

Sonochemical Reactions of Lead Tetracarboxylates with Styrene

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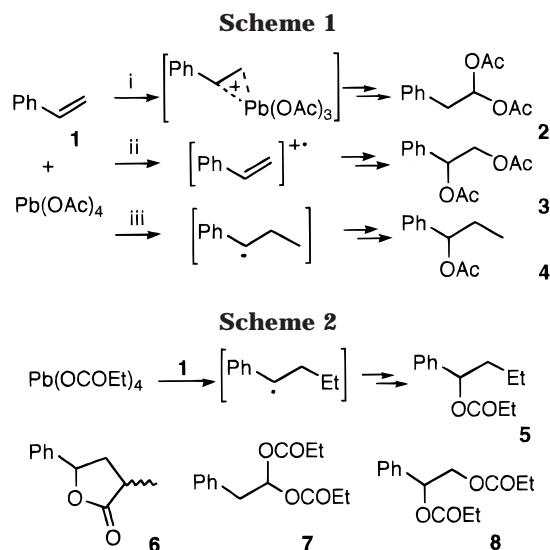
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Introduction

Because of their mechanistic diversity, the reactions of lead tetraacetate (LTA)¹ with various substrates constitute an ideal objective for sonochemical studies.² An example of this is the reaction of LTA with styrene **1** in acetic acid solution or suspension which is able to follow several mechanisms, each of which provides a different product (Scheme 1).³ Reaction i implies an ionic dissociation of the LTA oxidant, followed by an electrophilic attack of the olefinic bond. Reaction ii involves a preliminary one-electron oxidation of the olefin to a radical cation,⁴ although in this case it is also possible for the reaction to follow a polar pathway.^{3b} Whatever the mechanism, compound **3** is generally a minor constituent of the mixture. The key step of reaction iii consists of the addition to the double bond of a methyl radical resulting formally from a homolysis of LTA. Most of the published work shows that the pathway i is predominant, although not exclusive.

Because one of the important features of sonication is the enhancement of radical mechanisms,⁵ the oxidation of styrene by LTA under ultrasound irradiation would be expected to proceed with an increased selectivity in favor of compound **4** (and possibly **3**). This was indeed observed,^{2a} and this result constitutes an example of what has become known as sonochemical switching.⁶ All the



data also agree with a chain mechanism, easily inhibited by oxygen or *tert*-butylcatechol.^{2a,7-9}

Notwithstanding this observation, many aspects of these reactions, both conventional and sonochemical, remain unclear. Thus, in the literature there are several references to this type of reaction, some run simply by heating the styrene-LTA mixture,^{2a,7} whereas others report experiments performed in the presence of a base, the role of which is not clearly explained.^{2b-d,8} The present study was undertaken to provide more mechanistic elements, particularly with respect to the sonochemical effect. A specific aim was to determine the experimental conditions, sonochemical or conventional, that might confer useful selectivity to the reaction. In sonochemical reactions it is not firmly established where the key step occurs, i.e., in the continuous liquid phase or next to the cavitation bubble boundary, because activation is not expected to occur inside the cavity itself.^{2c} It has been shown that the sonolysis of LTA is extremely slow at temperatures up to 50 °C, leading to the conclusion that the homolytic process can occur only when LTA and styrene are present simultaneously,^{2c} an observation not explained by the currently accepted mechanism.

Results and Discussion

To detect possible ligand exchange reactions occurring during the reaction (see below), lead tetrapropanoate (LTP) was chosen as the reagent in place of LTA (Scheme 2).

