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THERMAL AND PHOTOLYTIC DECOMPOSITION OF ALKOXY-LEAD(IV)-ACETATES DERIVED FROM SATURATED ALIPHATIC ALCOHOLS[1]

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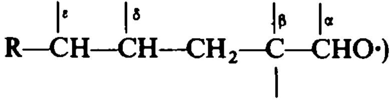
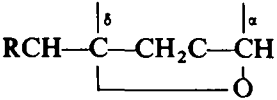
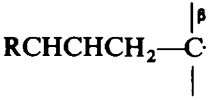
Abstract—Intramolecular formation of tetrahydrofuran-type ethers from saturated aliphatic alcohols and lead tetraacetate can be readily achieved at room temperature by UV irradiation of the reaction mixture in benzene. The yields of cyclic ethers and β-fragmentation products (when formed) are comparable to or even somewhat higher (under suitable conditions) than those observed in the thermal reaction, whereas the formation of carbonyl compounds (corresponding to the starting alcohols) is nearly completely suppressed.

WHEN an alcohol, $\mathrm{R{-}CH{-}CH{-}CH_2{-}C{-}CHOH}$ (I), is treated with lead tetraacetate it is converted, in the first (reversible) step, to an alkoxy-lead(IV) acetate $\mathrm{(R'O)_nPb(OAc)_{4-n}}$ (II).[2–4] This lead(IV) alkoxide (II), when heated in a nonpolar solvent (usually benzene or cyclohexane), decomposes homolytically[†] through a transition state or/and a species with alkoxy radical character III (e.g.  $\mathrm{R{-}\overset{|\varepsilon}{C}H{-}\overset{|\delta}{C}H{-}CH_2{-}\underset{|}{\overset{|\beta}{C}}{-}\overset{|\alpha}{C}HO\cdot}$), to give, depending on the structure of the starting alcohol, *cyclic ethers* [in the majority of cases tetrahydrofurans,  $\mathrm{RCH{-}\underbrace{\overset{|\delta}{C}{-}CH_2C{-}\overset{|\alpha}{C}H}_{O}}$ (IV), but also, when possible, small amounts of isomeric tetrahydropyrans (V), both ether products resulting from attack of the O-atom on a δ—C—H bond and ε—C—H bond, respectively, in the intermediate alkoxy radical (III)] and/or *β-fragmentation products*, i.e. a carbon radical fragment,  $\mathrm{RCHCHCH_2{-}\underset{|}{\overset{|\beta}{C}}\cdot}$ (VI) [which is usually further converted to an acetate (VIII) or/and an olefin], and a carbonyl fragment, $\mathrm{>\overset{\alpha}{C}{=}O}$ (VII), resulting from cleavage of the αC—βC bond in the intermediate alkoxy radical (III).[4,7–10,‡]

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[†] Since the Pb—O bonds in lead(IV) acylates (e.g. lead tetraacetate) exhibit ionic character,[5,6] this may also be the case for the Pb—O bond between lead and an alkoxy group in lead(IV) alkoxides of type II.[6] Therefore, the terms "homolysis" and "heterolysis" of the Pb—O bond involve actually a single and double electron transfer, respectively, from oxygen to lead.

[‡] For a detailed discussion and reaction schemes see Refs. 3, 4*a*, 7–9, 14.

TABLE 1. EFFECT OF THERMAL AND PHOTOLYTIC DECOMPOSITION (UNDER VARIOUS CONDITIONS) ON PRODUCT DISTRIBUTION IN THE LEAD TETRAACETATE REACTION OF SATURATED ALIPHATIC ALCOHOLS

