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### Facile Cleavage of N,N-Dimethylhydrazones to Ketones using Tetrabutylammonium Peroxydisulfate

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FACILE CLEAVAGE OF N,N-  
DIMETHYLHYDRAZONES TO KETONES USING  
TETRABUTYLAMMONIUM PEROXYDISULFATE

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**Abstract :** Tetrabutylammonium peroxydisulfate is turned out to be a good reagent for the conversion of N,N-dimethylhydrazones to ketones.

N,N-Dimethylhydrazones are useful intermediates in organic synthesis because they are utilized as protecting, activating, and directing groups in carbonyl chemistry<sup>1,2</sup>. Thus, the regeneration of carbonyl compounds from N,N-dimethylhydrazones is one of the important carbonyl protecting reactions and a variety of methods has been reported. Oxidative cleavage with nitronium and nitrosonium salts<sup>3</sup>, cupric ion-catalyzed hydrolysis<sup>4</sup>, singlet oxygen<sup>5</sup>,

sodium perborate<sup>6</sup>, magnesium monoperoxyphthalate<sup>7</sup>, Baker's yeast<sup>8</sup>, and others<sup>9</sup> are employed.

Tetrabutylammonium peroxydisulfate ((TBA)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) has been successfully prepared and shown to be a good source of the sulfate anion radical<sup>10</sup> which has the potential to be widely applicable in organic reactions. During the course of our study on tetrabutylammonium peroxydisulfate, sulfate anion radical from this peroxydisulfate was considered to oxidize the double bond of C=N. It has been found that the treatment of N,N-dimethylhydrazones with (TBA)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 1,2-dichloroethane at 70 °C gave the corresponding carbonyl compounds in excellent yields. The results obtained are shown in Table 1. The products were identified by comparison with authentic samples.

Because the reaction medium is nearly neutral, the cleavage reactions underwent smoothly toward the hydrazones which contain sensitive functional groups such as acetal ( Run 2) and olefin moiety ( Run 3). These sensitive units do not interfere with (TBA)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> cleavage.

The known peroxydisulfates such as potassium, sodium or ammonium peroxysulfate are not soluble in most of organic solvents. However, (TBA)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is very soluble in most of organic polar and nonpolar solvents. The reaction can be carried out in other organic solvents such as methylene chloride, acetonitrile, and benzene, giving excellent yields.

Tetrabutylammonium peroxydisulfate is readily prepared from potassium or sodium peroxydisulfate and n-tetrabutyl

Table 1. Conversion of N,N-dimethylhydrazones to ketones

Run	Substrates	Reaction time (h.)	Yields (%) <sup>a</sup>
1		1	90 <sup>b</sup>
2		0.6	97
3		1	95
4		3	90
5		1.5	89 <sup>b</sup>
6		0.5	92 <sup>b</sup>
7		3.5	93

a. Isolated yields. b. GC yields.

ammonium hydrogen sulfate<sup>10</sup> and the workup procedure is simple and easy. Though the reaction mechanism is not yet clear, the cleavage appears to be initiated *via* the addition of sulfate radical to the carbon of C=N, and the oxygen of

carbonyl product is probably originated from the peroxysulfate.

A typical procedure is as follows. To a solution of  $(\text{TBA})_2\text{S}_2\text{O}_8$  (1.0 mmol, 677 mg) in 3 ml of 1,2-dichloroethane was added a solution of 2-[2-(1,3-dioxolan-2-yl)ethyl] cyclohexanone N,N-dimethylhydrazone (0.5 mmol, 120 mg) in 1 ml of 1,2-dichloroethane. After being stirred at refluxing temperature for 0.6 h. under argon, the reaction mixture was poured into water and extracted with methylene chloride (5 ml X 3). The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated at reduced pressure to give the crude product, which was purified by column chromatography (ether : hexane = 1 : 1) to afford (96 mg, 97%) of 2-[2-(1,3-dioxolan-2-yl)ethyl] cyclohexanone.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  1.20-2.15 (m, 10H), 2.21-2.30 (m, 3H), 3.70-3.91 (m, 4H), 4.77 (t, 1H,  $J=4.64\text{Hz}$ ). IR ( $\text{CCl}_4$ ) : 1708, 1136, 1036  $\text{cm}^{-1}$ .

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## References.

1. E.J. Corey and D. Enders, *Tetrahedron Lett.*, 1976, 1, 3.
2. J. K. Whitesell and M. A. Whitesell, *Synthesis*, 1983, 518.
3. G. A. Olah and T. L. Ho, *Synthesis*, 1976, 610.

4. E. J. Corey and S. Knapp, *Tetrahedron Lett.*, 1976, 1, 3667.
5. E. Friedrich, W. Lutz, H. Eichenauer and D. Enders *Synthesis*, 1977, 893.
6. A. Mckillop and J. A. Tarbin, *Tetrahedron*, 1987, 43, 1753.
7. D. Enders and A. Plant, *Synlett*, 1990, 725.
8. A. Kamal and M. Meshram, *Tetrahedron Lett.*, 1991, 32, 2657.
9. T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, John Wiley & Sons, Inc., New York, 1991, Chapter 4, p 212-213.
10. J.C. Jung, H.C. Choi and Y.H. Kim, *Tetrahedron Lett.*, 1993, 34, 3581.

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