There is a distinct lack of accurate data concerning the reaction of LTP with styrene,¹⁰ and so a series of experiments were performed in the first instance to rectify this and the results are summarized in Table 1. The optimal stirring rate (600 rpm) was determined in a

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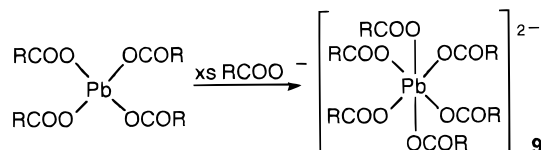
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Table 1. Effect of Potassium Propanoate on the Reaction Advancement

| run | EtCO ₂ K (mmol) | conditions ^a | remaining | | | product balance |
|-----|----------------------------|-------------------------|-----------|-----------------|-------|-----------------|
| | | | 1 (%) | 5 (%) | 6 (%) | |
| 1 | 0 | ↻, 45 °C | 48 | 0 ^b | 3 | 51 |
| 2 | 0 |))))) , 32 °C | 28 | 49 | 4 | 81 |
| 3 | 10 | ↻, 45 °C | 44 | 36 | 3 | 83 |
| 4 | 10 |))))) , 32 °C | 19 | 66 | 5 | 90 |
| 5 | 20 | ↻, 45 °C | 25 | 60 ^c | 4 | 89 |
| 6 | 20 |))))) , 32 °C | 7 | 78 | 6 | 91 |

^a ↻ stands for "stirring", and))))) for "ultrasonic irradiation".

^b Under the same conditions, LTA in AcOH yields **4** (11%) and **2** (6%). ^c Under the same conditions, LTA and AcOK in AcOH yield **4** (80%).

Scheme 3

preliminary study and kept constant throughout this work.^{11,12} Along with the normal product 1-phenylbutyl propanoate **5**, the lactones **6** were also found in small amounts. Products **7** and **8**, analogues to **2** and **3**, represent less than 2% of the mixture under any reaction conditions. The balance of the material consists of several minor unidentified constituents.

These results establish that the carboxylate anions directly influence the reaction in that the conversion of styrene occurs more rapidly than in their absence. The selectivity is also higher, as evidenced by an improved product balance, and the radical process is favored. These effects are further increased by sonication, even at lower temperatures, confirming that under these specified conditions sonochemical switching does occur. The diastereomeric mixture of lactones **6** is also the result of a free-radical process.

The enhancement of the radical reactivity of LTA under the influence of bases has been reported previously for several reactions, e.g., the oxidation of primary alcohols,¹³ the oxidative decarboxylation of carboxylic acids,^{1b,9} and the thermal decomposition itself.¹⁴ For reactions run in the presence of carboxylate anions, Benson et al.^{14b} proposed an explanation based on the formation of a hexaliganded complex of Pb(IV) (Scheme 3), even if only a few articles have described such high-coordination lead species.^{1b,15} Intermediates of this type are implicitly supposed to undergo homolysis preferentially.^{1b}

Higher propanoate concentrations favor the formation of **9** (R = Et), which reacts with styrene preferentially via a radical process. In parallel, the electrophilic attack of the double bond is significantly decreased. The reac-

tion shown in Scheme 3 should then represent the (or one of the) key step(s) of the radical formation and addition to styrene.

The higher conversion obtained under sonication in a heterogeneous medium can be assigned, in part, to the mechanical effects of sonication (crystal breakage of the solid reagents, mass transport, etc.), even if an additional chemical role cannot be excluded (see below). These conditions lead to an excellent selectivity with the yield of monoester **5** reaching almost 80%. Therefore the optimal conditions for the addition of an alkyl group to the styrene double bond would be the use of a mixture of alkali and lead(IV) carboxylates suspended in the corresponding acid. These requirements limit the generality of the reaction, however, particularly when expensive acids are used. A series of other reaction conditions were investigated (Table 2).

The *gem*- and *vic*-diacetates (Scheme 2) **2** and **3** are obtained in small amounts and are mentioned in Table 2 only when their percentage becomes significant. Only in one case (run 5) does the percentage of **2** reach a relatively high level (15%). However even then it is significantly diminished by sonication in accordance with expectations. This result shows that ultrasonic irradiation not only plays a mechanical role (which should be limited to a rate increase), but also produces the sonochemical switching. In the reactions of LTA in propanoic acid in the presence of potassium propanoate, two other esters can be formed, acetates **4** and **10**. 1-Phenylpropanol propanoate (**11**) was never observed. The di-propanoates **7** and **8** were not evident in the GC-MS spectra of the crude mixtures.

