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51. The Lead Tetraacetate Reaction of Alcohols Containing a Small Ring[1]). Part II[2]). Cyclobutane-methanols and Cyclopropane-ethanols

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(4. XI. 75)

Summary. The leadtetraacetate and lead tetraacetate/metal chloride oxidations of cyclobutane-methanol, cyclopropane-ethanol and the corresponding α,α-dimethyl alcohols have been investigated and compared with the oxidative reactions of cyclobutane-carboxylic acid, cyclopropane-acetic acid and 4-pentenoic acid, performed with the same reagents and under similar conditions. It was found that alcohol β-fragmentation and acid decarboxylation follow a remarkably similar mechanistic course, affording comparable results when the substrates are of the same structural type (**1**, **2** and **5**; **3**, **4** and **6**) or are converted to the same intermediate alkyl radical fragments (**3**, **4**, **6** and **7**). In addition, cyclization products formed from cyclopropane-ethanol (dihydropyran derivative **31**) and 4-pentenoic acid (γ-lactones **38**) have been isolated and identified.

In one of our previous publications [2] we presented partial results on the oxidation of cyclobutane-methanol (**1**) with lead tetraacetate (hereafter referred to as LTA). Because of some interesting features concerning the β-fragmentation process in this

[1]) Commun. 33 on 'Reactions with lead tetraacetate'. For Commun. 32 see [1].
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reaction, we have subsequently studied in greater detail the oxidative action of LTA and LTA/metal chloride combinations on cyclobutane-methanol (**1**), α,α-dimethyl-cyclobutane-methanol (**2**), cyclopropane-ethanol (**3**) and α,α-dimethylcyclopropane-ethanol (**4**), and compared the fragmentation products obtained with the decarboxylation products formed, under similar conditions, in the LTA and LTA/metal chloride oxidations of cyclobutanecarboxylic acid (**5**), cyclopropane-acetic acid (**6**) and 4-pentenoic acid (**7**). The results of these reactions (involving β-fragmentation, *i.e.* decarboxylation, cyclization and other processes) are summarized in Tables 1–3, and the products shown in *Schemes 1, 3, 4* and *6*.

Lead Tetraacetate Oxidations. – In benzene as solvent and irrespective of reaction conditions used (thermal at 80° without or in the presence of calcium carbonate or pyridine, UV.-photolytic at 20°), the cyclobutane ring-containing substrates, *i.e.* the primary alcohol **1** and the tertiary alcohol **2**, as well as the corresponding acid **5**[4]), afforded (Table 1) as fragmentation esters mixtures of 'homoallylic' [3] acetates (**14a**, **15a**, **16a**) and cyclobutanecarboxylates (**14b**, **15b**, **16b**) having essentially the *same* isomeric composition (approximate ratio **14/15/16** (**a** and **b**) = 4:42:54), and as fragmentation phenyl derivatives in high predominance or ex-

Table 1. *Products* (Scheme 1) *obtained in the lead tetraacetate oxidations* (in benzene) *of cyclobutanemethanol* (**1**), *α,α-dimethylcyclobutanemethanol* (**2**) *and cyclobutanecarboxylic acid* (**5**)

Reactant	Conditions and molar ratio: reactant/LTA (solvent benzene)	*Fragmentation products and yields (in %)*[a])		
		Acetates **14a+15a+16a** (**14a/15a/16a**)	*Carboxylates*[b]) **14b+15b+16b**	*Cyclobutylbenzene*[c]) **10**
	Thermal (80°)			
1	1:1 (:1 $CaCO_3$)	18 (4:41:55)	3	15
1	1:1 (:2 pyridine)	16 (5:42:53)	2	12
2	1:1 (:1 $CaCO_3$)	36 (3:46:51)	–	19
5	1:1	32 (4:41:55)	8	22
	UV.-Photolytic (20°)			
1	1:4	26 (5:43:52)	3	21
5	1:1	38 (4:42:54)	6	20

