We now would like to report that this reagent is useful for the conversion of aldehydes to 2,3-dihydroxyalkanoic acids under very mild conditions (Scheme B).

The reaction of silylated ketene acetics with aldehydes has been reported to be of use for the preparation of 3-hydroxyalkanoic acids and esters\(^1,\,^2\) and therefore by analogy, it was anticipated that the additional trimethylsilyloxy group present in 1 would allow a convenient preparation of 2,3-dihydroxyalkanoic acids. For example, the tin(IV) chloride-catalyzed reaction of a neat mixture of \(n\)-hexanal and an equivalent of reagent 1 is exothermic and furnishes 3 in 87\% yield. This product presumably arises by nucleophilic attack of the reagent on the aldehyde to give intermediate 2 which undergoes a silyl transfer as shown. Direct hydrolysis of the reaction mixture with aqueous acetic acid in tetrahydrofuran furnished the 2,3-hydroxyoctanoic acid (4) in 80\% yield after recrystallization.

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**Tris[trimethylsilyloxy]ethene: A Convenient Preparation of 2,3-Dihydroxyalkanoic Acids From Aldehydes**

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In a previous communication\(^1\) we reported the preparation of tris[trimethylsilyloxy]ethene (1) and its use for the conversion of carboxylic acid chlorides to hydroxymethyl ketones (Scheme A).
Table. Preparation of 2,3-Dihydroxyalkanoic Acids

<table>
<thead>
<tr>
<th>R</th>
<th>Yield [%]</th>
<th>m.p.</th>
<th>Molecular formula</th>
<th>I.R. (KBr) (v_{\text{c=O}} \text{ cm}^{-1})</th>
<th>1H-N.M.R. (acetone-(d_6)) (\delta \text{ ppm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-C(_5)H(_4)</td>
<td>80</td>
<td>106-111</td>
<td>(\text{C}_2\text{H}_2\text{O}_4) (176.2)</td>
<td>1710</td>
<td>5.90 (bs, 3H); 4.05 (m, 1H); 3.88 (m, 1H); 1.76-1.10 (m, 1H); 0.88 (m, 3H)</td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
<td>82</td>
<td>101-110</td>
<td>(\text{C}_9\text{H}_7\text{O}_4) (182.2)</td>
<td>1740</td>
<td>7.17 (m, 5H); 6.23 (bs, 3H); 5.08; 4.95 (2d, 1H, J = 3.0, 5.5 Hz); 4.37, 4.30 (2d, 1H, J = 5.5, 3.0 Hz)</td>
</tr>
<tr>
<td>3-O(_2)N C(_6)H(_5)</td>
<td>58a</td>
<td>189-190</td>
<td>(\text{C}_9\text{H}_7\text{NO}_4) (227.2)</td>
<td>1730</td>
<td>8.0 (m, 4H); 5.24 (d, 1H, J = 3.1 Hz); 4.35 (d, 1H, J = 3.1 Hz)</td>
</tr>
<tr>
<td>4-cyclohexyl</td>
<td>66</td>
<td>150-152</td>
<td>(\text{C}<em>9\text{H}</em>{12}\text{O}_4) (186.2)</td>
<td>1740</td>
<td>5.66 (bs, 2H); 4.29, 4.23 (2d, 1H, J = 2.0, 2.0 Hz); 3.63 (m, 1H); 2.0 (m, 7H)</td>
</tr>
<tr>
<td>C(_5)H(_3)-CH-CH(C(_2)H(_5))</td>
<td>78</td>
<td>113-118</td>
<td>(\text{C}<em>{12}\text{H}</em>{12}\text{O}_4) (222.2)</td>
<td>1730, 1690</td>
<td>7.22 (s, 5H); 6.60 (m, 1H); 4.35 (m, 2H)</td>
</tr>
<tr>
<td>(cis-C(_5)H(_3)-CH(_3))</td>
<td></td>
<td></td>
<td></td>
<td>1.92 (s, 3H)</td>
<td></td>
</tr>
</tbody>
</table>

* Reported yields are for recrystallized products.

