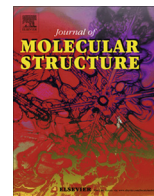




Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

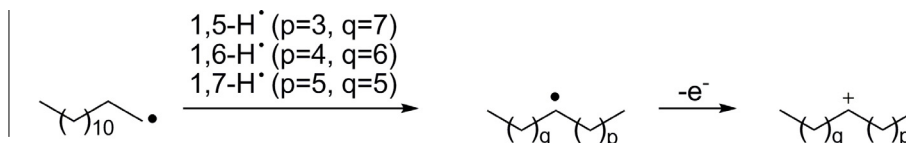
Stabilization of long-chain intermediates in solution. Tridecyl radicals and cations

Aleksandar V. Teodorović^{a,*}, Dalibor M. Badjuk^a, Nenad Stevanović^a, Radoslav Z. Pavlović^b^a Faculty of Science, University of Kragujevac, Radoja Domanovica 12, P.O. Box 60, 34000 Kragujevac, Serbia^b Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, P.O. Box 158, 11001 Belgrade, Serbia

HIGHLIGHTS

- Rearrangements of the long-chains radicals and cations.
- Monte Carlo simulation of the stabilization processes of 1-tridecyl radical.
- Thermal and UV-photolytic conditions for LTA decarboxylation.
- Ratios of homolytical rearrangements determined by Monte Carlo simulation.

GRAPHICAL ABSTRACT



thermal reaction: 1,5/1,6/1,7-H = 17.82 : 5.4 : 1.2
 photolytic reaction: 1,5/1,6/1,7-H = 1.81 : 0.45 : 0.1

ARTICLE INFO

Article history:

Received 25 August 2014
 Received in revised form 11 November 2014
 Accepted 11 November 2014
 Available online xxx

Keywords:

Carbocations
 Carbon centered radicals
 1-Tridecyl radical
 Rearrangements
 Lead(IV) acetate
 Monte Carlo simulation

ABSTRACT

Tetradecanoic acid was decarboxylated by means of lead(IV) acetate (LTA) under thermal (81 °C) and photolytic (r.t.) conditions in benzene solution. The mixture of products, obtained in thermal reaction, consists of esters (acetoxyalkanes and carboxylates), tridecenes, tridecane and phenyltridecane. Additionally, tetradecane and hexacosane, under photolytic conditions, were formed. The classes of products and their distribution might be explained by presence of intermediate 1-tridecyl radical which can undergo intramolecular (result in formation of rearranged carbon centered radicals) and intermolecular stabilization pathways. Experimentally obtained results were used as input data for computational Monte Carlo simulation study of the reaction. On the basis of these results, radical rearrangements, as well as hydride shifts in tridecyl system are discussed.

© 2014 Elsevier B.V. All rights reserved.

Introduction

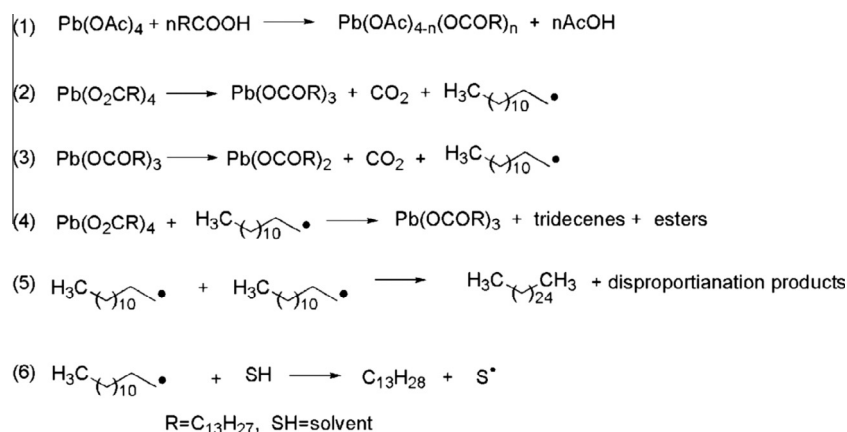
Intramolecular abstraction of a hydrogen atom by an alkyl group, especially 1,5- and 1,6-radical translocation passing through a six- and seven-membered cyclic transition state, respectively, in flexible long chain primary carbon centered radicals result in formation of more stable rearranged secondary alkyl radicals [1–3]. Stabilization by higher order rearrangements, for example 1,7- and 1,8-hydrogen atom transfer, are not excluded, but they happen with less probability, due to entropic factor. Fuch's synthe-

sis of alkenes applies alkyl radical translocations as key step [4]. 1,4-Hydrogen migration, involving a five-membered cyclic transition state is rare [3,5], but it was theoretically considered [3,6].

The oxidative decarboxylations of saturated carboxylic acids, RCOOH, with lead(IV) acetate (LTA) (under thermal or UV-photolytic conditions, in different solvents) have been the subject of numerous studies which have shown that the major fragmentation products obtained in these oxidations were, usually, esters (i.e. acetoxyalkanes, ROAc, and carboxylates, ROCOR) and alkenes, R(-H), in addition to saturated hydrocarbons, RH, and phenylalkanes, RPh (when benzene was used as a solvent) [7,8]. Since all these fragmentation products are derived from the initial carbon centered radical fragment R[•] (which is generated in a free-radical

* Corresponding author. Tel.: +381 34 335 039; fax: +381 34 335 040.

