OXIDATIVE DECARBOXYLATION OF DICARBOXYLIC ACIDS BY LEAD TETRAACETATE AND OXIDATION OF GENERATED CARBOXYALKYL RADICALS BY Pb(IV) AND Cu(II) CARBOXYLATES*

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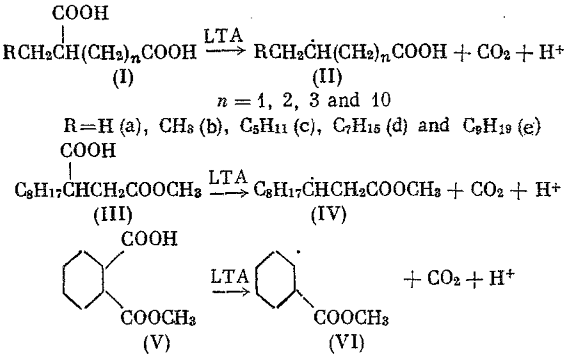
The oxidative decarboxylation of carboxylic acids by lead tetraacetate (LTA) is one of the simplest methods for the generation of alkyl radicals [2, 3]

$$\mathrm{RCOOH} \xrightarrow{\mathrm{LTA}} \mathrm{R}^{\cdot} + \mathrm{CO_2} + \mathrm{H}^+ \cdot$$

This method was used to generate radicals from unsubstituted alkanoic [4-6], acetoxyalkanoic [7], 1,2-alkane- and cycloalkanedicarboxylic [8, 9], disubstituted malonic [10], aralkylcarboxylic [5, 11], and other acids [2, 12]. Under the reaction conditions the formed radicals are partially oxidized by Pb(IV) carboxylates. The fraction of the radicals that undergoes oxidation, and the character of the obtained products, both depend to a large degree on the structure of the alkyl fragment, the presence of functional substituents, and their arrangement with respect to the radical center [2].

In order to ascertain the effect of these factors on the little-studied reactions of carboxyalkyl and carbalkoxyalkyl radicals, in the present paper we studied the oxidative transformations of radical (II), (IV), and (VI) under the influence of the Pb(IV) and Cu(II) carboxylates. These radicals were generated by the oxidative decarboxylation of the alkanedicarboxylic acids (I) and monomethyl esters of 2-octylsuccinic (III) and 1,2-cyclohexanedicarboxylic (V) acids with LTA



$$\underset{\text{(I)}}{\mathrm{RCH_2\overset{\displaystyle COOH}{\overset{|}{C}}H(CH_2)_nCOOH}} \xrightarrow{\mathrm{LTA}} \underset{\text{(II)}}{\mathrm{RCH_2\dot{C}H(CH_2)_nCOOH}} + \mathrm{CO_2} + \mathrm{H}^+$$

$n = 1$, 2, 3 and 10

R=H (a), CH_3 (b), C_5H_{11} (c), C_7H_{15} (d) and C_9H_{19} (e)

$$\underset{\text{(III)}}{\mathrm{C_8H_{17}\overset{\displaystyle COOH}{\overset{|}{C}}HCH_2COOCH_3}} \xrightarrow{\mathrm{LTA}} \underset{\text{(IV)}}{\mathrm{C_8H_{17}\dot{C}HCH_2COOCH_3}} + \mathrm{CO_2} + \mathrm{H}^+$$

(V) $\xrightarrow{\mathrm{LTA}}$ (VI) $+ CO_2 + H^+$

The reaction was run at 80°C in benzene, in an inert gas atmosphere, using approximately equimolar amounts of the decarboxylated acid and LTA (except Expts. 1 and 2, Table 1, and Expt. 5, Table 2), in the presence of pyridine (~1 mole/mole of LTA), which facilitates the decarboxylation [4]. In addition, in the experiments where the behavior of the radicals toward the Cu(II) carboxylates was studied we used cupric acetate in an amount of ~0.1 mole/mole of LTA. The obtained results are given in Tables 1 and 2.

It was established that the structure of R in the (I) acids is practically without effect on the reaction of (I). The decarboxylation of the (I) acids, which differ in a variable position of the COOH groups relative

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*See [1] for previous communication.