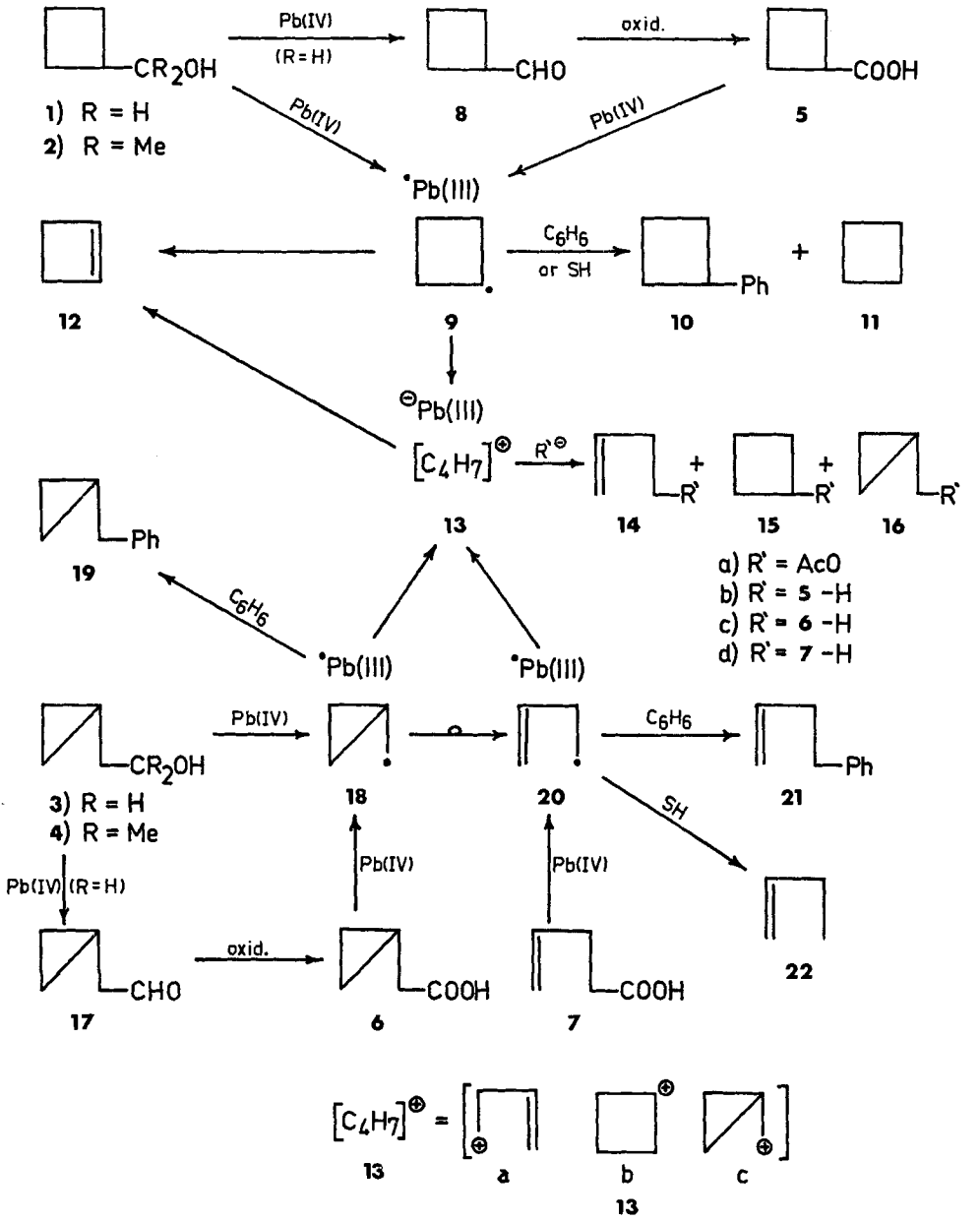
a) Other fragmentation products detected in all cases were 0.5–3% of cyclobutene (**12**) and 1.5–4% of cyclobutane (**11**). In reactions of alcohols **1** and **2** the corresponding acetates (15–30%) and formates (3–6%) were also formed (and 2–10% of alcohol was recovered). The primary alcohol **1** gave, in addition, 0.5–1% of aldehyde **8**, 1–2% of acid **5**, and 1–2% of cyclobutanecarboxylate of **1**. The tertiary alcohol **2** afforded 1–2% of fragmentation cyclobutyl methyl ketone (**24**).

b) The relative distribution of these esters (**14b/15b/16b**) was the same as that of the corresponding acetates **a** (*i.e.* 3–4:40–43:54–56).

c) Small amounts (trace-1.5%) of the isomeric fragmentation phenyl derivatives **19** and **21** were usually also detected.

4) The LTA oxidative reactions of acids **5**, **6** and **7** have been performed previously, under somewhat different reaction conditions [3]; the results reported for the decarboxylation products are comparable to those described in the present study. However, no mention was made [3] [8] of the acyloxy-γ-lactones **38a** and **38b** (*Scheme 6*), which are formed as predominant products from 4-pentenoic acid (**7**).

Scheme 1



Pb(z) = $Pb(OAc)_m$ or $R'_nPb(OAc)_m$; z = IV or III, m+n = 4 or 3 R' = **1**–**7**(–H), SH = Hydrogen donor.

clusively cyclobutylbenzene (**10**). These results are consistent with a common mechanistic course for the LTA β-fragmentation of both alcohols **1** and **2**[5]), and for the LTA decarboxylation of acid **5**[5]) (*Scheme 1*), namely with the initial formation of cyclobutyl radical fragments (**9**) (which react with solvent benzene and hydrogen donors to give cyclobutylbenzene (**10**) and cyclobutane (**11**), respectively [3] [4])[6]) followed by one-electron oxidation (by Pb(III) and Pb(IV) species) to the homoallylic cationic intermediates $[C_4H_7]^{\oplus}$ (**13**)[7]) which are converted, by addition of

Table 2. *Products* (Scheme 1) *obtained in the lead tetraacetate oxidations* (in benzene) *of cyclopropane ethanol* (**3**), *α,α-dimethylcyclopropaneethanol* (**4**), *cyclopropaneacetic acid* (**6**) *and 4-pentenoic acid* (**7**

