

REACTIONS OF OXIMES WITH TRIMETHYLSILYL IODIDE: DEHYDRATION AND BECKMANN REARRANGEMENT

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Abstract: Aldoximes are dehydrated in good yields to nitriles and certain ketoximes undergo Beckmann rearrangement when treated with trimethylsilyl iodide.

Trimethylsilyl iodide (TMSI, 1)³ has become a very useful reagent in organic synthesis, especially for the cleavage of carbon-oxygen bonds.⁴ It has also been found to be a good iodide nucleophile for various systems, e.g., cyclopropyl and cyclobutyl ketones,⁵ enones,⁵ aldehydes,⁶ and acid chlorides.⁷ In his recent review,^{3b} Olah described unpublished work of his on the reactions of nitroalkanes with TMSI to give oxime silyl ethers and products derived from them. This information prompts us to report our independent study of the reaction of oximes with TMSI.

When aldoximes 2 are allowed to react with TMSI, 1, in chloroform at 25°C for a few hours, a mixture of the corresponding nitrile 3 and starting material is obtained. By conducting the reaction at reflux (56°C), all starting material disappears and only the nitrile is produced, albeit in only fair yields (~40-50%). However, when the reaction is carried out in the presence of one equivalent of hexamethyldisilazane to act as a base,⁸ the yields are dramatically increased (84-88%) (Table I). Thus this is a reasonable alternative to the many methods for conversion of aldoximes to nitriles.⁹

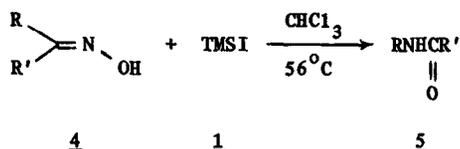
Table I
Dehydration of Aldoximes with TMSI

RCH=NOH	+	TMSI	$\xrightarrow[\text{4h}]{\begin{matrix} (\text{TMS})_2\text{NH} \\ 56^\circ\text{C} \\ \text{CHCl}_3 \end{matrix}}$	RCN
<u>2</u>		<u>1</u>		<u>3</u>
<u>Isolated Yield of 3</u>				
			Without (TMS) ₂ NH	With (TMS) ₂ NH
<u>a</u>	R = n-C ₈ H ₁₇		50%	88%
<u>b</u>	R = PhCH ₂		38.5%	84%
<u>c</u>	R = 3,4(OMe) ₂ C ₆ H ₃ CH ₂		45%	86%

Ketoximes undergo a somewhat different reaction course. Treatment of the oxime of benzophenone 4a with 1.3 equivalents of TMSI in chloroform at 25°C gave essentially no reaction. However upon refluxing the solution (56°C) for 4 hr, an excellent yield of the product of Beckmann

rearrangement, benzanilide 5a, was produced. A similar reaction course was observed for other aromatic ketoximes, e.g., acetophenone oxime 4b which gave acetanilide 5b. However, simple aliphatic ketoximes, e.g., acetone, cyclohexanone, 2-octanone and pinacolone oximes, do not undergo rearrangement under similar conditions (56°C, 10 hr). The initially formed silyl oxime is hydrolyzed in the workup to give back only starting material. It was further observed that the addition of hexamethyldisilazane had no effect on the rate or yield of these reactions.

Table II
Beckmann Rearrangement of Ketoximes with TMSI



<u>Compound</u>	<u>Time</u>	<u>Isolated Yield</u>
<u>a</u> R = Ph; R' = Ph	4h	80%
<u>b</u> R = Ph; R' = Me	4h	55%
<u>c</u> R = R' = (CH ₂) ₅	10h	NR
<u>d</u> R = Me; R' = Me	10h	NR
<u>e</u> R = <u>n</u> C ₆ H ₁₃ ; R' = Me	10h	NR
<u>f</u> R = <u>t</u> Bu; R' = Me	4h	NR

Further investigations in this area using other electrophilic silanes are under study.

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References and Notes

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