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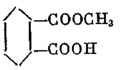
TABLE 1. Oxidative Decarboxylation of Acids (I), (III), and (V) by Lead Tetraacetate (LTA)*

Expt. No.	Acid	Reaction products, mole/mole of LTA†		Total yield (devoid of CO_2)
		CO_2	other products‡	
1	$HOOCCH_2CH_2CH(C_2H_5)COOH$ (I-2б)	0,85	(VII) 0,38; (VIII) + (IX) <0,01	0,38
2	$HOOC(CH_2)_3CH(C_2H_5)COOH$ (I-3б)	0,83	(Xb) 0,57; (XIb) 0,03; (XIIb) + + (XIIIb) 0,11; (XIVb) 0,08; (XVb) <0,01	0,79
3	$CH_3OOCCH_2CH(C_8H_{17})COOH$ (III)	0,62	(XVI) 0,02; (XVII) 0,19; (XVIII) + + (XIX) 0,06; (XIX)/(XVIII) ~3,9; (XX) 0,18	0,45
4	 (V)	0,60	(XXI) 0,18; (XXII) + (XXIII) 0,13; (XXIII)/(XXII) 0,65; (XXIV) 0,27	0,48

*Acid = 15 mmoles (Expts. 1 and 2) and 10 mmoles (Expts. 3 and 4), LTA and pyridine = 10 mmoles each in all of the experiments, solvent = benzene, 100 ml; 80°; reaction time from the start of adding the LTA to the cessation of CO_2 evolution (in the order of the experiments) = 6.5, 2, 15, and 15 h; time of adding the LTA = 3, 1, 5, and 5 h.

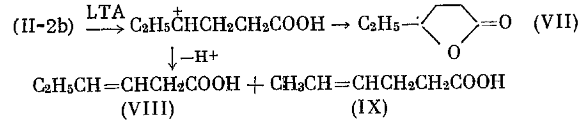
†The yield of the products was determined by analytical GLC.

‡Compound (VII) is γ-ethyl-γ-butyrolactone; (VIII) and (IX) are the 3- and 4-hexenoic acids (Xb) is δ-ethyl-δ-valerolactone; (XIb) is γ-propyl-γ-butyrolactone; (XIIb) and (XIIIb) are the 4- and 5-heptenoic acids; (XIVb) is heptanoic acid; (XVb) is 5-acetoxyheptanoic acid; (XVI) is methyl undecanoate; (XVII) is methyl 3-phenylundecanoate; (XVIII) and (XIX) are methyl 2-undecanoate and methyl 3-undecenoate; (XX) is methyl 3-acetoxyundecanoate; (XXI) is carbomethoxycyclohexane; (XXII) and (XXIII) are the 1- and 2-carbomethoxycyclohexenes; (XXIV) is 1-carbomethyoxy-2-acetoxycyclohexane.

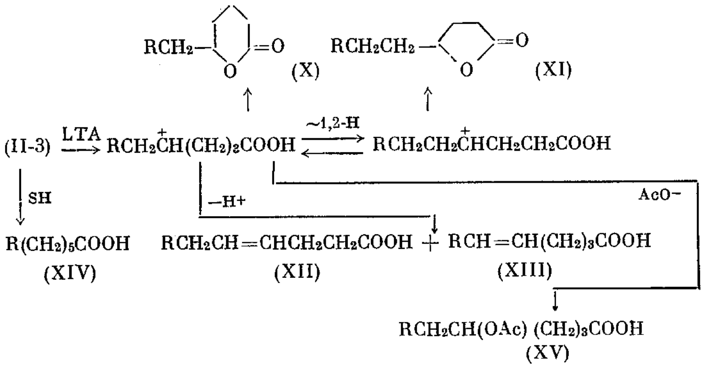
to each other, also proceeds just as smoothly if the reaction is run in the presence of copper ions and, in contrast, in their absence a substantial retardation of CO_2 elimination is observed as the COOH groups approach each other. Thus, under comparable conditions the decarboxylation of acids (III) and (V) is effected in 15 h, that of acids (I-2b)† in 6.5 h, and that of acids (I-3b) in 2 h. Of the two COOH groups in the (I) dicarboxylic acids the group attached to the secondary C atom is eliminated selectively under the experimental conditions [13].