From the comparison of runs 5–6 in Table 1 and runs 1–2 in Table 2, it appears that the selectivity in favor of ester **5** is practically unaffected by the replacement of LTP by LTA in the presence of propanoate anion and propanoic acid. With the system LTP-EtCOOK in AcOH (runs 3 and 4 in Table 2), although the addition of an ethyl group remains the preferred process, a significant amount of methylation occurs. Because the homolysis of the propanoate moiety occurs only in the lead carboxylate complex, we can conclude that a fast exchange must occur between LTA and the solvent and/or potassium propanoate (a shift to the right in Scheme 4).⁹

According to Kochi,^{9b} the selectivity of the cleavage is governed by the stability of the incipient alkyl radical. However the formation of 1-phenylpropanol acetate **4** in runs 3–8 shows that this preference is not respected in all cases. In the same experiments, the predominant pathway leads to compound **10** via the addition of an ethyl group and formation of the acetate ester. A second factor must have a determining role in this case. A structural effect in the intermediate complex can be envisaged as an hypothesis. The NMR spectra of **9** (R = CH₃) exhibit two signals for the acetate groups,^{15b} which is explained by the presence of two types of ligands, unidentate and symmetrically chelating bidentate. The preferential reaction of the less tightly bound ligand could then be invoked to explain the presence of 1-phenylpropanol acetate **4**. In the present case, this ligand could be the acetate or the propanoate, according to the rate of exchange (Scheme 4) and the order of addition of the ligands to the central atom (i.e., addition of propanoate ions to LTA or of acetate ions to LTP). Further modification of the system by replacement of potassium propanoate by acetate suppresses the formation of ester **5**,

(11) The conversion yield increases with the stirring rates (300, 600, 2400 rpm), but the relative amounts of the radical to ionic reaction products (see Table 2) is higher at 600 rpm. The parallel between ultrasonic and mechanochemical activations is not straightforward in this case.

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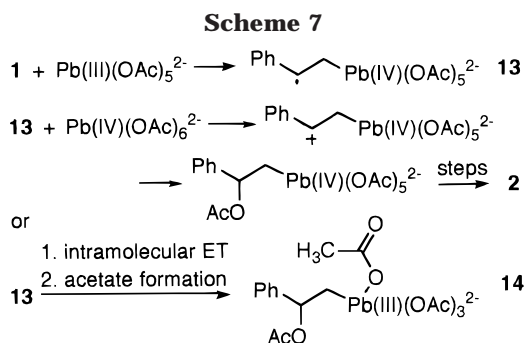
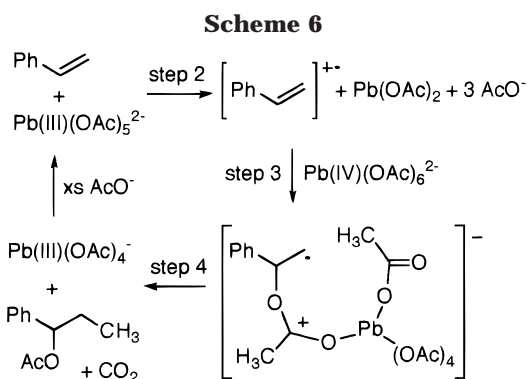
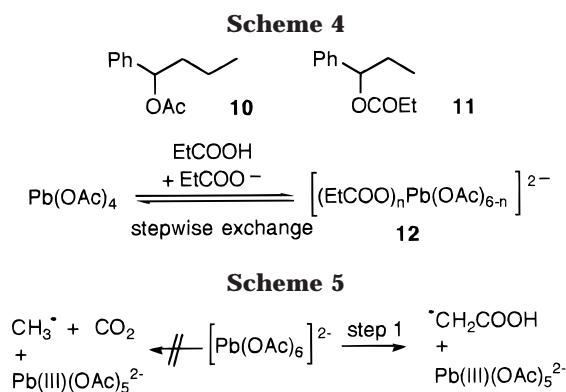
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Table 2. Reactions of LTP and LTA under Various Conditions

