (C_5F_5 , 39.7), and

124 (C_4F_4 , 100%), and δ_F (positive to low field of external $\text{CF}_3\text{CO}_2\text{H}$) -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 °C and <1 mmHg) and (**12**) (at 440 °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 N I H shift⁸

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¹ G. Camaggi, F. Gozzo, and G. Cevidalì, *Chem Comm*, 1966, 313, I. Haller, *J Amer Chem Soc*, 1966, **88**, 2070

² M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J C S Perkin I*, 1972, 2170

³ *Cf.*, the hydrocarbon analogue E. E. van Tamelen and D. Carty, *J Amer Chem Soc*, 1971, **93**, 6102

⁴ With *m/e* 202 (*M*⁺, 47.0) and 124 (C₄F₄, 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**, 107493s)

⁵ Compound (**6**) has δ_F 95.4 (COF), -71.5 (F-2,3), -88.6 (F-1,4), and -117.6 p.p.m (\geq CF), and (**7**) has 109.9 (COF), -16.6 (F-2), -57.5 (CF₂) -70.9 (F-4), and *ca* -78.5 [F-3, largely masked by an absorption of (**5**)] *cf.*, the chemical shifts of 1- and 5-chloro-pentafluorocyclopentadiene 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 difluoroanalogue 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

⁸ G. Guroff, J. W. Daley, D. M. Jerina, J. Renson, B. Witkop, and S. Udenfriend *Science*, 1967, **158**, 1524