In the experiments not using cupric acetate, among the products that are formed from radicals (II), (IV), and (VI) the following were identified and quantitatively determined via GLC, IR, NMR, and mass spectroscopy: alkyl-substituted γ-butyrolactones (VII) and (XI), δ-alkyl-δ-valerolactones (X), alkenoic acids (VIII), (IX), (XII), and (XIII), unsaturated acids (XIV), and other compounds (see Table 1). With the exception of the (XIV) acids, and esters (XVI) and (XXI), nearly all of them are the oxidation products of the corresponding radicals by lead tetraacetate. The processes for their formation from radicals (II-2b), (II-3), (IV), and (VI) apparently include the carbonium ions as intermediate particles, and can be depicted by the following schemes:

Scheme 1



Scheme 2



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† Adopted designations: the Roman numeral represents the general formula of the compound, while the Arabic numeral and letter, respectively represent the n and R values.

TABLE 2. Oxidative Decarboxylation of Acids (I), (III), and (V) by Lead Tetraacetate (LTA) in the Presence of $Cu(OAc)_2$*

Expt. No.	Acid	Reactants, mmoles				Reaction products, mole/mole of LTA		Total yield (devoid of CO_2)
		acid	LTA	$Cu(OAc)_2$	pyridine	CO_2	other products†	
1	$HOOCCH_2CH(C_8H_{17})COOH$ (I-1d)	30	30	4	25	0,85	(XXV-1d) + (XXVI-1d) 0,18; (XXV)/(XXVI) ~2; (XXVIIId)+ +(XXIXd) 0,10;	0,28
2	$CH_3OOCCH_2CH(C_8H_{17})COOH$ (III)	5	5	1	5	0,75	(XVIII) + (XIX) 0,36; (XIX)/ /(XVIII) ~2,8; (XVI) 0,01; (XVII)and(XX) <0,01	0,37
3	 (V)	10	10	2	5	0,90	(XXII) + (XXIII) 0,85; (XXIII)/(XXII) ~2,7; (XXI) 0,03; (XXIV) <0,01	0,88
4	$HOOCCH_2CH_2CH(C_2H_5)COOH$ (I-2b)	20	22	5	25	0,90	(VII) 0,25; (VIII) + (IX) 0,15; (IX)/(VIII) ~3	0,40
5	$HOOC(CH_2)_3CH(C_2H_5)COOH$ (I-3b)	15	10	2	10	0,95	(Xb) 0,18; (XXV-3b) + (XXVI-3b), 0,70; (XXV)/(XXVI) ~1,5; (XIb) <0,01	0,88
6	$HOOC(CH_2)_3CH(C_6H_{13})COOH$ (I-3c)	25	26	2,5	25	0,85	(Xc) 0,15; (XXV-3c) + (XXVI-3c) 0,50; (XIc) <0,01; (XXVIII-3c) + (XXX-3c) 0,07	0,72
7	$HOOC(CH_2)_3CH(C_8H_{17})COOH$ (I-3d)	40	44	5	40	0,84	(Xd) 0,18; (XXV-3d) + (XXVI-3d) 0,49; (XId) <0,01; (XXVII-3d) + (XXX-3d) 0,05; (XXX)/(XXVII) ~1,5	0,72
8	$HOOC(CH_2)_3CH(C_{10}H_{21})COOH$ (1-3e)	30	32	4	30	0,90	(Xe) 0,14; (XXV-3e) + (XXVI-3e) 0,42; (XIe) <0,01; (XXVII-3e) + (XXX-3e) 0,08; (XXX)/(XXVII) ~1,7	0,64
9	$HOOC(CH_2)_{10}CH(CH_3)COOH$ (I-10a)	25	27	2,5	25	0,90	(XXV-10a) + (XXVI-10a) 0,70; (XXV)/(XXVI) ~1,5; (XXVII-10a) + (XXX-10a) 0,10	0,80

