

A FACILE KETOXIME PREPARATION VIA THE REDUCTION OF
 α,β -UNSATURATED NITROALKENES USING SODIUM STANNITE

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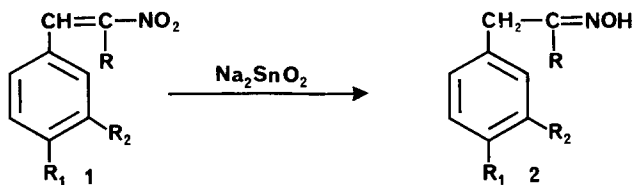
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Abstract: α,β -Unsaturated nitroalkenes are readily reduced by sodium stannite to ketoximes at room temperature.

Tin(II) halides have been used extensively to reduce a variety of compounds under acidic conditions.¹ However, only a few studies have been reported in which basic conditions were utilized (sodium stannite, Na_2SnO_2 , forms under basic conditions). These studies included the replacement of the diazonium group in aromatic compounds by hydrogen,² the reduction of nitroarenes to azo compounds³, and the reductive disproportionation of organomercuric halides.⁴ We decided to explore the utility of sodium stannite for the reduction of conjugated nitroalkenes in continuation of our studies involving these useful intermediates.⁵⁻¹³

We wish to report that nitroalkenes are readily reduced by sodium stannite to the corresponding ketoximes¹⁴ at room temperature. These results contrast those obtained when the reactions were carried out under acidic¹⁵ or neutral conditions¹⁰ which resulted in the formation of α -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 β -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 products¹⁶ were obtained. Further purification could be achieved by chromatography (silica gel: ether/petroleum ether). The results are summarized in Table I.



- a. R = CH₃; R₁ = R₂ = H
b. R = CH₃; R₁ = Br; R₂ = H
c. R = CH₃; R₁ = R₂ = OC₂H₅

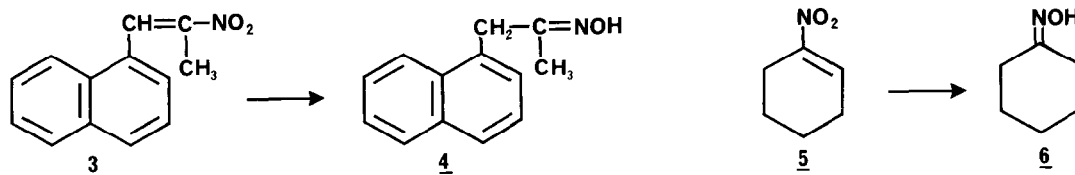


TABLE I. KETOXIMES FROM NITROALKENES VIA SODIUM STANNITE REDUCTION

Nitroalkene ^a	Product ^b	Time (Min)	Yield ^c [%]	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

^aPrepared by the published procedure.⁶ ^bAll products exhibited physical and spectral characteristics in accordance with the assigned structures. ^cIsolated and unoptimized yields.

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- Aldoximes could not be obtained under the reaction conditions; 8-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 CDCl₃ resulted in an equilibration favoring the (E)-isomer. The isomerization is presumably occurring in each of the compounds investigated and a similar phenomenon was noted for (Z)-phenylacetaldoxime.¹⁷
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