Synthetic Methods and Reactions: 108. Cleavage of Ethanediyl S,S-Acetals with Iodo(Bromo)trimethylsilane/Dimethyl Sulfoxide

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Ethanediyl S,S-acetals are useful in organic synthesis as masked acyl carbonates and as protecting groups for carbonyl compounds. Although a wide variety of reagents is available for hydrolytic cleavage of S,S-acetals to the corresponding carbonyl compounds there is still a need to develop improved mild and neutral reagents for this cleavage reaction.

We have previously demonstrated the use of bromodimethylsulfoxonium bromide and its in situ equivalents in the cleavage of ethanediyl S,S-acetals (1) to the corresponding carbonyl compounds (2). Our studies on the deoxygenation of dimethyl sulfoxide and other sulfoxides with bromotrimethylsilane and iodotrimethylsilane indicated that bromoiodo(dimethylsulfoxonium bromide (iodide) (3) could be the intermediates in these reactions. These observations have led us to develop a highly efficient reagent for the cleavage of ethanediyl S,S-acetals (1) by in situ generation of iodo(bromo)trimethylsulfoxonium iodide (bromide) (3) from iodo(bromo)trimethylsilane and dimethyl sulfoxide. The reaction is general for ethanediyl S,S-acetals of aliphatic, alicyclic, and aromatic carbonyl compounds. The reaction was faster with iodotrimethylsilane than with bromotrimethylsilane. However, both these reagents yielded the corresponding aldehydes and ketones (2) in excellent yields. We suggest the following mechanism for the cleavage of ethanediyl S,S-acetals.

\[
\begin{align*}
2 \text{X-Si(CH}_3)_3 & + \text{H}_2\text{C-S-CH}_3 \\
& \rightarrow \text{H}_2\text{C-S-CH}_3 \text{X}^\Theta
\end{align*}
\]

The present method provides a mild, efficient procedure for the conversion of ethanediyl S,S-acetals (1) to the corresponding carbonyl compounds (2) and further extends the utility of iodotrimethylsilane in organic synthesis.

Table. Carboxyl Compounds (2) from Their Ethanediyl S,S-Acetals (1) by Cleavage with Iodo(Bromo)trimethylsilane/Dimethyl Sulfoxide

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>X</th>
<th>Reaction time [h]</th>
<th>Yield [%]</th>
<th>b.p./torr [°C]</th>
</tr>
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* Yield of isolated product.
* Amounts of reagents are doubled.

Cleavage of Ethanediyl S,S-Acetals (1) to Carbonyl Compounds (2):

**General Procedure:**

The ethanediyl S,S-acetal (1; 1 mmol) is added to a stirred solution of iodo(bromo)trimethylsilane (35 mmol) and dimethyl sulfoxide (17.5 mmol) in carbon tetrachloride (5 ml) under a dry nitrogen atmosphere. The reaction mixture is heated at 75-80 °C and the reaction is monitored by TLC (silica gel, hexane eluent). Upon completion of the reaction, the mixture is quenched with water (15 ml) and extracted with carbon tetrachloride (2×10 ml). The organic extract is washed with saturated sodium thiosulfate solution (2×10 ml) and water (2×10 ml). The organic extract is dried with sodium sulfate and the solvent evaporated. The crude product is purified by column chromatography followed by crystallization or fractional distillation.

Support of our work by the National Science Foundation is gratefully acknowledged.

Received: January 29, 1982

0039-7881/82/1132-0965 $ 03.00 © 1982 Georg Thieme Verlag · Stuttgart · New York
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