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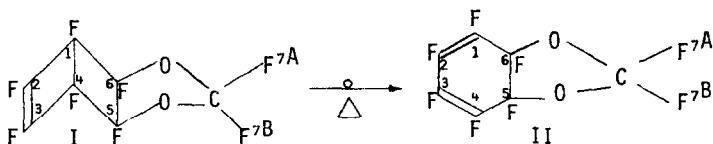
SHORT COMMUNICATION

THERMAL ISOMERIZATION OF A PERFLUOROBICYCLO[2.2.0]HEXENE DERIVATIVE

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In the course of our investigations on the addition reactions of bis(fluoroxy)difluoromethane to perfluorobicyclo[2.2.0]hexa-2,5-diene, we reported 5,6-difluoromethylenedioxyhexafluorobicyclo[2.2.0]hex-2-ene (I) as one of the volatile products [1]. In this paper we report that at 164°C I underwent first order irreversible ring expansion to 5,6-difluoromethylenedioxyhexafluorocyclohexa-1,3-diene (II).



I is a colorless liquid at room temperature with infrared absorption at 1740 for the olefinic bond, none at 1700 and a characteristic sharp strong absorption at 990 cm^{-1} , while II has two absorptions at 1740 and 1700 for the conjugated double bonds and almost no absorption at 990 cm^{-1} . The assignments of ^{19}F NMR of I were assisted by other known hexafluorobicyclo[2.2.0]-hexanes and -hexenes [2,3], and agreed with the recently reported value for I [1]: $\delta(1,4)$ 197.0, $\delta(2,3)$ 123.3, $\delta(5,6)$ 133.7, $\delta(7A)$ 51.3 and $\delta(7B)$ 62.2 ppm against external CFCl_3 . A gas chromatography-infrared analyzer (Perkin Elmer Model 567 and Sadtler CIRA 101) with the detector at 180°C, an infrared cell measured with a thermocouple at 164°C, an injection port at 160°C and a stainless steel column with 2% OV-210 on Chromsorb W at 100°C was used to record the infrared absorptions. The decreasing absorbance at 990 cm^{-1} (i.e. the characteristic peak for I) was observed with respect to time and with a new absorbance increasing at 1700 cm^{-1} (i.e. the characteristic peak for II). The semilog plots of the

absorbances ($A_0 - A$ at 1700 cm^{-1}) for II and (A at 990 cm^{-1}) for I versus time follow the first order dependence over four half lives. The half life at 164°C of I to II was 50 min.

The gas chromatography-mass spectrometry (LKB 9000 at 13eV) of molecule I showed a m/e value of parent ion at $268(\text{C}_7\text{F}_8\text{O}_2^+)$. After heating the sample at 190°C for 4 hr, the gas chromatography-mass spectral data recorded an identical m/e value of the parent ion at $268(\text{C}_7\text{F}_8\text{O}_2^+)$ but with different elution time and mass cracking patterns indicating the presence of isomer II. The ^{19}F NMR of II agreed with the recently reported value of II [4]; $\delta(1,4)$ 161.2, $\delta(2,3)$ 155.0, $\delta(5,6)$ 121.0, $\delta(7A)$ 58.7 and $\delta(7B)$ 63.8 ppm against external CFCl_3 .

Mass spectroscopic molecular weight (CEC21-110-B) of II: Found, 267.9788. Calculated for $\text{C}_7\text{F}_8\text{O}_2$, 267.9770.

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- 1 M.S. Toy and R.S. Stringham, J. Fluorine Chem., 13 (1979) in press.
- 2 M.G. Barlow, R.N. Haszeldine, W.D. Morton and R.D. Woodward, J. Chem. Soc. Perkin I, (1962) 2170.
- 3 L. Cavalli, J. Chem. Soc. (B), (1970) 1616.
- 4 M.S. Toy and R.S. Stringham, J. Polymer Sci Part A-I, 16 (1978) in press.