SYNTHESIS OF ar-NITROSTYRENES

By M. BUTCHER,* R. J. MATHEWS,* and S. MIDDLETON*†

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Abstract

The title compounds are conveniently prepared in high yield by reaction of the appropriate nitrobenzylidenetriphenylphosphorane with aqueous formaldehyde.

The synthesis of o-nitrostyrene is usually accomplished by decarboxylation of o-nitrocinamic acid,1,‡ by dehydrobromination of 2-(o-nitrophenyl)ethyl bromide,3 or by simultaneous decarboxylation and dehydrobromination of 3-bromo-3-(o-nitrophenyl)propionic acid.4 None of these methods is particularly suited, however, to the synthesis of isotopically labelled o-nitrostyrenes such as we required in our mass spectral investigations.5 We therefore investigated the possibility of obtaining o-nitrostyrene by means of a Wittig reaction between an appropriate phosphorane and formaldehyde.

\[
\begin{align*}
\text{(1)} & \quad \text{Br}^- \quad \text{CH}_2\text{P}^+\text{Ph}_3 \\
\text{(2)} & \quad \text{CH}==\text{PPh}_3 \\
\text{(3)} & \quad \text{CH}==\text{C}_2
\end{align*}
\]

Unlike other aliphatic aldehydes, formaldehyde does not undergo self-condensation under basic conditions, so that Wittig reactions in which it is used may be carried out6–8 by either the organometallic or metal alkoxide method to generate the required phosphorane from the appropriate phosphonium salt. However, although these procedures are potentially applicable to the synthesis of o-nitrostyrene from o-nitrobenzyltriphenylphosphonium bromide, a much simpler method is now reported. The success of the new procedure stems from the fact that although the o-nitrobenzylidenephosphorane (2; R = o-NO₂) is sufficiently nucleophilic to react readily

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‖‖ Butcher, M., Mathews, R. J., and Middleton, S., unpublished data.
|| Maercher, A., Org. React., 1965, 14, 393.

with carbonyl compounds, it is nevertheless sufficiently stable to be isolated from aqueous media. As a result, when the phosphorane is treated with aqueous formalin solution, a rapid reaction ensues and o-nitrostyrene is formed in high yield.

To the best of our knowledge, this is the first report of a Wittig reaction being carried out in an aqueous medium. Moreover, the extremely simple preparative procedure involved may be applicable to stable phosphoranes in general since we have found it to be equally successful when applied to the synthesis of \( p \)-nitrostyrene from the known \( p \)-nitrobenzylidenephosphorane \( 2; \ R = p\text{-NO}_2 \). Of even greater interest, however, is the finding that it is not essential that the phosphorane be isolable. Thus, although the \( m \)-nitrobenzylidenephosphorane \( 2; \ R = m\text{-NO}_2 \) is not sufficiently stable to be isolated as such, treatment of the corresponding phosphonium salt \( 1; \ R = m\text{-NO}_2 \) with formalin and aqueous sodium carbonate nevertheless gave \( m \)-nitrostyrene in high yield.

Clearly, the success of the new simplified procedure is largely due to the high reactivity of formaldehyde itself, a conclusion also suggested by our finding that the yields of alkenes obtained from the \( o \)-nitrobenzylidenephosphorane \( 2; \ R = o\text{-NO}_2 \) in aqueous media are markedly lower for aldehydes other than formaldehyde, and by the earlier finding\(^9\) that the reactions of \( p \)-nitrobenzylidenetriphenylphosphorane \( 2; \ R = p\text{-NO}_2 \) with a variety of aldehydes other than formaldehyde invariably gave lower yields of alkenes when water was added to the solvent used (ethanol).

**Experimental**

\( o \) - and \( p \) -Nitrostyrene

A suspension of \( o \)-nitrobenzyltriphenylphosphonium bromide\(^9\) \((3 \cdot 0 \text{ g})\) in aqueous sodium carbonate solution \((10\%, 100 \text{ ml})\) was stirred for 3 hr and the resulting purple phosphorane\(^9\) was filtered off. A suspension of the phosphorane in aqueous formalin solution \((40\%, 10 \text{ ml})\) was then stirred until the colour of the phosphorane was discharged \((15 \text{ min})\) whereupon the mixture was extracted with chloroform \((10 \text{ ml})\). The chloroform was evaporated and the residue purified either by distillation \((\text{b.p. } 105^\circ/10 \text{ mm})\) or, better, by chromatography on a column of alumina \((25 \text{ g})\) using light petroleum as eluent. The product thereby obtained \((0 \cdot 75 \text{ g}, 90\%)\) gave spectra identical with those obtained from an authentic sample of \( o \)-nitrostyrene (see Table 1).

<table>
<thead>
<tr>
<th>Iso-( \text{mer} )</th>
<th>( \gamma(\text{NO}_2) ) ( (\text{cm}^{-1})^a )</th>
<th>( \text{M}^{++} ) ( (m/e)^b )</th>
<th>N.m.r. spectra(^c) ( (\text{ABX multiplets}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
<td>1520, 1350</td>
<td>149</td>
<td>( 5 \cdot 4 ) ( 5 \cdot 7 ) ( 7 \cdot 2 )</td>
</tr>
<tr>
<td>meta</td>
<td>1520, 1350</td>
<td>149</td>
<td>( 5 \cdot 35 ) ( 5 \cdot 8 ) ( 6 \cdot 75 )</td>
</tr>
<tr>
<td>para</td>
<td>1520, 1350</td>
<td>149</td>
<td>( 5 \cdot 4 ) ( 5 \cdot 7 ) ( 6 \cdot 8 )</td>
</tr>
</tbody>
</table>

\(^a\) Liquid films.

\(^b\) Complete mass spectra to be published separately (ref. 5).

\(^c\) Measured at 60 MHz on \( \text{CCl}_4 \) solution with \( \text{SiMe}_4 \) as internal reference. \( \delta \) in p.p.m., \( J \) in Hz.

extracted with chloroform \((10 \text{ ml})\). The chloroform was evaporated and the residue purified either by distillation \((\text{b.p. } 105^\circ/10 \text{ mm})\) or, better, by chromatography on a column of alumina \((25 \text{ g})\) using light petroleum as eluent. The product thereby obtained \((0 \cdot 75 \text{ g}, 90\%)\) gave spectra identical with those obtained from an authentic sample of \( o \)-nitrostyrene (see Table 1).


Using the same procedure, \( p \)-nitrobenzyltriphenylphosphonium bromide\(^9\) readily afforded 
\( p \)-nitrostyrene, also in 90\% yield.

\textbf{m-Nitrostyrene}

A suspension of \( m \)-nitrobenzyltriphenylphosphonium bromide\(^9\) (3.0 g) in aqueous formalin solution (40\%, 10 ml) was added slowly with stirring to an aqueous sodium carbonate solution (10\%, 100 ml). The crude product was then isolated and purified as described above to give the required 
\( m \)-nitrostyrene (90\%).