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FREE RADICAL REACTIONS OF CYCLOPROPANOLS: THE FORMATION OF 1,2-DIOXOLANE DERIVATIVES

Dorothy H. Gibson and C. H. DePuy

Department of Chemistry, University of Colorado

Boulder, Colorado 80302

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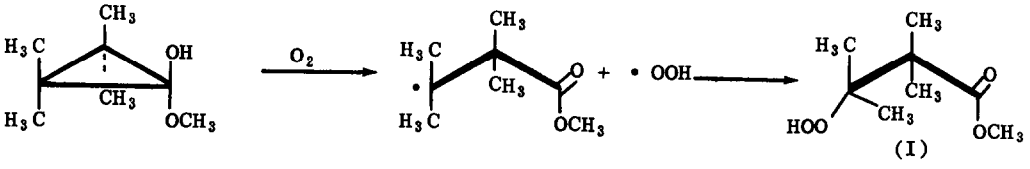
In another study we examined the behavior of radicals produced from cyclopropanol derivatives at low temperatures.[1] We now wish to report the free radical reactions of several members of this class of unusual alcohols with molecular oxygen. Whereas abstraction of a hydrogen atom from an alcohol by molecular oxygen is a well characterized process, abstraction occurs at the α-carbon of the alcohol and not at the hydroxyl group.[2] We now suggest that the presence of the adjacent cyclopropane ring renders the hydroxyl hydrogen of cyclopropanols much more labile than those of other alcohols and results in preferential reaction at this site accompanied by concerted ring opening.[3]

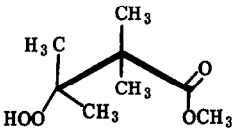
In the first example studied, tetramethylcyclopropanone methyl hemiketal[4] in hexane solution was allowed to react with atmospheric oxygen during 24 hours at room temperature. The sole reaction product (formed in 97% yield) was the ring opened β-hydroperoxy ester (I). The nmr spectrum of I (in CCl_4) exhibited singlets at τ 6.35, 8.75 and 8.78 whose relative ratios were 1:2:2; the infrared spectrum (CCl_4) showed ν_{OH} at 3560 and 3440 cm^{-1}.



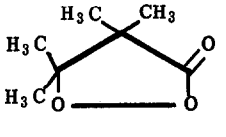
(I)

Support for the free radical nature of the ring opening was obtained by reacting the hemiketal with oxygen in the presence of bromotrichloromethane. This afforded the ring opened β-bromo ester[5] as the major product together with a small amount of I (75:25 mixture). Similarly, reaction in carbon tetrachloride solution afforded the β-chloro ester[6] as the predominant product.

Compound I is easily cyclized by sodium hydroxide in dioxane/water solution to a compound whose properties are in agreement with its formulation as tetramethylperoxypropiolactone (II). The infrared spectrum [$\nu_{C=O}(CCl_4)$ 1800 cm^{-1}] and nmr spectrum (in CCl_4 solution: two singlets of equal area at



(I)



(II)

τ 8.68 and 8.78) are consistent with the lactone formulation. When this work was initiated, the only previously known example of a member of this series was the β-methyl-β-phenyl derivative reported three years ago.[7a,7b] The intermediacy of compound II was suggested by Turro and his coworkers[4] to account for the formation of tetramethylethylene oxide and CO_2 from reactions of tetramethylcyclopropanone with oxygen; however, the lactone could not be isolated. In our hands the peroxylactone has been found to be thermally stable; it can be melted (85-86°) and recovered unchanged. It should also be noted that II is stable in the presence of methanol, thus eliminating the possible formation of I from II in the present study.

Reaction of 1,2,2-trimethylcyclopropanol[8] in hexane solution with atmospheric oxygen during 48 hours gave the known 3-hydroxy-3,5,5-trimethyl-1,2-dioxolane.[9] The nmr spectrum, obtained in carbon tetrachloride solution,

exhibited singlets of equal area at τ 8.68, 8.65 and 8.51 (CH_3 groups), an AB quartet centered at τ 7.61 (CH_2) and a broad singlet at τ 6.75 (OH). The mass spectrum exhibited the parent ion at m/e 132.

Pentamethyl cyclopropanol[1] was found to be as reactive toward atmospheric oxygen as the cyclopropanone hemiketal; complete conversion to 3-hydroxy-3,4,4,5,5-pentamethyl-1,2-dioxolane was evidenced after 24 hours at room temperature. The dioxolane was obtained as a white crystalline solid from hexane (m.p. 47-48°). The nmr spectrum (CCl_4 solution) exhibited a broad singlet at τ 3.50 (OH) and 5 additional singlets at τ 8.68, 8.72, 8.82, 8.97 and 9.00 (CH_3 groups); the mass spectrum is also consistent with the dioxolane formulation.

The relative rates at which these cyclopropanols react with atmospheric oxygen parallels the rate behavior of their nitrite esters toward homolysis.[1] Thus the hemiketal and pentamethyl compounds undergo complete reaction after 24 hours, the trimethyl compound requires 48 hours and the 1-phenyl derivative shows about 10% conversion after 10 days under analogous reaction conditions. The rate of reaction therefore seems to be dependent upon the stability of the incipient alkyl radical. We are now extending these studies to other cyclopropanols in order to examine the effect of substituents on the rates of these reactions and the propensity for cyclization to the dioxolanes.

Acknowledgment

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2. E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, Chapter 12.

3. These results are in accord with the observation that one electron oxidants open cyclopropanols by an apparently similar path; see S. E. Schaafsma, H. Steinberg and Th. J. DeBoer, Rec. Trav. Chim., 85, 70 (1966).

4. N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers and G. F. Vesley, J. Amer. Chem. Soc., 87, 2613 (1965).

5. The compound was identical with a sample prepared by reaction of the hemiketal with N-bromosuccinimide in the manner described previously: C. H. DePuy, W. C. Arney, Jr. and Dorothy H. Gibson, ibid., 90, 1830 (1968).

6. The compound was isolated by chromatography on florisil and compared to an authentic sample provided by H. L. Jones.

7. a. F. D. Greene, W. Adam and G. A. Knudsen, Jr., J. Org. Chem., 31, 2087 (1966). b. For a recent report of additional β-alkyl substituted peroxypropiolactones, see W. Adam, R. J. Ramirez and S. C. Tsai, J. Amer. Chem. Soc., 91, 1254 (1969).

8. See literature citation in reference 3.

9. The characterization of this dioxolane was first reported by G. B. Payne [J. Org. Chem., 23, 310 (1958)]; however, see A. Rieche, E. Schmitz and E. Grundemann, Chem. Ber., 93, 2443 (1960) for a better synthetic route to the compound.

10. For a recent review of cyclic peroxides see M. Schulz and K. Kirschke in "Advances in Heterocyclic Chemistry," Vol. 8, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1967, p 165.