

## SYNTHESIS AND PROPERTIES OF 1-VINYL-2, 2, 3, 3-TETRAFLUOROCYCLOBUTANE

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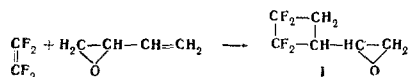
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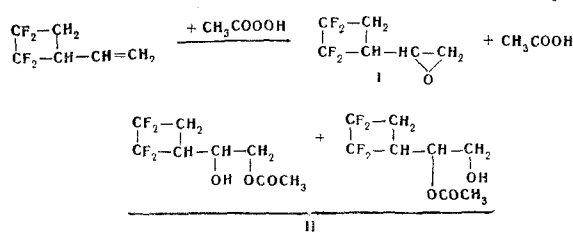
The oxidation, hydrobromination, and bromoacetylation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane are investigated, with a view to preparing its oxide. It is found that the most convenient method of preparing this oxide is acetyl hydroperoxide oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.

Oxidation of poly- and perfluoroolefins with hydrogen peroxide and oxygen is known to give [1-4] fluorinated epoxides. Oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane, one of the accessible fluoroolefins, has not been investigated. In addition, the method makes accessible both oxide and glycol, which are of interest for synthesizing fluorinated polyesters.

Originally 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane I was obtained by copolymerization of tetrafluoroethylene with butadiene monoxide [5].

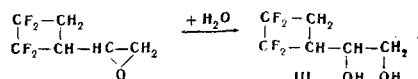


However, the yield was very low (9%). The present work studied acetylhydroperoxide oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane. The method made it possible to obtain a 60-70% yield of I. In addition there was isolated a low yield of a side reaction product, 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane monoacetate, arising by reaction of I with acetic acid.

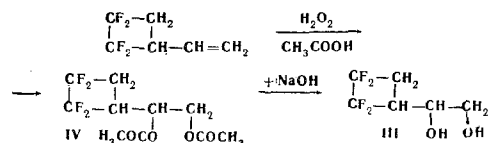


The rate of oxidation is greatly dependent on the temperature. Raising the temperature accelerates the process, the yield being practically unaltered (63-70%).

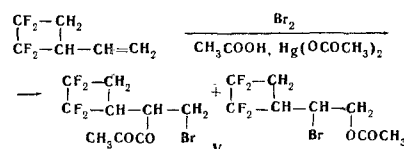
To confirm the structure of I it was hydrated, and glycol III was obtained in 50% yield.



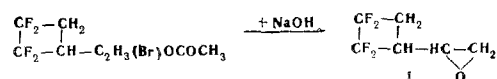
The glycol was also synthesized by oxidizing 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane with hydrogen peroxide in acetic acid solution, and then subjecting the resultant diacetate IV to alkaline hydrolysis.



Glycol III, as prepared by hydrating oxide I, and the glycol obtained by oxidizing 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane with hydrogen peroxide, were identical with respect to melting points and boiling points, IR spectra, elementary analyses, and molecular weights (see table and fig.). The literature [6] describes an indirect method of preparing fluorinated oxides from bromohydrins or bromoacetates by treating them with alkali. For example, this method was used to prepare trifluoropropene. It was of interest to compare this with the oxidation method. For this purpose the bromoacetate V was prepared by the following procedure

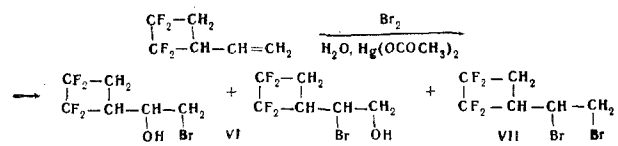


and it was cyclized with alkali under conditions similar to those used for trifluoropropene oxide [6].

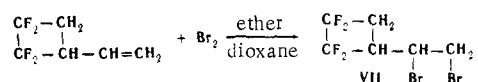


This gave only a 10% yield of oxide I. The main reaction product was polymer.

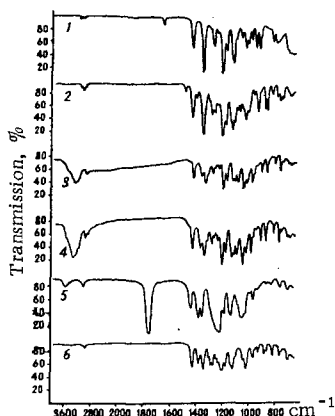
An attempt to hydrobrominate 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane to the bromohydrin, and cyclize the latter, gave a mixture of bromohydrin VI and dibromide VII, which could not be separated. Furthermore, cyclization of the bromohydrin was inconvenient.



The dibromide in the mixture was identified by brominating 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.



Thus, of the originally mentioned routes to 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane, the best results were given by acetyl peroxide oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.



