Tho Oxidation of Enol Ethers

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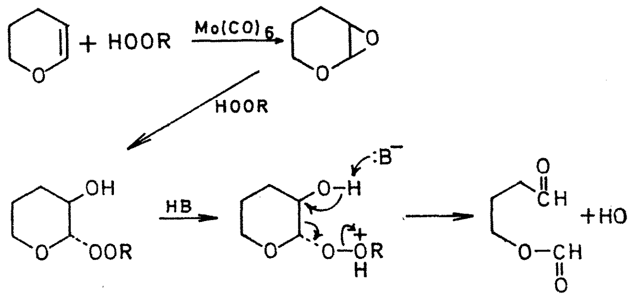
Summary Reaction of several enol ethers with t-butyl hydroperoxide or cumene hydroperoxide in the presence of molybdenum hexacarbonyl cleaves the double bond to give the corresponding dicarbonyl compound.

THE oxidation of olefins with hydroperoxides in the presence of molybdenum compounds has provided a very mild method for the preparation of epoxides.[1] We have found that this reaction when applied to enol ethers carries the oxidation further with cleavage of the double bond to yield a dicarbonyl compound. This novel reaction presents a convenient method for the preparation of 6-oxo-nonanolides from the corresponding 5,6,7,8-tetrahydrochromans. Medium-sized lactones constitute an important class of compounds which occur naturally as the aglycones in the macrolide antibiotics. One medium-ring lactone, 6-oxo-nonanolide, has been used by J. D. Dunitz in an *X*-ray study of the solid-state configuration of medium sized cyclic compounds.[2]

The reaction is accomplished by heating a mixture of an enol ether, the hydroperoxide and molybdenum hexacarbonyl in benzene at reflux for 48 hr. (Table). The molybdenum heaxcarbonyl concentration is of the order of 10^{-4}M. Higher concentrations of the catalyst accelerate the reaction but may lead to lower yields as a result of side reactions. In the case of 8-methyl-5,6,7,8-tetrahydrochroman, a side product has been isolated and is currently undergoing investigation. The reaction has been successfully carried out with t-butyl hydroperoxide and cumene hydroperoxide but the isolation of the products is simpler with the use of t-butyl hydroperoxide. A 10% excess of peroxide was employed in all reactions.

Following the reflux period, the benzene solution was washed several times with a 10% aqueous solution of ferrous sulphate to destroy any unreacted peroxide, and once with distilled water. After separation and drying of the organic phase, the solvent and t-butyl alcohol were removed on a rotary evaporator. Distillation of the residue afforded the product, with the exception of 6-oxo-nonanolide which crystallizes on cooling. The crystalline material was separated by suction filtration.



TABLE

Starting material	Solvent	Product	% Yield
8-Methyl-5,6,7,8-tetrahydrochroman	Benzene	2-Methyl-6-oxononanolide	62
5,6,7,8-Tetrahydrochroman	Benzene	6-Oxononanolide	50
4,5-Dihydropyran	Benzene	4-Formoxybutanal	25

The oxidation of 3,4-dihydropyran yielded a second carbonyl compound in addition to the formate ester of 4-hydroxybutanal. The structure of this compound is being investigated. The 4-formoxybutanal was identified by comparison of its physical properties with those in the literature.[3] The 6-oxononanolide and 2-methyl-6-oxononanolide were identified by a comparison of their i.r. spectra with those of authentic compounds.

The reaction may well proceed *via* an epoxide as shown. This type of mechanism has been postulated for the oxidation of 5,6,7,8-tetrahydrochroman with *m*-choloroperbenzoic acid.[4]

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