E-mail address: a.teodorovick@gmail.com (A.V. Teodorović).



Scheme 1. General accepted mechanism for LTA decarboxylation of carboxylic acids.

chain [8,9] and the corresponding, subsequently formed (by one-electron oxidation), carbocation (R⁺), whereby the relative product distribution is dependent on structural features of the starting acid and reaction conditions. In this type of reaction, oxidation with two electron oxidants, radicals can be also oxidized to corresponding alkyl cations which can be subjected to successive 1,2-hydride shifts. These processes can yield rearranged products, but their possible participation does not significantly influence the product distribution.

Monte Carlo (MC) simulation is powerful method for determination of many parameters and for study of complicated processes, for example (i) optimization in the refinement of molecular structure parameters from gas phase electron diffraction data [10], (ii) carbocation rearrangements [11], (iii) calculation of low-energy structures [12], (iv) simulation of consecutive metastable fragmentations [13], etc.

This paper deals with transfer of hydrogen and hydride in tridecyl radicals and cations, obtained by LTA reaction of tetradecanoic acid under thermal and photolytic conditions [14]. Because it was not possible to distinguish all branches in scheme of mechanism on the basis of experimentally products yields, the complex pathways of 1-tridecyl radical stabilization were analyzed by Monte Carlo simulation method to estimate primary involvement of 1,7-homolytical rearrangement if any exist. In our previous paper we put emphasis exclusively on intramolecular transposition of radical and cationic center [15] in octyl intermediates. Now, we also included some intermolecular processes of hydrogen abstraction. The yields of the products obtained experimentally were used as input data for Monte Carlo simulation.

Results and discussion

According with general accepted mechanism (Scheme 1) of LTA decarboxylation of fatty acids: (i) in the first step of the reaction, metathesis [8,16,17], the mixture of lead carboxylates were obtained (Eq. (1)), (ii) thermal or photolytic cleavage of Pb-OCOR as initiation step of free radical chain process (Eq. (2)) [18], (iii) Eqs. (3) and (4), depicted in Scheme 1, are propagation process.

In our previous paper we paid attention mainly on rearrangement of octyl intermediates (radicals and cations) obtained by decarboxylation of nonanoic acid by means of LTA in benzene solution under thermal conditions [15]. Now, we want to report the results obtained in the case of stabilization of 1-tridecyl radical (Schemes 3 and 4). Herein, beside thermal (with (A), benzene, 81 °C) and without solvent (C, 120 ± 2 °C), photolytic (B) reaction (benzene, room temperature) was examined. Intermediate 1-tridecyl radical can undergo to two different pathways of stabilization.

Intermolecular stabilization pathway

The high yields of tridecane (69%; C) and 1-phenyltridecane (51%; A) in thermal reactions are important and clear proof for intermolecular stabilization of 1-tridecyl radical by reaction with benzene [8,16,19] (A) and excess of tetradecanoic acid (C) (Scheme 1, Eq. (6)). The formation of tridecane is result of intermolecular abstraction of hydrogen or disproportionation of tridecyl radicals in all studied reactions. Toluene is also identified as product in A and B reactions. Tetradecane, as result of recombination of 1-tridecyl and methyl radicals, generated by UV-destruction of LTA and mixed Pb(IV) carboxylates, was also obtained. However, the main product of photolytic reaction is the result of another recombination of 1-tridecyl species, dimer (hexacosane) (Table 1 and Scheme 1, Eq. (5)). All these processes belong to termination stage of free radical chain reaction.

Intramolecular stabilization pathway

In order to study the properties of n-alkyl cations without the presence of alkyl radicals, the chemical reactivity of 1-decylamine was studied under deamination conditions in benzene solution (Table 2 and Scheme 2). Based on the distribution of isomeric products the following conclusions can be drawn:

- As expected, 1-decylamine gives rise mainly to unrearranged products under above experimental conditions.
- The formation of rearranged products can be explained via 1,2- and/or successive 1,2-hydride shifts in the corresponding ion. Rearrangements of higher order are not excluded

Table 1

Product distribution (%) in LTA reaction with tetradecanoic acid^a under thermal (A^b and C^b) and photolytic (B)^c conditions.^{d, e, f}

| | C ₁₃ H ₂₇ COOH → C ₁₃ H ₂₇ X + C ₁₃ H ₂₆ | | | | | |
|----------|--|---------------------|---------|--------|-------------------------------------|---------------------------------|
| | X = H | X = CH ₃ | X = OAc | X = Ph | X = C ₁₃ H ₂₇ | C ₁₃ H ₂₆ |
| A | 12.7 | – | 12.37 | 50.67 | – | 11.61 |
| B | 8.66 | 18.51 | 8.21 | 19.41 | 20.61 | 6.38 |
| C | 69.36 | – | 7.20 | – | – | 4.16 |

^a (A) Solvent: benzene; temperature: 81 °C, acid:LTA molar ratio = 1:1.

^b (C) Without solvent, excess of acid (120 ± 2) °C,

^c (B) Solvent: benzene; room temperature: 22 °C.

^d Yields calculated from analytical liquid–gas chromatograms.

^e For isomers see Tables 2 and 3.

^f Toluene was identified in reaction mixtures, but it was not quantified.

Download English Version:

<https://daneshyari.com/en/article/7809779>

Download Persian Version:

<https://daneshyari.com/article/7809779>

[Daneshyari.com](https://daneshyari.com)