Dethioketalization with O-Mesitylenesulfonylhydroxylamine

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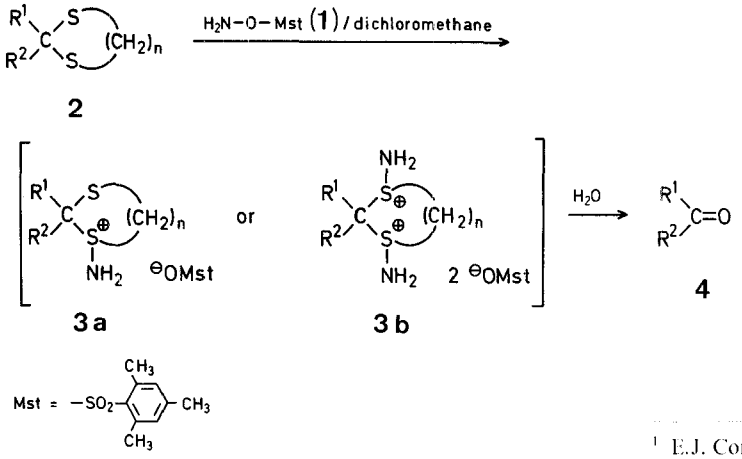
Recently, a number of efficient procedures for the conversion of thioketals into the original carbonyl compounds have been reported and the importance of dethioketalization in organic synthesis has been well documented. So far, reagents such as heavy-metal salts (mercuric chloride[1]), oxidizing agents (N-halogenosuccinimide[1], halogen[1], and ceric ammonium nitrate[2]), alkylating agents (methyl iodide[3], triethyloxonium tetrafluoroborate[4], and methyl fluorosulfonate[5]), and an aminating agent (chloramine T[6]) have been demonstrated to be effective for this conversion. We report now that O-mesitylenesulfonylhydroxylamine (**1**, MSH), a powerful aminating agent[7], can also be used as an alternative dethioketalizing agent.

Thus, thioketals (**2**, 1 mmol) were treated with MSH (1 or 2 mmol) in dichloromethane at room temperature for 30 to 60 min to give the parent carbonyl compounds in the yields listed in the Table.

The results indicate that this method can be effectively applied to the cleavage of thioketals derived from *α,β-unsaturated* ketones or aldehydes.

In view of the fact that MSH readily aminates various sulfides[8], regeneration of the carbonyl compounds presumably proceeds via unstable amine salts of thioketals (**3a** or **3b**), followed by hydrolytic cleavage.

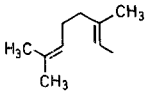
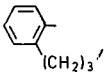


Dethioketalization Procedure:

To a solution of a thioketal (1 mmol) in dichloromethane (2 ml) was added dropwise a solution of O-mesitylenesulfonylhydroxylamine[a] (MSH; 1 or 2 mmol) in dichloromethane (2 ml) over 1 min under ice cooling. The mixture was stirred at room temperature for 30–60 min, ether (10 ml) was added, and the white precipitate formed (ammonium mesitylenesulfonate) was removed by filtration. The filtrate was thoroughly washed with saturated sodium chloride solution and dried with magnesium sulfate. The solvent was evaporated in vacuo, the residue was treated with 2,4-dinitrophenylhydrazine, distilled, or recrystallized.

[a] MSH usually contains 20–30% of water.

Table. Dethioketalization of Some Representative Thioketals

Thioketal (**2**) R[1]	R[2]	n	Molar equiv. of MSH	Yield (%) of Ketone or Aldehyde (**4**)
	H	3	2(1)	74 (46)[a]
	H	3	2	72[a]
	H	3	1(2)	74 (6)[a]
n-C_3H_7	H	3	1	27 (14)[a]
n-C_9H_{19}	H	3	1(2)	21 (7)[a]
	CH_3	2	2	66[b]
		2	1	85[c]
		2	1	60[d]
$-(CH_2)_4-$		2	1	[e]

[a] Isolated as the 2,4-dinitrophenylhydrazone.
[b] Isolated by distillation.
[c] Isolated by recrystallization.
[d] Isolated by preparative T.L.C.
[e] Distillation of the reaction mixture at 90–100°/0.2 torr afforded δ-valerolactam in 28% yield[9].

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