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HEXAKIS(TRIFLUOROMETHYL)BENZVALENE OZONIDE

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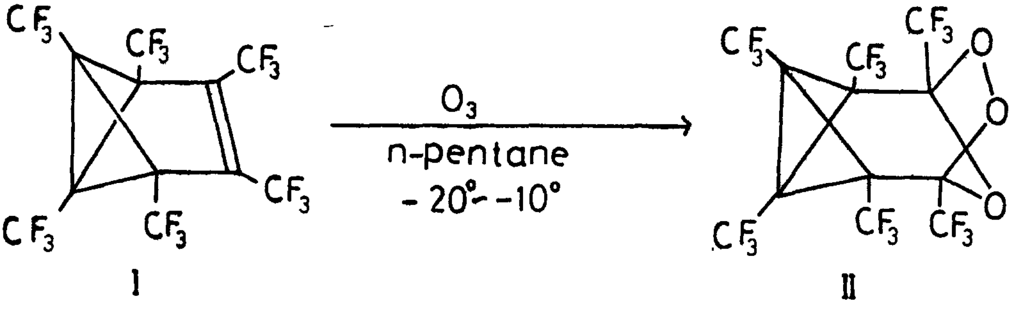
Attempted synthesis of non-substituted benzvalene ozonide was recently reported,[1] but the only compound that was isolated seemed to be a polymeric ozonide. Hexakis(trifluoromethyl)benzvalene (I)[2] is a very stable compound at room temperature owing to the perfluoroalkyl effect,[3] while non-substituted benzvalene itself is rather unstable.[4] We tried ozonolysis of I to obtain a stable ozonide of I, since such an ozonide was considered to be an interesting substrate for photoreaction.

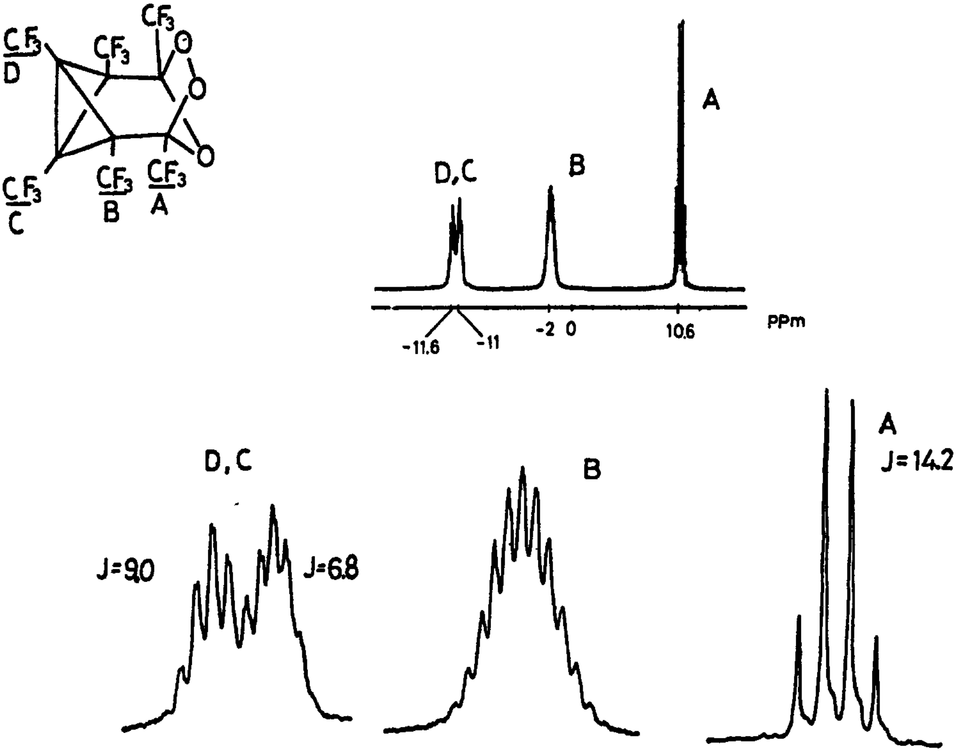
Bubbling of ozone into a solution of I in pentane at -20°to -10° gave hexakis(trifluoromethyl)benzvalene ozonide (II) quantitatively. II is a stable pale yellow liquid at room temperature and its IR spectrum shows weak absorp-



tion of a cyclopropane ring at 1538 cm^{-1}, without absorption in the carbon-carbon double bond region appearing in I. The structure of II was also supported without any inconsistency by the ^{19}F-NMR spectral data.[5] In the mass spectrum of II, no molecular-ion peak (mol. wt. 534) was observed, but m/e 324 peak corresponding to $C_4(CF_3)_4$ unit was observed in the fragmentation pattern. This fact means that the ozonide (II) could be a precursor of $C_4(CF_3)_4$ unit in photoreaction.

