Tetrahedron, 1966, Vol. 21, pp. 955 to 963. Pergamon Press Ltd. Printed in Northern Ireland

LEAD TETRA-ACETATE OXIDATION OF SATURATED ALIPHATIC ALCOHOLS[1]—V[2]

FACTORS INFLUENCING THE FORMATION OF CYCLIC ETHERS AND CARBONYL COMPOUNDS

M. Lj. Mihailović,[3] J. Bošnjak, Z. Maksimović,
Ž. Čeković and Lj. Lorenc
Department of Chemistry, Faculty of Sciences
and
Institute of Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

(*Received* 30 *September* 1965)

Abstract—Factors influencing the relative rates of the homolytic and heterolytic processes in the lead tetra-acetate oxidation of unbranched primary and secondary aliphatic alcohols have been investigated, with a view to determine the conditions giving optimal yields of cyclic ethers or carbonyl compounds.

UNBRANCHED primary and secondary alcohols (I) containing non activated δ-methylene (and ε-methylene) groups, when treated with lead tetra-acetate in non-polar solvents (e.g. in refluxing benzene) chiefly undergo intramolecular cyclization (*d*, Scheme 1), to give five-membered cyclic ethers (VII; in 33–50% yield) accompanied by small amounts (1–4% yield) of isomeric tetrahydropyran ethers (VIII), whereas the oxidation reaction (*b*, Scheme 1) to the corresponding carbonyl compounds (VI) is only of minor importance (1·5–5% yield).[4,5] In addition, secondary aliphatic alcohols (unbranched at the β-carbon atoms) afford also, in low yield (1–2%), fragmentation products (i.e. stabilization products (IX) of the primarily formed carbon radicals (V) and fragmentation carbonyl compounds (X); reaction *e*, Scheme 1).[5]

Even when the formation of cyclic ethers (VII and VIII; reaction *d*, Scheme 1) is very slow[5,2] (e.g. 1-butanol, 2-pentanol, 4-heptanol, 4,4-dimethyl-1-pentanol)[6] or when 1,5- (and 1,6-) cyclization is not possible[7] (e.g. 1-propanol, 2-propanol), the yields of carbonyl compounds (VI; reaction *b*) and their derivatives remain unsatisfactory

---

[1] Paper IX in the series "Reactions with lead tetra-acetate". For paper VIII see M. Lj. Mihailović and M. Miloradović, *Tetrahedron* **22**, 723 (1966).

[2] For part 4 see M. Lj. Mihailović, Ž. Čeković and D. Jeremić, *Tetrahedron* **21**, 2813 (1965).

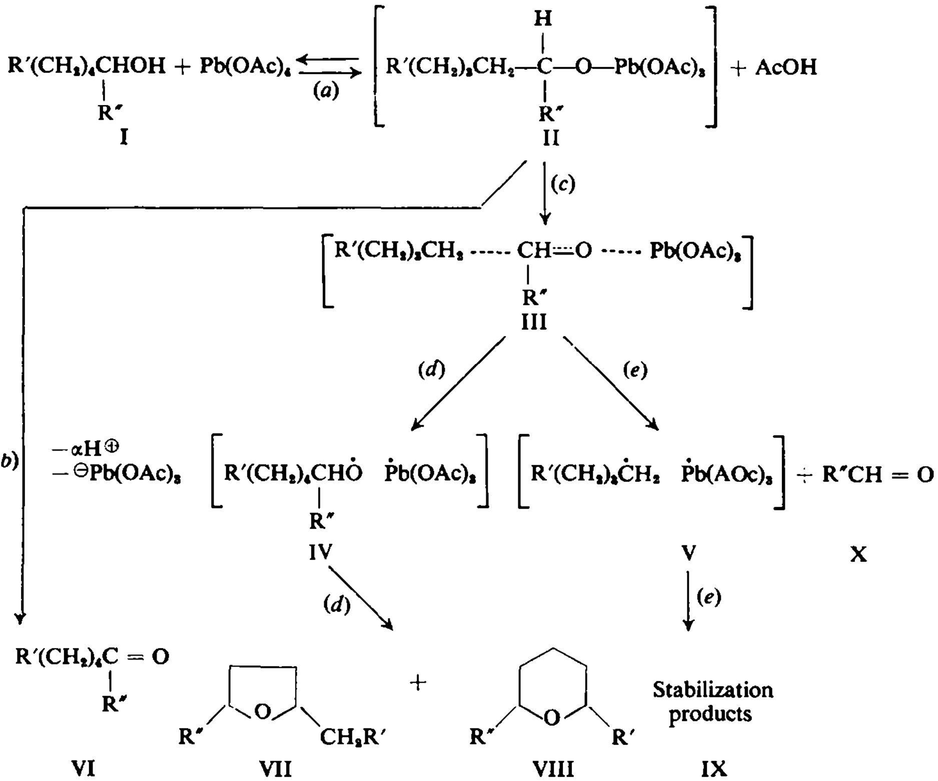
[3] To whom enquiries should be made. Full address: Department of Chemistry, Faculty of Sciences, Studentski trg 16, P.O. Box 550, Belgrade, Yugoslavia.

