Dethioacetalisation with Ceric Ammonium Nitrate

By TSE-LOK HO,* HONOR C. HO, and C. M. WONG

(*Department of Chemistry, University of Manitoba, Winnipeg* 19, *Manitoba, Canada*)

Summary A ready dethioacetalisation procedure employing ceric ammonium nitrate in aqueous acetonitrile at room temperature is described.

THE value of the thioacetal group for temporary masking the carbonyl function has increased recently through the development of versatile synthetic method based on the 1,3-dithian carbanion.[1] However, procedures for direct regeneration of carbonyl compounds from dithioacetals are still limited; methods most frequently used involve mercury(II) salts and *N*-halogenosuccinimides.[1] Chloramine T has also been used,[2] and dethioacetalisation *via* *S*-alkylation has been reported.[3]

In a study of the oxidation of organic compounds[4] by ceric ammonium nitrate (CAN) we have discovered a simple and convenient alternative. Thus, treatment of 1,3-dithiolans or 1,3-dithians (1·0 mmol) in 75% aqueous acetonitrile (12 ml) with CAN (4·0 mmol) at room temperature for 3 min, followed by dilution with water and extraction with ether, gave the parent carbonyl compounds in good yields (see Table). Pure products were isolated by distillation, or filtration through a neutral alumina column and recrystallisation, or as their 2,4-dinitrophenylhydrazones (2,4-DNP).

TABLE. *CAN cleavage of dithioacetals*

	Aldehyde or ketone	Yield (%) of parent compound
1,3-Dithiolans	Benzaldehyde[5]	73·4[a]
	Acetophenone[6]	80·0
	Benzophenone[8]	85·7
	Cyclohexanone[6]	87·0[a]
	Methyl 3′-oxononyl ketone[7]	80·0
1,3-Dithians	Phenylacetone[1]	85·0
	Cycloheptanone[1]	70·0

[a] Yield and identification based on isolated 2,4-DNP.

This work was supported by the National Research Council of Canada.

(*Received*, 15*th May* 1972; *Com.* 843.)

---

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

[2] W. F. J. Huurdeman, H. Wynberg, and D. W. Emerson, *Tetrahedron Letters*, 1971, 3449.

[3] T. Oishi, K. Kamemoto, and Y. Ban, *Tetrahedron Letters*, 1972, 1085; T. L. Ho and C. M. Wong, *Synthesis*, submitted for publication.

[4] P. Soucy, T. L. Ho, and P. Deslongchamps, *Canad. J. Chem.*, in the press; T. L. Ho, H. C. Ho, and C. M. Wong, *Synthesis*, in the press.

[5] H. Fasbender, *Ber.*, 1887, **20**, 460.

[6] E. E. Reid and A. Jelinek, *J. Org. Chem.*, 1950, **15**, 448.

[7] H. C. Ho, T. L. Ho, and C. M. Wong, *Canad. J. Chem.*, in the press.

[8] H. Fasbender, *Ber.*, 1888, **21**, 1473.