| run | reagent, additive, ^a solvent, conditions ^b | residual 1 (%) | polar reaction products (%) | radical reaction products (%) | material balance |
|-----|---|--------------------------|--------------------------------|---|---------------------|
| 1 | LTA, EtCO ₂ K, EtCO ₂ H, stirring | 7 | 3 (3) | 5 (57) + 6 (4) + 10 (9) | 80 |
| 2 | LTA, EtCO ₂ K, EtCO ₂ H,))))) | 2 | 3 (4) | 5 (73) + 6 (6) + 10 (9) ^c | 94 |
| 3 | LTP, EtCO ₂ K, AcOH, stirring | 21 | 2 (3) | 4 (14) + 5 (9) + 10 (44) ^c | 93 |
| 4 | LTP, EtCO ₂ K, AcOH,))))) | 3 | 2 (1) | 4 (10) + 5 (13) + 10 (61) ^c | 90 |
| 5 | LTP, AcOK, AcOH, stirring | 8 | 2 (15) + 3 (1) | 4 (22) + 10 (35) | 80 |
| 6 | LTP, AcOK, AcOH,))))) | traces | 2 (1) + 3 (3) | 4 (35) + 10 (55) | 91 |
| 7 | LTA, EtCO ₂ K, AcOH, stirring | 25 | 2 (9) + 3 (2) | 4 (13) + 10 (36) ^c | 83 |
| 8 | LTA, EtCO ₂ K, AcOH,))))) | 5 | 2 (2) + 3 (5) | 4 (19) + 10 (56) ^c | 82 |
| 9 | LTP, AcOK, EtCO ₂ H, stirring | traces | not found | 5 (80) + 6 (5) + 10 (8) | 93 |
| 10 | LTP, AcOK, EtCO ₂ H,))))) | traces | not found | 5 (79) + 6 (3) + 10 (11) | 93 |
| 11 | LTA, AcOK, EtCO ₂ H, stirring | 24 | 3 (2) | 5 (40) + 6 (3) + 10 (10) | 79 |
| 12 | LTA, AcOK, EtCO ₂ H,))))) | traces | 3 (7) | 5 (71) + 6 (7) + 10 (11) | 96 |

^a 20 equiv in all cases. ^b)))) stands for "ultrasonic irradiation". ^c Lactone **6** and 4-phenylbutyrolactone were detected in small amounts (<1% of each) by GC-MS of the crude mixture.



but 1-phenylbutanol acetate **10** remains the major product. This result confirms that the presence of a highly coordinated species of lead is necessary to the reaction, and the homolysis takes place essentially in this complex. Furthermore, even if it cannot be established that a complete exchange occurs, a mixed acetate-propanoate complex undergoes a preferential homolysis of the propanoate ligands. This selectivity is also demonstrated in runs 7 and 8 (Table 2).

Before a general scheme is proposed, a few important elements should be considered. (i) The existence of a chain mechanism was demonstrated previously by several authors,⁷⁻⁹ using inhibition [with benzoquinone and 4-*tert*-butyl catechol (4-BC)] and initiation experiments (with diisopropyl peroxydicarbonate). Some of us observed the complete quenching of the formation of **4** when benzoquinone or 4-BC (20% of the stoichiometric amounts) were added to the reaction mixture.^{2a} (ii) In the absence of styrene, LTA displays a surprising stability: an acetic acid solution heated at 50 °C under nitrogen for 1 h gives only 5% decomposition of LTA, and 7% under sonication at the same temperature (iodometric determination).^{2d} On the other hand, the hexaacetatoplumbate complex decomposes to the carboxymethyl radical, not to the methyl radical and carbon dioxide (Scheme 5).¹⁴ The presence of styrene is then necessary to induce the homolytic cleavage of the R-COO bonds, probably via the formation of a transitory species containing the lead reagent and the olefinic partner. Indeed, authors have observed previously that the UV-vis spectrum of a styrene-LTA mixture differs from the sum of those of the constituents with the presence of a low-intensity peak at 410 nm.⁷

From this, we can conclude that step 1 in Scheme 5 should constitute the initiation step of the reaction,

during which the carboxymethyl radical and a lead(III) species form in sufficient amounts. The former is responsible for the presence of lactones in detectable amounts in most of the experiments,¹⁶ and the latter should be the effective transfer agent in the propagation step (step 2, Scheme 6).⁴

In agreement with previous interpretations, the lead(III) complex should then oxidize styrene to its radical cation,^{4,17} able to react (step 3) with complex **9** to give an unstable intermediate, in which the methyl radical transfers to the styrenic moiety by a mechanism which deserves further study. The lead(III) species formed during this step can continue the chain sequence.