Run	Molar ratio ROH/LTA[c]	Conditions	Products[a] (yields in %)[b]			
			Cyclic ethers		β-Fragmentation	Carbonyl compound[g]
			THF[d] (IV)	[+THP[e] (V)]	Alkyl acetates[f] (VIII)	(IX)
		1-Octanol				
1	1:1	thermal[h] (+2 mol. equiv. $CaCO_3$)	49	(+4·5)	0	1·5
2	1:2	photolytic[i]	52	(+5·5)	0	traces
3	1:1	photolytic (+1·5 mol. equiv. pyridine)	46	(+4)	0	traces
4	1:2	photolytic (+4 mol. equiv. pyridine)	57	(+5·5)	0	traces
5	1:2	photolytic (+10 mol. equiv. pyridine)	42	(+3·5)	0	4·5
6	1:3	photolytic (+2 mol. equiv. pyridine)	52	(+5)	0	traces
		2-Octanol				
7	1:1	thermal[h] (+1 mol. equiv. $CaCO_3$)	39–43[j,k]	(+ ~1)[l]	1·4[m]	3–1·5[j]
8	1:1	thermal (+2 mol. equiv. AcOH)	44	(+ ~1)	1·5	traces
9	1:1	thermal (+2 mol. equiv. pyridine)	31	(*n*)	1·1	19
10	1:1	thermal (+5 mol. equiv. pyridine)	9	(*n*)	0·3	46
11	1:1	room temperature (in pyridine alone)	2	(*n*)	0	58
12	1:2	photolytic[i]	48·5[k]	(+3)[l]	1·5[m]	traces
13	1:2	photolytic (+3 mol. equiv. pyridine)	46	(+2)	1·4	traces
14	1:2	photolytic (+10 mol. equiv. pyridine)	40	(+ ~1)	1·3	4
		2-Methyl-1-pentanol				
15	1:1	thermal[h] (+1 mol. equiv. $CaCO_3$)	36[o]	(+0)	10[p]	2
16	1:1	thermal at 50° (in pyridine alone)	6	(+0)	2	38
17	1:2	photolytic[i]	40[o]	(+0)	10[p]	traces
18	1:2	photolytic (+2 mol. equiv. pyridine)	35	(+0)	8	traces
19	1:2	photolytic (+8 mol. equiv. pyridine)	32	(+0)	7	4

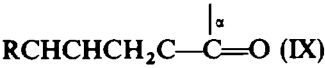
[a] Other products were also obtained, such as unchanged starting alcohol, the corresponding acetate, small amounts of formate, etc.[7, 9]

[b] Yields were calculated from gas-chromatograms and are based on the total amount of alcohol introduced into the reaction mixture (i.e. reacted + recovered alcohol).

[c] LTA = lead tetraacetate.

[d] THF = tetrahydrofuran.

[e] THP = tetrahydropyran.

The formation of an aldehyde or ketone (corresponding to the starting alcohol),  $\overset{|\alpha}{\mathrm{RCHCHCH_2C—C{=}O}}$ (IX), under these conditions, is not favoured and proceeds in relatively low yield. On the other hand, when the lead tetraacetate reaction of alcohols is performed in benzene in the presence of excess pyridine or in pyridine alone, the cyclization and β-fragmentation processes are suppressed, whereas good yields of aldehyde or ketone (IX) are obtained, either upon heating or even at room temperature.[6,8,11–13] These and other results have been taken as evidence that carbonyl compound (IX) formation proceeds predominantly by heterolytic decomposition* of the initially formed alkoxy-lead(IV) acetate (II) (or is coordination complex with pyridine[13]) with elimination of an α-proton, and only to a minor extent (if at all) by the homolytic process involving loss of an αH-atom from the intermediate alkoxy radical (III).[3,6,8,12,13,†]

Heusler and Kalvoda have recently shown that in rigid polycyclic systems with geometrically fixed reacting centers, such as steroid alcohols, intramolecular cyclic ether formation and β-fragmentation by means of lead tetraacetate could be brought about thermally and photolytically,[6,12,15] and Partch has reported[14] that UV irradiation of a 1:1 (molar) mixture of 1-pentanol and lead tetraacetate (*without* solvent) in a quartz flask yielded the same products and in the same ratio (tetrahydrofuran ether, aldehyde, unchanged alcohol and its acetate) as those obtained from the thermal oxidation in solution.

We have now investigated in more detail the effect of changes in reaction conditions on the relative rates of intramolecular cyclic ether formation (IV and V), β-fragmentation (VI, i.e. VIII, and VII) and carbonyl compound formation (IX) in the reaction of lead tetraacetate with three different saturated aliphatic alcohols (I), namely with 1-octanol, 2-octanol and 2-methyl-1-pentanol. As can be seen from Table 1, photolytic decomposition (by UV irradiation) in benzene at room temperature, with or without the addition of 1–4 molar equivalents of pyridine,‡ affords cyclic ethers

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* See footnote † on p. 2269.

† See footnote ‡ on p. 2269.

‡ This amount of pyridine was added to neutralize acetic acid formed in the course of the reaction, i.e. in order to ensure a sufficient concentration of alkoxy-lead(IV) acetate (II).

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[f] Resulting from the initially formed alkyl carbon radical fragment (VI).

[g] Aldehyde or ketone corresponding to the starting alcohol.

[h] In refluxing benzene (for *n* moles of alcohol *n*.1000–*n*.2000 ml of benzene were used). Reaction times for disappearance of Pb (IV): 0·5–7·5 hr, depending on the starting alcohol, amount of solvent and presence of pyridine or acetic acid.

