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$MoO_2(acac)_2$ Complex as a Reagent for Oxidative Cleavage of vic-Diols

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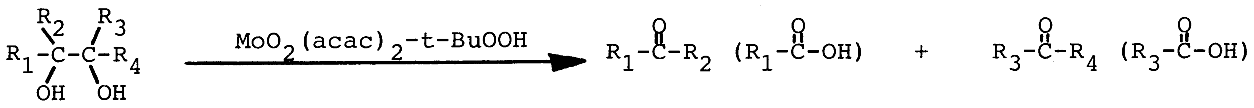
$MoO_2(acac)_2$-t-BuOOH system has high activity for oxidative cleavage of tertiary and secondary vic-diols. $MoO_2(acac)_2$ cleaves the diols to give carbonyl compounds in the absence of t-BuOOH.

We have reported that $MoO_2(acac)_2$ compound oxidatively cleaved olefinic double bonds in the presence of t-BuOOH.[1)] In relation to carbon-carbon bond cleavage reactions, we also found that the $MoO_2(acac)_2$-t-BuOOH system could induce the oxidative cleavage of vic-diols to give carbonyl compounds. The catalyst system has high activity for t- and/or s-diols, compared with diols involving primary hydroxy group. It should be noted that $MoO_2(acac)_2$ itself cleaves the carbon-carbon bonds of the diols in the absence of t-BuOOH.



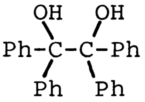
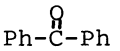
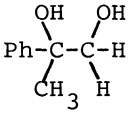
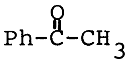
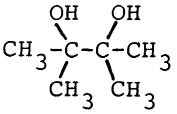
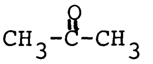
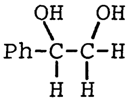
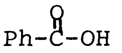
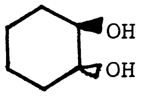
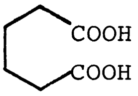
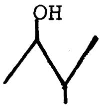
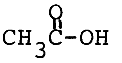
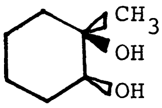
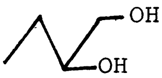
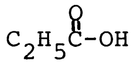
Typical results for the diol oxidation using the $MoO_2(acac)_2$-t-BuOOH are summarized in Table 1. Various vic-diols gave ketones and carboxylic acids derived from cleavage of carbon-carbon bonds attached to hydroxy groups in high yields. Especially, di-t-diols are exclusively cleaved to give ketones.
We confirmed that carboxylic acids were formed from the corresponding aldehydes. Diols with primary hydroxy group except styrene glycol and α-methylstyrene glycol gave low yields of expected carboxylic acids because overoxidation occurred.
High reactivity for t- and s-diols might be due to facile formation of molybdenum-alkoxides from these diols.[2)]

We examined the metal effect on the cleavage reaction of styrene glycol in the presence of t-BuOOH. Other metals, e.g., $TiO(acac)_2$ and $Zr(acac)_4$ gave benzoic acid in low to moderate yields.[3)] Solvents strongly affected this cleavage reaction: CCl_4 and chlorobenzene are good solvent.

The $MoO_2(acac)_2$ could cleave the carbon-carbon bonds of diols in the absence of t-BuOOH; the stoichiometric reaction of styrene glycol with $MoO_2(acac)_2$ gave 78% yield of benzaldehyde under a nitrogen atmosphere. We think that Mo(VI) species reacts with diols to give carbonyl compounds and Mo(IV) species, and in the catalytic reaction, the Mo(IV) is oxidized to the Mo(VI) by t-BuOOH.

This $MoO_2(acac)_2$-t-BuOOH catalyst system is one of useful reagents for oxidative cleavage of t- and s-vic-diols.[4)]

Table 1. Oxidation of vic-Dilos Using $MoO_2(acac)$-^{t}BuOOH System[a)]

Substrate	Product(yield/%)	Substrate	Product
 $\mathrm{Ph{-}\underset{Ph}{\overset{OH}{C}}{-}\underset{Ph}{\overset{OH}{C}}{-}Ph}$	 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}Ph}$ (96)	 $\mathrm{Ph{-}\underset{CH_3}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}H}$	 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$ (93)
 $\mathrm{CH_3{-}\underset{CH_3}{\overset{OH}{C}}{-}\underset{CH_3}{\overset{OH}{C}}{-}CH_3}$	 $\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$ (99)	 $\mathrm{Ph{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}H}$	 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}OH}$ (83)
	 (79)		 $\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}OH}$ (92)
	 (62)		 (59)
			 $\mathrm{C_2H_5\overset{O}{\overset{\|}{C}}{-}OH}$ (37)

a) To a stirred solution of $MoO_2(acac)_2$(0.05 mmol) and diol(0.5 mmol) in chlorobenzene(10 ml) was added t-BuOOH(4 mmol) in chlorobenzene(5 ml) under N_2. The resulting solution was stirred at 60 °C for 24 h. The oxidation products were analyzed by GLPC and ^{1}H NMR.

References

1) K.Jitsukawa, K.Kaneda, and S.Teranishi, J.Org.Chem., 48,389(1983). 2) Vanadium and molybdenum complexes favor t- and s-hydroxyls more than primary ones in the formation of metal alkoxides: R.K.Mittal and R.C.Mehrotra, Z.Anorg.Allg.Chem., 355,328(1967). 3) Zviely have reported that $VO(acac)_2$-t-BuOOH cleaved only di-t-diols: M.Zviely and E.Glotter, J.Chem.Soc., Perkin Trans. 1, 1986,229.

4) For typical examples of metal-catalyzed diol cleavage, see: a) G. de Vries and A.Schore, Tetrahedron Lett., 1968, 5689, Co-O_2; b) E.S.Huyser and L.G.Rose, J.Org.Chem., 37,851(1972), Ag-$S_2O_8^{2-}$; c) D.H.Barton, J.Finet, B.Motherwell, and C.Pichon, Tetrahedron, 42,5627(1986), Bi-NBS; d) C.Venturello and M.Ricci, J.Org.Chem., 51,1599(1986), W-H_2O_2.

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