This mechanism offers several advantages by giving evidence of (i) the role of the base, here the carboxylate ions, (ii) the relationship of the selectivity to the structure

(16) In addition to lactone **6**, 4-phenylbutyrolactone was detected in runs 3, 4, 7, 8 in small amounts (<1%) by GC-MS spectrometry.

(17) An addition of the Pb(III) complex to the olefinic bond seems incompatible with experiment (Scheme 7): (i) the radical **13**, further oxidized by a second molecule of **9** (R = CH₃), would give a carbocation precursor of compound **2**; (ii) **13** can be transformed to **14** via an intramolecular disproportionation. The collapse of **14** would lead to the formation of **4** and a "lead(I)" species.

of the intermediate hexacoordinated lead complex, and (iii) the chain character, consistent with previous observations. A question is still open, the origin of the sonochemical effect. The more simple interpretation based only on the mechanical phase mixing is not sufficient, because other results demonstrate a sonochemical effect even in homogeneous solutions.¹⁸ The sonochemical activation cannot occur out of the bubble, ruling out the activation of the unvolatile lead compound. This necessitates the activation of the volatile styrene itself, possibly by ionization to the radical cation (indeed this species has a crucial role in the mechanism) in the bubble gas phase. Styrene radical cation was evidenced spectroscopically in radiolysis experiments,^{19,20} and analogies in the chemical effects of ultrasound and ionizing radiation (the radiomimetic effect of sonication) are known.²¹ The sonochemical reaction would then be initiated by this ionization, by-passing step 1 (Scheme 5) and step 2 (Scheme 6). The higher efficiency of the sonochemical reaction, the switching in favor of the radical pathway, and the role of volatility of the substrate¹⁸ should find a reasonable explanation here.

Experimental Section

Chemicals and solvents were purchased from Aldrich. LTA (95% pure) was recrystallized from acetic acid. LTP was prepared from lead(II,III)oxide, propanoic acid, and anhydride,²² and recrystallized in propanoic acid. Potassium acetate and

propanoate, LTA, and LTP were dried in vacuo before use. Acetic and propanoic acids were distilled in the presence of their anhydrides on chromic anhydride or potassium permanganate, respectively. All the experiments were run in the dark under argon. Reactions under stirring were run at 45 °C in a thermostated vessel, with a mixture of styrene (2.5 mmol), LTP (3 mmol), and potassium propanoate (0 to 20 mmol) suspended in propanoic acid (10 mL). The sonochemical experiments were performed at 32 °C in a thermostated cell, with a "Heat & Systems" generator delivering a 20-kHz continuous wave. The intensity was measured calorimetrically²³ and kept to the constant value of 30 W. In both series of experiments, the excess of oxidant was quenched after 3 h by addition of an aqueous ammonium chloride solution, and the organic compounds were extracted with ether. The ethereal layer was washed twice (NaHCO₃, then water) and the mixture analyzed by vapor-phase chromatography, on a DB 624 "J&W" column with dodecane as an internal standard, with the following temperature sequence: 80 °C isotherm, 4 min; temperature raise 15 °C per min; 210 °C final isotherm, 10 min. The products were identified by comparison with literature data and GC-MS spectrometry.

1-Phenylpropyl acetate **4**⁷: *m/z* 178, 149, 136, 117, 107.
1-Phenylbutyl propanoate **5**¹⁰: *m/z* 206, 163, 150, 132, 117, 107.
4-Phenyl-2-methylbutyrolactone **6**²⁴: *m/z* 176, 132, 117, 105.
1-Phenylbutyl acetate **10**²⁵: *m/z* 192, 150, 117, 107.

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