in carbon tetrachloride; the infrared spectrum exhibited a band at 1630 cm.$^{-1}$ ($>C=C<$ stretching).

Preparation of 1,1,3,3-Tetrafluoro-2,2,4,4-tetramethylcyclobutane (III).—Tetramethylcyclobutanedione (160 g.) and 2 ml. of water were placed into a 1.8-l. rocking autoclave and cooled −78° under N_2. After addition of 450 g. of sulfur tetrafluoride, the reaction was carried out for 60 hr. at 160°. After venting the unreacted gas, 230 g. of a brown, crystalline product was recovered. Two distillations yielded a colorless product, 153.7 g., 73%, m.p. 65°, b.p. 110°. The infrared spectrum had major bands at 845, 970, 1065, 1095, 1260, 1390, and 1480 cm.$^{-1}$ The n.m.r. spectrum showed a quintet at 72 c.p.s. below TMS in carbon tetrachloride (J = 1.6 c.p.s.).

Anal. Calcd. for $C_8H_{12}F_4$: C, 52.2; H, 6.5; F, 41.3. Found: C, 52.4; H, 6.8; F, 41.3.

Pyrolysis of 1,1,3,3-Tetrafluoro-2,2,4,4-tetramethylcyclobutane (III).—III (19.4 g.) was passed through an unpacked 50-cm. long tube at 690° (wall temperature) and 0.08–0.1 mm. Injection was through a capillary tube into the hot zone in order to have better control. The pressure of III was kept below 1 mm. by cooling. The pyrolysis vapors were passed through a −70° cold trap (13.1 g. of starting material was recovered) and then through a liquid N_2 trap (5.2 g. recovered). Vapor phase chromatography showed the second trap contents to be 85% 1,1-difluoro-2-methylpropene[11,7] (V). Its infrared spectrum showed a strong band at 1760 cm.$^{-1}$ ($>C=C<$ stretching).

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Cyclization of Methallyloxyethanol

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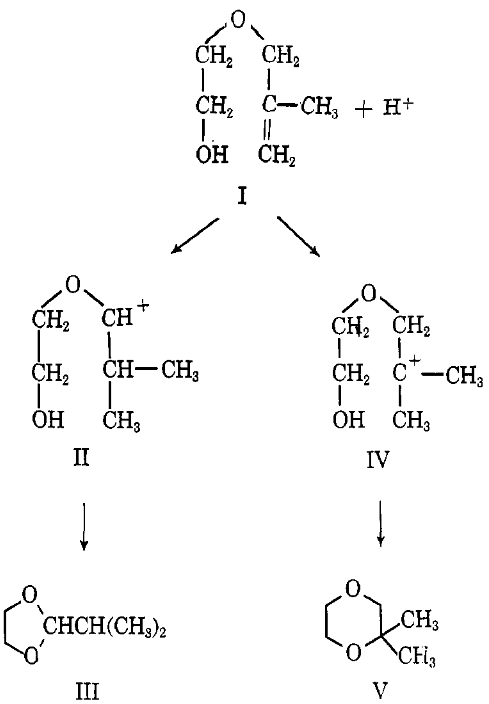
Several methods for the preparation of the derivatives of dioxolane have been described.[1] The present Note reports on the synthesis of 2-isopropyldioxolane and corrects some information appearing in the literature.

It has been reported[2] that cyclization of methallyloxyethanol (I) with concentrated sulfuric acid yields 2,2-dimethyldioxane-1,4 (V). We have repeated the synthesis according to the described procedure[2] and have obtained a product which has the same physical properties as that described in the original paper.

However, the spectrographic data are not in agreement with the proposed structure. The n.m.r. spectrum shows some features which are characteristic of the existence in the molecule of an isopropyl group. Namely, (1) there is a multiplet centered at 1.75 p.p.m. which integrates to an intensity of 1 and can be attributed to the proton adjacent to the two methyl groups. Such a proton would not be found in compound V. (2) There is a doublet at 0.95 p.p.m. with intensity of 6 which is assigned to the two methyl groups of an isopropyl group. (3) There is a doublet centered at about 4.6 p.p.m. with an intensity of 1, whose low-field position can be attributed to methine hydrogen which is in position related to the two ether oxygens as shown in III and which is split by the adjacent methine hydrogen to give a doublet. Such a single low-field hydrogen would not be expected in compound V and the splitting would not be expected. The examination of the infrared spectrum shows a band at 1365 cm.$^{-1}$ which can be correlated to the existence of the isopropyl group. The band at higher frequency is masked by a more intense band.



Chemical evidence for the cyclic acetal structure was obtained by hydrolysis to isobutyraldehyde and by synthesis from ethylene glycol and isobutyraldehyde.[3] The product had properties and spectra identical with the compound obtained from I.

It can be concluded that the compound described by Meltzer as 2,2-dimethyldioxane-1,4 is instead 2-isopropyldioxolane. The results of our work show that in acid environment the methallyloxyethanol is isomerized preferentially to 2-isopropyldioxolane. This particular cyclization can be explained if one postulates the formation of a hypothetical intermediate ion (II) which is more probable than the corresponding ion (IV), because the positive charge in intermediate II is stabilized by the neighboring oxygen.

Experimental Section

Methallyloxyethanol was prepared and isomerized according to Meltzer, *et al.*[2] The purity of the obtained compound has been found by gas chromatography to be 97%. The compound has been further purified with a preparative gas-chromatographic column [Perkin-Elmer 154 modified, 300 × 2.5 cm., Celite 545 (60–80 mesh)–diisodecyl phthalate (20:80), 80°, helium at 300 cc./min.]. The purified compound has b.p. 122°, n^{25}_{D} 1.4094.

Hydrolysis of 1.2 g. of 2-isopropyldioxolane with dilute hydrochloric acid on a steam bath for 3 hr. gave isobutyraldehyde as shown by the formation of a 2,4-dinitrophenylhydrazone whose m.p. 178–180° was not depressed by an authentic sample.

The infrared spectrum was obtained on a pure liquid sample (thickness, 0.01 mm.) with a Perkin-Elmer Model 221 spectrophotometer with NaCl optics. The n.m.r. spectrum was recorded from a 20% solution in CCl_4 with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

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