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FACILE CONVERSION OF N, N-DIMETHYLHYDRAZONES
TO CARBONYL COMPOUNDS
BY CUPRIC ION-CATALYZED HYDROLYSIS

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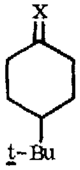
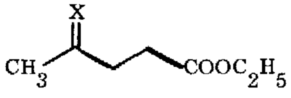
The versatility and usefulness of N, N-dimethylhydrazones (DMH's) as intermediates in organic synthesis has been shown by recent studies[1-3] which detail a number of reactions for carbon-carbon bond formation and also a method for the oxidative hydrolysis of DMH's to carbonyl compounds at pH 7 using periodate a the oxidizing agent. We describe herein still another process for efficient generation of carbonyl compounds from DMH derivatives under very mild conditions. This method is based on the discovery that the hydrolysis of DMH's is powerfully catalyzed by cupric ion.[4] The following experiment is illustrative of the magnitude a utility of this catalytic effect.

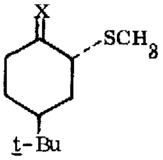
To a stirred solution of cupric acetate (200 mg, 1 mmole) in 10 ml of water (pH 5.4) was added 4-*t*-butylcyclohexanone DMH (98 mg, 0.5 mmole) in 10 ml of tetrahydrofuran (THF). The color of the reaction mixture changed from blue to dark green to tan and a tan precipitate was deposited over 15 min. Concentrati under reduced pressure to remove THF, addition of aqueous ammonium chloride-ammonium hydroxide soluti (pH 8) and extraction with methylene chloride gave after drying and concentration of the extract a product whi afforded upon sublimation (50°, 0.1 torr) 75 mg (97%) of 4-*t*-butylcyclohexanone, mp 43-45°. The hydrolys is significantly slower if the amount of cupric acetate or the proportion of water in the reaction mixture is de



(1 hr, 96%)



(2 hr, 100%)



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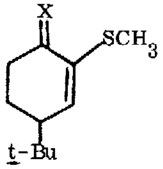
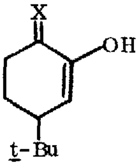


(15 hr, 99%)



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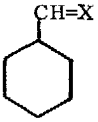
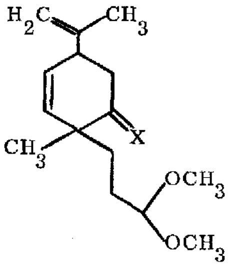


(15 hr, 100%)

PhCH=CHCH=X

(6 hr, 50°, 98%)



(15 hr, 85%)

The cupric ion-catalyzed hydrolysis of DMH derivatives is not only efficient but also mild enough to work well with sensitive substrates. From the above examples it can be seen that α-dicarbonyl, α-thiocarbonyl, acetal and aldehydic formyl units do not interfere with DMH cleavage. Further, in the case of aldehyde DMH's the formation of nitriles is not a significant side reaction.[6]

References and Notes

1. E. J. Corey and D. Enders, *Tetrahedron Letters*, 3 (1976).
2. E. J. Corey, D. Enders and M. G. Bock, *ibid.*, 7 (1976).
3. E. J. Corey and D. Enders, *ibid.*, 11 (1976), and references cited therein.
4. For a review of metal-catalyzed hydrolytic reactions see, A. E. Martell, *Pure and Applied Chemistry*, **17**, 129 (1968).
5. See, D. Petridis, A. Burke and A. L. Balch, *J. Am. Chem. Soc.*, **92**, 428 (1970).
6. This research was assisted financially by a grant from the National Science Foundation.