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

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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. However, only a few studies have been reported in which basic conditions were utilized (sodium stannite, Na₂SnO₂, forms under basic conditions). These studies included the replacement of the diazonium group in aromatic compounds by hydrogen, the reduction of nitroarenes to azo compounds, and the reductive disproportionation of organomercuric halides. We decided to explore the utility of sodium stannite for the reduction of conjugated nitroalkenes in continuation of our studies involving these useful intermediates.

We wish to report that nitroalkenes are readily reduced by sodium stannite to the corresponding ketoximes at room temperature. These results contrast those obtained when the reactions were carried out under acidic or neutral conditions 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 products were obtained. Further purification could be achieved by chromatography (silica gel: ether/petroleum ether). The results are summarized in Table I.

\[
\begin{align*}
\text{CH} &= \text{C-NO}_2 \\
\text{R} &\quad \text{Na}_2\text{SnO}_2 \\
\text{CH}_2 &= \text{C-NOH} \\
\text{R} &
\end{align*}
\]

1. R = CH₃; R₁ = R₂ = H
2. R = CH₃; R₁ = Br; R₂ = H
3. R = CH₃; R₁ = R₂ = OC₂H₅
TABLE I. KETOXIMES FROM NITROALKENES VIA SODIUM STANNITE REDUCTION

<table>
<thead>
<tr>
<th>Nitroalkene a</th>
<th>Product b</th>
<th>Time (Min)</th>
<th>Yield c [%]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>2a</td>
<td>25</td>
<td>82</td>
<td>13</td>
</tr>
<tr>
<td>lb</td>
<td>2b</td>
<td>40</td>
<td>84</td>
<td>13</td>
</tr>
<tr>
<td>lc</td>
<td>2c</td>
<td>90</td>
<td>71</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>45</td>
<td>68</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>15</td>
<td>86</td>
<td>13</td>
</tr>
</tbody>
</table>

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

REFERENCES AND NOTES


14. Aldoximes could not be obtained under the reaction conditions; 8-nitrostyrene gave mainly polymeric material.


16. 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 similar phenomenon was noted for (Z)-phenylacetaldoxime.¹⁷