Reactant	Conditions and molar ratio: reactant/LTA (solvent benzene)	*Fragmentation products and yields (in %)*[a])		
		Acetates **14a**+**15a**+**16a** (**14a**/**15a**/**16a**)	*Carboxylates*[b]) **14c**+**15c**+**16c**	*4-Phenyl-1-butene*[c]) **21**
	Thermal (80°)			
3	1:1 (:1 $CaCO_3$)	7 (21:21:58)	1.5	30
4	1:1 (:1 $CaCO_3$)	16 (20:25:55)	–	18
6	1:1	8 (21:22:57)	2	32
6	1:1 (:2 pyridine)	6 (30:15:55)	1.5	28
7	1:1	4 (25:23:52)	–[d])	5
	UV.-Photolytic (20°)			
3	1:4	11 (20:22:58)	2	22
6	1:2	13 (24:23:53)	3	29

[a]) Other fragmentation products in all cases were 5% (for **7**) to 20% of butene (**22**) and trace amounts of 1,3-butadiene. In reactions of alcohols **3** and **4** the corresponding acetates (10–30%) and formates (3–6%) were also formed (and 5–15% of unchanged alcohol was recovered). The primary alcohol **3** gave, in addition, 1–3% of aldehyde **17**, 1–2% of acid **6**, 1–2% of cyclopropaneacetate of **3**, and 6–10% of 3,4-dihydro-2*H*-pyran-4-yl acetate (**31**, *Scheme 3*). The tertiary alcohol **4** afforded 1–2% of fragmentation 1-cyclopropyl-2-propanone (**25**). 4-Pentenoic acid (**7**) furnished as major reaction products 75–85% of the acetate and 4-pentenoate ester of 5-hydroxymethyl-tetrahydro-2-furanone (**38a** and **38b**, *Scheme 6*)[4]).

[b]) The relative distribution of these esters (**14c**/**15c**/**16c**) was approximately the same as that of the corresponding acetates **a**.

[c]) Small amounts (trace-1.5%) of the isomeric fragmentation phenyl derivatives **10** and **19** were usually also detected.

[d]) In this reaction (of acid **7**) the fragmentation carboxylates (**14d**, **15d**, **16d**) could not be detected.

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[5]) For discussions of the mechanisms of the LTA and LTA/metal chloride reactions see [2] [4–6] for the oxidation (including β-fragmentation) of alcohols, and [3] [4] [7] [8] for the oxidative reactions (including decarboxylation) of carboxylic acids.

[6]) The formation of small amounts of the isomeric phenyl derivatives **19** and **21** in the LTA reactions of **1**, **2** and **5**, and of **10** and **19** in reactions of **3**, **4**, **6** and **7**, is probably the result of electrophilic attack of the cation(s) **13** on benzene (as solvent) [3] [4], although in the case of substrates **3**, **4** and **6** product **19** could also arise directly from the unrearranged radical **18**.

[7]) The 'homoallylic' cation(s) $[C_4H_7]^{\oplus}$ **13** has been formulated either as a nonclassical ion (resonance hybrid of various structures such as **13a**, **13b** and **13c**) (*Scheme 1*) or as a system of three-equilibrating cations (**13a** $\rightleftharpoons$ **13b** $\rightleftharpoons$ **13c**) [2] [9].

acetate and cyclobutanecarboxylate ions[8]), to the corresponding isomeric fragmentation esters **14**, **15** and **16** (**a** and **b**, respectively).

A similar situation is encountered in the LTA reaction of the cyclopropane ring-containing alcohols **3** and **4**, and of the corresponding acid **6**[4]) (Table 2), with that difference that the initially produced cyclopropanemethyl radical **18** is rapidly isomerized to the 3-buten-1-yl radical **20** (*Scheme 1*) [10][9]), which then either reacts with solvent (benzene) or hydrogen donor to give 4-phenyl-1-butene (**21**)[6]) or 1-butene (**22**), respectively, or undergo one-electron oxidation to the homoallylic cation(s) **13**[7]), these being finally converted[8]) to the fragmentation esters **14**, **15** and **16** (**a** and **c**). This has been confirmed on the ground of similar homoallylic acetates distribution (**14a**, **15a**, **16a**) observed in the LTA oxidation of 4-pentenoic acid (**7**)[4]) (Table 2). Since the relative amounts of the fragmentation esters **14** and **15** depend on whether the precursor radical species is 3-buten-1-yl (**20**) (generated in the LTA reaction of **3**, **4**, **6** and **7**) or cyclobutyl (**9**) (produced in the LTA reaction of **1**, **2** and **5**), whereas the proportion of the cyclopropanemethyl esters **16** remains essentially constant, irrespective of the substrate used (Tables 1 and 2), it appears that the extra part of the olefinic esters **14**, formed in the LTA reactions of **3**, **4**, **6** and **7**, arises, as a consequence of unsaturation in the 3-buten-1-yl radical (**20**), from a direct ligand transfer process (without rearrangement) involving complex species such as **23** (*Scheme 2*)[10]).

Scheme 2

$$\underset{\mathbf{20}}{R''\bullet} + Pb(OAc)_n \rightleftharpoons \underset{\mathbf{23}}{R''Pb(OAc)_n} \longrightarrow \underset{\mathbf{14}}{R''OAc} + Pb(OAc)_{n-1}$$

$n = 3$ or 4

β-Fragmentation can also involve (to a minor degree) the elimination of methyl radicals, as actually observed in the LTA reaction of the tertiary alcohols **2** and **4**, which afford in low yield (1–2%) cyclobutyl methyl ketone (**24**) and 1-cyclopropyl-2-propanone (**25**), respectively.

