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REACTIONS WITH LEAD TETRAACETATE—IV[1]

OXIDATION OF SATURATED ALIPHATIC ALCOHOLS—II[2]; ALCOHOLS OF LOW MOLECULAR WEIGHT

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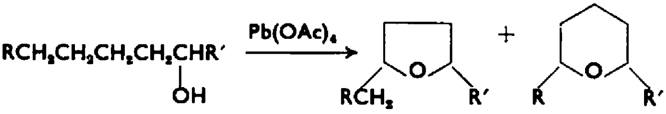
Abstract—The action of lead tetraacetate on ethanol, 1-propanol, 2-propanol and 2-butanol has been studied under various experimental conditions, and it was found that the tetravalent lead compound reacts with alcohols in ways not so far observed. The possible reaction schemes are discussed in terms of homolytic and heterolytic cleavage of the intermediate alkoxy lead acetate complexes.

INTRODUCTION

IN OUR previous paper[2] it was shown that saturated primary and secondary aliphatic alcohols (I) with sufficiently long n-alkyl chains are oxidized by lead tetraacetate, in benzene solution, to give as major products 2-alkyl or 2,5-dialkyl tetrahydrofurans (II), accompanied by small amounts of isomeric tetrahydropyrans (III). Other products include the corresponding carbonyl compounds (2–5% yield), the acetates of the starting alcohols, unreacted alcohol and high boiling unidentified material containing acetate groups.



I II III

In order to examine in more detail some of the by-products formed in these side reactions, competing with cyclization, we have now studied the lead tetraacetate oxidation of alcohols of low molecular weight, the structures of which do not permit intramolecular substitution with formation of five-membered and six-membered cyclic ethers.

RESULTS AND DISCUSSION

By using a 1:1 molar ratio of reactants in boiling benzene and in the presence of excess of anhydrous calcium carbonate, 1-propanol (IVa) and 2-propanal (IVb) react slowly with lead tetraacetate to give, after completion of the oxidation, a variety of products, which are listed in Table 1.[4] These products were isolated by fractional distillation followed by preparative gas-chromatographic separation, and were identified on the basis of analytical data and by comparison of their chemical and physical properties (including IR and NMR spectra) with those of authentic reference

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[1] Paper III: M. Stefanović, M. Gašić, Lj. Lorenc and M. Lj. Mihailović, *Tetrahedron* **20**, 2289 (1964).

[2] Part 1: V. M. Mićović, R. I. Mamuzić, D. Jeremić and M. Lj. Mihailović, *Tetrahedron* **20**, 2279 (1964).

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[4] In the absence of $CaCO_3$ a similar distribution of products was obtained.

compounds, which were either commercially available or synthesized by independent routes.

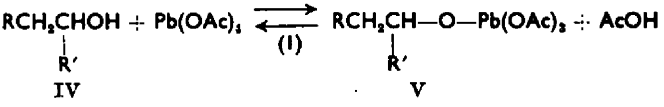
Assuming that the first step in the lead tetraacetate oxidation of monohydroxylic alcohols consists in the conversion of the alcohol (IV) to the corresponding alkoxy lead triacetate[5–7] (V), in an equilibrium controlled reaction (1), the possible reaction courses leading to the observed products can be interpreted in terms of homolytic and heterolytic decomposition of the intermediate alkoxy complex (V).[8]

TABLE 1. PRODUCTS OBTAINED IN THE OXIDATION OF 1-PROPANOL (IVa) AND 2-PROPANOL (IVb) WITH LEAD TETRAACETATE IN BENZENE, IN THE PRESENCE OF ANHYDROUS CALCIUM CARBONATE[a,b]

1-Propanol (IVa)		2-Propanol (IVb)	
Product	Yield (%)	Product	Yield (%)
1-Propyl acetate (IVa)	35	2-Propyl acetate (VIb)	31
—		2-Propyl phenyl ether (Xb)	2
—		Acetone (XIIb)	10
1,1-Dipropoxypropane (XIIIa)	10	—	
Propionic acid (XVa)	1·5	—	
1-Propyl propionate (XVIa)	4	—	
1-Propyl formate (XVIIa)	1	2-Propyl formate (XVIIb)	2
2-Acetoxy-1-propanal (XVIIIa)	2·5	1-Acetoxy-2-propanone (XVIIIb)	7
2-Acetoxypropionic acid (XIXa)	1	—	
—		1-Isopropoxy-2-propanone (XXb)	2
—		1-Isopropoxy-2-propanol (XXIVb)	1·5
2-Ethyl-4-methyl-1,3-dioxolane (XXVa)	3·5	2,2,4-Trimethyl-1,3-dioxolane (XXVb)	2·5
Hexane (XXVIa)	5	2,3-Dimethylbutane (XXVIb)	4
Propene (XXVII)[c]	7	Propene (XXVII)[c]	4
2-Propyl acetate (VIb)	2	—	
1-Propylbenzene (XXVIIIa)	2·5	2-Propylbenzene (XXVIIIb)	2·5
1-Propanol (IVa)[d]	15	2-Propanol (IVb)[d]	17

