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MOLYBDENUM PEROXIDE-CATALYZED REACTION OF 1,2-DIOLS WITH DIMETHYL SULFOXIDE

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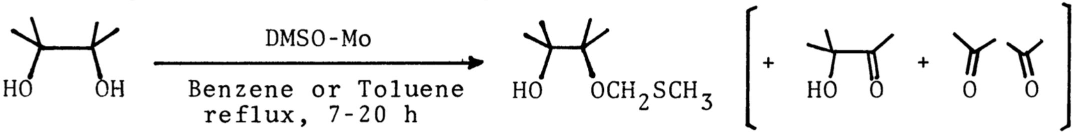
The reaction of 1,2-diols with dimethyl sulfoxide-catalytic molybdenum peroxide in refluxing toluene generally resulted in monoprotection of diols to give 2-methylthiomethoxy-1-ols (Course A). Exceptionally, a) cis-1,2-cyclooctanediol and benzopinacol, and b) 1,2-cyclododecanediol caused C-C bond cleavage (Course B) and monooxidation (Course C), respectively as Scheme 1.

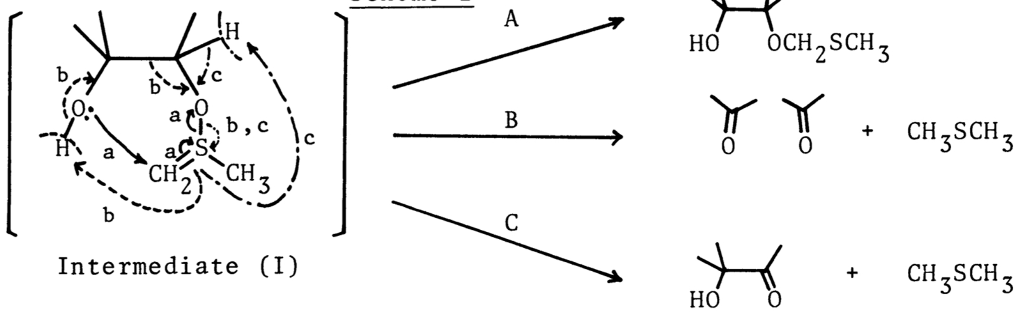
In a previous paper, we reported dimethyl sulfoxide (DMSO)-catalytic molybdenum peroxide was an excellent reagent for the oxidation of various alcohols to carbonyl compounds.[1)] Molybdenum peroxide is of greater advantage than other electrophiles[2)] such as acetic anhydride, oxalyl chloride, DCC and so on for catalysis and stability to water.[1)] Here we describe the possibility of monoprotection and oxidation of 1,2-diols using DMSO-cat. molybdenum peroxide system.



A typical procedure was as follows: 0.1g (0.64 mg atom Mo) of molybdenum peroxide[1)] was added to a solution of 0.46g (4 mmol) of cis-1,2-cyclohexanediol and 4 cm^3 of DMSO in 20 cm^3 of toluene. The solution was allowed to reflux for 8 h to separate water as the toluene azeotrope. Next, the solution was diluted with 50 cm^3 of ether, washed with water, and dried over magnesium sulfate. Evaporation of the solvent and column chromatography(silica gel-hexane:EtOAc=1:1) of the residue gave 0.37g (53%) of 2-methylthiomethoxy-1-cyclohexanol.

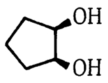
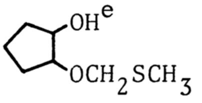
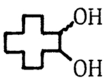
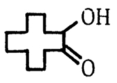
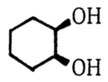
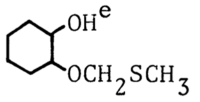
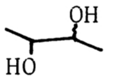
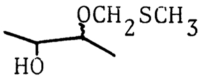
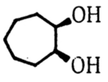
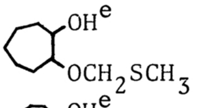
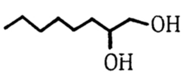
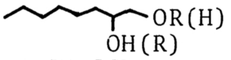
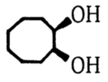
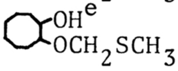
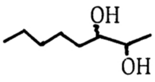
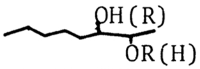
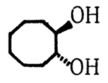
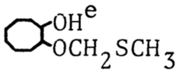
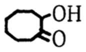
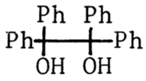
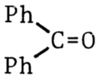
The results of monoprotection and/or oxidation of various 1,2-diols are summarized in Table 1.

Scheme 1



Intermediate (I)

Table 1 Reaction of various 1,2-diols with DMSO-Mo[3)]

Diol	Product	Yield(%)[a]	Diol	Product	Yield(%)[a]
		35[b] (62)[c]			81
		53 (61)[d]			32
		70		 R: CH_2SCH_3	60[f]
	 	6 37		 R: CH_2SCH_3	61[f]
	 	60 18			89

conditions: Toluene, reflux, 7-20 h

a) Other by-products were not detected under these conditions. Elongation of the reaction time produced the corresponding 2-methylthiomethoxy-1-ones.

b) Pentanedial was obtained in 10% yield. c) Benzene as a solvent was used.

d) Cyclohexanediol(cis:trans=1:1) was used. e) Stereochemistry was not confirmed.

f) The ratio of regioisomers was 1:1.

As was distinct from normal Moffatt-type oxidation of 1,2-diols (Course C),[4)] this reaction with DMSO-Mo generally provided only 2-methylthiomethoxy-1-ols (Course A) in Scheme 1. This reaction should be affected by the conformation of diols and the interaction of molybdenum peroxide and intermediate (I).[5)]

Further studies of dehydration and oxidation of other functional groups using this DMSO-Mo system are in progress.

References

1) Y. Masuyama, A. Tsuhako, and Y. Kurusu, Tetrahedron Lett., 22, 3973 (1981).

2) J. G. Moffatt, "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., 1971, p 1-64; J. B. Hendrickson and S. M. Schwartzman, Tetra. Lett., 273 (1975) and references cited therein.

3) The yields shown are for the isolated products and the purification is carried out by means of column chromatography. All new compounds obtained here exhibited satisfactory spectral (IR, NMR, MS) and physical properties.

4) E. J. Corey and C. U. Kim, Tetrahedron Lett., 287 (1974).

5) Mechanism to intermediate (I), that is, catalytic action of molybdenum peroxide was given in the paper of reference 1.

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