Synthesis of Bis(aryloxy)chloromethanes via Radical-Induced Chlorinations of Formaldehyde Diaryl Acetals

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Bis(aryloxy)chloromethanes 2 and bis(aryloxy)dichloromethanes 3 are prepared via radical-induced chlorination of the formaldehyde diaryl acetals 1 with chlorine or sulfuryl chloride.

The chlorinated acetals 2 and 3, derivatives of formic and of carbonic acid, respectively, are useful reagents in organic synthesis (2,1-6;3,7-12) and various methods for their preparation have been published (2,7,13,14;3,15,16,17). We report now that these compounds can more easily be prepared via radical-initiated chlorination of the formaldehyde acetals 1,19 though treatment of 1c with chlorine in acetic acid was reported to proceed with electrophilic aromatic substitution, and the reaction of 1c with sulfuryl chloride gave only 46% of 3c.16

When chlorine was passed through refluxing solutions of 1a-c and traces of 2,2'-azobisisobutyronitrile (AIBN) in tetrachloromethane the dichloromethanes 3a-c were formed in 95–96% yield. Since 1a, b react considerably faster than 2a, b, the intermediate monochlorinated compounds 2a, b can be isolated with > 70% yield when the reaction is monitored (e.g., 1H-NMR) and interrupted after the signals of 1a, b have disappeared. This method has not been successful for an efficient preparation of 2c. As shown for the synthesis of 3b, the chlorinations can also be carried out at ambient temperature when the chlorine radicals are generated photolytically. In analogy to radical-induced chlorinations of alkanes, sulfuryl chloride can be employed in place of chlorine, whereby similar yields of the compounds 2b and 3b have been obtained.

Since the formaldehyde diaryl acetals 1 can be prepared via phase-transfer-catalyzed reactions of phenols with dichloromethane,26 the title compounds are now readily available. Publications on further applications of these compounds in organic synthesis are in preparation.

Bis(aryloxy)chloromethanes 2 and Bis(aryloxy)dichloromethanes 3: General Procedure:

Both procedures are carried out in a flask flushed with dry nitrogen.

Method A: Chlorine is passed through a solution of formaldehyde diaryl acetal 1 (30 mmol) and AIBN (0.45 mmol) in dry CCl4 (50 mL) at 80–85 °C until the wanted degree of chlorination is achieved (spectroscopic control). After evaporation of the solvent, the residue is distilled.

Method B: Compound 1 (20 mmol), sulfuryl chloride (2 equivalents per hydrogen to be substituted), and AIBN (0.30 mmol) in dry CCl4 (30 mL) are heated under reflux until the wanted degree of chlorination is achieved (1.5–4.5 h, spectroscopic control). After evaporation of the solvent, the residue is distilled.

We thank the Deutsche Forschungsgemeinschaft for support of this work.

Table. Radical-Induced Chlorinations of Formaldehyde Diaryl Acetals 1a–c

<table>
<thead>
<tr>
<th>Prod-Me thod</th>
<th>Reaction Time (min)</th>
<th>Yield (%)</th>
<th>bp (C mbar)</th>
<th>Lit. bp (C mbar)</th>
<th>mpa (C solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>30</td>
<td>72</td>
<td>120–122/0.1</td>
<td>128–130/0.2</td>
<td>65–67.5</td>
</tr>
<tr>
<td>2b</td>
<td>30</td>
<td>73</td>
<td>145–150/0.1</td>
<td>170/0.8</td>
<td>(pentane)</td>
</tr>
<tr>
<td>3a</td>
<td>90</td>
<td>95</td>
<td>100–105/0.07</td>
<td>183–185/16</td>
<td>40–42</td>
</tr>
<tr>
<td>3b</td>
<td>90</td>
<td>95</td>
<td>170–175/0.4</td>
<td>30.5–31.5</td>
<td>(pentane)</td>
</tr>
<tr>
<td>3c</td>
<td>20</td>
<td>95</td>
<td></td>
<td>82–86/20</td>
<td>82–89/16</td>
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Received: 20 September 1988

References: