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FACILE CONVERSION OF TOSYLHYDRAZONES TO CARBONYL COMPOUNDS BY THE POTASSIUM PEROXYMONOSULFATE-ACETONE SYSTEM

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ABSTRACT : Tosylhydrazones of carbonyl compounds were found to be readily cleaved into the corresponding carbonyl compounds in good yields under the mild conditions by treatment with dimethyldioxirane which is generated in situ from the reaction of acetone with potassium peroxymonosulfate.

Earlier, the formation of dioxirane has been mentioned occasionally as elusive reaction intermediates in oxidation reaction.[1] The observation that acetone reacted with potassium peroxymonosulfate (oxone : $KHSO_5$) to form dimethyldioxirane became accepted as relatively stable entities. Thus numerous oxidations using dimethyldioxirane have been performed in situ for a wide-ranging development of the chemistry of these interesting cyclic peroxides.

Derivatives of carbonyl compounds such as tosylhydrazones serve as important synthetic intermediates and are at the same time very useful for purification and characterization of ketones.[2] Recovery of the parent ketones has, therefore, received considerable attention. A number of methods have been developed to bring about such cleavage.[3]

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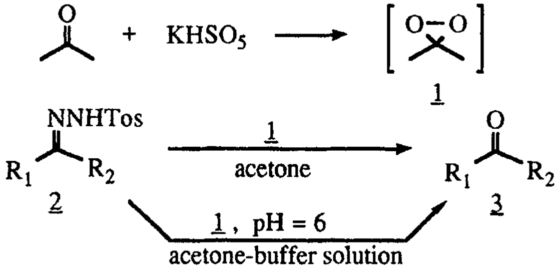
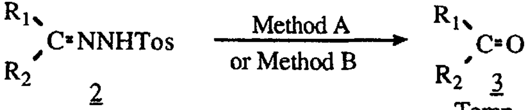
Recently, we reported that peroxysulfur intermediates (R-S(O)$_2$-OO$^\cdot$ or R-S(O)$_2$-OO$^-$), are efficient reagents for the cleavage of various tosylhydrazones to the corresponding carbonyl compounds.[4] We have now found that various readily diaryl and aryl-alkyl tosylhydrazones react readily with dimethyl dioxirane (1), which is generated in situ by the reaction of acetone with potassium peroxymonosulfate (KHSO$_5$), to form the corresponding ketones. The reaction can be carried out under mild conditions by controlling pH value using phosphate buffer solution (pH 6). The work-up is simple ; products are readily separable from the organic solvent layer in nearly quantitative yields.

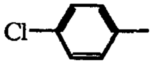
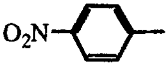
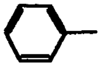
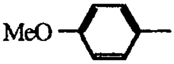
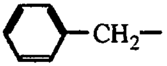
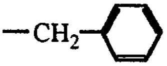
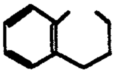


The following experimental procedure is representative. Method A: The mixture of acetophenone tosylhydrazone (202 mg, 0.7 mmol) and potassium peroxymonosulfate (1.3 g, 4.2 mmol) in acetone (10 ml) was stirred at 10 °C. After being stirred for 24 h at 10 °C, a saturated aqueous solution of NaHCO$_3$ (10 ml) was added to the reaction mixture, and then was extracted with CH$_2$Cl$_2$ (3 x 20 ml). The combined organic layers were dried over MgSO$_4$ and filtered. Removal of solvent under reduced pressure gave the crude acetophenone. Separation by preparative TLC (Merck, silica gel, 60 GF$_{254}$, 1mm x 20 cm x 20 cm, n-hexane/ether = 2/1, v/v) gave pure acetophenone (82 mg, 98 %). The product obtained was identified by comparing its IR and ^{1}H NMR with those of authentic sample. Method B: The same procedure described in method A was carried out in

Table 1. Oxidative cleavages of 2 in potassium peroxymonosulfate-acetone system



$$R_1R_2C{=}NNHTos \xrightarrow[\text{or Method B}]{\text{Method A}} R_1R_2C{=}O$$

Run	R_1	R_2	Method	Temp. (°C)	Time (h)	Yields (%)[c]
1		$-CH_3$	A	25	24	98[d]
2			A	10	36	99
3		$-CH_3$	A	10	96	99
4		$-CH_3$	A	10	24	99
5			B	25	12	99
6		$-CH_3$	A	10	10	97
7			A	10	144	67
8			B	25	72	90
9			A	10	120	95
10			B	25	48	90
11			A	10	120	75
12			B	25	13	98

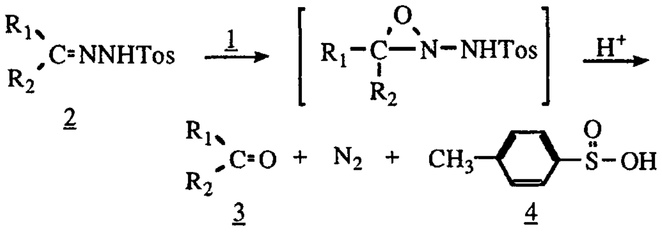
a) Method A; 6 equivalent of $KHSO_5$, CH_3COCH_3, 10 °C.

b) Method B; 6 equivalent of $KHSO_5$, CH_3COCH_3, phosphate buffer solution (pH 6), 25 °C.

c) Isolated yields. d) Substrate; p-Chloroacetophenone hydrazone

phosphate buffer solution (pH 6) at 25 °C. The results obtained are summarized in Table 1.

When the reaction was carried out in acetonitrile which is more polar than acetone, tosylhydrazone (2) was recovered quantitatively.



The regeneration of the carbonyl groups from the tosylhydrazones appears to be initiated *via* the oxidation with 1 which is generated in acetone-potassium peroxymonosulfate system. Tosylhydrazones may be oxidized into the corresponding oxaziridines. The oxaziridines may be immediately decomposed to the ketones[4] together with toluene sulfonic acid[5] by fragmentation reaction induced by potassium peroxymonosulfate which is known to be quite acidic. The acid catalyzed elimination reaction of oxaziridines has already been examined in depth by several group before this work.[6] It was also known that imines are oxidized readily to the corresponding oxaziridines by dioxirane.[7]

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Reference and Notes

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5. 4-Toluene sulfinic acid was actually oxidized to 4-toluene sulfonic acid under the same reaction conditions. The crude 4-toluene sulfonic acid was isolated and confirmed by its molecular peak in mass spectrum (m/z, 172, 11.4 %).
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