† All compounds gave satisfactory elemental analyses (C \(\pm 0.4\%), H \(\pm 0.3\%), N \(\pm 0.3\%\)) with the exception of the last entry in the Table (C \(\pm 1.4\%), H \(\pm 0.02\%\)); this compound gave a satisfactory high resolution mass spectrum. Calc. for \(\text{C}_2\text{H}_2\text{O}_4\) (M + \(\text{H}_2\text{O}\)) 204.0786; found: 204.0779.

‡ While in this case a single isomer was obtained on recrystallization, inspection of the silylated mixture before hydrolysis indicated both isomers were present in comparable amounts; consequently, the low yield reflects fractionation of isomers during recrystallization.

The results obtained with a number of additional aldehydes are presented in the Table. In all cases, inspection of the silylated mixture prior to hydrolysis indicated that the products are mixtures of the erythro and threo isomers, the isomers being present in comparable amounts.

This procedure for the preparation of 2,3-dihydroxyalkanoic acids complements the literature methods. Such compounds have been prepared by oxidation of \(\omega\)-unsaturated acids and esters with a variety of oxidants.\(^a\) With respect to these oxidative methods, the procedure described here is likely to be advantageous if the required \(\omega\)-unsaturated compound is not available, is difficult to prepare, or contains other functionality which is susceptible to oxidation. For example, it is unlikely that the last two entries in the Table could be prepared by such oxidative procedures. However, unlike these literature procedures which can provide 2,3-dihydroxyalkanoic acids stereospecifically depending on the stereochemistry of the starting \(\omega\)-unsaturated compound and the nature of the oxidizing agent,\(^b\) the procedure described here is non-stereospecific.

2,3-Dihydroxyalkanoic acids have also been prepared from aldehydes using a Dattels condensation followed by alkaline hydrolysis of the resulting \(\omega\)-epoxy esters.\(^c\) The new procedure described here can accomplish the same transformation under much milder conditions.

**2,3-Dihydroxyoctanoic Acid (4): Typical Procedure**

To a stirred mixture of \(n\)-hexanol (30 g, 30 mmol) and tris[trimethylsilyloxyl]ethene (11; 8.8 g, 30 mmol) is added three drops of titanIV chloride (ethoctic acid). After stirring 3 h, 2:2:1 acetic acid/tetrahydrofuran/water (20:ml) is added. The solution is stirred for 10 min and the solvents are removed at reduced pressure at 50-60°C. Toluene is added and removed twice. The residue is recrystallized from chloroform/tetrahydrofuran (two crops) to give 4; yield: 4.19 g (80%). Analytical and spectral data are given in the Table.

**Trimethyksilyl 2,3-Bis[trimethylsilyloxy]octanoate (3):**

The above reaction is repeated using \(n\)-hexanal (1.5 g, 15 mmol), I (4.4 g, 15 mmol), and one drop of titanIV chloride. After 3 h, the mixture is subjected to molecular distillation (bath temperature 120°C, 0.3 torr); yield: 5.12 g (87%).

C\(_5\)H\(_3\)I\(_2\)O\(_4\)Si\(_3\) calc. C 51.99 H 10.27 found 51.92 10.18


1. R (neat); \(v_{\text{max}}\) = 1740 cm\(^{-1}\).

1H-N.M.R. (CDCl\(_3\)); \(\delta = 4.00\) (m, 2H, OC\(_2\)H\(_5\)); 1.25 (m, 8H, \(\text{CH}_2\)\(_2\)); 0.80 (m, 3H, \(\text{CH}_3\)\(_2\)O), 0.29, 0.15, 0.12, 0.08, 0.00 ppm [5s, 27H, Si(CH\(_3\))\(_3\)].

We wish to thank Mr. L. M. Bruncone and his staff (E. Ross, E. T. Palestro) for microanalyses, Messrs. W. Fulmor and G. O. Morton and Dr. R. T. Hargreaves and staff (H. M. Smith, G. D. Livingston, K. A. Angyal) for spectral data.

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