[4] V. M. Mićović, R. I. Mamuzić, D. Jeremić and M. Lj. Mihailović, *Tetrahedron Letters* No. 29, 2091 (1963); *Tetrahedron* **20**, 2279 (1964).

[5] M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, Lj. Lorenc and R. I. Mamuzić, *Tetrahedron* **21**, 2799 (1965).

[6] Because in these alcohols a methyl carbon atom, which is less reactive than a methylene carbon atom, is involved in cyclization.[5,2]

[7] M. Lj. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović and Lj. Lorenc, *Tetrahedron* **21**, 1395 (1965).



Scheme 1

(below 20%). However, when alcohols of low mol. wt. (such as 1-propanol and 2-propanol) are oxidized by lead tetra-acetate in excess of starting alcohol (without solvent), in benzene in the presence of dry pyridine (using a 4:1 molar ratio of base to oxidant) or in pyridine alone, at 80–100°, the corresponding carbonyl compounds are formed in very good yields (75–98%) and the reactions proceed rapidly to completion.[7] Similar results have been reported by Partch[8] and Heusler[9] for the lead tetra-acetate oxidation of various alcohols in non-polar solvents and in the presence of pyridine. These facts and other evidence, together with the observation that good yields (66–77%) of aldehydes are obtained in the lead tetra-acetate oxidation of 2-, 3- and 4-pyridinemethanols in refluxing benzene,[10] suggest that the formation of cyclic ethers (VII and VIII) is a homolytic process (*cd*, Scheme 1), taking place *via* alkoxy radicals (IV),[11,5] and that the conversion of alcohols (I) to carbonyl compounds (VI) proceeds predominantly by heterolytic cleavage of the polarized O–Pb bond in the intermediate alkoxy lead triacetate (II) with elimination of an α-proton,[12,13] this

---

[8] R. E. Partch, *Tetrahedron Letters* No. 41, 3071 (1964).

[9] K. Heusler, *Tetrahedron Letters* No. 52, 3975 (1964).

[10] V. M. Mićović and M. Lj. Mihailović, *Rec. Trav. Chim.* **71**, 970 (1952).

[11] K. Heusler and J. Kalvoda, *Angew. Chem.* **76**, 518 (1964); *Ibid.* (Intern. English Ed.) **3**, 525 (1964), and Refs. therein.

[12] R. Criegee, *Angew. Chem.* **70**, 173 (1958), and Refs. therein.

