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### Facile Transformation of N,N-Dimethylhydrazones and Tosylhydrazones to Ketones with Dimethyl Sulfate and Potassium Carbonate

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**FACILE TRANSFORMATION OF N,N-DIMETHYLHYDRAZONES AND  
TOSYLHYDRAZONES TO KETONES WITH DIMETHYL SULFATE  
AND POTASSIUM CARBONATE.**

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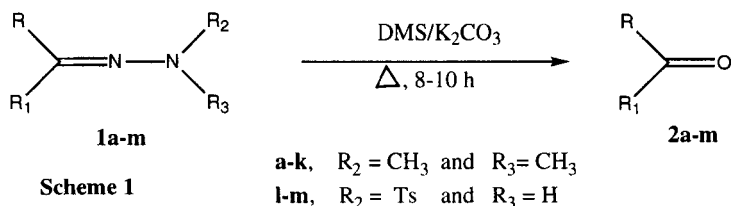
**Abstract:** N,N-Dimethylhydrazones and tosylhydrazones can be converted to their ketones in good to excellent yields with dimethylsulfate and  $K_2CO_3$ .

N,N-Dimethylhydrazones<sup>1</sup> and tosylhydrazones<sup>2</sup> are important intermediates in many synthetic transformations. The versatility and usefulness of N,N-dimethylhydrazones have been proven by some applications to carbon-carbon bond formation and other reactions<sup>3</sup> like epoxidations, hydroboration, oxidation, reduction and hydrolysis. However, very often these conversions require the regeneration of the carbonyl functionality. The formation of N,N-dimethylhydrazones and tosylhydrazones is generally required for protection and/or the separation and purification of carbonyl compounds; purification of these derivatives followed by regeneration of their parent ketone is a useful process for recovery of the desired ketone from a complex reaction mixture<sup>4</sup>. As a result there has been considerable interest in the development of efficient

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techniques for the conversion of N,N-dimethylhydrazones and tosylhydrazones into their ketones<sup>5,6</sup>. Most of the known methods of regenerating carbonyl compounds from their nitrogen derivatives need strongly acidic<sup>7</sup>, oxidizing<sup>8</sup> or reducing<sup>9</sup> conditions, or tedious procedures and/or expensive reagents<sup>10</sup>. It is desirable, in particular to avoid toxic reagents eg. (PhSeO)<sub>2</sub>O<sup>11</sup> and use of expensive transition metals .

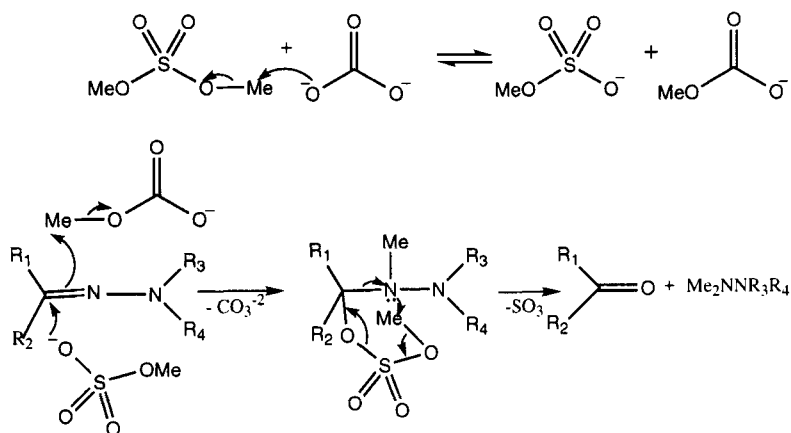


In our earlier studies, we described the use of baker's yeast for the regeneration of carbonyl compounds from their corresponding hydrazones<sup>12</sup> and oximes<sup>13</sup>. In continuation of these efforts, we now wish to report a new facile and convenient method for the regeneration of ketones from their N,N-dimethylhydrazones and tosylhydrazones in presence of dimethyl sulfate (DMS) and K<sub>2</sub>CO<sub>3</sub> in quantitative yields. The possible mechanism is depicted in Scheme 2 and the results are summarized in the Table. In case of entries **c-f** simultaneous O-methylation takes place along with the deprotection of hydrazones. In case of hydrazones of aldehydes this reaction gives nitriles by oxidative cleavage<sup>14</sup>.

Interestingly, in summary this new method for the regeneration of ketones has some practical merits over previously reported methods. Particularly, the use of inexpensive reagents which are very convenient in both small and large scale operations, and the procedure involves very simple work up.

#### General procedure for the deprotection of hydrazones .

To a solution of hydrazone **1** (5mmol) in CH<sub>3</sub>CN (15ml) was added DMS (0.477ml, 5mmol) and K<sub>2</sub>CO<sub>3</sub> (0.64g, 5mmol). This reaction mixture was



Scheme 2

**Table** : Oxidative Cleavage of N,N-Dimethylhydrazones and Tosylhydrazones with DMS/ K<sub>2</sub>CO<sub>3</sub>

Entry	Substrate	Product	Yield <sup>a</sup> (%)
a.	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	97
b.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NN(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	94
c.	2-OH-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	95
d.	2,4-(OH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,4-(OCH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> COCH <sub>3</sub>	93
e.	2-OH,5-OCH <sub>3</sub> ,C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,5-(OCH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> COCH <sub>3</sub>	94
f.	2-OH,4-OCH <sub>3</sub> ,C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,4-(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COCH <sub>3</sub>	93
g.	2-NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	96
h.	2-NH <sub>2</sub> ,5 NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,NH <sub>2</sub> ,5 NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	90
i.	2-NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2,NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>5</sub>	95
j.	2-NH <sub>2</sub> ,2,5-(Cl) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	2-NH <sub>2</sub> ,2,5-(Cl) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	94
k.	(CH <sub>3</sub> ) <sub>2</sub> 2-CH=CH(CH <sub>3</sub> )C=NN(CH <sub>3</sub> ) <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> 2-CH=CHCOCH <sub>3</sub>	95
l.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NNHTs	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	92
m.	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )C=NNHTs	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	94
n.	4-Me,2-COOH,C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C=NN(Me) <sub>2</sub>	4-Me,2-COOH,C <sub>6</sub> H <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	93
o.	3-Cl,2-COOH,C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C=NN(Me) <sub>2</sub>	3-Cl,2-COOH,C <sub>6</sub> H <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	95

<sup>a</sup> Yields of isolated products. <sup>b</sup> Tosylhydrazones were prepared by known methods.<sup>15</sup><sup>c</sup> Products were characterised by comparison of their melting points, IR, and<sup>1</sup>H-NMR spectra with authentic samples.

refluxed for (10-15 h). On completion of the reaction the solid was separated by filtration and the filtrate was evaporated in reduced pressure to afford the crude product. This was purified by column chromatography (silica, EtOAc-hexane, 2:8) to give pure compound **2a-m**.

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