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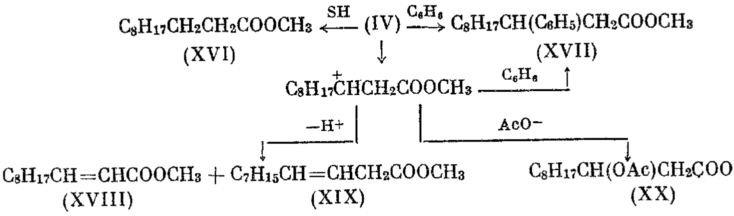
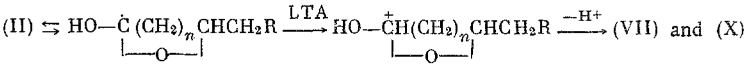
*Solvent = benzene, 100 ml; 80°; reaction time from start of adding LTA to cessation of CO_2 evolution = ~3 h; time of adding LTA = 2 h.

†See footnote to Table 1 for (VII)-(IX) and (XVI)-(XXIV); (Xb-e) are respectively the δ-ethyl-δ-hexyl-, δ-octyl-, δ-decyl-δ-valerolactones; (Xb-e) are respectively the γ-propyl-, γ-heptyl-, γ-nonyl-, and γ-undecyl-γ-butyrolactones; (XXV-3b-e) are respectively the $\Delta^{5,6}$-heptenoic, $\Delta^{5,6}$-undecenoic, $\Delta^{5,6}$-tridecenoic, and $\Delta^{5,6}$-pentadecenoic acids; (XXVI-3b-e) are respectively the $\Delta^{4,5}$-hepteonic, $\Delta^{4,5}$-undecenoic, $\Delta^{4,5}$-tridecenoic, and $\Delta^{4,5}$-pentadeconic acids; (XXV-10a) and (XXXVI-10a) are the 12- and 11-trideconoic acids; (XXVII 3c-e) are the deca-, dodeca-, and tetra-1,4-decadienes; (XXX-3c-e) are the deca-, dodeca-, and tetra-1, 3-decadienes; (XXVII-10a) and (XXX-10a) are the 1,11- and 1,10-dodecadienes; (XXVIIId) is 2-decenyl acetate; (XXIXd) is 3-acetoxy-1-decane.

Scheme 3



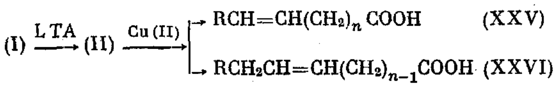
The application of Scheme 3 to the (VI) radicals can explain their conversion to the methyl esters of the cyclohexanecarboxylic (XXI), the 1- and 2-cyclohexenecarboxylic (XXII) and (XXIII), and the 2-acetoxycyclohexanecarboxylic (XXIV) acids. Taking into consideration the tendency of the 3- and 4-carboxyalkyl radicals to undergo intramolecular cyclization [14], it is possible to assume an alternate path for the conversion of radicals (II-2) and (II-3) to lactones (VII) and (X)



$$(II) \leftrightarrows HO{-}\dot{C}(CH_2)_nCHCH_2R \xrightarrow{LTA} HO{-}\overset{+}{C}H(CH_2)_nCHCH_2R \xrightarrow{-H^+} (VII) \text{ and } (X)$$

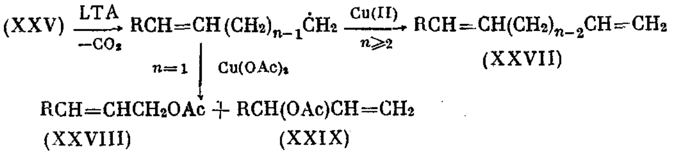
The oxidation of the 1,3- and 1,4-dicarboxylic acids by LTA to the γ- and δ-lactones was observed in [12], where, as in the present paper, the involvement of carbonium ions in the formation of the lactones is postulated.

