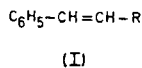


Vinyl radicals: the oxidative decarboxylation of α,β -unsaturated acids

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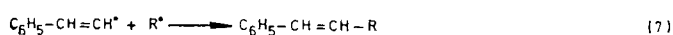
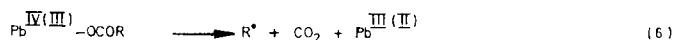
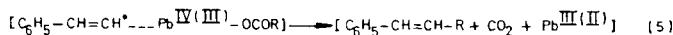
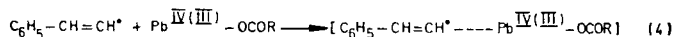
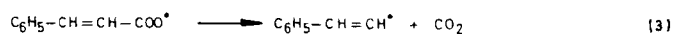
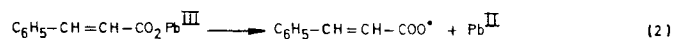
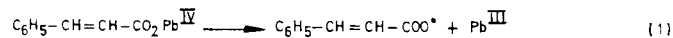
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In an investigation of the reactivity of lead tetraacetate (LTA), it was noticed that the oxidative decarboxylation¹ of *trans*- and *cis*-cinnamic acids² leads to the unexpected formation of β -methylstyrene (I, R=Me) as major product. The partial non-sensitivity of the course of the reaction to



radical scavengers led to the hypothesis² that compound (I, R=Me) is formed by two concomitant processes: (i) coupling (equation 7) of the 'free' radicals $\text{C}_6\text{H}_5-\text{CH}=\text{CH}^\bullet$ and CH_3^\bullet formed according to the reactions (3) and (6); (ii) transfer of a CH_3^\bullet radical from the Pb(IV, III) species on the radical $\text{C}_6\text{H}_5-\text{CH}=\text{CH}^\bullet$ through the formation of a labile complex (equations 4 and 5).

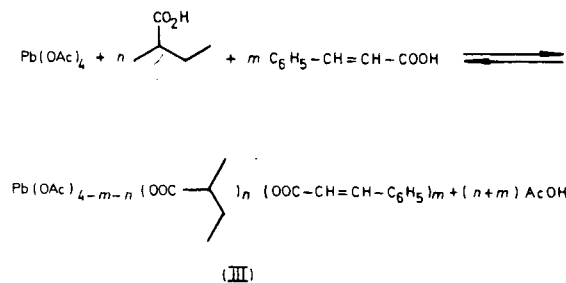
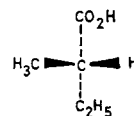
Scheme



However, whether compound (1) is formed only when R=CH₃ is oxidised with difficulty,³ or whether its formation is a general process taking place even when R is a radical

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.



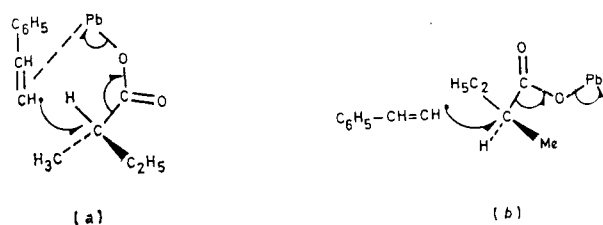
Homolysis of compound (III) gives rise, in addition to phenylvinyl and methyl radicals, to *sec*-butyl radicals which are known³ to be easily oxidised by LTA. Moreover, 2-methylbutanoic acid was used in the optically active form in order to examine the possible existence in process (2) of transfer mechanisms such as those (a) and (b) represented in

Table - Oxidative decarboxylation of α,β -unsaturated acids^a

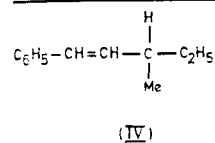
Experiment No	Time ^b	Reagents	Products ^c	Yield ^f in moles per cent with respect to (A)
1	70'	(A) <i>S</i> -(+)-2-methylbutanoic acid, 0.25M (B) cinnamic acid, 0.25M (C) LTA, 0.375M	1-phenyl-3-methylpent-1-ene (IV) ^d 1-phenylprop-1-ene (I, R=Me)	34 3.5
2	40'	(A) as in experiment 1 (B) as in experiment 1 (C) as in experiment 1 (D) Cu(OCOMe)H ₂ O, 0.044M	1-phenyl-3-methylpent-1-ene (IV) 1-phenylprop-1-ene (R=Me)	8 <1
3	15'	(A) phenylpropionic acid, 0.25M (B) LTA, 0.125M	phenylacetylene (V) 1-phenylprop-1-yne (VI)	25.6 14.8
4	15'	(A) as in experiment 3 (B) <i>S</i> -(+)-2-methylbutanoic acid, 0.25M (C) LTA, 0.375M	1-phenyl-3-methylpent-1-yne (VII) ^e phenylacetylene (V) 1-phenylprop-1-yne (VI)	32 <1 <1

^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; ν_{max} . 3040, 2975, 2940, 2880, 1595, 1490, 1450, 1380, 1120, 970, 750, 690cm⁻¹; n.m.r. spectrum δ 7.23 (s, 5H, aromatic protons); 6 and 6.33 (AB, $J=16$ Hz, 2H, vinylic protons); 2.15 (m, 1H, allylic proton); 1.34 (m, 2H, CH₂ of ethyl group); 1.00 (t, $J=6$ Hz, CH₃ of ethyl group); 0.95 (d, $J=6$ Hz, 3H, allylic CH₃). ^e Compound (VII), not known in the literature, was isolated by distillation of the crude product of the reaction; bp 115-120°/15mm Hg; ν_{max} . 3055, 2980, 2950, 2890, 2250, 1600, 1495, 1450, 1380, 1340, 1075, 960, 920, 760, 695cm⁻¹; n.m.r. spectrum δ 7.28 (s, 5H, aromatic protons); 2.52 (m, 1H, tertiary proton adjacent to triple bond); 1.50 (m, 2H, CH₂ of ethyl group); 1.24 (d, $J=6$ Hz, 3H, CH₃ adjacent to triple bond); 1.16 (t, $J=6$ Hz, 3H, CH₃ of ethyl group). ^f Determined by g.l.c. with suitable internal references

Fig



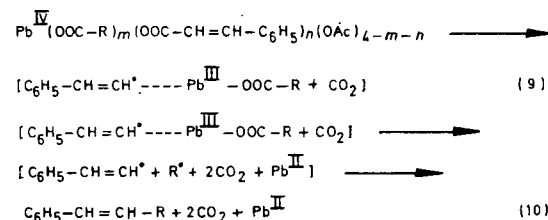
the Figure in which the group R is not free to racemise. As shown in the Table (experiment 1), the main product of the reaction is 1-phenyl-3-methylpent-1-ene (IV). Then formation of the β -alkylstyrenes (I) can be considered a general reaction when R is an alkyl group. To distinguish the extent to which



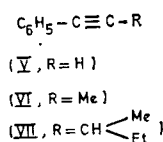
processes (1) and (2) are operating the decarboxylation was effected in the presence of 0.044M Cu (II) (see Table, experiment 2), which is known to oxidise free alkyl radicals, e.g. *sec*-butyl radical,³ to the corresponding cations. In these conditions the formation of the β -alkylstyrene (IV) fell 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 \cdot , coming from decomposition of the Pb (III) species, and the phenylvinyl radical are in close proximity

to give the β -alkylstyrenes (I).



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 methylphenylacetylene (VI), and in the latter case the main product was 1-phenyl-3-methylpentyne (VII). As with the



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

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