Synthetic Methods and Reactions; XXI[1]. Oxidative Cleavage of Tosylhydrazones with Sodium Peroxide

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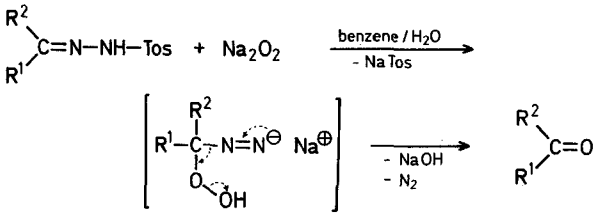
Current interest in the recovery of carbonyl compounds from tosylhydrazones has resulted in a number of methods. Thus, lead(IV) acetate[2], sodium methoxide/dimethyl sulfoxide[3], titanium(III) chloride[4], sodium hypochlorite[5], *N*-bromosuccinimide/methanol[6], acetone[7], and uranium(VI) fluoride[8] have been used for oxidative cleavage or exchange reactions.

The hypochlorite procedure[5] apparently involves activation of the tosylated N-atom which induces S_N2' displacement by hydroxide ion present in the reaction medium, and subsequent fragmentation. It occurred to us that a powerful nucleophile could also initiate the S_N2' reaction directly on tosylhydrazones with extrusion of the toluenesulfinate anion, and the use of a peroxide nucleophile would eventuate in fragmentation of the intermediates in the opposite direction. This possibility has been put to test and the regeneration of ketones from tosylhydrazones has now been realized by employing sodium peroxide as the reagent. The reaction was carried out in the two-phase system pentane/water in which the tosylhydrazones are solubilized in the aqueous layer via the ionic intermediate, while the products are returned to the organic layer. Copious evolution of nitrogen accompanies the reaction.



The yields of recovered ketones given in the Table indicate that some further oxidation of the products must have taken place by a Kharasch-Sosnovsky-type process[9].

Oxidative Cleavage of Ketone Tosylhydrazones with Sodium Peroxide:

To a stirred suspension of the tosylhydrazone (10 mmol) in pentane (20 ml)/water (20 ml) is added sodium peroxide (1.56 g, 20 mmol). The resultant mixture is heated on a steam bath for 6 h, and then allowed to cool. The two layers are separated, the aqueous solution is extracted with ether (2 × 30 ml), and the combined organic solution is dried and evaporated under a Vigreux column. The residue is filtered through a short column of neutra alumina (eluent: ether) to give the pure ketone.

Table. Oxidative Cleavage of Tosylhydrazones with Sodium Peroxide

Ketone	Yield[a] [%]
Cyclohexanone	72
2-Methylcyclohexanone	70
Cycloheptanone	73
Cyclooctanone	69
Acetophenone	70

[a] Isolated product, identified by comparison with authentic sample.

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[1] Part XX: G. A. Olah, T. L. Ho, *Synthesis* **1976**, 610.
[2] A. Bhati, *J. Chem. Soc. Chem. Commun.* **1965**, 476.
[3] R. Oda, M. Mieno, Y. Hayashi, *Tetrahedron Lett.* **1967**, 2363.
[4] B. P. Chandrasekhar, S. V. Sunthankar, S. G. Telang, *Chem. Ind. (London)* **1974**, 87.
[5] T.-L. Ho, C. M. Wong, *J. Org. Chem.* **39**, 3453 (1974).
[6] G. Rosini, *J. Org. Chem.* **39**, 3504 (1974).
[7] S. R. Maynes, L. Pelavin, G. Erker, *J. Org. Chem.* **40**, 3302 (1975).
[8] G. A. Olah, J. Welch, T.-L. Ho, submitted for publication.
[9] M. S. Kharasch, G. Sosnovsky, *J. Org. Chem.* **23**, 1322 (1958).