[a] Formulae corresponding to "a" have R = CH_3, R′ = H, and those to "b" have R = H, R′ = CH_3.

[b] In addition, toluene, benzyl acetate, phenyl acetate and biphenyl, resulting from attack of lead tetraacetate on solvent (benzene), were isolated, in approximate yields (based on lead tetraacetate) of 1%, 4%, 1% and 1%, respectively. [c] As the dibromide. [d] Recovered after completion of the oxidation.



$$\underset{\text{IV}}{RCH_2\underset{\substack{|\\R'}}{C}HOH} + Pb(OAc)_4 \underset{(1)}{\rightleftarrows} \underset{\text{V}}{RCH_2\underset{\substack{|\\R'}}{C}H{-}O{-}Pb(OAc)_3} + AcOH$$

(a) R = CH_3, R′ = H; (b) R = H, R′ = CH_3
(Valid for all equations in this paper)

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[5] The formation of complex lead alkoxides of this type was first postulated and in part demonstrated by R. Criegee, L. Kraft and B. Rank, *Liebigs Ann.* **507**, 159 (1933).

[6] For further discussion on intermediate alkoxy lead derivatives see J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.* 102 (1953); H. B. Henbest, *Annual Reports* **53**, 146 (1956); E. J. Moriconi, F. T. Wallenberger and W. F. O'Connor *J. Amer. Chem. Soc.* **80**, 656 (1958); **82**, 3122 (1960).

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

[8] For simplicity reasons most reactions are formulated and discussed as termination steps rather than propagation steps.

(a) *Acetates of starting alcohols*

Acetates (VI) are the major reaction products of the lead tetraacetate oxidation (in benzene) of 1-propanol (IVa) and 2-propanol (IVb) (Table 1),[9] but they are also formed (in lower yields) from alcohols which afford in non-polar solvents predominantly cyclic ethers.[2,18] One possible route leading to the acetates (VI) is direct esterification of the starting alcohol (IV) or reaction of the intermediate alkoxide (V) with acetic acid,[12] produced from lead tetraacetate in the course of the oxidation.[19] This process (with acetic acid) probably takes place to a certain extent when oxidation is carried out in benzene or in excess of the starting alcohol[20] (and in the absence of any other solvent) (Table 2). However, simple esterification with acetic acid is not the only reaction involved in the formation of acetates (VI) as demonstrated by carrying out the lead tetraacetate oxidation of 1-propanol (IVa) and 2-propanol (IVb) in benzene in the presence of excess of pyridine[21] or in pyridine alone (Table 2; runs 9–12), the acetates (VI) being again isolated (in 3–7% yields), although free acetic acid cannot be present in the reaction mixture[22] and the oxidations proceed very rapidly to completion (3–5 minutes).[23] Therefore, in the presence of pyridine the acetates (VI) must be formed by another reaction path. The isolation of a small amount of acetic anhydride upon lead tetraacetate oxidation of 1-propanol (IVa) and 2-propanol (IVb) in the presence of pyridine (Table 2) suggests that the formation of the corresponding acetates (VI) may be, at least in part, interpreted as a simple base-catalysed esterification step involving acetic anhydride (i.e. the acetyl cation $CH_3\overset{\oplus}{C}{=}O$) and the starting alcohol or the intermediate alkoxy lead triacetate (V).

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[9] Other authors have also observed acetate formation in the lead tetraacetate oxidation of alcohols performed in acetic acid[10–13] or benzene solution.[13–17]

[10] R. Criegee, *Liebigs Ann.* **481**, 263 (1930); E. Montignie, *Bull. Soc. Chim. Fr.* [5] **1**, 1280 (1934).

[11] W. A. Mosher and H. A. Neidig, *J. Amer. Chem. Soc.* **72**, 4452 (1950).

[12] W. A. Mosher, C. L. Kehr and L. W. Wright, *J. Org. Chem.* **26**, 1044 (1961).

