Vinyl radicals: the oxidative decarboxylation of \( \alpha,\beta \)-unsaturated acids

Bruno Danieli, Paolo Manitto, Fiamma Ronchetti and Giovanni Russo

Istituto di Chimica Organica, Facoltà di Scienze, Università di Milano, Via C Saldini 50, 20133 Milan, Italy

In an investigation of the reactivity of lead tetraacetate (LTA), it was noticed that the oxidative decarboxylation\(^1\) of trans- and cis-cinnamic acids\(^2\) leads to the unexpected formation of \( \beta \)-methylstyrene \((1, R = \text{Me})\) as major product. The partial non-sensitivity of the course of the reaction to easily oxidised by Pb (IV), to esters and olefins via the corresponding cation, remained an open question. To answer this question the decarboxylation of trans-cinnamic acid with LTA in the presence of \( S-(+) \)-2-methylbutanoic acid (II), from which the mixed salts (III) are generated (see equation below) was studied.

![Scheme]

radical scavengers led to the hypothesis\(^3\) that compound \((1, R = \text{Me})\) is formed by two concomitant processes: (i) coupling (equation 7) of the 'free' radicals \( C_6H_5-\text{CH}=\text{CH}^* \) and \( CH_3^* \) formed according to the reactions (3) and (6); (ii) transfer of a \( CH_3^* \) radical from the Pb (IV, III) species on the radical \( C_6H_5-\text{CH}=\text{CH}^* \) through the formation of a labile complex (equations 4 and 5).

**Scheme**

\[
\begin{align*}
(1) & \quad C_6H_5-\text{CH}=\text{CH}-\text{CO}_2^+ + \text{Pb}^{IV} \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{Pb}^{III} \\
(2) & \quad C_6H_5-\text{CH}=\text{CH}-\text{CO}_2^{**} + \text{Pb}^{IV} \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{CO}_2 \\
(3) & \quad C_6H_5-\text{CH}=\text{CH}^* + \text{CO}_2 \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{CO} \\
(4) & \quad C_6H_5-\text{CH}=\text{CH}^* + \text{Pb}^{IV} \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{Pb}^{III} \\
(5) & \quad C_6H_5-\text{CH}=\text{CH}^* + \text{Pb}^{IV} \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{Pb}^{III} \\
(6) & \quad \text{Pb}^{IV} \rightarrow \text{Pb}^{III} + \text{CO}_2 + \text{Pb}^{IV} \\
(7) & \quad C_6H_5-\text{CH}=\text{CH}^* + \text{CO}_2 \rightarrow C_6H_5-\text{CH}=\text{CH}^* + \text{CO} \\

\end{align*}
\]

Homolysis of compound (III) gives rise, in addition to phenylvinyl and methyl radicals, to sec-butyl radicals which are known\(^3\) to be easily oxidised by LTA. Moreover, 2-methylbutanoic acid was used in the optically active form in order to examine the possible existence in process (2) of transfer mechanisms such as those (a) and (b) represented in

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**Table - Oxidative decarboxylation of \( \alpha,\beta \)-unsaturated acids**

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Time</th>
<th>Reagents</th>
<th>Products</th>
<th>Yield (in moles per cent with respect to (A))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70'</td>
<td>(A) S-(+)2-methylbutanoic acid, 0.25M</td>
<td>1-phenyl-3-methylpent-1-ene (IV)(^d)</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(B) cinnamic acid, 0.25M</td>
<td>1-phenylprop-1-ene (1, R = Me)</td>
<td>3-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C) LTA, 0.375M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>40'</td>
<td>(A) as in experiment 1</td>
<td>1-phenyl-3-methylpent-1-ene (IV) (^d)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(B) as in experiment 1</td>
<td>1-phenylprop-1-ene (R = Me)</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C) as in experiment 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D) Cu(OOC)Me ( \cdot )H(_2\O) 0.044M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15'</td>
<td>(A) phenylpropionic acid, 0.25M</td>
<td>phenylacetylene (V)</td>
<td>25-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(B) LTA, 0.125M</td>
<td>1-phenylprop-1-ynyl (VI)</td>
<td>14-8</td>
</tr>
<tr>
<td>4</td>
<td>15'</td>
<td>(A) as in experiment 3</td>
<td>1-phenyl-3-methylpent-1-ynyl (VII)(^e)</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(B) S-(+)2-methylbutanoic acid, 0.25M</td>
<td>phenylacetylene (V)</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C) LTA, 0.375M</td>
<td>1-phenylprop-1-ynyl (VI)</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

