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ALLENE OXIDES. THE PERACID OXIDATION OF TETRAMETHYLALLENE

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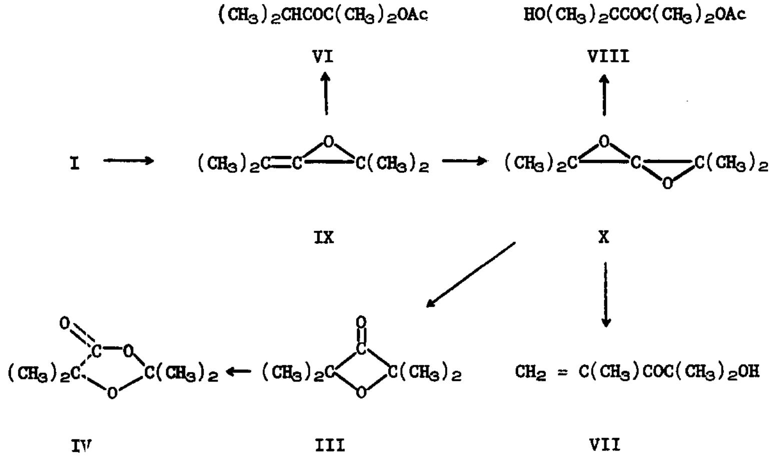
In connection with synthetic studies directed toward obtaining a stable molecule with an allene oxide structure[1], we have examined the peracid oxidation of allenes[2]. The present report describes some results of this work which provide evidence regarding the existence and reactivity of this strained heterocyclic system. A point of particular interest involves the possibility of interconversion of allene oxides with their formal valence tautomers, cyclopropanones[3].

Peracetic acid oxidation of a methylene chloride solution of tetramethylallene (I) in the presence of powdered sodium carbonate as a buffering agent[4] resulted in a mixture of products of widely differing physical properties. The infrared spectrum of the crude product exhibited striking carbonyl absorption of medium intensity at 5.49 and 5.57 μ, in addition to more common, longer wavelength carbonyl bands. Preparative gas chromatography provided the 5.49 μ component as a volatile, crystalline solid, mp 45-6°, whose nmr spectrum consists of a single, sharp resonance at τ 8.60. While the spectroscopic data were in accord with expectation for tetramethylcyclopropanone (II)[3], which was an unknown entity at the time of this observation; further examination revealed that the compound is, in fact, the known oxetanone

III^5. The 5.57 μ material was subsequently identified as lactone IV [Found: C, 58.09; H, 8.29. Nmr: equivalent singlets at τ 8.48 and 8.60]. Baeyer-Villiger oxidation of III with peracetic acid also produced IV. Other major products were determined to be 2-acetoxy-2,4-dimethyl-3-pentanone^6 (VI), 4-hydroxy-2,4-dimethylpent-1-en-3-one (VII) [Found: C, 65.37; H, 9.65. IR: 2.86, 3.33, 6.02 and 6.12 μ. Nmr: τ 3.92 (1,m), 4.23 (1,m), 5.86 (1,s), 8.11 (3,m) and 8.56 (6,s), UV: λ_{max}(EtOH) 221 mμ (ϵ 7700)], and 2-acetoxy-4-hydroxy-2,4-dimethyl-3-pentanone (VIII) [Found: C, 57.32; H, 8.64. IR: 2.9, 5.75, 5.83 and 7.9 μ. Nmr: singlets at τ 6.84 (1), 7.93 (3), 8.36 (6) and 8.55 (6)]. With the exception of VI these compounds all represent higher oxidation states than the desired allene oxide IX.

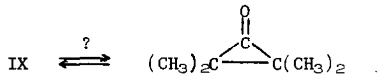
CHART I



Thus, a satisfactory explanation of the product data appears to require the existence of a real intermediate which is capable of being further oxidized and eventually converted to the observed materials. Tetramethylallene oxide (IX) satisfies this requirement uniquely and a scheme utilizing IX as the key intermediate is shown in Chart I. After formation of the allene oxide, this reactive species is partitioned between addition of acetic acid to give VI and reaction with a second equivalent of peracid. An attractive hypothesis which economically accounts for the more highly oxidized products is that epoxidation of IX leads to the 1,4-dioxaspiropentane[7] X. This interesting intermediate conveniently provides a second branching point in the reaction scheme from which rearrangement to the oxetanone III and the unsaturated ketone VII can occur. These transformations (which may be thermal or acid-catalyzed processes) are in competition with the addition of acetic acid to X to generate VIII. Appropriate control experiments have demonstrated that III is not the precursor of VII or VIII, whereas it does produce IV under the reaction conditions. In addition VI and VIII were shown to be stable to the reaction and isolation conditions. The experimental conditions for the epoxidation have been varied over a wide range. Suffice it to say for the present that the variation in products observed is in general accord with the proposed scheme.

Our results lead us to propose that allene oxide IX is a molecule of finite existence which intercedes in the epoxidation of allenes and which can reasonably be expected to be isolable under the appropriate experimental conditions. A similar statement can be made concerning

X but with much less conviction. Studies designed to substantiate these predictions by actual isolation are currently in progress.



II

The important question raised earlier regarding the possibility of valence tautomerism between IX and II unfortunately cannot be answered with any certainty at the present time due to the paucity of information concerning these interesting chemical species. However, the present work provides no positive evidence implicating cyclopropanones as intermediates in allene epoxidation reactions.

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7. An early claim for this ring system [D. Vorlander and P. Weinstein, Ber., 56, 1124 (1923)] has been shown to be incorrect by G. B. Hoey, D. O. Dean and C. T. Lester, J. Am. Chem. Soc., 77, 391 (1955). A similar proposal incorporated into Ref. 2b is not adequately documented and this structure, as well as that of the precursor allene, is highly suspect.