[13] J. Tadanier, *J. Org. Chem.* **28**, 1744 (1963).

[14] P. B. Sollman, *J. Org. Chem.* **28**, 3559 (1963).

[15] H. Immer, M. Lj. Mihailović, K. Schaffner, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **45**, 753 (1962).

[16] A. Bowers and E. Denot, *J. Amer. Chem. Soc.* **82**, 4956 (1960).

[17] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith and P. M. Zanet, *J. Org. Chem.* **28**, 55 (1963); this oxidation was carried out in heptane solution.

[18] K. Heusler, J. Kalvoda, C. Meystre, P. Wieland, G. Anner, A. Wettstein, G. Cainelli, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **44**, 502 (1961); D. Hauser, K. Schaffner and O. Jeger, *Ibid*, **47**, 1883 (1964); D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner and O. Jeger, *Ibid.* **47**, 1961 (1964); K. Kitahonoki and A. Matsuura, *Tetrahedron Letters* No. 33, 2263 (1964).

[19] In the latter case the resulting tetravalent lead derivative, $HO{-}Pb(OAc)_3$, could either reform lead tetraacetate, react directly as oxidizing agent or decompose to a divalent lead compound.

[20] In excess of alcohol the amount of acetate (VI) was increased, in spite of a short reaction time, when the oxidation was performed with a larger concentration of lead tetraacetate and at a higher temperature (Table 2, run 5).

[21] Four moles of base per mole of lead tetraacetate were used. Two moles of pyridine are necessary to neutralize acetic acid, if in the course of the reaction both acetoxy groups from lead tetraacetate are converted to acetic acid.

[22] As expected, by heating 1-propanol or 2-propanol with acetic acid in pyridine or benzene–pyridine for 3 hr the corresponding acetates are not formed.

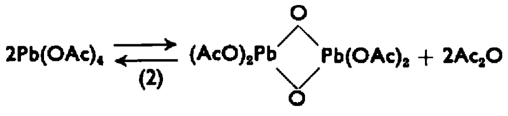
[23] Similar results were obtained with higher aliphatic alcohols and various aromatic alcohols (to be published).

Table 2. Product distribution in the lead tetraacetate oxidations of aliphatic alcohols of low molecular weight, under various experimental conditions

Run no.	Alcohol	Reaction time	Temp (°C)	Yields of reaction products[a] (%)			
				Carbonyl compound	Acetal[b]	Acetate[c]	Acetic anhydride
	In excess of starting alcohol						
1	Ethanol	25 hr	20	(83)			
2	Ethanol	8 min	45	79 (78)	6	5	*d*
3	1-Propanol	25 hr	20	(77)			
4	1-Propanol	15 min	45–50	69 (66)	7	11	*d*
5	1-Propanol[e]	15 min	80	48	19	27	*d*
6	1-Propanol[f]	7 min	50	(87)			
7	2-Propanol	15 min	50	(98)			
8	2-Butanol	20 min	60	(95)			
	In benzene in the presence of pyridine[g]						
9	1-Propanol	5 min	80	82	2	7	2
10	2-Propanol	5 min	80	86	—	6	3
	In pyridine						
11	1-Propanol	3 mon	> 100	87	3	4	2
12	2-Propanol	3 min	> 100	93	—	4	2

[a] Yields were calculated from gas-chromatograms. For carbonyl compounds the yields were also obtained, in separate runs, by the quantitative determination of solid derivatives (values given in parentheses); in these runs other products were not investigated. [b] Acetal of starting alcohol and corresponding aldehyde. [c] Acetate of starting alcohol. [d] Not investigated. [e] In this run the concentration of lead tetraacetate was larger than usual (see Experimental) i.e. 0·03 mole (13·3 g) per 10 ml. of alcohol. [f] Dry pyridine was added in a ratio of 2 moles for 1 mole of lead tetraacetate. [g] A 4:1 molar ratio of pyridine to lead tetraacetate was used.

Acetic anhydride might arise from the equilibrium reactions (2) or (3), the latter equation affording possibly a more correct interpretation of the structure of the lead containing product (VIII) formed in the course of this process, since organo-lead compounds with very similar structures to VIII have been isolated and identified, e.g. $(R_3Pb)_2O$[24] and particularly $(Ph_2PbOAc)_2O$.[25]



VII

$$2Pb(OAc)_4 \underset{(3)}{\rightleftarrows} (AcO)_3Pb{-}O{-}Pb(OAc)_3 + Ac_2O$$

VIII

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[24] Yu. A. Aleksandrov, T. G. Brilkina and V. A. Shushunov, *Dokl. Akad. Nauk SSSR* **136**, 89 (1961); T. G. Brilkina, M. K. Safonova and V. A. Shushunov, *Zh. Obshch. Khim.* **32**, 2684 (1962); N. N. Vyshinskii, Yu. A. Aleksandrov and N. K. Rudnevskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **26**, 1285 (1962).

