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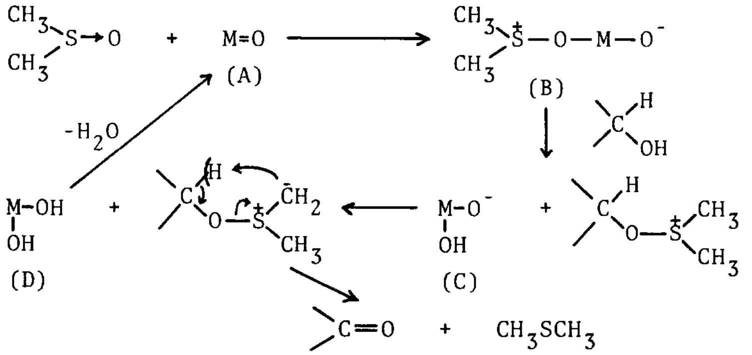
DIMETHYL SULFOXIDE-CATALYTIC MOLYBDENUM PEROXIDE: A NEW SYSTEM FOR THE FACILE OXIDATION OF ALCOHOLS

Yoshiro Masuyama, Akira Tsuhako, and Yasuhiko Kurusu
Department of Chemistry, Sophia University
7-1 Kioicho, Chiyoda-ku, Tokyo 102, Japan

Summary: In the dimethyl sulfoxide (DMSO)-metal oxide oxidation of alcohol to carbonyl compound, molybdenum oxides were the only useful catalytic reagents, an various alcohols were oxidized to the corresponding carbonyl compounds in high yields.

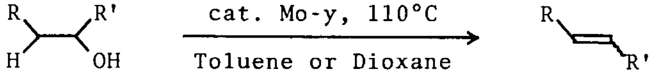
Sulfoxonium salt derived from DMSO and acetic anhydride (or certain other anhydrides) can oxidize alcohols to carbonyl compounds[1]. However, these reactions need anhydrides in stoichiometric amounts. To avoid this problem, a catalytic electrophile for dehydration should be developed in this reaction.



(1)

Metal oxides (A) may give as an effective complex (B) as the DMSO-anhydride complex in the oxidation of alcohol and may be produced to activate again by the dehydration of (D) in equation 1.

Recently we found molybdenum peroxide (Mo-y)[2] was a good dehydration catalyst for alcohols (equation 2)[3].



(2)

On the other hand, it is known that molybdenum has a strong affinity for sulfur and anionic compounds[4]. Molybdenum compounds should therefore be more reactive for DMSO than alcohols.

This communication deals with the investigations about molybdenum compounds as a dehydration catalyst in the oxidation of cyclohexanol to cyclohexanone using DMSO and the application to the oxidation of various alcohols.

The following was a general experimental procedure for investigating the activity of metal oxides: To the solution of 0.217 g (2.17 mmol) of cyclohexanol and 5 ml of DMSO in a 20 ml screw-capped test tube was added 0.4-2.0 mmol of metal oxide. The solution was stirred vigorously at 120°C in a aluminum-block thermostat. After 90 h, the product cyclohexanone was analyzed by glpc[5].

The results of the oxidation of cyclohexanol using various metal oxides are summarized in Table 1.

Table 1. Oxidation of cyclohexanol with various metal oxides

Metal Oxide	mg	⬡=O Yield%	Molar Ratio ⬡=O/Metal	Metal Oxide	mg	⬡=O Yield%	Molar Ratio ⬡=O/Metal
Mo-y*	101	76	2.58	MnO_2	111	0	-
MoO_3	106	75	2.21	WO_3	108	0	-
Mo	93	71	1.58	H_2WO_4	96	0	-
Na_2MoO_4	101	0	-	BaO_2	191	0	-
$CaMoO_4$	99	0	-	TiO_2	103	0	-
$H_2MoO_4H_2O$	107	0	-	ZnO	104	0	-
CrO_3	95	28	0.64	MgO	95	0	-
V_2O_5	153	6	0.15	CaO	81	0	-
Al_2O_3	110	0	-	CuO	103	0	-

*) Average weight per one atom Mo is 158 (This was determined by the titration of Mo.)

As shown in Table 1, only some molybdenum compounds (not basic and hydrated ones) were effective as a catalytic electrophile in the DMSO-metal oxide system

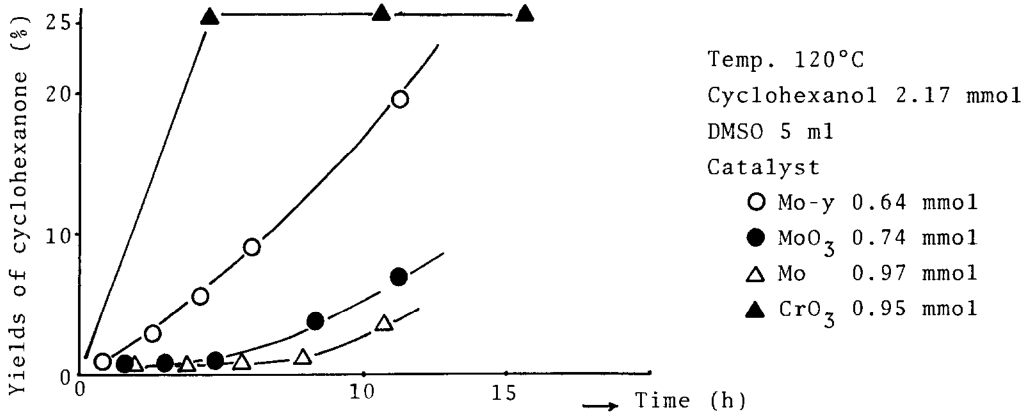


Figure 1. Oxidation with Mo oxides and CrO_3

for the oxidation of cyclohexanol to cyclohexanone. Neither acidic nor basic metal oxides except molybdenum compounds reacted with DMSO under similar conditions. The reaction rate using Mo-y was faster than that using MoO_3 or Mo metal in the initial stages of reaction (Figure 1). One factor affecting these initial stages should be difference of acidity. Mo-OH and Mo-O-OH groups that consisted in Mo-y might increase the acidity[2]. Further, an effect of the solubility should be closely associated in this reaction (Solubility for DMSO: Mo-y $>$ MoO_3 $>$ Mo). This order should depend on molecular size of these compounds.