Independent of the mutual arrangement of the COOH groups, the decarboxylation of the (I) acids in the presence of $Cu(OAc)_2$ leads to their predominant conversion to unsaturated acids (XXV) and (XXVI)



$$\text{(I)} \xrightarrow{\text{LTA}} \text{(II)} \xrightarrow{\text{Cu(II)}} \left[\begin{array}{ll} \rightarrow \text{RCH=CH(CH}_2)_n\text{COOH} & \text{(XXV)} \\ \rightarrow \text{RCH}_2\text{CH=CH(CH}_2)_{n-1}\text{COOH} & \text{(XXVI)} \end{array}\right.$$

In like manner, the main oxidation products of acid (III) become the methyl esters of the 2- and 3-undecenoic acids, while in the case of acid (V) the methyl esters of the 1- and 2-cyclohexenecarboxylic acids are the main products. The formation of unsaturated and acetoxyalkanoic acids is almost completely suppressed, and the fraction of lactones in the total reaction product decreases. The formed unsaturated acids (XXV) undergo partial decarboxylation and subsequent transformation to alkadienes (XXVII) and alkenyl acetates (XXVIII) and (XXIX)



$$\begin{tikzcd} \text{(XXV)} \arrow[r, "\text{LTA}", "-\text{CO}_2"'] & \text{RCH=CH(CH}_2)_{n-1}\dot{\text{C}}\text{H}_2 \arrow[r, "\text{Cu(II)}", "n\geqslant 2"'] \arrow[d, "n=1"', "\text{Cu(OAc)}_2"] & \underset{\text{(XXVII)}}{\text{RCH=CH(CH}_2)_{n-2}\text{CH=CH}_2} \\ & \underset{\text{(XXVIII)}}{\text{RCH=CHCH}_2\text{OAc}} + \underset{\text{(XXIX)}}{\text{RCH(OAc)CH=CH}_2} & \end{tikzcd}$$

In a similar manner, alkadienes $RCH_2CH{=}CH(CH_2)_{n-3}CH{=}CH_2$ (XXX) are formed from the unsaturated acids (XXVI) when n ≥ 3, while alkenyl acetates $RCH_2CH{=}CHCH_2OAc$ (XXXI) and $RCH_2CH(OAc)CH{=}CH_2$ (XXXII) are formed when n = 2. The unsaturated acids (XXV-1) and (XXVI-2), with the double bond in the 3,4 position, are more inclined to undergo the same secondary reactions. For this reason in Expts. 2 and 4 (see Table 2), where acids of this type are the products of the first decarboxylation step, they are obtained in low yield. Judging by the yield of alkadienes (XXVII) and (XXX), acids (XXV) and (XXVI), with a C=C bond in the 4,5 and more distant position, are decarboxylated to the extent of ~10-20% under the experimental conditions.

