

Hydrolysis of Thioacetals with Silver Oxide

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Summary A convenient procedure for the hydrolysis of thioacetals using silver oxide in aqueous methanol is described.

THE usefulness of the thioacetal group in organic synthesis is well known¹ and it is largely due to the fact that in recent years several methods have become available to effect its removal under a variety of conditions.^{1,2}

During a recent study of the reaction of cysteine derivatives with silver oxide and silver carbonate to yield α -acylaminoacrylic esters,³ it became apparent that thioacetals should hydrolyse to the corresponding ketone under similar conditions.

We have found that silver oxide in 1:10 aqueous methanol does effect the conversion of this protective grouping into the corresponding ketone in good yield.

In a typical experiment (see Table) a suspension of pregnenolone ethylenedithioacetal (392 mg, 1.0 mmol) in aqueous methanol (55 ml, 1:10) was heated to reflux for 16 h with a ten-fold excess of silver oxide to give pregnenolone (73%).

TABLE. Hydrolysis of thioacetals

Thioacetal derivative of ketones	Reaction time	Yield of parent ketone (%) ^a
Bicyclo[3,3,1]nonan-2-ol-9-one, (<i>endo</i>)	24 h	75 ^b
5-Pregnen-3 β -ol-20-one	.. 16 h	73
5-Androsten-3 β -ol-17-one	.. 4 days	76
Cyclohexanone 20 h	85 ^d

^a Recrystallized. ^b Pure *endo*. ^c First day, 10 mol silver oxide added, then 3 mol per day. ^d 2,4-Dinitrophenylhydrazone derivative.

Finally, it may be noted that silver carbonate does not show the same reactivity as silver oxide, the thermodynamic stability of the starting thioacetal and/or steric hindrance may play an important role in this reaction, and acetates are very slowly hydrolysed under these reaction conditions.

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¹ D. Seebach, *Synthesis*, 1969, 17 and references therein.

² W. F. J. Hurdeman, H. Wynberg, and D. W. Emerson, *Tetrahedron Letters*, 1971, 3449; T. Oishi, K. Kamemoto and Y. Ban, *Tetrahedron Letters*, 1972, 1085; T. L. Ho and C. M. Wong, *Synthesis*, submitted for publication; M. Fetizon and M. Jurion, *J.C.S. Chem. Comm.*, 1972, 382; Hsin-Lan Wang Chang, *Tetrahedron Letters*, 1972, 1989; S. J. Daum and R. L. Clarke, *Tetrahedron Letters*, 1967, 165; P. R. Heaton, J. M. Midgley, and W. B. Whalley, *Chem. Comm.*, 1971, 750; T. L. Ho, H. C. Ho, and C. M. Wong, *J.C.S. Chem. Comm.*, 1972, 791.

³ D. Gravel, R. Gauthier, and C. Berse, preceding communication.