though we were able to affect formylation of 2 in only low yield (possibly for steric reasons).

\[ \text{Scheme A} \]

2-Formyl-1,3-dithiane (5) is known\(^4\), but its alkylation chemistry has not been reported. We have found that addition of 2-lithio-1,3-dithiane to dimethylformamide at \(-20^\circ\text{C}\), followed by treatment with 3-bromocyclohexene (4) yielded after workup 70–75% of the aldehyde 1 directly (Scheme A). This reaction has been extended (Scheme B) to a variety of other allylic halides.

\[ \text{Scheme B} \]

As evident from the Table, the alkylations with unsymmetrical allylic halides 6 yield products 7 corresponding to S_{\text{E2}}\(^2\) reaction. This is probably the result of S-alkylation of the lithium enolate of 5 by the allylic halides followed by a [2,3]-type rearrangement\(^7\).

It should be noted that any unreacted 2-formyl-1,3-dithiane can be easily removed from the alkylation product by washing the crude reaction mixture with aqueous (10%) sodium hydroxide. From G.L.C. analysis it was concluded that 2-formyl-1,3-dithiane (5) is completely deprotonated by aqueous sodium hydroxide solution and can be extracted from ether solution. Acidification liberates 5 which can be isolated by ether extraction.

Swedish chemists\(^6\) have reported that reaction of alkylmagnesium bromides with dialkylformamides yields enamines which, in certain cases, can be alkylated \textit{in situ} in high yield. They report, however, that alkyllithium reagents in hexane react with dialkylformamides to form the amino-alcohohlates which did not undergo elimination to form enamines.

We favor a mechanism that involves addition of 2-lithio-1,3-dithiane to dimethylformamide to yield the amino-al-
Table. In Situ Alkylation of 2-Formyl-1,3-dithiane (5)

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield* [%]</th>
<th>b.p. [°C]/torr</th>
<th>Molecular formula*</th>
<th>δ [ppm]</th>
<th>M.S. m/e (M⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a'</td>
<td>50</td>
<td>105°/1</td>
<td>C₇H₁₀O₂S₂ (188.3)</td>
<td>9.0 (s, 1 H); 5.8 (m, 1 H); 5.1 (m, 2 H)</td>
<td>—</td>
</tr>
<tr>
<td>7b</td>
<td>48</td>
<td>120°/1</td>
<td>C₇H₁₀O₂S₂ (202.0)</td>
<td>9.0 (s, 1 H); 5.8 (m, 1 H); 5.1 (m, 2 H); 1.1 (d, 3 H)</td>
<td>202.04831 (calc. 202.04858)</td>
</tr>
<tr>
<td>7c</td>
<td>69</td>
<td>115°/1</td>
<td>C₇H₁₀O₂S₂ (202.0)</td>
<td>9.1 (s, 1 H); 4.9 (m, 2 H); 1.9 (s, 3 H)</td>
<td>202.04869 (calc. 202.04858)</td>
</tr>
<tr>
<td>7d</td>
<td>54</td>
<td>123°/1</td>
<td>C₇H₁₀O₂S₂ (216.1)</td>
<td>9.2 (s, 1 H); 6.0 (dd, 1 H); 5.1 (m, 2 H); 1.1 (s, 6 H)</td>
<td>216.06355 (calc. 216.06424)</td>
</tr>
</tbody>
</table>

* Yield of isolated product of >96% purity as determined by ¹H-N.M.R. (220 MHz) and G.L.C. (conditions: OV 101, programmed 40-250 °C).

The microanalyses were in satisfactory agreement with the calculated values (C ± 0.26, H ± 0.26, S ± 0.26).

Cohololate, which breaks down to form the stable enolate (Scheme C).

\[ \begin{array}{cc}
\text{S} & \text{Li} \\
\text{H} & \text{Li} \\
\text{H} & \text{H} \\
\text{C} & \text{N-CHO} \\
\end{array} \rightarrow \begin{array}{cc}
\text{S} & \text{Li} \\
\text{H} & \text{H} \\
\text{H} & \text{N-CHO} \\
\end{array} \]

Scheme C

2-(3-Cyclohexenyl)-2-formyl-1,3-dithiane (1); Typical Procedure:

A solution containing 1,3-dithiane (3.12 g, 0.01 mol) in anhydrous tetrahydrofuran (20 ml) is cooled with stirring under nitrogen to –30 °C (Dry ice/isopropyl alcohol) and treated dropwise with 2.4 molar n-butyllithium in hexane (4.2 ml, 0.01 mol). After 1 h of additional stirring, dimethylformamide (2.8 g, 0.04 mol) in tetrahydrofuran (5 ml) is added. The mixture is stirred at –20 °C for 2 h and then kept at 0 °C (refrigerator) for 12 h. To the resulting white suspension under nitrogen is added 3-bromocyclohexene (4.2 ml, 3.2 g, 0.02 mol). After stirring for 16 h at 25 °C, the reaction mixture is poured into ice/water (25 ml) and extracted with ether (2 x 20 ml). The ether extract is washed with 2 normal hydrochloric acid (2 x 20 ml) and then with 10% sodium hydroxide solution (2 x 20 ml). The organic extract is finally washed with water and dried with magnesium sulfate. Evaporation of the ether gives a yellow oil (1.85 g), and distillation gives analytically pure 1; yield: 1.7 g (72%); b.p. 135 °C/1 torr.

C₇H₁₀O₂S₂

Calc. C 57.89 H 7.01 S 28.07

Found 57.60 7.05 28.43

M.S.: m/e 228.06424 (M⁺; calc. 228.06412).

¹H-N.M.R. (CHCl₃): δ = 9.1 (s, 1 H, CHO); 5.8 ppm (m, 2 H).

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