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DETHIOACETALIZATION WITH ISOAMYL NITRITE

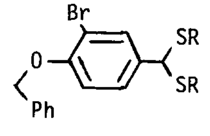
Kaoru Fuji, Kohei Ichikawa, and Eiichi Fujita*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611 Japan

Being stable under both acidic and basic conditions dithioacetal grouping is suitable as a protecting group of carbonyl compounds. The important synthetic utilities of dithioacetals as masked acyl anion equivalents[1] have also been demonstrated. These facts have stimulated the development of a number of new methods of dethioacetalization.[2]

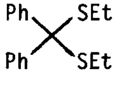
Here we describe a new method of dethioacetalization with isoamyl nitrite. A typical experimental procedure is exemplified: To a solution of dithioacetal 1 in dichloromethane was added isoamyl nitrite (1 equiv.) and the mixture was stirred for 15 min. at room temperature. To the resulting red solution was added water (3 equiv.) and stirring was kept for an additional 15 min. Usual work-up of the reaction mixture gave the corresponding aldehyde in 93% yield. Other dithioacetals listed in Table I also afford good yields of the parent carbonyl compounds. It is note-worthy that isoamyl nitrite has a remarkable chemospecificity. Thus, a mixture of equimolar amount of 3 and 2 in dichloromethane was treated with 1 equivalent of isoamyl nitrite gave rise to 74% of 4 and less than 5% of 5 as expected. Dithioacetal 6 was converted into 7 with 1 equivalent of isoamyl nitrite in 80% yield.

Table I. Reaction Conditions and Yields of the Parent Carbonyl Compounds

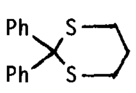


R = Et (1) (93%)
CH_2Cl_2/r.t./0.5h

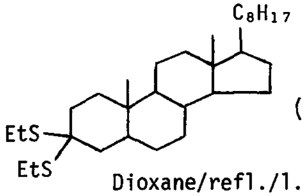
R = CH_2Ph (87%)
CH_2Cl_2/r.t./1.5h



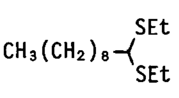
(84%)
CH_2Cl_2/r.t./0.5h



(65%)
CH_2Cl_2/refl./2.5h

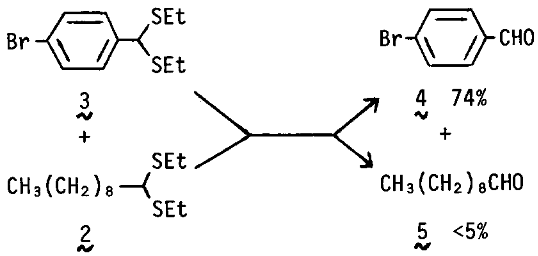


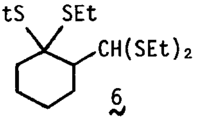
(72%)
Dioxane/refl./1.5h



$CH_3(CH_2)_8CH(SEt)_2$

(2) (89%)
CH_2Cl_2/r.t./0.5h





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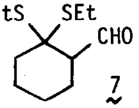

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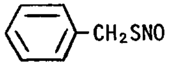

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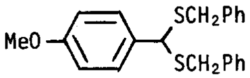

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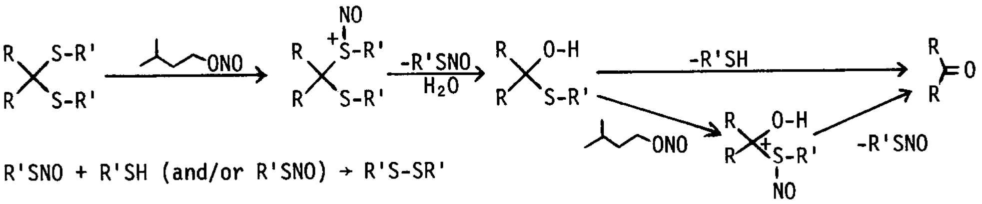
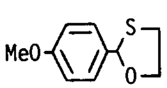
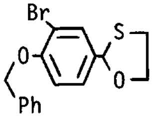
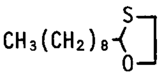
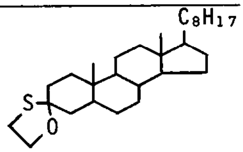
The presence of nitrosyl mercaptide 8 was observed[3,4] in the NMR spectrum of the red solution resulting from the reaction of dithioacetal 9 with isoamyl nitrite in $CDCl_3$. Disulfide was always obtained in 70-80% yield from this dethioacetalization. Taken together these results indicate that the reaction mechanism shown in the following scheme is most plausible.



R'SNO + R'SH (and/or R'SNO) → R'S-SR'

Oxathiolanes were also cleaved to afford the corresponding carbonyl compounds in reasonable yields as summerized in Table II.

Table II. Cleavage of Oxathiolanes*

Oxathiolane				
Isoamyl Nitrite (mol eq.)	3.5	3	3	2
Reaction time/Yield	1.2h/93%	1.25h/70%	1.5h/64%	1.5h/67%

*All reactions were carried out in dichloromethane at room temperature

References and Note

1. B. T. Gröbel and D. Seebach, Synthesis, 357 (1977).
2. Y. Tamura, K. Sumoto, S. Fujii, H. Satoh, M. Ikeda, Synthesis, 312 (1973).
3. H. Lecher and W. Siefken, Chem. Ber., 59, 1314 (1926).
4. Identified with authentic speciemen prepared from benzyl mercaptan and isoamyl nitrite. Nitrosyl mercaptide is red-colored and converted into disulfide on heating or with oxygen.

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