According to *Dreiding* models of the alkoxy radicals **26** and **27** (*Scheme 3*) (which are the first radical intermediates generated in the LTA reaction of alcohols **1** and **3**, respectively [2] [4–6]), the optimal distance (of about 2.5–2.7 Å) between the oxygen atom and the δ-carbon atom, necessary for intramolecular 1,5-hydrogen abstraction and cyclic ether formation [5] [6], is not possible in the cyclobutanemethoxy radical (**26**) but is easily attainable in the cyclopropaneethyl radical (**27**). In agreement with these considerations, no cyclic ether or derived products could be detected in the

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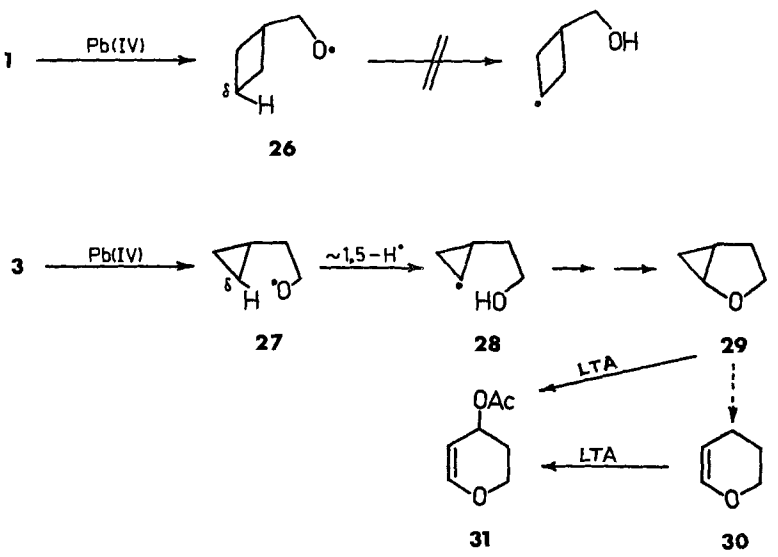
[8]) Ester groups which add to cation(s) **13** are derived from Pb(III)- or Pb(IV)-acetate and -carboxylate species, or directly from AcOH and acids **5** and **6** [2–8]. In the LTA oxidations of the primary alcohols **1** and **3**, the acids **5** and **6**, respectively, are formed by further oxidation of the corresponding aldehyde products **8** and **17** (*Scheme 1*).

[9]) Isomerization of cyclopropanemethyl radicals (**18**) to cyclobutyl radicals (**9**) has not been hitherto observed [10] (except in one, unconfirmed case [11], where such a rearrangement (to a moderate extent) was tentatively suggested).

[10]) Similar to 3-buten-1-yl-copper acetate complexes postulated as possible intermediates in direct acetate transfer processes [12].

Scheme 3



LTA oxidation of cyclobutane-methanol (**1**), whereas in the case of cyclopropane-ethanol (**3**) 3,4-dihydro-2*H*-pyran-4-yl acetate (**31**) was isolated in 6–10% yield. This compound (**31**), which was identical with one of the products obtained in the LTA oxidation of 3,4-dihydro-2*H*-pyran (**30**) [13], arises either from direct attack of LTA on the (unknown) ether 2-oxabicyclo[3.1.0]hexane (**29**)[11]), or upon eventual isomerization of **29** to **30** [15] and subsequent reaction with LTA[12]).

Reactions with Lead Tetraacetate/Metal Chloride Combinations. – In the thermal oxidation of the four-membered ring alcohols **2** and acid **5** with LTA and lithium chloride one obtains (Table 3) as only fragmentation chloride the unrearranged chlorocyclobutane (**33**)[13]) (*Scheme 4*). 4-Pentenoic acid (**7**) under these conditions is converted (in low yield) without isomerization to 4-chloro-1-butene (**32**) (Table 3)[13]). When the cyclopropane ring-containing alcohols **3** and **4** and acid **6** are treated thermally with LTA in the presence of lithium chloride or sodium chloride (in benzene) or N-chlorosuccinimide (in dimethylformamide/acetic acid) [17], they undergo chlorofragmentation to a moderate extent, affording (Table 3) in high predominance the expected 4-chloro-1-butene (**32**) (from the rearranged 3-buten-1-yl radical **20**) and only a very small amount of (chloromethyl)cyclopropane (**34**) (from the intact

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[11]) It is known that cyclopropane rings are opened by LTA [2] [14], whereby this oxidative C—C bond cleavage of the three-membered ring is particularly facile in strained systems, such as bicyclo[n.1.0]alkanes [14].

[12]) Other products are probably also formed in the LTA oxidation of **29** or **30** (*e.g.* tetrahydro-2*H*-pyran-2,4-diol diacetate, 3,6-dihydro-2*H*-pyran-2-yl acetate, etc. [13]), but are subsequently converted, under the reaction conditions used, to compound **31** or are hydrolyzed to sensitive unsaturated hydroxy-aldehydes.

[13]) The LTA/LiCl halodecarboxylation of acids **5** and **7** has been previously reported [7b]. Except for 2% of **32**, other products from acid **7** were not identified [7b].