An analysis of the obtained results makes it possible to conclude that the copper salt substantially changes the character of the transformations of the radicals that are generated from acids (I), (III), and (V) under the influence of Pb(IV). It is known that Cu(II), when compared with other variable valence metals, has a much greater capacity to oxidize alkyl radicals [15], and in this respect is far superior to Pb(IV) [16]. The direction of the reaction of LTA with dicarboxylic acids changes in the presence of $Cu(OAc)_2$, while the transformations of the formed radicals that are observed here actually give information regarding their reaction with Cu(II). As a result, it was found that the mutual arrangement of the functional group and radical center in radicals (II), (IV), and (VI) exerts a very interesting effect on their competing oxidative β-deprotonation under the influence of copper ions respectively to the isomeric unsaturated acids (XXV) and (XXVI), esters (XVIII) and (XIX), and esters (XXII) and (XXIII). This effect is primarily manifested in the fact that the reaction is directed predominantly toward the formation of (XXV), (XIX), and (XXIII), i.e., unsaturated acids and their esters where the C=C bond is further away from the carboxy of carbalkoxy group, as the result of the functional group of the radical inhibiting the competing oxidative reaction, which leads to (XXVI), (XVIII), and (XXII). Thus, in the case of the (II-1) radicals the 2-alkenoic acid (XXVI-1) is formed only in an amount equal to ~25% of the isomeric 3-alkenoic acid (XXV-1), if its amount, converted to alkenyl acetates (XXVIII) and (XXIX), is taken into account (see Table 2, Expt. 1). However, this effect of the COOH groups decreases rapidly with increase in their distance from the radical center, and becomes barely noticeable even for the 4-carboxyalkyl radicals. For example, the 4- and 3-alkenoic acids (XXV-2) and (XXVI-2) are formed from the 3-carboxyalkyl radicals (II-2) in an ~3 : 1 ratio, while the 5- and 4-alkenoic acids (XXV-3) and (XXVI-3) are formed from the 4-carboxyalkyl radicals (II-3) in an ~1.5 : 1 ratio (Expts. 4 and 5, see Table 2). The carbomethoxyl groups exert a smaller effect than the carboxyl groups in analogous reactions. Thus, if the 2- and 3-alkenoic acids (XXVI-1) and (XXV-1) are formed from the 2-carboxyalkyl radicals (II-1) in an ~1 : 4 ratio, then the oxidation of the 2-carbomethoxyalkyl radicals (III) under analogous conditions leads to a mixture of the methyl esters of these acids in an ~1 : 3 ratio. The same ratio of the esters of the $\Delta^{2,3}$- and $\Delta^{3,4}$-acids is observed in the oxidation of the 2-carbomethoxycyclohexyl radicals (VI). A similar intramolecular effect of a functional group on the oxidative β-deprotonation of functionally substituted alkyl radicals under the influence of Cu(II) was observed previously for the acetoxyalkyl radicals [7]. The mechanism by which the acetoxyl group, as well as the carboxyl and carbomethoxyl groups, exert an effect on the oxidative β-deprotonation of radicals is apparently the same in all cases. Its interpretation as applied to the oxidation of acetoxyalkyl radicals is given in [7].

EXPERIMENTAL METHOD

For the GLC analysis we used a chromatograph equipped with a flame-ionization detector and 2 m × 4 mm stainless columns packed with 15% PEGS, 10% Tween-40, 15% FFAP, and 15% Silicone Oil DS-550 deposited on acid-washed Chromosorb W (0.16-0.20 mm). The carrier gas was nitrogen. The NMR spectra were obtained on a Varian DA-60-IL instrument at 60 MHz, using ~30% CCl_4 solutions and HMDS as the internal standard; the IR spectra were taken on a UR-10 spectrophotometer as a thin layer and in CCl_4 solution; the mass spectra were taken on MX-13-03 and Varian MAT-111 instruments.

The characteristics of the employed LTA, $Cu(OAc)_2 \cdot H_2O$, pyridine, and benzene are given in [7].

2-Ethylglutaric Acid (I-2b). This was obtained by the saponification of 4,4-dicarbethoxycaproic acid and subsequent thermal decarboxylation, bp 190° (20 mm), mp 50-51° (from benzene). Found: C 52.20; H 7.70%; neutralization equivalent (NE) 82. $C_7H_{12}O_4$. Calculated: C 52.50; H 7.50%; NE 80.

2-Ethyladipic Acid (I-3b). This was obtained by the homolytic alkylation of butyric acid with vinylacetic acid as described in [17]; yield 42%; bp 135-140° (0.5 mm); mp 47-48° (from benzene). Found: NE 90.2. $C_8H_{14}O_4$. Calculated: NE 87.

2-Octylsuccinic (I-1d), 2-Methyltridecanoic (I-10a), and 2-Alkyladipic (I-3c-e) Acids. These were obtained by the saponification of the methyl esters of the corresponding acids. The synthesis of the esters of acids (I-1d), (I-3e), and (I-3d) is described in [17]. The ester of acid (I-10a) was prepared as described in [17] from propionic acid and methyl undecenate in 55% yield, bp 160-165° (0.1 mm), while the ester of acid (I-3c) was obtained by a similar procedure from dimethyl adipate and 1-hexene in 60% yield, bp 110-116° (0.08 mm). The dicarboxylic acids were purified by recrystallization from benzene and petroleum ether, and their purity was checked by the NE. The melting points of the synthesized acids were: (I-1d) 75-77°; (I-10a) 84°; (I-3c) 48-49°; (I-3d) 58-60°; (I-3e) 63-65°.