[13] It is possible that a fraction of the carbonyl compound (VI) arises by stabilization (e.g. α-hydrogen atom elimination) of the corresponding alkoxy radical (IV).[7]

process (*b*, Scheme 1) being favoured in the presence of polar and basic solvents, which displace the equilibrium of the first stage of the oxidation (*a*, Scheme 1) in favour of the complex lead alkoxide formation (II), polarize this intermediate and aid in the removal of the α-proton.[7]

TABLE 1. DEPENDENCE OF PRODUCT DISTRIBUTION ON THE BASICITY AND POLARITY OF SOLVENT IN THE LEAD TETRA-ACETATE OXIDATION OF β-UNBRANCHED PRIMARY AND SECONDARY SATURATED ALCOHOLS

Alcohol[a]	Products[b] (in %)	Solvent					
		Benzene (80°)	Bz-Py[c,d] (reflux)	Bz-Py[e] (reflux)	Pyrid.[f] (~100°)	Pyrid. (20°)	No Solvent[g] (~80°)
1-Pentanol	Cycl. ether	37–43				2	18
	Aldehyde	8–4				66[h]	38
1-Hexanol	Cycl. ethers[i]	52					26
	Aldehyde	2					20
1-Heptanol	Cycl. ethers[i]	53	35	15	5	4	32
	Aldehyde	2	15	37	46	55	16
1-Octanol	Cycl. ethers[i]	52					30
	Aldehyde	1·5					13
4,4-Dimethyl-1-pentanol	Cycl. ethers[j]	7	3·5				
	Aldehyde	4	19				
2-Octanol	Cycl. ethers[i]	40	31	9	3	2	20
	Ketone	3	19	46	54	58	18
	Fragmentation products[k]	1·4	1·1	0·3	0·1		0·6
4-Heptanol	Cycl. ether	15·5		0·1	0·1		8
	Ketone	7·5[l]		57	58		63
Cyclohexanol	Cycl. ether[m]	1	0	0	0		0
	Ketone	5	39	62	63		90

[a] In benzene and pyridine a 1:1 molar ratio of alcohol to lead tetra-acetate was used. In most runs 0·05 mole of alcohol was oxidized in 50 ml of benzene (+ the necessary amount of pyridine) or in 50 ml of pyridine alone. [b] Other products are also obtained, such as unchanged alcohol, the corresponding acetate, etc.[5,8] [c] Bz = benzene; Py = pyridine. [d] Molar ratio pyridine to lead tetra-acetate 2:1. [e] Molar ratio pyridine to lead tetra-acetate 5:1. [f] Usually, upon heating at 80–100° the reaction became strongly exothermic and was completed in a few min. [g] In excess of starting alcohol (0·02 mole of lead tetra-acetate in 20 ml of alcohol). [h] Reported yield 70%.[8] [i] Tetrahydrofuran + tetrahydropyran ethers.[5] [j] Tetrahydropyran derivative + rearranged five-membered cyclic ether.[3] [k] Total yield of 1-hexyl acetate + rearranged 2-hexyl acetate.[6] [l] In addition, 7–8% of the corresponding α-acetoxy ketone was present in the reaction mixture.[5] [m] 1,4-Epoxycyclohexane.

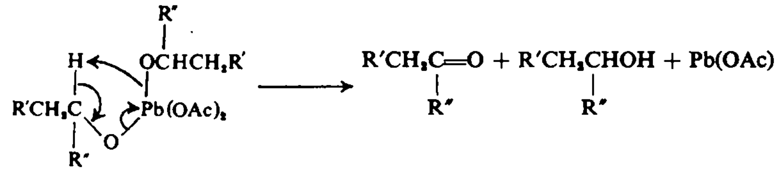
This duality of mechanisms (*b* and *cd*, Scheme 1) in the lead tetra-acetate oxidation of alcohols has been confirmed in the present study, in which unbranched primary and secondary aliphatic alcohols (and cyclohexanol) have been subjected to the action of lead tetra-acetate (one molar equiv) in solvent systems of varying polarity and basic strength. As can be seen from Table 1, by increasing the proportion of pyridine in benzene (with respect to the amount of lead tetra-acetate), the yield of cyclic ethers (VII and VIII) decreases and that of carbonyl compounds (VI) increases, the largest difference being observed in pyridine alone (suppressed ether formation) and in benzene alone (suppressed carbonyl compound formation).[14] In addition, with increasing

