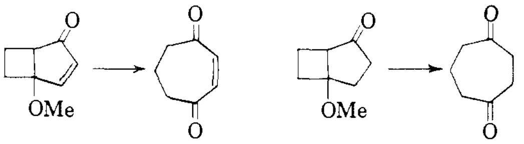
ten-1,4-dione was synthesized by an unequivocal method.[6] Dilute aqueous acid at room temperature rapidly converted IV to cycloheptan-1,4-dione (VI) which was characterized by the bis-2,4-dinitrophenylhydrazone previously reported by Cope.[7] This transformation is so facile that treatment of IV with a solution of 2,4-dinitrophenylhydrazine in cold ethanolic acid gives directly the bis-2,4-dinitrophenylhydrazone of VI. The acid catalyzed openings of the bicyclic system in II, III and IV reported above are in sharp contrast to the reported failure of such reactions in related systems.[8] The success of the reaction in the present cases presumably is due to the strategic location of the methoxyl group.



III V IV VI

Satisfactory analyses have been obtained for all new compounds either directly or for the 2,4-dinitrophenylhydrazones

The anomalous ultraviolet spectrum of II and additional transformations of II will be discussed in a forthcoming paper.

Acknowledgment.—The authors are pleased to acknowledge financial support of this work by the Research Corporation through a Frederick Gardner Cottrell grant.

(6) O. L. Chapman and D. J. Pasto, unpublished results.

(7) A. C. Cope, J. A. Liss and G. W. Wood, THIS JOURNAL, **79**, 6287 (1957).

(8) See the reference in footnote 3 to the work of Forbes.

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O. L. CHAPMAN
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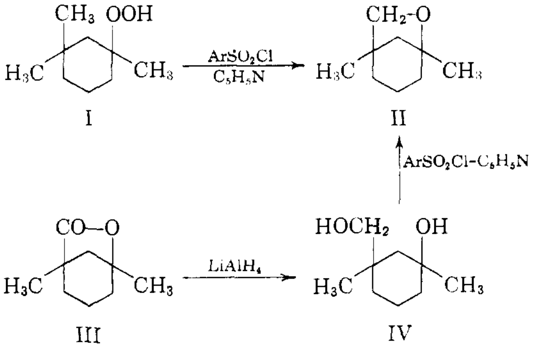
RECEIVED NOVEMBER 14, 1958

CATIONIC DISPLACEMENT OF HYDROGEN BY OXYGEN AT A SATURATED CARBON ATOM

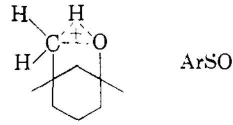
Sir:

Although the oxygenation of paraffinic groups via free radical chain reactions is well known,[1] the replacement of alkyl hydrogen by oxygen using cationic oxygen species does not appear to have been realized. This note reports evidence that such an ionic substitution process can be effected and that intramolecular attack can be directed at a specific carbon atom.

The substance used in this study of oxidation by cationic oxygen was 1,3,3-trimethylcyclohexyl hydroperoxide (I), obtained from 1,3,3-trimethylcyclohexanol[2] using freon—25% hydrogen peroxide in 50% sulfuric acid[3] (70% yield); *p*-nitrobenzoyl derivative, m.p. 113.5–114° (dec.), found: C, 62.53; H, 6.75; infrared max. 1755 cm.$^{-1}$. Reaction of the hydroperoxide I with *p*-nitrobenzenesulfonyl chloride in cold pyridine–methylene chloride produced the *bicyclic ether II*, which was synthesized unambiguously for comparison from the known lactone III[4] by reduction (lithium aluminum hydride) to the diol IV, m.p. 78–78.5°, found: C, 68.41; H, 11.59; followed by cyclization (*p*-toluenesulfonyl chloride); found for II: b.p. 66.5–67° (31 mm.), $n^{20}\text{D}$ 1.4466; C, 77.15; H, 11.66. The identity of the products obtained from the hydroperoxide I and the lactone III was established by identical vapor chromatographic constants on nonyl phthalate and Carbowax columns at six different temperatures and from the correspondence of the characteristic infrared and nuclear magnetic resonance spectra. The latter spectrum exhibits a quartet centered at +48 c.p.s. (at 40 mc., relative to water) due to $-CH_2-O-$, two methyl peaks at +138 and +146 c.p.s. and a peak from the remaining eight protons at +129 c.p.s. The yields of II obtained from the hydroperoxide I have been in the range 5–10%; however, optimum conditions have not yet been determined.



Since O–O cleavage of the *p*-nitrobenzenesulfonyl derivative of I is doubtless heterolytic under the conditions used,[5] we consider the change I → II as proceeding via a cationic transition state such as V, a mechanism intermediate between the extremes for attack of cationic oxygen (1) exclusively on hydrogen and (2) exclusively on carbon. We have not been able to detect II as a product of thermal or photochemical decomposition of I or its *p*-nitrobenzoate.



V

The reaction I → II is particularly interesting as a possible chemical counterpart of enzymatic hydroxylation at a saturated carbon which also appears to involve electrophilic oxygen[6] and which proceeds by frontal displacement as implied by V.[7–9] It also may be related to the ozone–decalin reaction.[10]

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RECEIVED NOVEMBER 10, 1958

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(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 9.

(2) A. W. Crossley and C. Gilling, *J. Chem. Soc.*, **97**, 2220 (1910).

(3) We are indebted to Prof. N. A. Milas for suggesting this procedure.

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(11) National Science Foundation Predoctoral Fellow 1956–58. This work was supported also by U. S. Public Health Grant 4565.