Table 3. *Isomeric (homoallylic) fragmentation chlorides* (**32**, **33**, **34**) *obtained in the thermal lead tetraacetate/metal chloride reactions of alcohols* **2**, **3** *and* **4**, *and acids* **5**, **6** *and* **7** (Scheme 4)

Reactant	Metal chloride MCl_m	Solvent and molar ratio: reactant/LTA/MCl_m (temp. 80°)		Fragmentation chlorides [a]: Total yield (%) (**32**+**33**+**34**)	Fragmentation chlorides [a]: Isomeric composition (**32**/**33**/**34**)
2	LiCl	PhCl	1:1:1	70	0:100:0
2	$CuCl_2$	PhCl	1:1:1	60	1:97:2
5	LiCl	PhMe	1:1:1	93	0:100:0
5	$CuCl_2$	PhMe	1:2.5:2	89	0:99:1
3	LiCl	PhMe	1:1:1	16	97:0:3
3	$CuCl_2$	PhMe	1:1:0.5	14	95:1:4
4	LiCl	PhCl	1:1:1	35	99:0:1
6	LiCl	PhMe	1:1:1	20	98:0:2
6	NaCl	PhMe	1:1:1	14	97:0:3
6	$CuCl_2$	PhMe	1:1:0.5	18	94:2:4
6	NCS [b]	DMF+AcOH [b]	1:1:6	17	100:0:0
7	LiCl	PhCl	1:1:1	6	100:0:0
7	$CuCl_2$	PhMe	1:1:0.5	5	97:1:2

[a] Products obtained in the oxidations with LTA alone (see Tables 1 and 2) were also formed (with a similar relative distribution of the isomeric fragmentation esters and phenyl derivatives) in most of these reactions, but in reduced yields. 4-Pentenoic acid (**7**) afforded, in addition, 14–20% of the γ-lactone 5-(chloromethyl)dihydro-2(3*H*)-furanone (**38c**, *Scheme 6*).

[b] NCS = N-chlorosuccinimide, DMF = dimethylformamide; DMF/AcOH = 5:1 (*v*/*v*).

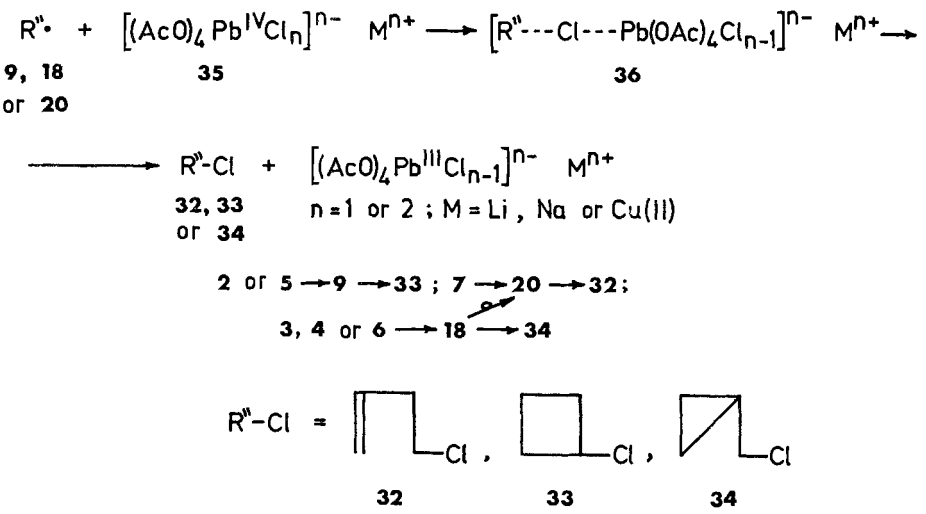
cyclopropanemethyl radical **18**) (ratio **32**/**34** = (96–100):(4–0)[14]). All these results of chlorofragmentation are consistent with a homolytic oxidative mechanism [4] [7] [8] [10c] which involves (*Scheme 4*) direct chlorine transfer (without rearrangement) from chlorine-containing Pb(IV)-complex species (such as **35**), *via* transition state **36**, to the (initially produced) radicals **9**, **18** or **20**[15]). It should be noted that in the LTA oxidation of all these substrates (**2**–**7**) in the presence of cupric chloride, which can itself effect chlorine transfer to radicals **9** and **20**, but with extensive rearrangement [10c] [16], the chloro compounds expected from the homolytic process (*Scheme 4*) were again formed almost exclusively (with only trace amounts of the isomeric chlorides; Table 3), indicating that here also chlorine is predominantly transferred *via* the free radical type transition state **36** (*Scheme 4*) (atom transfer of ligand), rather than through alkyl-metal chloride intermediate species which would allow the alkyl moiety (R″) to have carbenium ion character and undergo substantial rearrangement (oxidative displacement in ligand transfer [10c] [16]).

As shown in separate control experiments, the substrates used in the present study (**1**, **2**, **5**; **3**, **4**, **6**; **7**), the isomeric fragmentation esters (**14**, **15**, **16**), phenyl derivatives (**10**, **19**, **21**) and chloro products (**32**, **33**, **34**) do not undergo isomerization or rearrangement under the conditions of the LTA and LTA/metal chloride (or

[14] This being in agreement with the above-discussed radical isomerization (**18** → **20**) and formation of the phenyl-alkene **21** from **3**, **4** and **6** (Table 2, *Scheme 1*).