In a large excess of DMSO, the reaction rate using Mo-y seems not to be affected by the concentration of cyclohexanol (Figure 2), but to depend on the concentration of Mo-y (Figure 3). For 8.87 mmol of cyclohexanol, the yield was 74% and cyclohexanone/Mo-y molar ratio was 13.9 after 90 h (Figure 2).

Chromium trioxide exhibited reactivity. However, considering the time course of the reaction, chromium trioxide serves not as a catalytic electrophile but only as a stoichiometric oxidant (Figure 1).

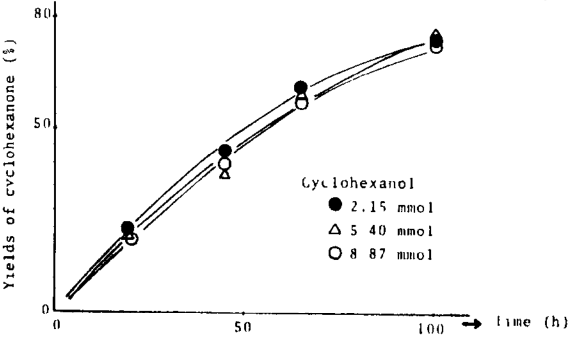


Figure 2
Oxidation of cyclohexanol in various concentrations
Mo-y 75 mg, DMSO 5ml, Temp 120°C

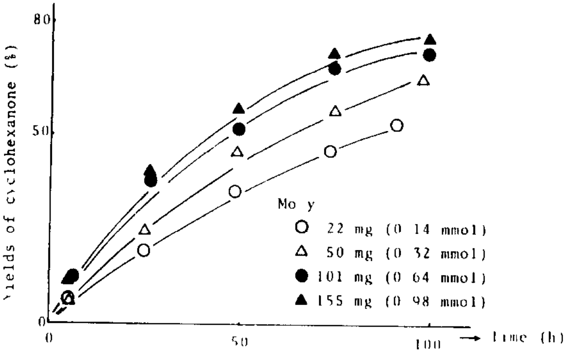
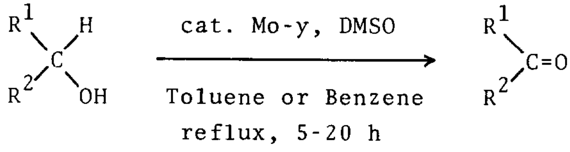


Figure 3
Oxidation of cyclohexanol with various amounts of Mo-y
(cyclohexanol 2.17 mmol, DMSO 5ml, Temp 120°C

Next, we demonstrate the applicability of this method to the oxidation of various alcohols by means of azeotropic reaction (equation 3).

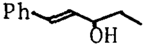
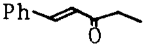
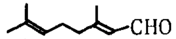
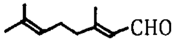


(3)

A typical procedure was as follows: 70 mg (0.45 mmol) of Mo-y was added to the solution of 0.63 g (4 mmol) of L-menthol in 3 ml of DMSO and 20 ml of toluene. The solution was allowed to reflux for 10 h to separate water as the toluene azeotrope. Next, the solution was diluted with 50 ml of ether, washed with water, and dried over magnesium sulfate. Evaporation of solvent and column chromatography (silica gel-hexane:EtOAc=10:1) provided 0.53 g (86%) of menthone.

The results of the oxidation of various alcohols are summarized in Table 2.

Table 2. Oxidation of Alcohols with DMSO-Mo-y[6]

Alcohol	Solvent	R. Time h	Product	Yield %
2-Octanol	Toluene	12	2-Octanone	88
Cyclododecanol	Toluene	16	Cyclododecanone	91
Borneol	Toluene	13	Camphor	81
L-Menthol	Toluene	10	Menthone	86
1-Phenylethanol	Toluene	7	Acetophenone	90
1-Phenylethanol	Benzene	20	Acetophenone	83
	Benzene	20		41[a]
	Toluene	5		77[b]
Geraniol	Toluene	10		40[c]
Geraniol	Benzene	15		78[c]
1-Decanol	Toluene	16	Decanal	79

a) only E isomer by NMR; 1-Phenyl-1,3-pentadiene was obtained in 15% yield. b) only E isomer by NMR, c) E:Z=1:1 (by NMR)

This oxidation gave only carbonyl compounds without the by-products, methylsulfenylmethyl ethers, which were often obtained by the DMSO-anhydride oxidation[1]. So, it is advantageous for large-scale work.

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

References

1. 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, Tetrahedron Lett., 273 (1975) and references cited therein.
2. Y. Kurusu, Bull. Chem. Soc. Jpn., 54, 293 (1981).
3. Y. Kurusu, K. Shiraki, and Y. Masuyama, unpublished results.
4. P. C. H. Mitchell, "Proceedings of the First International Conference on the Chemistry and Uses of Molybdenum," P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, 1973, p 1.
5. In these reaction conditions, no by-product was observed and the yields based on the conversion of cyclohexanol were over 95%.
6. The yields shown are for the isolated products and the purification is carried out by means of recrystallization or column chromatography. All products obtained here were identified by comparison of the physical properties with those of the authentic samples.

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