Oxidation of Dihydropyran with MoO_5·HMPA

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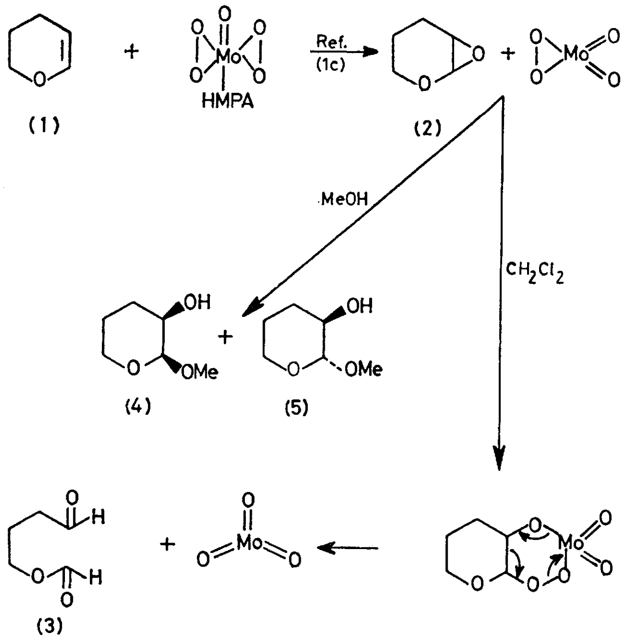
Summary The reaction of dihydropyran with MoO_5·HMPA yields 4-formyloxybutanal, in inert solvents; in methanol, however, the solvolysis products of the epoxide of dihydropyran are obtained.

We report that the reaction of 3,4-dihydro-2*H*-pyran (**1**) with oxodiperoxohexamethylphosphoramidemolybdenum[1] (MoO_5·HMPA) in CH_2Cl_2 or $CHCl_3$ yields only the corresponding cleavage product, 4-formyloxybutanal (**3**). The reaction was carried out at room temperature by adding a solution of MoO_5·HMPA (slight excess) dropwise to a solution of the enol ether (**1**). The solvent was removed under reduced pressure and the product isolated by bulb-to-bulb distillation under high vacuum. Compound (**3**) was the sole product obtained in high yield and was identical with an authentic sample obtained from the ozonolysis of (**1**). We suggest that the reaction proceeds by the mechanism in the Scheme, which may rationalize results obtained in several other systems (*vide infra*).



Scheme

Rapp and Borowitz obtained (**3**) when they oxidized dihydropyran with t-butyl or cumene hydroperoxide and molybdenum hexacarbonyl [$Mo(CO)_6$] in refluxing benzene.[2] However, since hydroperoxides are not present under our conditions, they cannot be the source of oxygen. That the reaction proceeds *via* the corresponding epoxy-ether (**2**) is clearly demonstrated by the fact that the oxidation of (**1**) with MoO_5·HMPA in methanol exclusively yields *cis*- and *trans*-2-methoxy-3-hydroxytetrahydropyran (**4**) and (**5**) in a ratio of 1 : 4. The same two products, in a 1 : 9 ratio, are obtained from the *m*-chloroperbenzoic acid epoxidation of dihydropyran in methanol.[3]

Mimoun and his co-workers [1b,4] have suggested that peroxo species of molybdenum, tungsten, and vanadium are generated *in situ* during epoxidations of olefins when organic hydroperoxides and catalytic quantities of salts of these metals are used. This would thus implicate these peroxo species as the key intermediates in this whole family of oxidation reactions. If one assumes the correctness of this hypothesis, the mechanism detailed in the Scheme may serve as an alternative explanation for the isolation of 4-formyloxybutanal (**3**) in the oxidation of dihydropyran by hydroperoxides and [$Mo(CO)_6$] mentioned above.

The oxidation of tetracyclone by chromium pentoxide [CrO_5·L] has been studied by several groups.[5] In light of the above discussion it would seem that the formation of *cis*-dibenzoylstilbene in this reaction is clearly expected and proceeds in a fashion analogous to that detailed in the Scheme.

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[2] R. D. Rapp and I. J. Borowitz, *Chem. Comm.*, 1969, 1202.

[3] A. A. Frimer, unpublished results.

[4] See also J. Kaloustian, L. Lena, and J. Metzger, *Tetrahedron Letters*, 1975, 599, and refs. cited therein.

[5] J. E. Baldwin, J. C. Swallow, and H. W.-S. Chan, *Chem. Comm.*, 1971, 1407 and refs. cited therein.