[i] At room temperature (15–18°) in benzene (for *n* moles of alcohol *n*.10,000 ml of benzene were used). Irradiation was carried out in a Pyrex vessel with a high pressure mercury lamp Hanau Q 81, in a central water-cooled Pyrex jacket. Reaction times for disappearance of LTA: 2–10 hr, depending on starting alcohol, amount of LTA, etc.

[j] Depending on the concentration of reactants in benzene.[8]

[k] Mixture of *cis*- and *trans*-2-methyl-5-n-propyltetrahydrofurans, in a ratio of 38–40:62–60 (in all thermal and photolytic reactions).[7,8]

[l] Mixture of *cis*- and *trans*-2-ethyl-6-methyltetrahydropyran (in all thermal and photolytic reactions).

[m] Mixture of 1-hexyl acetate and 2-hexyl acetate[7] (in all thermal and photolytic runs).

[n] Not determined.

[o] Mixture of *cis*–*trans* isomers of 2,4-dimethyltetrahydrofuran, ratio 60:40, configurations not assigned[10] (in all thermal and photolytic runs).

[p] 2-Pentyl acetate.[10]

(tetrahydrofurans IV and tetrahydropyrans V) and β-fragmentation products (acetates VIII) in yields that are comparable to an often somewhat higher than those observed in the thermal decomposition in (refluxing) benzene, whereas the formation of carbonyl compounds (aldehydes or ketones IX corresponding to the starting alcohols) appears to be even more suppressed under photolytic conditions.

Even addition of excess pyridine (to benzene) did not markedly affect the course of the photolytic reaction (runs 5, 14 and 19), the favoured products being again cyclic ethers (IV) (and the β-fragmentation acetate (VIII) in the case of 2-methyl-1-pentanol), and the yield of aldehyde or ketone (IX) remaining low. This contrasts with the thermal decomposition in the presence of pyridine or in pyridine alone (runs 9, 10, 11 and 16), which, as mentioned above, suppresses cyclization and β-fragmentation but favours the formation of carbonyl compounds (IX) (and which proceeds even at room temperature when a large excess of pyridine is added to benzene or pyridine alone is used as solvent[8,11]).

It should be noted that the ratio of intramolecular ether formation to β-fragmentation for a given substrate (which can undergo both reactions) remains remarkably constant under photolytic and thermal conditions [about 30:1 in the case of 2-octanol (runs 7, 8, 12–14) and about 4:1 in the case of 2-methyl-1-pentanol (runs 15, 17–19)], and even in the presence of pyridine or in pyridine alone, under thermal conditions (runs 9–11 and 16, respectively), this ratio does not change noticeably, whatever the actual yields of products may be.

These results support the fact that both the thermal decomposition and photolytic decomposition of the initially formed alkoxy-lead(IV) acetate (II) from an aliphatic alcohol (I) and lead tetraacetate proceed homolytically in the same way and by a mechanism involving an intermediate species with alkoxy radical character III (see above), to give cyclization and β-fragmentation products in comparable yields, and that a similar reaction course is followed when the coordination complex of alkoxy-lead(IV) acetate with pyridine is subjected to UV irradiation; under thermal conditions, however, such a pyridine containing lead (IV) alkoxide species decomposes preferentially by heterolytic cleavage of bonds to an aldehyde or ketone IX (corresponding to the starting alcohol).

Intramolecular tetrahydrofuran formation from saturated aliphatic alcohols and lead tetraacetate, under photolytic conditions, may be a useful synthetic method, particularly in those cases when the substrate or/and products are sensitive to heat.

EXPERIMENTAL

The preparation of Pb(OAc)$_4$, drying of the reagents and solvents, and the thermal oxidations in benzene, benzene–AcOH, benzene–pyridine and pyridine alone were carried out as reported previously;[7,8,3,11,16] see also footnote *h* in Table 1. The photolytic reactions were performed with 0·02 moles alcohol in 200 ml benzene, at room temp, as described in footnote *i* in Table 1, and with amounts of Pb(OAc)$_4$ and pyridine which are given in the same Table for each run. The reaction mixture was worked out, depending on the presence or absence of pyridine, according to general procedures published previously.[7,8,3,11,16] After removal of ether and most of the benzene from the "neutral part"[7] by fractional distillation, the products in the residue were separated by gas chromatography (instrument: Perkin–Elmer Model 116-E; column: polyethylene glycol 435 on Chromosorb P; carrier gas: dry H_2; temp: 82–130° (depending on the alcohol used as substrate) and identified by comparison of their gas-chromatographic retention times, IR spectra and NMR spectra with those of authentic compounds, either synthesized by independent routes or isolated in previous Pb(OAc)$_4$ reactions.

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