MoO2(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.

 $R_{1} \xrightarrow{R_{2}}_{OH} \xrightarrow{R_{3}}_{OH} MOO_{2}(acac)_{2} - t - BuOOH = R_{1} - C - R_{2} (R_{1} - C - OH) + R_{3} - C - R_{4} (R_{3} - C - OH)$

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 molybdenumalkoxides 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: ${\rm CCl}_4$ and chlorobenzene are good solvent.

The MoO₂(acac)₂ could cleave the carbon-carbon bonds of diols in the absence of t-BuOOH; the stoichiometric reaction of styrene glycol with MoO₂(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 MoO₂ (acac)-^tBuOOH System^{a)}

Substrate	Product(yield/%)	Substrate	Product
OH OH Ph-C-C-Ph Ph Ph	0 Ph-C-Ph (96)	Ph-C-C-H CH ₃ H	0 Ph-C-CH ₃ (93)
CH ₃ -C-C-CH ₃ CH ₃ CH ₃	сн ₃ -С-сн ₃ (99)	OH OH Ph-C-C-H I H H	Рh-С-ОН (83)
ОН	Соон (79)	OH OH	Сн ₃ С-он (92)
СН ₃ ОН	COOH (62)		Соон (59) С ₂ н ₅ С-он (37)

a) To a stirred solution of $MoO_2(acac)_2(0.05 \text{ mmol})$ and diol(0.5 mmol) in chlorobenzene(10 ml) was added t-BuOOH(4 mmol) in chlorobenzene(5 ml) under N₂. The resulting solution was stirred at 60 °C for 24 h. The oxidation products were analyzed by GLPC and ¹H NMR.

References

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