IR spectra of compounds prepared, determined with a DS-301 instrument, between NaCl plates, layer thickness 5–10 $\mu$ . 1) 1-Vinyl-2, 2, 3, 3-tetrafluorocyclobutane; 2) oxide I; 3) glycol III (an oxidation product of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane); 4) glycol III (hydration product of oxide I); 5) diacetate IV; 6) dibromide III.

The IR spectra of most of the compounds prepared were determined (see figure). The spectrum of the oxide I showed the characteristic absorption band of the epoxide group in the 6.6  $\mu$  region, in accord with the literature data [2] regarding fluorinated epoxides.

## EXPERIMENTAL

**1-Vinyl-2, 2, 3, 3-tetrafluorocyclobutane** was synthesized from tetrafluoroethylene and butadiene by the method described in the literature [5].

The purities of the compounds synthesized were checked with a LKhM-7 gas-liquid chromatograph, made by SKB IOKh AN SSSR (Special Design Office, Institute of Organic Chemistry, AS USSR). Compounds containing two different substituents gave two separate peaks, showing the presence of  $\alpha$  and  $\beta$  isomers (e. g., in the cases of the monoacetate, bromoacetate, bromohydrin ex 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane). The table gives constants and elementary analyses.

**Oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane with acetyl hydro-peroxide.** A flask was charged with 61.6 g (0.4 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane, which was vigorously stirred, and 42 ml 78% acetylhydroperoxide in 20 ml ether added dropwise at room temperature (18°–20° C), when the temperature rose to 26°. After all the peroxide had been added, the products were allowed to stand

for 15–17 days, and at the end of that period, the hydroperoxide content of the mixture was about 4%. If the reactants were heated at 40°–50° for 6 hours daily, the reaction took 8 days, while if the heating was at 50°–70°, it took 3 days. Then the products were diluted with ether, and treated with water until they gave a negative reaction for hydroperoxide. The ether solution was dried over  $K_2CO_3$ , the ether distilled off, and the residue vacuum-distilled. Yield of oxide 60–70%, calculated on the reacted 1-vinyl-2, 2, 3, 3-tetrahydrocyclobutane. In addition to the oxide, a mixture of isomeric monoacetates of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane was obtained, yield 2%. M (cryoscopic) 232, 228 (calculated 230).

**Hydration of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane oxide.** A flask was charged with 7.7 g (0.045 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane oxide, 15 ml (0.83 mole) water, and 0.08 g conc.  $H_2SO_4$ , and the whole stirred for 4 hr at 80°–90° C, after which the hydration product was extracted with ether. The ether solution was washed with water until neutral, then dried over  $MgSO_4$ , the ether distilled off, and the residue vacuum-distilled. The glycol of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane was a pleasant smelling white waxy compound, mp 48°–49°, soluble in water, EtOH, dioxane, acetone, ether, and insoluble in benzene, heptane,  $CCl_4$  and  $CHCl_3$ . Mp 48°–49°, M (cryoscopic) 187, 190 (calculated 188). Yield of glycol III, 50%.

**Oxidation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane by hydrogen peroxide.** A 3-necked flask was charged with 20.8 g (0.2 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane, 200 ml glacial AcOH, and 4.5 g conc.  $H_2SO_4$ . The whole was vigorously stirred, and 27 ml 28%  $H_2O_2$  added at 40° C, dropwise. The products were heated and stirred daily, for 6 days, for 6 hr a day, until the  $H_2O_2$  content was 0.38%. Then the AcOH was distilled off, (52°–56°/104 mm). An intermediate reaction product was 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane diacetate, which was saponified with 10% alkali (20 ml) at 100°, for 1 hr. After treatment with 10% HCl, the products were extracted with ether, the ether solution washed with water until neutral, dried over  $MgSO_4$ , the ether distilled off, and the residue vacuum-distilled, to give a 50% yield of glycol, mp 48°–50°, M (cryoscopic) 188, 190 (calculated 188).

**Bromoacetylation of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.** A 3-necked flask was charged with 50 ml glacial acetic acid and 20 g mercuric acetate. The flask was cooled with ice-water and 16 g (0.10 mole) bromine and 16 g (0.10 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane added with vigorous stirring. The reaction temp. was maintained at 16°–20°. When the reaction was completed, the mercuric bromide precipitate was filtered off, and washed with water and ether. 200 ml ice-water was added to the filtrate and the organic layer separated from the aqueous layer. The latter was neutralized with alkali and extracted with ether. The organic layer was mixed with the ether extracts, washed with water and  $Na_2CO_3$  solution

