Pergamon

Tetrahedron Letters, Vol. 37, No. 11, pp. 1897-1898, 1996
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0040-4039/96 $15.00 + 0.00

S0040-4039(96)00146-3

An Exceptionally Simple and Convenient Method for Dethioacetalization

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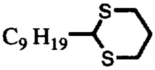
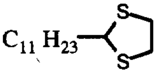
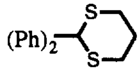
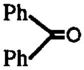
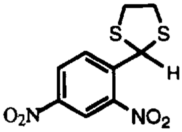
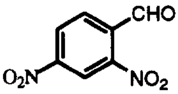
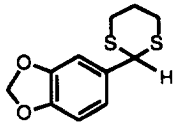
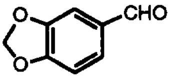
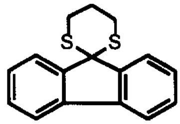
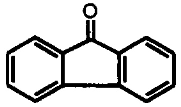
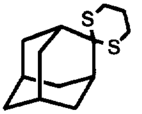
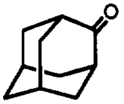
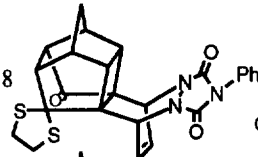
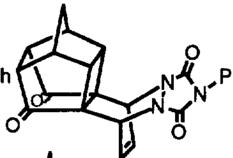
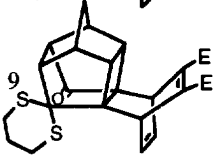
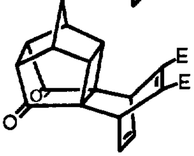
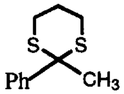
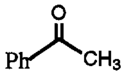
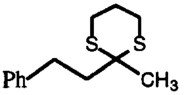
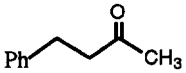
Abstract: Thioacetals derived from aldehydes and ketones can be unmasked to the corresponding carbonyl compounds in high yield on exposure to a solution of 'oxides of nitrogen' in dichloromethane.

Cyclic S,S-acetals e.g., 1,3-dithiolanes and 1,3-dithianes, are regarded as advantageous protecting groups and functionalities in the armoury of synthetic chemists in view of their robustness towards hydrolytic cleavage and the ability of 1,3-dithianes in particular to promote metallation for effecting 'umpolung' of the carbonyl reactivity.[1] However, one of the limiting factors in their widespread use is the occasionally encountered refractoriness and waywardness towards regeneration of the carbonyl functionality, despite the availability of many reagents and recipes for deprotection based on the enhancement of nucleofugacity of sulfur through metal-coordination, alkylation and oxidation; thus underscoring the need to buttress the existing repertory of the procedures for dethioacetalization.[2]

During an ongoing project, we attempted dethioacetalization in a polycyclic substrate (entry 9), but the existing methods were found to be ineffective. During a search for alternatives, we stumbled on a chance observation that exposure of this thioacetal to a dichloromethane (DCM) solution of 'nitrogen oxides'[3,4] resulted in clean dethioacetalization. This prompted us to explore the generality of this simple, rapid and convenient dethioacetalization procedure, which merely requires a titration of the substrate solution with a solution of 'oxides of nitrogen' in DCM and aqueous work-up. The yields are consistently good (Table) and the procedure seems to be particularly well suited for 1,3-dithianes and 1,3-dithiolanes of aldehydes and non-enolizable ketones. However, in the case of thioacetals of methyl ketones (entries 10 & 11) only a modest yield was obtained.

General Procedure: To a stirred solution of the thioacetal (~1 mmol) in dichloromethane (DCM, 10 ml), cooled in an ice-bath (0-5°C), was added drop-wise a solution of 'nitrogen oxides' in DCM.[3] In the case of 1,3-dithiane substrates the reaction mixture turns pink and the reagent addition is continued till the color is discharged. However, in the case of 1,3-dithiolanes, color change was not observed and the reaction was monitored by tlc. After the completion of the reaction (5-20 min), the reaction was quenched with ice-cold aq.$NaHCO_3$ and extracted with additional DCM. The organic layer was separated, dried (Na_2SO_4) and the residue obtained after the removal of solvent was filtered through a small silica-gel pad to furnish the dethioacetalized product, which was characterized

Table

Entry	Substrate	Product	Yield(%)
1		$C_9H_{19}CHO$	96
2		$C_{11}H_{23}CHO$	81
3			97
4			87
5			95
6			94
7			96
8			73
9			62
10			40
11			40

through spectral comparison with authentic specimen.

In short, we have reported a simple, mild and rapid method for dethioacetalization which should find extensive preparative use and is a useful addition to the existing procedures.

References and Notes

1. (a) Kocienski, P.J. "Protecting Groups" George Thieme Verlag, Stuttgart, 1994. (b) Jarowicki, K.; Kocienski, P. *Contemporary Organic Synthesis*, **1995**, *2*, 315.
2. Some of the newly introduced dethioacetalization procedures: Ravindranathan, T.; Chavan, S.P.; Tejwani, R.B.; Varghese, J.P. *J. Chem. Soc. Chem. Commun.*, **1991**, 1750; Tanemura, K.; Dohya, H.; Imamura, M.; Suzuki, T.; Horaguchi, T. *Chem. Lett.*, **1994**, 965; Kamata, M.; Murakami, Y.; Tamagawa, Y.; Kato, M.; Hasegawa, E.; *Tetrahedron*, **1994**, *50*, 12821.
3. 'Nitrogen Oxides' were prepared according to the literature procedure[4] by treating arsenious oxide with conc.HNO_3 and the resulting gaseous mixture was bubbled through dichloromethane cooled in an ice-bath (0-5°C). A bottle-green solution was obtained and could be stored at 0-5°C for several months without loss of activity and was repeatedly used for the dethioacetalization experiments.
4. Dox, A.W. *Organic Synthesis*, Col. Vol. 1, **1941**, 266. The 'Oxides of Nitrogen' are usually regarded as a mixture of N_2O_4, N_2O_3 and NO_2, see: Fieser, L.F.; Fieser, M. ***Reagents for** Organic Synthesis*, John-Wiley, New York, **1967**, 737.

(*Received in UK* 18 *December* 1995; *accepted* 26 *January* 1996)