---

[14] Similar results have been observed in the lead tetra-acetate oxidations of steroid alcohols.[9]

amounts of pyridine (at refluxing temp) the reaction times (necessary for complete consumption of tetravalent lead) decrease considerably. The results obtained in pyridine at 100° and in pyridine at room temperature (procedure of Partch[8]) do not differ markedly. In the former case (heating at 100°) the reaction is much faster and is usually completed in a few minutes, while at room temperature the oxidations are slow taking from 8 to 18 hr.[15] The formation of carbonyl compounds (VI) by the lead tetra-acetate oxidation of alcohols (I) in pyridine or benzene-pyridine solution may be used for preparative purposes, particularly when the aliphatic aldehydes or ketones can be separated from other reaction products in the form of solid derivatives (e.g. bisulphite compounds).

In excess of starting alcohol (in the abscence of solvent), at 80°, the yields of cyclic ethers are reduced to about half while the yields of carbonyl compounds are increased 6–10 times over the yields of the corresponding products obtained in refluxing benzene (Table 1). These results (and shorter reaction times) indicate that in excess of starting alcohol the equilibrium (*a*, Scheme 1) of the first stage of the reaction is also shifted to the right, because of the large concentration of alcohol and probably, to a certain extent, because of removal by esterification of the acetic acid formed, and that, in addition, the polar properties of the starting alcohol facilitate heterolytic decomposition of the lead alkoxide (II). Moreover, the alkoxide (II) may further react with excess alcohol to give the dialkoxy lead diacetate (XI, Scheme 2); decomposition of this intermediate *via* a cyclic-type transition state to give the carbonyl compound (VI) and lead diacetate, with recovery of one molecule of alcohol (I), should be assisted by the presence of the second alkoxy group attached to lead in XI. The use of excess alcohol as solvent, however, does not suppress cyclic ether formation and improve carbonyl compound formation as efficiently as when the lead tetra-acetate oxidations of aliphatic alcohols are performed in the presence of basic pyridine (see Table 1).



XI VI I

Scheme 2

It is interesting to note that the ratio of cyclic ethers (VII and VIII) to fragmentation products (IX) does not depend on the nature of the solvent system (see 2-octanol in Table 1), indicating that cyclization (*d*, Scheme 1) and fragmentation (*e*) have a common precursor, i.e. the transition state or intermediate with alkoxy radical character (III), which arises (*c*) from the complex lead alkoxide (II) and then collapses by path (*d*) to the alkoxy radical (IV) or by path (*e*) to the carbon radical (V) and carbonyl compound (X).[14]

[15] The method of Partch[8] (pyridine, room temp), because of its extremely mild conditions, is particularly appropriate for the preparation of sensitive and unstable carbonyl compounds.

When benzene is used as solvent, product distribution is also not noticeably affected by temp; after 9 days at 20° and 16 hr at 40° (when the reaction was completed) 2-octanol afforded 2·5% 2-octanone and 37% of cyclic ethers. (Compare with results in benzene at 80° in Table 1.)

As a consequence of the different behaviour of alcohols towards lead tetra-acetate when the reaction is carried out in benzene solution (nonpolar solvent) or without solvent in excess of starting alcohol (polar medium), one would expect the amount of nonpolar solvent (up to a certain limit) to affect the distribution of reaction products (carbonyl compounds VI, cyclic ethers VII and VIII, possibly acetates of starting alcohols, etc.). This has been confirmed by performing the lead tetra-acetate oxidation of 2-octanol in different concentrations in benzene solution. As can be seen from Table 2, by increasing the dilution of the alcohol (and lead tetra-acetate) in benzene, the yield of the corresponding ketone (heterolytic process) decreases, whereas the yield of cyclic ethers (formation *via* free radicals) increases,[16] and, moreover, the reaction times are prolonged. These facts suggest once again that a decrease in polarity of the reaction medium displaces the ratio of competing mechanisms (polar and free radical) in favour of the homolytic process (*cd*, Scheme 1). By increasing the amount of benzene over 200 ml per 0·1 mole of 2-octanol (and lead tetra-acetate) the yields of reaction products are not further affected.