Monomethyl Ester of 2-Octylsuccinic Acid (III). This was obtained in quantitative yield by treating 2-octylsuccinic anhydride with methanol [18]. Acid (III) is an oil with n_D^{20} 1.4462. Found: NE 252. $C_{13}H_{24}O_4$. Calculated: NE 242. Infrared spectrum ($\nu_{C=O}$): 1712 and 1745 cm^{-1}. 2-Octylsuccinic anhydride was obtained in the homolytic alkylation of succinic anhydride with 1-octene by the following method. To a heated mixture of 50 g (0.5 mole) of succinic anhydride and 10 ml of chlorobenzene was added a solution of 3 g (0.02 mole) of tert-butyl peroxide in 11.2 g (0.1 mole) of 1-octene in 4 h, the mixture was heated for another 1 h, and then 50 ml of chlorobenzene was added to it at one time, the mixture was cooled, the precipitate was filtered and washed with ether, and the ether extract and chlorobenzene solution were evaporated in vacuo. Recrystallization from petroleum ether gave 8.5 g (40%) of 2-octylsuccinic anhydride, mp 58-60°. Found: anhydride equivalent 211 (determined as described in [19]). $C_{12}H_{20}O_3$. Calculated: 212. Infrared spectrum ($\nu_{C=O}$): 1782 and 1865 cm^{-1}.

Monomethyl Ester of 1,2-Cyclohexanedicarboxylic Acid (V). This was obtained by the catalytic hydrogenation over Raney nickel (50 atm, 6 h) of a methanol solution of the monomethyl ester of 4-cyclohexene-1,2-dicarboxylic acid; yield 95%; mp 65-67° (benzene–petroleum ether). Found: NE 177. $C_9H_{14}O_4$. Calculated: NE 186. Infrared spectrum ($\nu_{C=O}$): 1710 and 1740 cm^{-1}. The monomethyl ester of 4-cyclohexene-1,2-dicarboxylic acid was prepared as described in [18] by treating the anhydride of the corresponding acid, the adduct of butadiene and maleic anhydride [20], with methanol; the yield of the ester was 98%; mp 76-79° (petroleum ether).

General Method for the Oxidative Decarboxylation of Carboxylic Acids. This was described in [7]. On conclusion of adding the LTA the refluxing (~80°) of the reaction mixture was continued until the CO_2 evolution ceased (1-13 h), after which the mixture was cooled, treated with an ~3-fold molar excess of 1 : 1 HCl solution, the precipitate was filtered, and the organic layer of the filtrate was diluted with ether, washed with water, and dried over $MgSO_4$. After distilling off the solvents the residue was analyzed employing GLC, NMR, IR, and mass spectrometry, either directly or after fractional distillation in vacuo or by preparative GLC. The chromatographic determination of the amount of compounds in the residue was accomplished using internal standards, while the amounts in the fractions were determined using the internal normalization method. The results of studying the reaction products by the indicated physical methods are summarized in Table 3. The ratio of the unsaturated acids (XXV) and (XXVI), esters (XVII) and (XIX), (XXII) and (XXIII), and alkadienes (XXVII) and (XXX), was established both chromatographically and from the integral intensities of the signals of the protons, characteristic for the corresponding compounds (see Table 3).

