plete reaction showed only the diphenylpropane and starting material.

**Reaction of the Unknown with Alcohols.**—A solution of 23.9 mg. of the unknown in 2.0 ml. of absolute, reagent grade methanol was maintained at room temperature, and the reaction was monitored by thin layer chromatography using silica gel plates. The plates were developed with 50:50 ether–petroleum ether. The first sample was taken after 1 min. Appreciable bis(2,3-diphenylcyclopropenyl) ether had already formed at that time. After 35 min. there was no detectable trace of the starting material left. The thin layer showed only one spot corresponding to the bis ether. The identity of the product was confirmed by removing the solvent and comparing the residue with the known material.

When the unknown was dissolved in isoamyl alcohol instead of methanol, it was possible to follow production of the other anticipated reaction product, the alkyl nitrite. Isoamyl nitrite was indeed observed by g.l.p.c. and, although the yield was not determined precisely, it appeared to be nearly quantitative.

**Acknowledgment.**—J. W. K. wishes to thank the Ford Foundation for financial support during a portion of the time when this research was underway. The authors wish also to thank Dr. W. S. Brey, Jr., for conducting the n.m.r. investigations.

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## Preparation of 1,1-Dihalo-2-methylpropenes

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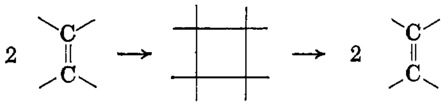
The high reactivity of many olefinic compounds somewhat restricts potential reactions at their functional groups. If such reactions have to be carried out, it is necessary to eliminate the olefinic double bond temporarily. A convenient route for this purpose is reported in this note.

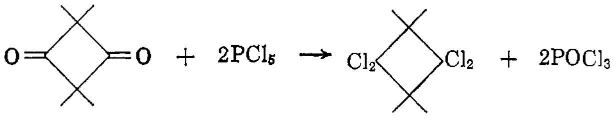
It is well known that under proper conditions many ethylene derivatives can be dimerized, forming cyclobutane derivatives.[2–3] At higher temperatures this reaction can be reversed.[4–7]



Reactions at the functional groups can be carried out with the cyclobutane derivatives and following this the reaction product may be cleaved.

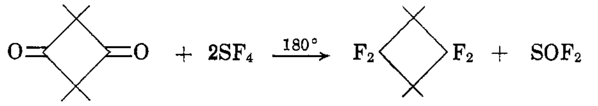
This route is especially suited for ethylenes which form symmetrical cyclobutanes by head-to-tail dimerization. The feasibility of this route has been shown by the conversion of dimethylketene into dimethyldihaloethylene.

Dimethylketene can be easily dimerized to 1,1,3,3-tetramethylcyclobutanedione (I).[8] The reaction of the dione I with phosphorus pentachloride in refluxing carbon tetrachloride forms 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane (II) in almost quantitative yield.



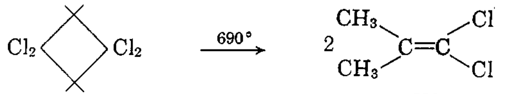
I II

More vigorous conditions have to be applied for the preparation of 1,1,3,3-tetrafluoro-2,2,4,4-tetramethylcyclobutane (III). I has to be heated with a twofold excess of sulfur tetrafluoride in the presence of hydrogen fluoride at 160° for 60 hr. None of III is isolated if the reaction is carried out without catalyst.[9]



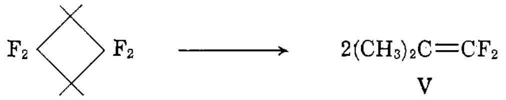
I III

The pyrolysis of II is carried out at 690° (wall temperature) and 0.1–0.5 mm. The formation of side products is reduced if the pyrolysis is run in an unpacked tube. The yield of IV is 34% at a conversion of 39%.



II IV

1,1-Difluoro-2-methylpropene (V) is isolated in 23% yield at a conversion of 33%.



