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SYNTHESIS OF TRI(ARYLOXY)METHANES

BY

J. W. SCHEEREN, M. J. H. M. VAN ROY

and

A. P. M. VAN DER VEEK

A convenient synthetic procedure is described for the preparation of triphenoxy-methanes from aryl dichloromethyl ethers\(^1\) and sodium phenolates in dimethoxy-ethane.

Although the first reports on triphenoxymethanes already appeared in the 19th century\(^2-^4\), a useful preparative method for this type of compound has not yet been described.

Several compounds of this type have been mentioned in the literature as minor side-products in Reimer-Tiemann reactions\(^2-^11\), and in syntheses of aryl difluoromethyl ethers\(^12\). Triphenoxy-methane has also been obtained from diphenoxymethyl chloride\(^13\). The latter compound, however, can be prepared in a simple manner only from triphenoxy-methane\(^14\).

The well-known exchange reaction for the preparation of higher boiling aliphatic orthoformates from methyl or ethyl orthoformate\(^15,16\) gives low yields, if used in the syntheses of aryl orthoformates.

\(^2\) F. Tiemann, Ber. 15, 2686 (1882).
\(^3\) A. Weddige, J. Prakt. Chem. [2], 26, 444 (1882).
\(^4\) K. Auwers, Ber. 18, 2655 (1885).
\(^7\) J. E. Driver, J. Am. Chem. Soc. 46, 2090 (1924).
\(^12\) T. G. Miller and J. W. Thanassi, ibid. 25, 209 (1960).
The reason is, that the transition states (which are carboxonium ion in character), in the successive exchange reactions

\[
\begin{align*}
[\text{RO—C—OR}]^+ & \quad [\text{RO—C—O} \cdot] + \quad [\text{O—C—O} \cdot] + \quad (R=\text{CH}_3 \text{ or } \text{C}_2\text{H}_5) \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

become more and more unstable due to the electron-withdrawing effect of the phenyl group (compare disproportionation of orthoformates\(^{17}\)).

Aliphatic orthoformates can also be prepared in reasonable yields from sodium alkoxides and chloroform\(^{18}\). With phenolates, however, the intermediate dichlorocarbene\(^{19}\) will be attached to the phenyl ring (Reimer-Tiemann reaction) which yields (ortho- and para-) \(\text{Cl}_2\text{CH—C}_6\text{H}_4\cdot\text{OH}\), and not to the phenolate oxygen giving dichloromethyl phenyl ether. The primary products can react further with sodium phenolate giving rise to substitution products \(\text{HOC}_6\text{H}_4\text{CH(OPh)}_2\) or, by analogous carbene and substitution reactions producing \(\text{HC(C}_6\text{H}_4\text{OH)}_2\text{OPh}\) and \(\text{HC(C}_6\text{H}_4\cdot\text{OH)}_2\). The carbene reactions are stimulated by the stabilizing effect of the phenyl group. If, in any way aryl dichloromethyl ether should have been formed, further substitution should be favoured rather than \(\alpha\)-elimination if the base is not too strong.

In a previous paper\(^1\), we described the synthesis of several aryl dichloromethyl ethers. By treating them with sodium phenolates in dimethoxy ethane, tri(aryloxy)methanes could be obtained in good yields:

\[
\text{HCCl}_2\text{OPh} + 2 \text{NaOPh} \rightarrow \text{HC(OPh)}_3 + 2 \text{NaCl}
\]

It is important to use sodium phenolate which is free from water or alcohol and to use it in excess. Completion of the reaction is necessary, because residual aryl dichloromethyl ether (when exposed to moisture\(^1\)) produces hydrogen chloride, which causes triphenoxymethanes to rearrange to leucaurines, probably as follows:

\[
\text{HC(OPh)}_3 + \text{H}^+ \rightarrow [\text{HC(OPh)}_2]^+ + \text{PhOH} \rightarrow (\text{PhO})_2\text{CH—C}_6\text{H}_4\cdot\text{OH} \text{ etc.}
\]

By a procedure similar to that described, some mixed aryl orthoformates have also been prepared.


