A Convenient Method for Hydrolysis of 1,3-Dithiane Derivatives Using Cupric Chloride

Koichi Narasaka, Takeshi Sakashita, and Teruaki Mukaiyama
Laboratory of Organic Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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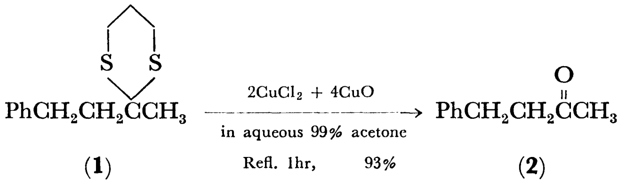
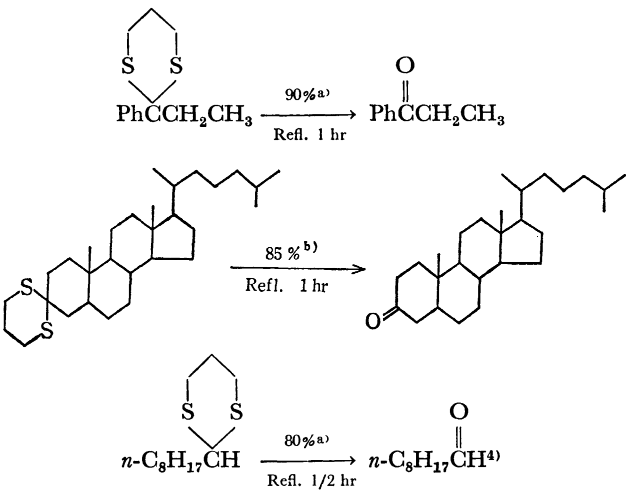
A variety of methods for generation of carbonyl compounds from 1,3-dithiane derivatives has been developed, however, none of these methods is general.[1] Therefore, in connection with the studies on the activation of carbon-sulfur bond with cupric chloride[2], we investigated the hydrolysis of 1,3-dithiane derivatives with cupric chloride.

The mixture of 5 mmol of 2-methyl-2-phenethyl-1,3-dithiane (**1**), 10 mmol of cupric chloride and 20 mmol of cupric oxide in 50 m*l* of aqueous 99% acetone[3] was refluxed for 1 hr. A precipitate was filtered off and the filtrate was condensed under reduced pressure. Ether was added to the residue and the resulting precipitate was filtered off. The filtrate, which was homogeneous by tlc and vpc, was distilled and benzylacetone (**2**) was obtained in 93% yield. When the reaction was carried out at room temperature for 2 hr, **2** was isolated in 83% yield.



(**1**) (**2**)

The hydrolysis of several other 1,3-dithiane derivatives was examined by the same procedure to test the generality of this method.



a) Yield of pure carbonyl compound isolated by distillation.

b) Yield of recrystallized product.

From the results shown in the above equations, it was confirmed that this method is applicable to hydrolysis of a wide variety of 1,3-dithiane derivatives and the corresponding carbonyl compounds were isolated in good yields by the simple procedure.

In addition, it was found that 2-*n*-octyl-1,3-dithiane is readily hydrolyzed with cupric chloride to the corresponding aldehyde in higher yield as compared with the cases of the hydrolyses of 2-monoalkyl-1,3-dithianes, such as 2-benzyl-1,3-dithiane and 2-*n*-hexyl-1,3-dithiane with mercuric chloride[1e,f], *n*-hexyl-1,3-dithiane with boron trifluoride–mercuric oxide[1f] and 2-*n*-octyl-1,3-dithiane with silver perchlorate.[5]

In conclusion, it is noted that this method affords a convenient method for hydrolysis of 1,3-dithiane derivatives, a useful synthetic intermediates, to carbonyl compounds. The further application is now in progress.

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[1] a) K. Kuhn and F. A. Neugebauer, *Chem. Ber.*, **94**, 2629 (1961): b) D. Seebach, *Synthesis*, **1**, 17 (1969): c) M. L. Wolform, *J. Amer. Chem. Soc.*, **51**, 2188 (1929): d) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968): e) E. J. Corey and B. W. Erickson, *ibid.*, **36**, 3553 (1971): f) E. Vedejs and P. L. Fuchs, *ibid.*, **36**, 366 (1971): g) W. Huurdeman and H. Wynberg, *Synthetic Commun.*, **2**, 7 (1972): h) T. Mukaiyama, S. Kobayashi, K. Kamio and H. Takei, *Chem. Lett.*, **1972**, 237.

[2] T. Mukaiyama, K. Narasaka, and H, Hokonoki, *J. Amer. Chem. Soc.*, **91**, 4315 (1969); T. Mukaiyama, K. Maekawa and K. Narasaka, *Tetrahedron Lett.*, **1970**, 4669.

[3] The reaction proceeds in various aqueous organic solvents (acetone, acetonitrile, methanol, and tetrahydrofuran), but it was noted that benzylacetone is obtained in the best yield in the case of aqueous 99% acetone.

[4] In this case, the reaction was carried out under an argon atmosphere for 30 min.

[5] T. Mukaiyama, S. Kobayashi, and K. Kamio, Unpublished work.