

A FACILE KETOXIME PREPARATION VIA THE REDUCTION OF  
 $\alpha,\beta$ -UNSATURATED NITROALKENES USING SODIUM STANNITE

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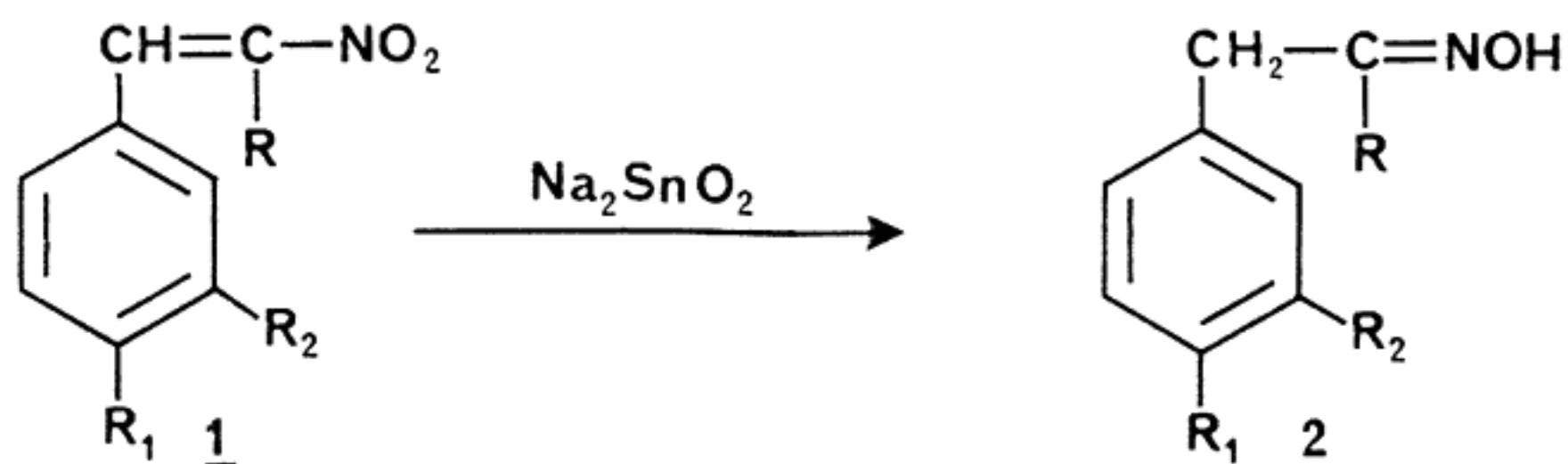
Tetrahedron Letters, Vol. 26, No. 49, pp 6013-6014, 1985

Abstract:  $\alpha,\beta$ -Unsaturated nitroalkenes are readily reduced by sodium stannite to ketoximes at room temperature.

Tin(II) halides have been used extensively to reduce a variety of compounds under acidic conditions.<sup>1</sup> However, only a few studies have been reported in which basic conditions were utilized (sodium stannite,  $\text{Na}_2\text{SnO}_2$ , forms under basic conditions). These studies included the replacement of the diazonium group in aromatic compounds by hydrogen,<sup>2</sup> the reduction of nitroarenes to azo compounds<sup>3</sup>, and the reductive disproportionation of organomercuric halides.<sup>4</sup> We decided to explore the utility of sodium stannite for the reduction of conjugated nitroalkenes in continuation of our studies involving these useful intermediates.<sup>5-13</sup>

We wish to report that nitroalkenes are readily reduced by sodium stannite to the corresponding ketoximes<sup>14</sup> at room temperature. These results contrast those obtained when the reactions were carried out under acidic<sup>15</sup> or neutral conditions<sup>10</sup> which resulted in the formation of  $\alpha$ -substituted oxime derivatives.

The following procedure is representative: a sodium stannite solution was prepared by addition of aqueous sodium hydroxide (50 mmol, 2 g in 15 mL of water) to aqueous stannous chloride (5 mmol, 1.12 g in 15 mL water); the initially formed precipitate dissolved to form a clear solution. This solution was gradually added to the  $\beta$ -nitrostyrene derivative (2 mmol, in 10 mL THF) at room temperature; a mildly exothermic reaction ensued. The reaction mixture was stirred for the specified time, saturated brine solution added, the product extracted into ether (3 x 45 mL), and then worked up in the usual manner. Essentially pure products<sup>16</sup> were obtained. Further purification could be achieved by chromatography (silica gel: ether/petroleum ether). The results are summarized in Table I.



- a. R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>2</sub> = H  
b. R = CH<sub>3</sub>; R<sub>1</sub> = Br; R<sub>2</sub> = H  
c. R = CH<sub>3</sub>; R<sub>1</sub> = R<sub>2</sub> = OC<sub>2</sub>H<sub>5</sub>

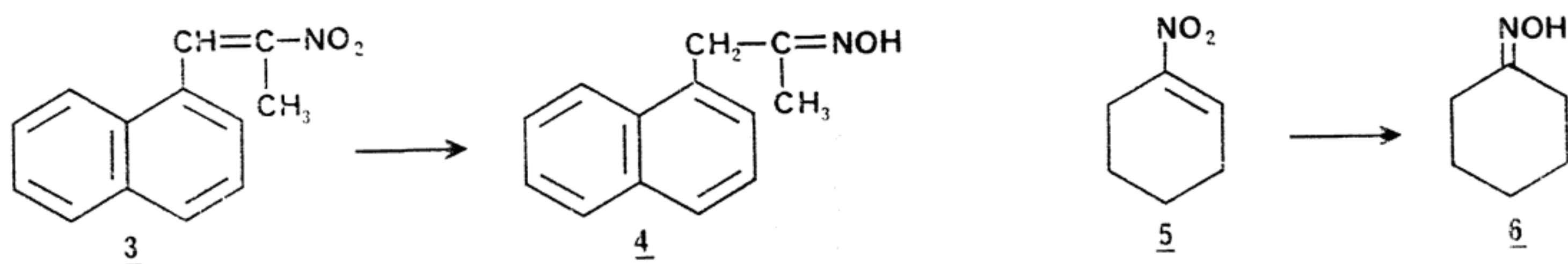


TABLE I. KETOXIMES FROM NITROALKENES VIA SODIUM STANNITE REDUCTION

Nitroalkene <sup>a</sup>	Product <sup>b</sup>	Time (Min)	Yield <sup>c</sup> [%]	Ref
<u>1a</u>	<u>2a</u>	25	82	13
<u>1b</u>	<u>2b</u>	40	84	13
<u>1c</u>	<u>2c</u>	90	71	13
<u>3</u>	<u>4</u>	45	68	13
<u>5</u>	<u>6</u>	15	86	13

<sup>a</sup>Prepared by the published procedure.<sup>6</sup> <sup>b</sup>All products exhibited physical and spectral characteristics in accordance with the assigned structures. <sup>c</sup>Isolated and unoptimized yields.

#### REFERENCES AND NOTES

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- Aldoximes could not be obtained under the reaction conditions;  $\beta$ -nitrostyrene gave mainly polymeric material.
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- It is interesting to note that freshly prepared solutions of 2a and 2b exhibited only the low field methylene and high field methyl resonances corresponding to the thermodynamically less stable (Z)-isomer; overnight storage in CDCl<sub>3</sub> resulted in an equilibration favoring the (E)-isomer. The isomerization is presumably occurring in each of the compounds investigated and similar phenomenon was noted for (Z)-phenylacetaldoxime.<sup>17</sup>
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