Physical Properties and Elementary Analyses of Compounds Prepared

| Compound   | Bp, °C<br>(pressure<br>mm) | $d_4^{20}$ | $n_D^{20}$ | $M_R$ |                 | Formula              | Found, %       |              |                |                | Calculated, % |      |       |       |
|--|----------------------------|------------|------------|-------|-----------------|----------------------|----------------|--------------|----------------|----------------|---------------|------|-------|-------|
|  |                            |            |            | found | calcu-<br>lated |                      | C              | H            | F              | Br             | C             | H    | F     | Br    |
| 1-Vinyl-2, 2, 3, 3-<br>tetrafluoro-<br>cyclobutane <sup>1*</sup> | 82—84                      | 1.1848     | 1.3503     | 27.99 | 27.25           | $C_6H_6F_4$          | 46.80<br>46.60 | 3.72<br>3.92 | 49.12<br>49.51 | —              | 46.75         | 3.89 | 49.35 | —     |
| I <sup>2*</sup>  | 37—39 (8)                  | 1.3763     | 1.3686     | 27.84 | 27.44           | $C_8H_6F_4O$         | 42.53<br>42.42 | 3.88<br>3.97 | 44.50<br>44.80 | —              | 42.35         | 3.52 | 44.70 | —     |
| II <sup>3*</sup>   | 113 (8)                    | 1.3941     | 1.3993     | 39.93 | 40.29           | $C_8H_{10}F_4O_3$    | 41.72<br>41.95 | 4.52<br>4.74 | 35.10<br>34.80 | —              | 41.73         | 4.25 | 33.04 | —     |
| IV   | 90 (2)                     | 1.3252     | 1.3984     | 49.58 | 49.81           | $C_{10}H_{12}F_4O_4$ | 43.90<br>44.17 | 4.50<br>4.61 | 27.86<br>27.74 | —              | 44.11         | 4.41 | 27.94 | —     |
| III <sup>4*</sup>  | 87—89 (2.5)                | —          | —          | —     | —               | $C_8H_8F_4O_2$       | 38.80<br>38.60 | 4.67<br>4.54 | 40.70<br>40.60 | —              | 38.29         | 4.25 | 40.22 | —     |
| V  | 75—77 (2)                  | 1.6312     | 1.4262     | 46.04 | 46.48           | $C_6H_8F_4O_2$       | 38.20<br>38.40 | 4.17<br>4.36 | 40.30<br>40.65 | —              | 38.29         | 4.25 | 40.22 | —     |
| VII  | 57—58 (3)                  | 1.9818     | 1.4612     | 43.49 | 43.15           | $C_8H_6Br_2F_4$      | 32.20<br>31.95 | 2.94<br>2.97 | 25.80<br>26.00 | 27.25<br>27.21 | 32.76         | 3.07 | 25.93 | 27.27 |
|  |                            |            |            |       |                 | $C_8H_6Br_2F_4$      | 23.07<br>22.86 | 2.20<br>2.14 | 24.09<br>24.10 | 51.20<br>51.00 | 22.92         | 1.91 | 24.20 | 50.95 |

1\* Literature: bp 83°–85° C;  $d_4^{25}$  1.1866,  $n_D^{25}$  1.3480.

2\* Literature: bp 74°–75° C (67 mm);  $n_D^{25}$  1.3730.

3\* Mixture of isomers.

4\* Hydration product of oxide I.

5\* Oxidation product of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.

and again with water till neutral. After drying with  $MgSO_4$  the ether was distilled off, and the residue vacuum-distilled. Yield 25 g (87%) of a mixture of isomeric bromoacetates.

**Hydrobromination of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.** A reaction vessel was charged with 50 ml water and 20 g mercuric acetate. The mixture was stirred at room temperature, and the following added simultaneously: 16 g (0.1 mole) Br and 16 g (0.1 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane. The reaction products were worked up as described above, for the previous experiment. It was impossible to isolate pure bromohydrin. A mixture of isomeric bromohydrins and dibromide was formed.

**Bromination of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane.** A flask was charged with 8 g (0.05 mole) 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane in 40 ml ether and 20 ml dioxane, and 8 g (0.05 mole) Br added at 5°–10° C. The products were left overnight, then washed with  $Na_2CO_3$  solution and water. The ether solution was dried over  $MgSO_4$ , the ether distilled off, and the residue vacuum-distilled, to give a 50% yield of dibromide.

**Synthesis of 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane oxide from 1-vinyl-2, 2, 3, 3-tetrafluorocyclobutane bromoacetate.** A Claisen flask was charged with 11 g (0.037 mole) bromoacetate, which was heated to 100° C in a current of N at 30 mm, and 20 ml 75% aqueous alkali added, dropwise. When all the alkali had been added, the temperature was raised to 120°, and the resultant oxide distilled off, along with water. The product obtained by distilling off was treated with ether, the ether solution washed till neutral, dried

over  $K_2CO_3$ , and distilled. Yield 0.68 g (10%) oxide I, bp 37° (7 mm)  $n_D^{20}$  1.3686. The residue in the reaction flask was treated with 10% HCl until slightly acid, extracted with ether, the ether extract washed with water till neutral, then dried over  $MgSO_4$ . After the ether had been distilled off, a viscous mass remained in the flask, and on distilling it changed to a brittle resin.

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