III V

### Experimental Section

**Preparation of 1,1,3,3-Tetrachloro-2,2,4,4-tetramethylcyclobutane (II).**—A mixture of 200 g. of tetramethylcyclobutanedione, 1000 g. of phosphorus pentachloride, and 2 l. of carbon tetrachloride was heated at reflux temperature for 3 hr. Carbon tetrachloride and most of the phosphorus oxychloride were distilled off. The remaining liquid was poured with stirring over crushed ice. The solid was isolated by filtration and recrystallized from a mixture of ethanol and water: yield 317 g., 89%, m.p. 234–236°.

*Anal.* Calcd. for $C_8H_{12}Cl_4$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.4; H, 4.5; Cl, 56.6.

The infrared spectrum showed major bands at 955 (breathing vibration, cyclobutane ring), 1370, and 1385 (*gem*-dimethyl) cm.$^{-1}$, besides 840, 880, 1205, and 1450 cm.$^{-1}$. The n.m.r. spectrum has a singlet at 92 c.p.s. with carbon tetrachloride as solvent and tetramethylsilane as the internal standard using a Varian A-60 n.m.r. spectrometer.

**Pyrolysis of 1,1,3,3-Tetrachloro-2,2,4,4-tetramethylcyclobutane (II).**—During a 2-hr. period 40 g. of II was passed through a 30-cm. long tube, which was heated at 700° at 0.1–0.5 mm. The vapors were condensed in a Dry Ice–acetone trap. Fractionation yielded 13.7 g. (34%) of dichloromethylpropene (IV), b.p. 108–110°,[10] and 24.2 g. of starting material.

The n.m.r. spectrum showed a singlet at 113 c.p.s. below TMS

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[1] Farbenfabriken Bayer A.-G., Werk Uerdingen, Wissenschaftliches Hauptlaboratorium, Krefeld, Germany.

[2] A. L. Henne and R. P. Ruth, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[3] M. Prober and W. T. Miller, *ibid.*, **71**, 598 (1949).

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[5] R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

[6] B. F. Gray and H. O. Pritchard, *J. Chem. Soc.*, 1002 (1956).

[7] J. L. Anderson, U. S. Patent 2,733,278 (1956).

[8] H. Staudinger and E. Suter, *Ber.*, **53**, 1085 (1920).

[9] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[10] J. Faworski, *Chem. Zentr.*, 606 (1899).

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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[11] R. S. Corley, S. G. Cohen, M. S. Simon, and H. T. Wolosinski, *J. Am. Chem. Soc.*, **78**, 2608 (1956).

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# Cyclization of Methallyloxyethanol

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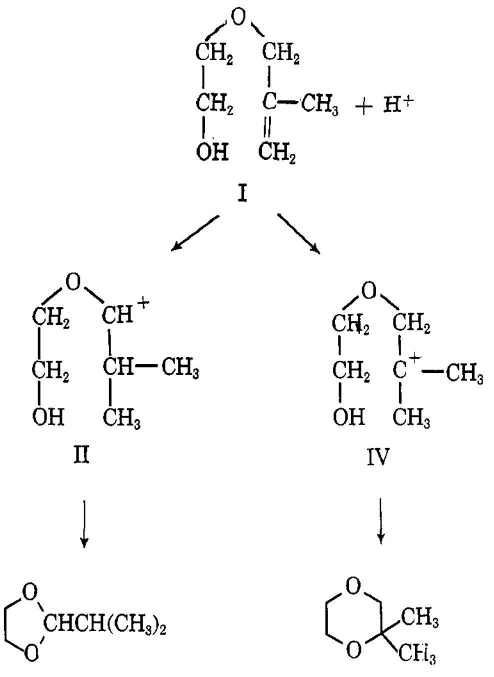
Several methods for the preparation of the derivatives of dioxolane have been described.[1] The present Note reports on the synthesis of 2-isopropyldioxolane and corrects some information appearing in the literature.

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.



I II IV III V

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°, $n^{25}\mathrm{D}$ 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.

**Acknowledgments.**—This work has been supported by the U. S. Department of Army, European Office, Contract DA 91-591-EUC-3079.

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[2] R. I. Meltzer, A. D. Lewis, and A. Fischman, *J. Org. Chem.*, **24**, 1763 (1959).

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