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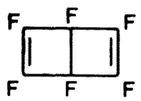
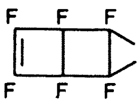
Summary Photochemical oxidation of hexafluorobenzene in the vapour phase yields the title compound, which undergoes thermal rearrangement into hexafluorocyclohexa-2,4-dienone and two acid fluorides, attack by diethyl ether at the oxiran ring, and cycloaddition to its C=C double bond.

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.


(**1**)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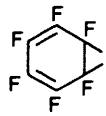
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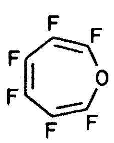
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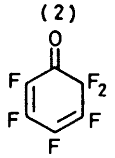
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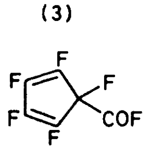
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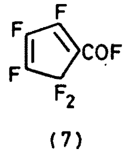
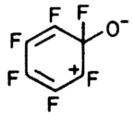
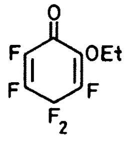
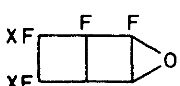

(**7**)

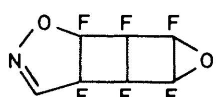

(**8**)

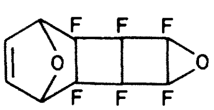

(**9**)

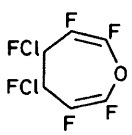
The oxide (**2**), which is conveniently separated from its presumed precursor (**1**) by reaction of the latter with bromine in the dark,[2] has $\nu_{max.}$ 1755 cm^{-1} (C=C stretch), *m/e* 202 ($M^{+\cdot}$, 60·8), 174 (C_5F_6, 40·9), 155 (C_5F_5, 39·7), and 124 (C_4F_4, 100%), and δ_F (positive to low field of external CF_3CO_2H) $-43·3$ (=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.

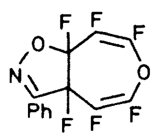
The oxiran (**2**) shows the expected reactivity at the C=C double bond in comparison to compound (**1**),[2,6] adding photochemically chlorine or bromine in carbon tetrachloride to give (**10**) (70%) or (**11**) (75%) (mainly the *cis-exo*-isomers), forming the adduct (**12**) with benzonitrile oxide,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


(**10**) X = Cl
(**11**) X = Br


(**12**)


(**13**)


(**14**)


(**15**)

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 shift[8]

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[1] G Camaggi, F Gozzo, and G Cevidalli, *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 (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**, 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 ($\geqslant$CF), and (**7**) has 109 9 (COF), -16 6 (F-2), -57 5 (CF_2) $-70{\cdot}9$ (F-4), and *ca* -78 5 [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 difluoroanalogue of (**10**) has recently been described M S Toy 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