TABLE 2. INFLUENCE OF AMOUNT OF BENZENE (NONPOLAR SOLVENT) ON PRODUCT DISTRIBUTION IN THE LEAD TETRA-ACETATE OXIDATION OF 2-OCTANOL[a]

Amount of 2-octanol (in moles)	Amount of benzene (in ml)	Reaction time (in min)	Yields of reaction products (in %)		
			2-Octanone	Cyclic ethers[b]	2-Octyl acetate
0·7	None[c]	45–60[d]	18	20	29[e]
0·1	50	90	6	32	15
0·1	100	135–150[d]	3	40	9
0·1	200	165–180[d]	1·5	44	6

[a] Reactions in boiling benzene were carried out with an equimolar proportion of 2-octanol and lead tetra-acetate. [b] Total yield of 2-methyl-5-n-propyl-tetrahydrofuran (*cis*- and *trans*-isomers) and 2-ethyl-6-methyltetrahydropyran (*cis*- and *trans*-isomers).[1] [c] This reaction was performed at ~80° in excess of starting alcohol (0·7 mole of 2-octanol and 0·1 mole of lead tetra-acetate). [d] Reaction times (until disappearance of tetravalent lead) varied slightly from run to run. [e] In this case most of the ester is probably formed by direct esterification of the starting alcohol (large excess) with acetic acid produced in the course of the reaction.[7]

It was found that the addition of glacial acetic acid to benzene increases the reaction times of the lead tetra-acetate oxidations of 1-heptanol and 2-octanol (Table 3), reduces the yield of the corresponding carbonyl compound (VI) and increases (by about 5%) the yield of cyclic ethers (VII + VIII).[17] This is understandable, since acetic acid lowers the concentration of the alkoxy lead triacetate (II, Scheme 1) by displacing the equilibrium (*a*) in the direction of the starting alcohol (I) and, being an acid, does not assist heterolytic cleavage of the alkoxide (II) in the sense of α-proton elimination (*b*) and carbonyl compound formation. On the other hand, acetic acid

---

[16] Although the yield of 2-octyl acetate was also found to decrease with increasing dilution (Table 2), it is not at present possible to explain this change in terms of a particular mechanism. Namely, various routes leading to the acetates of the starting alcohols are possible (including polar mechanisms), but they have not yet been investigated in detail.[7]

[17] 1-Propanol and 2-propanol gave only traces of the corresponding carbonyl compound when treated with lead tetra-acetate in glacial acetic acid at 60–65° for 25 hr.[7]

should not markedly prevent homolytic decomposition (*c*) of the same alkoxide (II), followed by cyclization (*d*) and fragmentation (*e*).

Erratic yields of cyclic ethers (VII + VIII) and fragmentation products (IX + X) were frequently obtained in repeated lead tetra-acetate oxidations of the same alcohols,[18] suggesting that the acetic acid content of the lead tetra-acetate used must have a considerable influence on the possible reaction courses.[9,19] With lead tetra-acetate dried *in vacuo* at 20–30 mm over phosphorus pentoxide and potassium hydroxide (and which still contains some acetic acid[19]) usually good yields of cyclic ethers were obtained (Tables 1, 2 and 3),[5] whereas with samples dried in a high vacuum (below 10^{-1} mm) and practically acetic acid free, the yields of homolytically formed products were often considerably lower (and those of carbonyl compounds somewhat higher); in this case, glacial acetic acid should be added to benzene (according to Table 3), in a molar proportion (relative to lead tetra-acetate) of 1:1 or 2:1. It follows, therefore, that in the lead tetra-acetate oxidations of aliphatic alcohols high dilutions of reactants in benzene (or other nonpolar solvents) and some acetic acid are necessary for obtaining optimal yields of cyclic ethers.[20]