\(^a\) The reactions were effected by heating under reflux under nitrogen a solution of the reagents in benzene-pyridine (9:1). \(^b\)Time of complete consumption of the oxidant. \(^c\)The products of the reaction were identified by g.l.c.-mass spectrometry. \(^d\)Compound (IV), not known in the literature, was isolated by distillation of the crude product of the reaction: bp 150/15mm Hg. v\(_{max}\) 3040, 2975, 2940, 2880, 1595, 1490, 1450, 1380, 1120, 970, 750, 690cm\(^{-1}\); n.m.r. spectrum \( 6 7.23 \) (s, 5H, aromatic protons); 6 and 6.33 (AB, J = 16 Hz, 2H, vinyllic protons); 2.15 (m, 1H, allylic proton); 1.34 (m, 2H, CH\(_2\) of ethyl group); 1.00 (t, J = 6 Hz, CH\(_2\) of ethyl group); 0.95 (d, J = 6 Hz, 3H, allylic CH\(_3\)) (Compound (VII), not known in the literature, was isolated by distillation of the crude product of the reaction: bp \( 135-120^\circ /15\)mm Hg, \( v_{max}\) 3055, 2980, 2950, 2890, 2250, 1600, 1495, 1450, 1380, 1340, 1075, 960, 920, 760, 690cm\(^{-1}\); n.m.r. spectrum \( 6 7.28 \) (s, 5H, aromatic protons); 2.52, 2.31 (q, 2H, tertiary proton adjacent to triple bond); 1.50 (m, 2H, CH\(_2\) of ethyl group); \( 124 \) (d, J = 6 Hz, 3H, CH\(_3\) adjacent to triple bond); 1.16 (t, J = 6 Hz, 3H, CH\(_3\) of ethyl group). \( ^{\text{e}} \) Determined by g.l.c. with suitable internal references.
the Figure in which the group R is not free to racemise. As shown in the Table (experiment 1), the main product of the reaction is 1-phenyl-3-methylpent-1-ene (IV). Then formation of the alkylstyrenes (I) can be considered a general reaction when R is an alkyl group. To distinguish the extent to which processes (1) and (2) are operating the decarboxylation was effected in the presence of 0.04M Cu (II) (see Table, experiment 2), which is known to oxidise free alkyl radicals, e.g. sec-butyl radical,² to the corresponding cations. In these conditions the formation of the β-alkylstyrene (IV) fell from 34 to 8 per cent, indicating that a substantial amount (ca. 25 per cent) of (IV) is formed via process (2). In each case (IV) was shown to be optically inactive: the complete racemisation of the asymmetric centre excludes that process (2) takes place according to mechanisms (a) or (b), or any other in which the sec-butyl group is not free to racemise.

Therefore, it is concluded that process (2) consists of the formation of a labile complex between phenylvinyl radical and a Pb (III) species, probably derived from homolysis of the same Pb (IV) species (equation 9), owing to the fact that the process is a short chain process.² Under these conditions the radical R⁺, coming from decomposition of the Pb (III) species, and the phenylvinyl radical are in close proximity and offer optimal opportunity for coupling⁴ (equation 10) to give the β-alkylstyrenes (I).

\[ \text{R} - \text{COOC} = \text{R} \stackrel{\text{II}}{\longrightarrow} \text{R} - \text{C} = \text{CH} - \text{C}_2\text{H}_5 \]

\[ \text{R} = \text{Me} \]

The oxidative decarboxylation of phenylpropionic acid, either with LTA (see Table, experiment 3) or with LTA in the presence of 2-methylbutanoic acid (see Table, experiment 4) afforded phenylacetylene (V) and in the former case methylenphenylacetylene (VI), and in the latter case the main product was 1-phenyl-3-methylpentene (VII). As with the

\[ \text{C}_n\text{H}_5 - \text{C} = \text{C} - \text{R} \]

(\(\text{V}, \text{R} = \text{H}\))

(\(\text{VI}, \text{R} = \text{Me}\))

(\(\text{VII}, \text{R} = \text{CH} = \text{C}_2\text{H}_5\))

β-alkylstyrenes, the above acetylenes can be easily isolated by distillation.

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References
4. An analogous possibility was also postulated by Kochi, J. K. et al to explain dimer formation during photochemical decarboxylation of acids with thallium III; Kochi, J. K. & Bethea, T. W., J. org. Chem., 1968, 33, 75