Table 1

Triphenoxy methanes \( \text{HC(OR}_1\text{)(OR}_2\text{)}_2 \)

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>M.P</th>
<th>M.P</th>
<th>Ref.</th>
<th>( \text{H—C(—O—)}_3 ) in ( \text{CCl}_4 )</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl</td>
<td>phenyl</td>
<td>74–75°</td>
<td>71–72°</td>
<td>2</td>
<td>6.5</td>
<td>80%</td>
</tr>
<tr>
<td>( p )-cresyl</td>
<td>( p )-cresyl</td>
<td>112–113°</td>
<td>112°</td>
<td>5</td>
<td>6.3</td>
<td>80%***</td>
</tr>
<tr>
<td>( p )-chloro-</td>
<td>( p )-chloro-</td>
<td>109–110°</td>
<td>106°</td>
<td>10</td>
<td>6.4</td>
<td>70%</td>
</tr>
<tr>
<td>( p )-nitro-</td>
<td>( p )-nitro-</td>
<td>241–243°</td>
<td>232°</td>
<td>3</td>
<td>*</td>
<td>60%***</td>
</tr>
<tr>
<td>phenyl</td>
<td>phenyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-dimethyl-</td>
<td>2,6-dimethyl-</td>
<td>189–191°</td>
<td></td>
<td></td>
<td>5.85</td>
<td>75%</td>
</tr>
<tr>
<td>phenyl</td>
<td>phenyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4,6-trimethyl</td>
<td>2,4,6-trimethyl</td>
<td>193–194°</td>
<td>185–186°</td>
<td>11</td>
<td>5.85</td>
<td>75%</td>
</tr>
<tr>
<td>phenyl</td>
<td>( \alpha )-naphthyl</td>
<td>240–241°</td>
<td></td>
<td></td>
<td>**</td>
<td>75%</td>
</tr>
<tr>
<td>phenyl</td>
<td>( p )-chloro-</td>
<td></td>
<td></td>
<td></td>
<td>6.40</td>
<td>80%</td>
</tr>
<tr>
<td>phenyl</td>
<td>( p )-nitro-</td>
<td></td>
<td></td>
<td></td>
<td>6.8</td>
<td>55%</td>
</tr>
</tbody>
</table>

* Measured in DMSO.
** Identified by mass spectrum.
*** Identified by carbon-hydrogen analyses.

Experimental

1. Tri(aryloxy)methanes (Table 1)

A solution of sodium phenolate is prepared by carefully adding an equimolar amount of sodium to a solution of 30 g phenol in 100 g of dimethoxyethane. If necessary, dissolution of sodium was completed by refluxing. An aryl dichloromethyl ether is then added drop by drop to the solution while stirring. The phenolate is always used in excess (at least 10%). After the addition, the mixture is boiled for half an hour, the solvent is distilled off under reduced pressure (15 mm) and water and ether are added to the residue. The ethereal solution is washed with water several times and dried with sodium sulfate.

After removing the ether, the practically pure triaryloxymethane remains behind. Because sodium \( p \)-nitrophenolate dissolves only partly in dimethoxyethane under these experimental conditions, the dichloro-ether solution is slowly added to the sodium phenolate in boiling dimethoxyethane and boiling is continued for 4 hours.

2. Tri(\( \alpha \)-naphthyl)oxymethane

Crude \( \alpha \)-naphthyl formate* is prepared from \( \alpha \)-naphthol and the formic acid-acetic anhydride (reaction) mixture as described for the synthesis of phenyl formates20 but now the low boiling components are removed at such low pressure that the temperature of the

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formate remains below 80°. The crude product is treated with PCl₅ as described previously¹
and POCl₃ was again removed from the reaction mixture at low pressure. The remaining
 crude dichloro ether* dissolved in dimethoxyethane was added to the sodium α-naphtholate as described above.

Acknowledgement

We thank Prof. Dr. R. J. F. Nivard for discussing the work.

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* Both α-naphthyl formate and α,α-dichloromethyl 4 naphthyl ether decompose during distillation under diminished pressure.