TABLE 3. PRODUCT DISTRIBUTION IN THE LEAD TETRA-ACETATE OXIDATION OF 1-HEPTANOL AND 2-OCTANOL IN BENZENE-ACETIC ACID[a]

Alcohol (0·1 mole)	Solvents		Reaction time (in min)	Yields of reaction products (in %)	
	Benzene (ml)	Acetic acid (moles)		Cyclic ethers (VII + VIII)	Carbonyl compound (VI)
1-Heptanol	100	—	45	53	2
1-Heptanol	100	0·1	180	55	1·5
1-Heptanol	100	0·2	265	58	traces
2-Octanol	100	—	150	40	3
2-Octanol	100	0·1	370	43	1·5
2-Octanol	100	0·2	450	45	traces

[a] Reactions were carried out at reflux temperatures with a 1:1 molar ratio of alcohol to lead tetra-acetate.

By comparing the yields of cyclic ethers, carbonyl compound, unreacted alcohol, the corresponding acetate and high-boiling residue,[5,21] in reactions carried out in refluxing benzene (100 ml) under various experimental conditions, with 0·1 mole of

---

[18] Similar results were also observed by other authors.[9]

[19] It was recently suggested that "normal" (acetic acid stabilized) lead tetra-acetate probably contains two molecules of acetic acid and corresponds to $H_2[Pb(OAc)_6]$; K. Heusler, H. Labhart and H. Loeliger, *Tetrahedron Letters* No. 32, 2875 (1965).

[20] After this work was completed, R. E. Partch, *J. Org. Chem.* 30, 2498 (1965), has described the lead tetra-acetate oxidation of 1-pentanol in various reaction media, and his results concerning the proportion of products in dependence of solvent are, on the whole, similar to our results. However, the reported yields of cyclic ethers are lower and those of carbonyl compounds higher than the yields of corresponding compounds obtained in our studies,[5] possibly because of somewhat different experimental conditions and for reasons mentioned above.

[21] These residues, consisting of products boiling above the acetates of the starting alcohols, were obtained (in 15–25% yield) in all the lead tetra-acetate oxidations of aliphatic alcohols.[5]

The yields of carbonyl compounds (VI), under various experimental conditions discussed below, remained low and did not change appreciably.

lead tetra-acetate and 0·1 mole of alcohol, it was found that the yields of cyclic ethers and other products did not change noticeably by varying the mode of addition of reactants (as compared to the usual procedure of first mixing the reactants in benzene and then heating to reflux),[5] on condition that the starting alcohol is added to the oxidant in boiling benzene either in one portion or in the course of 3–5 minutes, or that lead tetra-acetate is added to the refluxing solution of alcohol in benzene in a few portions (of 4–5 g) at short time intervals. The presence of calcium carbonate does not improve (or only slightly) the yields of cyclic ethers. However, when the alcohol was added dropwise over a long period of time, the yields of cyclic ethers were noticeably lower (by about 15–20%) and those of unreacted alcohol + acetate and of high-boiling residue higher (by about 5–10% and 10–15%, respectively), similar results being also observed when lead tetra-acetate was added in small portions (of 0·4 to 0·8 g) over long time intervals. By using two moles of lead tetra-acetate for one mole of alcohol the time required for complete consumption of the oxidant was considerably increased, but the yields of cyclic ethers were not improved (as compared to the yields obtained when a 1:1 molar ratio was employed), in spite of the fact that less starting alcohol was recovered after the reaction; however, under these conditions the amounts of acetate of starting alcohol and of high-boiling products were considerably larger.