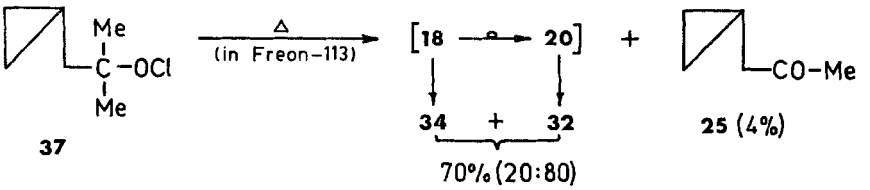
[15] In the LTA/NCS reaction it is possible that chlorine transfer occurs directly from N-chlorosuccinimide molecules.

Scheme 4



LTA/N-chlorosuccinimide) reactions. Also, in the free radical decomposition [4] of α,α-dimethylcyclopropane-ethyl hypochlorite (**37**, *Scheme 5*), fragmentation occurs as expected, giving chlorides **32** and **34** (and no chlorocyclobutane **33**)[16].

Scheme 5

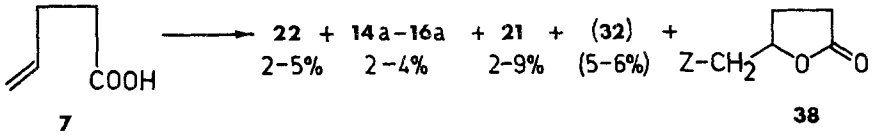


γ-Lactone Formation in the Lead Tetraacetate and Lead Tetraacetate-Metal Chloride Oxidation of 4-Pentenoic Acid (**7**). As can be seen from Tables 2 and 3, and *Scheme 6*, the LTA and LTA/LiCl (or $CuCl_2$) oxidation of 4-pentenoic acid (**7**) afford decarboxylation products in rather poor overall yield (11–14%)[4][13]. A more detailed study has disclosed that the major products of these reactions were γ-lactones **38** (*Scheme 6*), which arise from intramolecular cyclizative addition of the carbonyl oxygen to the nearer olefinic carbon. With LTA alone these lactone products were the acetate and 4-pentenoate ester of 5-(hydroxymethyl)dihydro-2(3*H*)-furanone (**38a** and **38b**) (the ratio of which depends on the relative amount of LTA and on the presence of acetic acid in the reaction mixture; see *Scheme 6*), whereas with LTA/MCl, in addition to those two products, 5-(chloromethyl)dihydro-2(3*H*)-furanone (**38c**) was also obtained (in a yield increasing with the relative amount of metal chloride used; see *Scheme 6*). The structures of these lactones **38** were established on the basis of spectral

[16] Similar thermal decomposition of the hypochlorite of α,α-dimethylcyclobutanemethanol (**2**) gives, as expected, only the unrearranged chlorocyclobutane (**33**) [18].

data (see Exper. Part), and, moreover, the acetoxy-lactone **38a** was synthesized independently by oxidative lactonization of tetrahydrofurfuryl acetate by means of ruthenium tetroxide.

Scheme 6



7 **38**

a) Z = AcO
b) Z = 7-H
c) Z = Cl

7/LTA/LiCl	Total yield (%) of **38**	Ratio **38a/38b/38c**
1 : 1 : 0	85	35 : 65 : 0
1 : 1.3 : 0	75	46 : 54 : 0
1 : 1 : 0 (+12 AcOH)	63	67 : 33 : 0
1 : 1 : 1	81	25 : 58 : 17
1 : 1 : 2	87	21 : 52 : 27
1 : 1 : 5	82	7 : 18 : 75

Only a few examples of acetoxy-γ-lactone formation in the LTA oxidations of γ,δ-unsaturated acids have been reported so far [8] [19], but our results (described above) appear to be the first case in which an acyclic Δ^4-olefinic acid has been used as substrate, and the first example of chloro-γ-lactone formation by the LTA/metal chloride oxidation. Because of high conversion yields, these reactions (under optimal conditions) could find useful synthetic application.

A similar situation is encountered with 4-penten-1-ol; when treated with LTA or LTA/metal chloride, it affords, by way of intramolecular addition (of the hydroxyl oxygen to the double bond), cyclic ethers as predominant products [19c] [20], and (in the LTA reaction) only 1–2% of fragmentation acetates (in a **14a/15a/16a** ratio similar to that observed in the LTA decarboxylation of acid **7**) or (in the LTA–LiCl or $CuCl_2$ reaction) 1–2% of 4-chloro-1-butene (**32**). These results show that in the LTA oxidations of Δ^4-olefinic acids and alcohols intramolecular addition of oxygen to a spatially accessible carbon-carbon double bond (whatever the mechanism of these reactions may be) is much preferred to acid decarboxylation and alcohol β-fragmentation, respectively.

The authors are grateful to the *Serbian Academy of Sciences and Arts* and the *Serbian Republic Research Fund* for financial support.