[25] K. A. Kocheshkov, E. M. Panov and N. N. Zemlyanskii, *Izy. Akad. Nauk SSSR, Otd. Khim. Nauk.* 2255 (1961); E. M. Panov, N. N. Zemlyanskii and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR* **143**, 603 (1962).

Similarly, in benzene alone,[26] reactions (2) or (3) followed by esterification of the starting alcohol (IV) or the corresponding alkoxide (V) by acetic anhydride may account, in part, for the formation of acetates (VI),[27] although acetic anhydride can not be detected during the oxidation of IV (a and b) in boiling benzene solution.

(b) *Oxidation products*

The carbonyl compounds (XII) corresponding to the starting alcohols are undoubtedly primary oxidation products of 1-propanol (IVa) and 2-propanol (IVb), but are largely or completely converted, upon prolonged heating with starting alcohol and lead tetraacetate, to carbonyl compound derivatives, such as acetals (XIII; 7), or further oxidized to acid and ester (XVa and XVIa, when $R' = H$; 8, 9, 10), and to α-acetoxy (XVIII and XIXa: 11, 12) or α-alkoxy derivatives (XX; 13). Thus, in the case of 1-propanol (IVa) free propionaldehyde (XIIa) is not present in the reaction mixture after completion of the lead tetraacetate oxidation, but only in the form of its acetal (XIIIa); however, when the reaction is interrupted after 90 min, about 3–4% of free aldehyde may be isolated. As evident from Table 1, the total yield of carbonyl compound (XII), acetal (XIII) and products formed by subsequent oxidation (XV, XVI, XVIII–XX) do not exceed 20%, similar results having also been reported for other lead tetraacetate oxidations of aliphatic[2] and alicyclic alcohols[1,13–16,28–30] in non-polar solvents, except in those cases[16,31] when the formation of the carbonyl group results in considerable energy gain associated with release of steric compression,[32] and therefore the yields of ketones obtained are much higher.

Decomposition of the alkoxy lead triacetate (V) in non-polar solvents consists preferentially in homolytic cleavage of the O—Pb bond (4) to give as intermediate product the alkoxy radical (IX),[33,34] which can stabilize in different ways,[33] for example by intermolecular substitution with solvent. The isolation of a small amount

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[26] As already mentioned, the presence of anhydrous $CaCO_3$ does not affect product distribution, thus indicating that addition of this base to benzene (resulting in a heterogeneous system) does not noticeably change the polarity of the reaction medium.

[27] Other routes to acetate formation would involve C—O bond cleavage in the intermediate lead alkoxide (V). In the light of other results (*vide infra*) this possibility cannot be *a priori* disregarded and is now being investigated.

[28] R. E. Partch, *J. Org. Chem.* **28**, 276 (1963).

[29] G. Cainelli, B. Kamber, J. Keller, M. Lj. Mihailović, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **44**, 518 (1961).

[30] A. Bowers, E. Denot, L. C. Ibanez, M. E. Cabezas and H. J. Ringold, *J. Org. Chem.* **27**, 1862 (1962); G. B. Spero. J. L. Thompson, W. L. Schneider and F. Kagan, *Ibid.* **28**, 2225 (1963); R. M. Moriarty and T. D. D'Silva, *Ibid.* **28**, 2445 (1963).

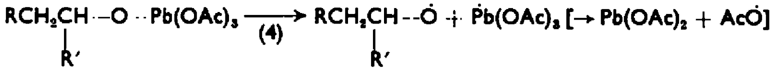
[31] K. Heusler, J. Kalvoda, G. Anner and A. Wettstein, *Helv. Chim. Acta* **46**, 352 (1963). See also J. F. Bagli, P. F. Morand and R. Gaudry, *J. Org. Chem.* **28**, 1207 (1963).

[32] J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta* **38**, 1529 (1955).

[33] K. Heusler and J. Kalvoda, *Angew. Chem.* **76**, 518 (1964); *Ibid*, (Interna. Ed.) **3**, 525 (1964).