These results, i.e. the facts (a) that the starting alcohol is always recovered to a certain extent (even when 2 moles of lead tetra-acetate per one mole of alcohol are used), and (b) that the amount of high-boiling residue increases and the yield of cyclic ethers decreases when lead tetra-acetate is in excess over the starting alcohol in the course of the reaction or/and when the reaction mixture is allowed to be in contact with the oxidant over considerable periods of time,[22] may be accounted for by assuming the following: (i) The first stage of the reaction (i.e. alcoholysis) does not involve only mono-alkoxy lead derivatives (II, Scheme 1), but also dialkoxy intermediates (XI, Scheme 3; see also Scheme 2) from which, upon homolytic decomposition (*f* and *g*, Scheme 3), part of the alcohol (I) would be recovered.

$$\underset{\textbf{XI}}{(\mathrm{RO})_2\mathrm{Pb(OAc)}_2} \xrightarrow[(f)]{} \underset{\textbf{IV}}{\mathrm{RO}\cdot} + \mathrm{RO{-}Pb{-}OAc} + \mathrm{AcO}\cdot$$

$$\mathrm{RO{-}Pb{-}OAc} \xrightarrow[(g)]{\mathrm{AcOH}} \underset{\textbf{I}}{\mathrm{ROH}} + \mathrm{Pb(OAc)}_2$$

Scheme 3

(ii) The alkoxy radicals (IV) may partly reconvert to the corresponding alcohols (I) by abstracting hydrogen from their environment, and (iii) In competing reactions lead tetra-acetate attacks the primarily formed products, alkoxy radicals (IV) and cyclic ethers (VII + VIII), to produce acetoxylated compounds. Since the major reaction products from the lead tetra-acetate oxidation of alcohols (starting from 1-butanol) are five-membered cyclic ethers, the high-boiling residues would be expected

---

[22] When lead tetra-acetate is added in small portions over long time intervals (see above), after a while the equilibrium (*a*, Scheme 1) will be shifted to the side of reactants, because of the acetic acid formed (about two moles per mole of oxidant used) and because of decreased concentration of starting alcohol. Therefore, the small amounts of added lead tetra-acetate will only slowly undergo alcoholysis (*a*, Scheme 1) to II and will be "free" to attack other species present in the reaction mixture.

to contain derivatives formed by subsequent reaction of these tetrahydrofurans with lead tetra-acetate.[23,24] This was confirmed by isolating, from the high-boiling fraction obtained in the lead tetra-acetate oxidation of 1-butanol, a product, b.p. 90–95° at 0·5 mm, which was identical with authentic 2,5-diacetoxytetrahydrofuran,[25,26] and which afforded the bis-2,4-dinitrophenylhydrazone of succinedialdehyde (m.p. 275–277°)[26] when treated with 2,4-dinitrophenylhydrazine in aqueous sulphuric acid. Residues from the oxidations of other primary and secondary aliphatic alcohols also contained products with acetate (and hydroxyl) groups (according to IR spectra), which liberated acetic acid upon heating, thus suggesting the presence of α-acetoxylated tetrahydrofurans.[27] The relative amounts of high-boiling residues obtained from secondary alcohols were usually larger than those formed in the lead tetra-acetate oxidation of primary alcohols; this is understandable, since 2,5-dialkyl-tetrahydrofurans (VII, R″ = alkyl; Scheme 1) (produced from secondary alcohols), with two tertiary α-carbon atoms, should be more susceptible to lead tetra-acetate attack than 2-alkyl-tetrahydrofurans (VII, R″ = H; Scheme 1) (formed from primary alcohols), which contain only one tertiary α-carbon atom.[28] This difference in reactivity was demonstrated by measuring the rate of oxidant consumption in the reaction between lead tetra-acetate and various tetrahydrofurans in boiling benzene (Table 4).

TABLE 4. RATE OF OXIDANT CONSUMPTION IN THE REACTION OF SOME TETRAHYDROFURANS WITH LEAD TETRA-ACETATE IN BENZENE SOLUTION[a]

Time (in min)	Consumption of lead tetra-acetate (in %) THF[b]	2-Methyl-THF	2-n-Propyl-THF	2-Methyl-5-n-propyl THF
30	0·55	3·63	5·84	6·28
90	0·72	5·69	8·57	12·64
150	0·77	8·69	11·38	22·51
210	0·84	10·20	14·98	27·54

[a] See Experimental. [b] THF = tetrahydrofuran.