TABLE 3. Infrared, NMR, and Mass Spectra of Reaction Products

No.		Product	Infrared spectrum, ν_{max}, cm^{-1}	NMRspectrum, δ, ppm (integral intensity)*	Mass spectrum, m/e (relative intensity)
expt.	Table				
1	1	(VII)	1780	0,9 t (3H), ~2,1—2,6 m (6H), 4,35 m (H)	—
2	1	(Xb)+ (XIIb)+ + (XIIIb)	1654, 1712, 1742	4,35 m (~0,27 H), 5,3 m (~0,7 H)	—
3	1	(XVII)	1742, 3030	—	202(100), 91(67), 121(50), 44(50), 57(48), 118(42), 104(37), 69(30), 276(28, M$^+$), 105(27), 216(17), 163(14)
4	1	(XXII) + + (XXIII) + + (XXIV)	1654, 1725, 1745, 3040	1,85 s (2H), 5,7 m (~0,5H)	—
2	2	(XVIII)+(XIX)	1660, 1742, 3035	0,9 t (3H), 2,9 m (1,5H) 3,6 s (3H), 5,3 m (1,5H), 5,8 m (0,25H), 6,7 m (0,25H)	—
3	2	(XXII) + (+XXIII)	1654, 1725, 1745, 3040	5,7 m (1,5H), 6,9 m (0,5H)	—
4	2	(VII) + (VIII)+ + (IX)	1712, 1780	0,9 t (2H), 1,2—2,7 m (~6H), 2,9 m (~0,2H), 4,3 m (0,6H), 5,3 m (0,7H), 9 s (~0,4H)	—
5	2	(Xb)	1740	0,9 t (3H), 2,1—2,6 m (8H), 4,35 m (H)	99(100), 42(64), 71(56), 55(50), 128(7, M$^+$)
5	2	(XXV-3b) + + (XXVI-3b)	1640, 1712, 3080	0,9 t (1,2H), 1,6 m (1,8H), 5,3 m (2H), 10,5 s (H)	—
6	2	(Xc)	1740	0,9 t (3H), 1,2—2,2 m (16H), 4,35 m (H)	99(100), 55(49), 42(44), 70(42), 44(27), 40(29), 71(21), 29(21), 114(8)
6	2	(XXV-3c) + + (XXVI-3c) †	1710	0,9 t (3H), 1,25 m (14H), 5,3 m (2H), 10,25 s (H)	—
7	2	(XXVII-3d) + +(XXX-3d) †	1645	0,9 t (3H), 1,25 m (11H), 2,65 m (0,6H), 4,6—6,3 m (5H)	—
9	2	(XXV-10a) + +(XXVI-10a)	1645, 1712	1,25 m (15,2H), 1,57 m (1,2H), 1,92 m (2H), 2,22 t (2H), 4,7—4,95 m (1,2H), 5,25 m (0,6H), 5,5—6 m (0,8H), 10,25 s (H)	—

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*The intensity of the signals of the characteristic protons of a mixture of two or three products is given on the basis of the ratio to the total integral of the given mixture.

†The spectra of lactones (Xd) and (Xe) resemble the spectra of lactone (Xc), the spectra of the mixtures (XXV-3d) + (XXVI-3d) and (XXV-3e) + (XXVI-3e) resemble the spectrum of the mixture (XXV-3c) + (XXVI-3c) and the spectra of alkadienes (XXVII-3e) and (XXX-3e) resemble the spectrum of alkadienes (XXVII-3d) and (XXX-3d).

CONCLUSIONS

1. The reaction of lead tetraacetate with dicarboxylic acids of general formula $RCH_2CH(COOH)(CH_2)_n$-COOH (R = Alk, n = 1, 2, 3 or 10) in the presence of pyridine led to their selective oxidation decarboxylation and the generation of carboxyalkyl radicals $RCH_2\dot{C}H(CH_2)COOH$. In a similar manner, the 1-(carbomethoxymethyl)nonyl and 2-carbomethoxycyclohexyl radicals were obtained from the monomethyl esters of the 2-octylsuccinic and cyclohexane-1,2-dicarboxylic acids.

2. The main products when the radicals are oxidized with the Pb(IV) and Cu(II) carboxylates are alkenoic acids and their esters, γ- and δ-lactones (in the oxidation of the carboxylalkyl radicals with n = 2 and 3), and esters of acetoxy-substituted monocarboxylic acids (when oxidation is with Pb(IV) carboxylates).

3. The carboxy and carbomethoxy groups in the 2- and 3-carboxy- and 2-carbomethoxyalkyl radicals direct the oxidative β-deprotonation of these radicals under the influence of copper ions predominantly toward the formation of alkenoic acids or of their esters, where the double bond is further away from the functional group.

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