Experimental Part[17])

Previous papers contain details on the techniques used for the separation, isolation and identification of products [4], and on the procedures for the LTA and LTA/metal chloride oxidations of alcohols [2] [4] [5] and decarboxylations of acids [3] [4] [7] [8]. The LTA reactions were performed (a) in preparative runs with 0.05 mol of substrate in 70–100 ml of solvent, and (b) in

[17]) Spectral measurements were performed in the Laboratories for Instrumental Analysis (directed by Prof. *D. Jeremić*), and elemental microanalyses in the Microanalytical Laboratory (Dr. *R. Tasovac*) of the Chemistry Department.

small-scale runs with 0.005 mol of substrate in 15–20 ml of solvent for thermal reactions, and in 100–120 ml of solvent for photolytic oxidations. The reaction products were separated and analysed (isolated when necessary) by GLC., using Carbowax 20M and Silicone GE XE-60 columns. The molar proportions of reactants, general reaction conditions (solvent, temp., additive, thermal or photolytic decomposition) and product distribution are given in Tables 1–3 and *Scheme 6*.

Most of the starting materials and products were known compounds, synthesized according to literature procedures (or in some cases commercially available). Their purity, before use, was checked by elemental analysis, spectral data and GLC.

α,α-Dimethylcyclopropane-ethanol (**4**) was prepared either by the *Simmons-Smith* reaction [21] with 2-methyl-4-penten-2-ol, or by the *Grignard* reaction from the methyl or ethyl ester of cyclopropane-acetic acid (**6**) and MeMgI, in the usual way (*e.g.* as described for the preparation of the tertiary alcohol **2** [18] [22]), followed by preparative GLC. (Carbowax 20M, 80°). – IR. (CCl_4): ν_{max} = 3620 and 3400 (OH), 3080 (cyclopropyl), 1380 and 1370 (2 Me), 1130, 1020, 895 cm^{-1}. – NMR. (CCl_4, 60 MHz): 2.85 (*s*, 1 H of OH); 1.32 (*d*, 2 H of the side-chain β-CH_2); 1.20 (*s*, 6 H of the two CH_3); −0.1 to 0.9 (complex absorption, 5 H, ring protons).

$C_7H_{14}O$ (114.18) Calc. C 73.63 H 12,36% Found C 73.40 H 12.38%

α,α-Dimethylcyclopropane-ethyl hypochlorite (**37**) in Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane, b.p. 47–48°), was prepared from **4** and NaOCl + AcOH, according to standard procedures [4]. Its thermal decomposition [4] was carried out by refluxing the solution (under N_2) for 3 h (an incandescent 100 Watt tungsten lamp being used as heat source). The major products obtained are shown in *Scheme 5*.

The esters cyclobutanemethyl cyclobutanecarboxylate (from the LTA oxidation of **1** [2], Table 1) and cyclopropane-ethyl cyclopropane-acetate (from the reaction of **3**, Table 2), and the fragmentation cyclobutanecarboxylates **14b**, **15b**, **16b** (derived from **1** and **5**, Table 1) and cyclopropaneacetates **14c**, **15c**, **16c** [23] (from **3** and **6**, Table 2) were prepared by treating the corresponding acid chloride (obtained from acid **5** or **6** and thionyl chloride) with an equimolar amount of the required alcohols (**1**, **3**, 3-buten-1-ol, cyclobutanol or cyclopropane-methanol) in pyridine for 2–4 h at 0–5°, followed by the usual work-up [23].

3,4-Dihydro-2H-pyran-4-yl-acetate (**31**) was obtained (as one of the products) from the LTA oxidation of 3,4-dihydro-2*H*-pyran (**30**) in benzene (at 20°) [13].

5-(Hydroxymethyl)dihydro-2(3H)-furanone acetate (**38a**) was prepared by adding dropwise a solution of ruthenium tetroxide in CCl_4 (prepared from 1.25 g of hydrated[18] ruthenium dioxide in 75 ml of CCl_4 and 5 g of sodium metaperiodate in 75 ml of water [24]) to a stirred and ice-cooled solution of tetrahydrofurfuryl acetate (0.72 g, 0.005 mol) in CCl_4 (15 ml) [25], stirring at 20° for another 5 h, filtering, drying ($CaSO_4$) and removing the solvent *in vacuo*. Preparative GLC. (Silicone GE XE-60, 170°) afforded **38a** in 75% yield. – IR. (CCl_4): ν_{max} = 1785 (γ-lactone C=O), 1745 (acetate C=O), 1235, 1180, 1160, 1080, 1045, 945 cm^{-1} [26]. – NMR. (CCl_4, 60 MHz): 4.56 (*m*, 1 H, H–C–O); 4.10 (*m*, 2 H, H_2C–O); 2.03 (*s*, 3 H, AcO); 1.8–2.65 (complex *m*, 4 H, $-CH_2CH_2-$). – MS. (*m/e*): 159 (*M*+1), 115 (*M* − Ac), 98 (*M* − AcOH), 85 (*M* − $AcOCH_2$), 43 (Ac).