Therefore, we carried out the photolysis of II according to the methods used in the case of other types of ozonide.[6] The solution of II in 3-methylpentane, sealed in vacuum in a Pyrex tube, was irradiated at -196° for 8 hr with a high-pressure mercury lamp. On irradiation of this matrix, yellow coloration was observed, and this yellow color persisted at -196° after the lamp was switched off. When matrix was thawed gradually, the yellow color disappeared and

^{19}F NMR of Hexakis(trifluoromethyl)benzvalene ozonide



crystals came out immediately. These crystals were tetrakis(trifluoromethyl)-cyclobutadiene dimer (III); yield, 37.5% [colorless prisms, mp 204-205°; ^{19}F-NMR (hexafluorobenzene) -1.6 and -3.8 ppm, singlets of equal intensity; IR (Nujol), 1710 cm^{-1} (cyclobutenic double bond); mass spectrum, m/e 648 (M^{+})].

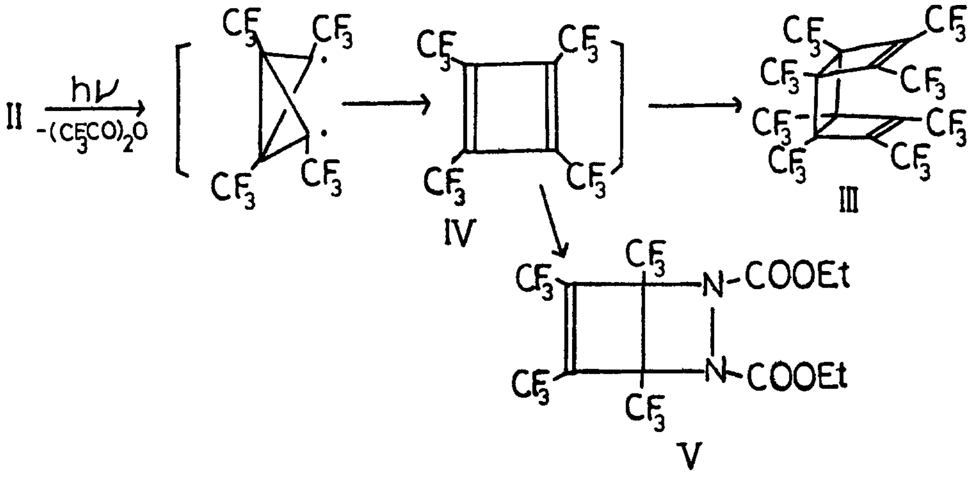
In this reaction, only one of two geometrical isomers (syn- and anti-) of tetrakis(trifluoromethyl)cyclobutadiene dimer was obtained. The spectral data and melting point of III are very similar to those of the dimer assigned as the anti-isomer by Miller and Pelosi.7) This fact seemed to be peculiar, since the Diels-Alder reaction of cyclobutadiene has been known to give the syn-dimer mainly.8) Therefore, X-ray analysis was carried out and the structure of III was established as the syn-type. The lattice constants and space group were determined by a Philips four-circle X-ray diffractometer (Cu Kα radiation) giving a=8.52Å, α=67.40' and R$\bar{3}$. The density of the crystal was calculated to be 2.12 g.cm^{-3}, assuming that one molecule was contained in the unit cell, which was consistent with the observed value. This is rather a surprising result since the symmetry of the space group requires an inversion triad axis for the molecule. However, in the syn-tetrachlorocyclobutadiene dimer, a similar result was obtained by Scherer and Meyers9), who assumed a random orientation of the diad axis of the molecule in the cubane-type crystal structure.

The present crystal may therefore be considered to have the same type of structure as with the syn-tetrachlorocyclobutadiene dimer. For comparison, the lattice constants of the three related crystals are given below.

Cubane10): a=5.34Å, α=72.26°, R$\bar{3}$, Z=1. Tetrachlorocyclobutadiene dimer11); a=7.20Å. α=72.3°. Present compound: a=8.52Å, α=67.7°.

In order to obtain the evidence that the tetrakis(trifluoromethyl)cyclobutadiene (IV) is an intermediate, photolysis of II was carried out in the presence of ethyl azodicarboxylate at room temperature. In this photolysis, 1:1 adduct (V) of IV and ethyl azodicarboxylate was obtained; 54.3% in yield, [colorless oil; ^{19}F-NMR (pentane) +7.4 and 0 ppm, singlets of equal intensity; ^{1}H-NMR (CCl_4), typical ethyl group signal; IR (film) 1695 cm^{-1} (cyclobutenic double bond), 1710 and 1790 cm^{-1} (C=O), 1200-1260 cm^{-1} (C-F); mass spectrum, molecular ion peak is not observed, m/e 453 (M-OEt)].

These results show that tetrakis(trifluoromethyl)cyclobutadiene (IV) is a precursor of III in the photoreaction, and the formation pathway of III is postulated as shown below.



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