It follows, therefore, that for obtaining good yields of cyclic ethers from aliphatic

---

[23] That aliphatic, cyclic and benzyl ethers are attacked by lead tetra-acetate with the formation of α-acetoxy derivatives was shown by several authors. See, for example, M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.* **16**, 533 (1951); H. E. Barron, G. W. K. Cavill, E. R. Cole, P. T. Gilham and D. H. S. Solomon, *Chem. & Ind.* 76 (1954); G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall and A. Robertson, *J. Chem. Soc.* 4573 (1954); G. W. K. Cavill and D. H. Solomon *Ibid.* 1404 (1955); W. Frass, Ph.D. Thesis, Karlsruhe (1960); J. Jadot, A. David and J. Kasperszyck, *Bull. Soc. Roy. Sci. Liège* **29**, 196 (1960); M. Lj. Mihailović and M. Miloradović, *Tetrahedron* **22**, 723 (1966).

[24] Carbonyl compounds may also be subsequently attacked by lead tetra-acetate to give α-acetoxy derivatives.[7,8] However, because of low yields of carbonyl compounds formed in the lead tetra-acetate oxidation of aliphatic alcohols in benzene, the amount of oxidizing agent consumed in this side reaction should not be large.

[25] N. Clauson-Kaas, Si-Oh Li and N. Elming, *Acta Chem. Scand.* **4**, 1233 (1950); N. Elming and N. Clauson-Kaas *Ibid.* **6**, 535 (1952).

[26] H. Gross, *Chem. Ber.* **95**, 83 (1962).

[27] G. Sosnovsky, *Tetrahedron* **13**, 241 (1961), has reported that α-acetoxylated tetrahydrofurans and tetrahydropyrans are decomposed upon heating.

[28] For example, 2,5-dimethyltetrahydrofuran reacts considerably faster with lead tetra-acetate than unsubstituted tetrahydrofuran. W. Frass, Ph.D. Thesis, Karlsruhe (1960).

alcohols, a 1:1 molar ratio of substrate to oxidant should be used (with possibly a small excess (2–5%) of lead tetra-acetate),[29] both reactants being added to benzene before starting the oxidation (i.e. before applying heat).

EXPERIMENTAL

The preparation of lead tetra-acetate, drying of the reactants and solvents, and the lead tetra-acetate oxidations in benzene, benzene–pyridine and excess of starting alcohol (in the absence of solvent) were carried out according to general procedures described previously,[5,2,7,8] and with amounts of substrate, oxidant and solvents given in Tables 1, 2 and 3, and in the text above.

The reaction products, isolated by fractional distillation and/or gas chromatographic separation, were identified by comparison of their physical properties (b.ps, refractive indices, retention times, IR and NMR spectra, m.ps of solid derivatives) with those of authentic compounds. In a few cases the formed carbonyl compounds were separated from the reaction mixture by conversion to the corresponding bisulphite derivatives.

For rate measurements in the reaction of cyclic ethers with lead tetra-acetate, the pure tetrahydrofurans[4,5] (0·0025 mole) were allowed to react, under reflux and with stirring, with a 0·05 molar solution of lead tetra-acetate in benzene, containing 0·0025 mole of oxidizing agent (about 50 ml). The procedure used for determining the consumed lead tetra-acetate, at definite time intervals, was that described by Wessely *et al.*,[30] with the remark that stirring was interrupted and the reaction mixture cooled in ice-water for 5 min before taking 2 ml samples for titration. The results of these measurements are presented in Table 4.

Acknowledgement—The authors are grateful to the Yugoslav Federal Research Fund for financial support.

[29] Apparently cyclic ethers in a fused ring system (i.e. steroid skeleton) are far more stable towards lead tetra-acetate than simple tetrahydrofuran ethers, since cyclizations of various steroid alcohols have been usually carried out satisfactorily with a large excess of oxidizing agent (up to 5 moles of oxidant per mole of substrate).[9] (See also Refs. in 11.)

[30] F. Wessely, G. Lauterbach-Keil and F. Sinwel, *Monatsh.* **81**, 811 (1950).