$_7H_{10}O_4$ (158.15) Calc. C 53.16 H 6.37% Found C 53.02 H 6.53%

The major reaction products of the LTA oxidation (for conditions see *Scheme 6*) of 4-pentenoic acid (**7**) were separated and isolated by preparative GLC. (Silicone GE XE-60), and consisted of the above-described acetoxy-lactone **38a** and of 5-(hydroxymethyl)dihydro-2(3*H*)-furanone 4-pentenoate (**38b**, *Scheme 6*). – IR. (CCl_4): ν_{max} = 1780 (γ-lactone C=O), 1740 (acetate C=O), 1175 (sh), 1155, 1080, 920 cm^{-1}. – NMR. (CCl_4, 60 MHz): 5.60 (*m*, 1 H, H–C=C); 4.88 and 4.83 (two *q*, J_{trans} = 16.5, J_{cis} = 8, J_{gem} = 1.5, 2 H, H_2C=C); 4.48 (*m*, 1 H, H–C–O); 4.04 (*q*, 2 H, H_2C–O); 1.75–2.60 (complex *m*, 8 H, C=C–CH_2CH_2–COO and ring CH_2CH_2). – MS. (*m/e*): 199 (*M*+1), 198 (*M*), 115 (*M* − CH_2=$CHCH_2CH_2CO$), 99 (*M* + 1 − CH_2=$CHCH_2CH_2COOH$), 98 (*M* − CH_2=$CHCH_2CH_2COOH$), 85 (*M* − CH_2=$CHCH_2CH_2COOCH_2$), 83 (CH_2=$CHCH_2CH_2CO$).

$C_{10}H_{14}O_4$ (198.21) Calc. 60.60 H 7.12% Found C 60.70 H 7.15%

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[18] The nonhydrated form of RuO_2 *does not* afford RuO_4 by this procedure [24b].

The LTA/LiCl oxidation of acid **7**, followed by preparative GLC., furnished the γ-lactones **38a** and **38b**, and, in addition, 5-(chloromethyl)dihydro-2(3*H*)-furanone (**38c**) *Scheme 6*). – IR. (film): ν_{max} = 1800 (γ-lactone C=O), 1175, 1050, 920, 745 (C—Cl), 660 (C—Cl) cm^{-1}. – NMR. (CCl_4, 60 MHz): 4.66 (*m*, 1 H, H–C–O); 3.64 (*d*, *J* = 5.5, 2 H, H_2C–Cl); 1.85–2.70 (complex *m*, 4 H, $-CH_2CH_2-$). – MS. (*m/e*): 134 and 136 (*ca.* 3:1) (*M* (^{35}Cl) and *M* + 2 (^{37}Cl)), 85 (*M* – CH_2Cl), 49 (CH_2Cl).

$C_5H_7O_2Cl$ (134.56) Calc. C 44.63 H 5.24% Found C 44.55 H 5.33%

The LTA oxidations in the presence of N-chlorosuccinimide [17] were carried out with 1.0 g (0.01 mol) of acid **6** (using a 1:1:6 molar ratio of **6**/LTA/NCS) in 7.5 ml of dimethylformamide and 1.5 ml of glacial AcOH. After completion of the reaction, *i.e* disappearance of Pb(IV), the resulting solution was directly subjected to fractional distillation (without previous work-up) and the first fractions analyzed by GLC.

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52. Concerning the Conformation of Isolated Benzylideneaniline[1])

by **Thomas Bally**[2]), **Edwin Haselbach**[2])[4]), **Suzana Lanyiova**[2]), **Freimuth Marschner**[3]) and **Michel Rossi**[2])

(16. IX. 75)

Summary. From PE.-spectroscopical studies the torsional angle φ of the N-phenyl ring in isolated benzylideneaniline **1** has been found to be definitely smaller than $\varphi = 90°$. An approximate value $\varphi = 36°$ has been estimated which is even smaller than the one observed in the crystal ($\varphi = 55°$) and suggested to prevail also in solutions of **1**. A reevaluation of the gas phase optical spectrum of isolated **1** supports a torsional angle similar to that found in the other phases.

Calculations of the most stable conformation of **1** as well as of stilbene and azobenzene by the MINDO/3-technique lead to torsional angles $\varphi = 90°$ for both phenyl rings in all cases. These results are at variance with the experimental results and suggest that MINDO/3–like its less advanced precursor MINDO/2 or like CNDO/2–is unreliable for low energy processes involving rotation of π-systems connected by essential single bonds.

It is concluded that the π-energy of benzylideneaniline, like that of stilbene or azobenzene, would favor a planar conformation. The increased torsional angle in **1** as compared to the other two *iso*-conjugate systems arises from a larger steric interaction between phenyl- and bridge-protons.

Introduction. – Crystalline benzylideneaniline (**1**) exhibits – in contrast to its *iso*-electronic and essentially planar analogues *trans*-stilbene (**2**) [2] and *trans*-azobenzene (**3**) [3] – an angle of twist $\varphi = 55°$ of the N-phenyl-ring about the C–N essential single bond [4]. This deviation from planarity was already postulated on the basis of the marked differences between the optical spectra of **1** and **2** or **3** [5] and by the resemblance of the optical absorption spectrum of **4**, where planarity is enforced by bridging, to those of **2** and **3** [6]. That the angle of twist for **1** in solution is not too different from that in the solid is suggested by the similarity between its solution and its crystal reflectance spectrum [7]. A recent illuminating study employing derivatives of **1** and of the planar reference system **4** has indicated that the angle of twist varies markedly for different substituents in the *p,p'*-positions, $\varphi \approx 0°$ being presumably realized for 'push-pull' substitution which increases the bond order of the relevant C_{sp^2}–N_{sp^2} bond [8].

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