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Deprotection of Thioacetals and 1,3-Dithianes with Dimethylsulphoxide

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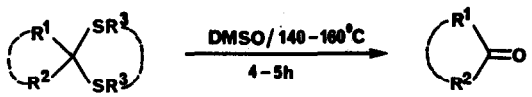
Abstract: *The dialkylthioacetals, cyclic ethanediylthioacetals and 1,3-dithianes are shown to undergo facile dethioacetalization on heating in dimethylsulphoxide under neutral conditions to afford the corresponding carbonyl compounds in good yields.*

The dithioacetals of aldehydes and ketones play an important role either as protecting groups[1] or as masked acyl anions[2] in organic synthesis. In both the cases, the ultimate step involves the cleavage of the dithioacetal functionality to restore the original carbonyl group. Unlike their oxygen counterparts, the corresponding thioacetals and ketals pose some practical difficulties in classical acid-assisted hydrolytic cleavage[2]. Among the various reagents employed for this purpose, dimethylsulphoxide in the presence of iodine[3] or t-butyl chloride[4] are known to cleave thioacetals under neutral conditions. Scorrano and co-workers[5] have described a facile cleavage of 1,3-dithianes with dimethylsulphoxide/HCl in aqueous dioxane. The halodimethylsulphonium ion (generated *insitu*) appears to have been the active intermediate species for oxidative cleavage of thioacetals in these reactions[5]. Apparently, efforts to discover milder and more efficient neutral reagents to cleave the dithioacetals are being continued[6]. We have now observed that just the dimethylsulphoxide itself, in the absence of any other reagent, is capable of cleaving both acyclic and cyclic thioacetals to the corresponding carbonyl compounds in high yields under thermal and neutral conditions. We herein report the results of our preliminary studies on this reaction.

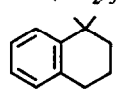
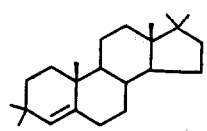
In a typical experiment, a solution of thioacetal (0.01 mol) in dry dimethylsulphoxide (10 ml, pH=7) was heated at high temperature (140-160°C, Table) for 4-5 hr (monitored by TLC). The reaction mixture after cooling was poured into water (50 mL), extracted with $CHCl_3$ (2x25 mL), dried and evaporated to give crude carbonyl compound which was further purified by passing through silica gel column (hexane as eluent) followed by distillation or crystallization[7]. A variety of acyclic and cyclic thioacetals derived from various ketones and aldehydes were thus deprotected and yields are shown in Table.

It is not possible at this stage to suggest the actual mechanism of this interesting thioacetal cleavage. Precautions were taken to exclude acidic and other contaminants in dimethylsulphoxide. In view of the importance of thioacetals and 1,3-dithianes in organic synthesis, the present method is a useful compliment to the variety of methods available for their cleavage under neutral conditions. Further work to study the scope and mechanism of this reaction is in progress.



1 2

Table. Deprotection of Thioacetals 1 to Carbonyl Compounds 2

Entry	Substrate	R^1	R^2	R^3	Reaction Temp(°C)	Reaction Time(h)	Yield[a](%) 2
1	1a	C_6H_5	H	Et	140	4.0	94
2	1b	C_6H_5	H	Bu	160	4.0	88
3	1c	C_6H_5	H	$-(CH_2)_3-$	160	4.5	86
4	1d	C_6H_5	Me	$-(CH_2)_2-$	160	4.0	88
5	1e	$C_6H_5CH=CH-$	H	$-(CH_2)_2-$	160	4.0	82
6	1f	$C_6H_5CH=CH-$	H	$-(CH_2)_3-$	160	4.0	89
7	1g	Et	Et	Et	140	4.0	90
8	1h	Et	Et	$-(CH_2)_2-$	160	5.0	87
9	1i	Et	Et	$-(CH_2)_3-$	160	4.0	91
10	1j	$Me(CH_2)_2-$	H	Et	160	4.0	83
11	1k	$Me(CH_2)_2-$	H	$-(CH_2)_2-$	160	5.0	79
12	1l	$Me(CH_2)_{10}-$	H	Et	160	5.0	81
13	1m	$Me(CH_2)_{10}-$	H	$-(CH_2)_2-$	160	4.5	81
14	1o	$-(CH_2)_5-$		$-(CH_2)_2-$	160	4.5	84
15	1p			Et	160	4.0	89
16	1r			$-(CH_2)_2-$	160	5.0	66

[a] Yield of pure isolated product.

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References and Notes

1. Grobel, B.T.; Seebach, D. *Synthesis* **1977**, 357-402.
2. Greene, T.W. *Protective Groups in Organic Synthesis*, John Wiley and Sons; New York, **1981**, pp. 129-138, 311-314.
3. Chattopadhyaya, J.B.; Ramarao, A.V. *Tetrahedron Lett*. **1973**, **58**, 3735- 3736.
4. Olah, G.A.; Mehrotra, A.K.; Narang, S.C. *Synthesis* **1982**, 151-152.
5. Prato, M.; Quently, V.; Scorrano, G.; Suraro, A. *Synthesis* **1982**, 679-680.
6. Kamata, M.; Otogawa, H.; Hasegawa, E. *Tetrahedron Lett*. **1991**, **32**, 7421-7424.
7. All the hydrolyzed carbonyl compounds were characterized by comparison of their physical and spectral data with those of authentic samples.

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