[34] This (IX) and other species resulting from the decomposition of the alkoxide (V) probably exist in the form of radical pairs (or/and ion pairs), the other partner in the pair being the corresponding lead containing residue.[33] Therefore, it should be more correct to consider the formation of most of the oxidation and other products as actually involving reactions of such pairs, which may be either resonance structures of the alkoxide (V) in the transition state or else discrete intermediates, possibly with some degree of covalent interaction between the partners in the pair. However, for simplicity reasons, the various ways in which the alkoxide (V) can react are mainly discussed in terms of the reactive lead free species derived from the starting alcohol.

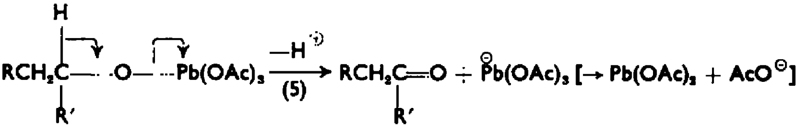
of isopropyl phenyl ether (X), upon lead tetraacetate oxidation of 2-propanol (IVb) in benzene, confirms this possibility.[35]



$$\underset{\substack{|\\ R'}}{RCH_2CH}-O-Pb(OAc)_3 \xrightarrow[(4)]{} RCH_2\underset{\substack{|\\ R'}}{CH}-\dot{O} + \dot{P}b(OAc)_3\,[\rightarrow Pb(OAc)_2 + Ac\dot{O}]$$

V IX

The rather low yields of aldehydes and ketones (and their derivatives) in non-polar solvents indicate that alkoxy radicals (IX) are not readily converted (if at all) to the corresponding carbonyl compounds by α-hydrogen atom elimination[36] or oxidation to oxonium ions[37] followed by loss of an α-proton. Therefore, lead tetraacetate oxidation of alcohols to carbonyl compounds should be predominantly a heterolytic process, taking place (5) by elimination of an α-proton from the alkoxy lead triacetate (V),[7] with concerted heterolysis of the polarized O—Pb bond.[38] In the absence of other proton acceptors acetic acid would be produced from the resulting proton and acetate anion. (The formation of carbonyl compound (XII), acetic acid and lead diacetate from the alkoxide (V) might also be envisaged as a synchronous process involving a cyclic five-membered transition state in V).



V XII

This mechanism (5) is substantiated by the observation that in excess of starting alcohol (in the absence of benzene) or in pyridine (alone or in benzene solution), i.e. in polar (and basic) solvents favouring separation of charges, the lead tetraacetate oxidation of 1-propanol, 2-propanol, as well as ethanol and 2-butanol, are fast and afford the corresponding carbonyl compounds in very good yields (Table 2).[39–41] Pyridine with its proton acceptor properties strongly displaces the equilibrium of the first stage of the oxidation (1) to the side of the complex lead alkoxide (V) formation

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[35] A similar intermolecular ether formation between solvent and starting alcohol was observed when 3α-hydroxy-17β-acetoxy-5β-androstane was oxidized with lead tetraacetate in cyclohexane solution.[15]

[36] Lead tetraacetate oxidation of alcohols to carbonyl compounds *via* alkoxy radicals (of type IX) was proposed by M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.* **16**, 533 (1951).

[37] H. E. De La Mare, J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.* **85**, 1437 (1963), have reported that alkoxy radicals are unaffected by cupric salts, which are known to oxidize easily carbon free radicals to the corresponding cations.

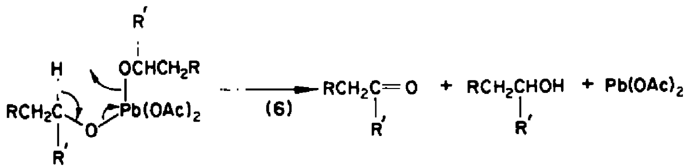
[38] When conversion of the hydroxyl group to the carbonyl group releases considerable steric compression in the molecule, heterolytic decomposition of the lead alkoxide (V) is favoured even in non-polar solvents[16,31] although in these cases the possibility that the α-hydrogen might depart from alkoxide (V) (or from IX) in the radical form cannot be *a priori* rejected.

[39] This fact was actually suggested by our earlier results obtained in studying the lead tetraacetate oxidation of the 2-, 3- and 4-pyridinemethanols. See V. M. Mićović and M. Lj. Mihailović, *Rec. Trav. Chim. Pays-Bas* **71**, 970 (1952).

[40] Similar results were also observed with higher aliphatic alcohols, which upon lead tetraacetate oxidation in non-polar solvents yielded predominantly cyclic ether and only a few per cents of carbonyl compound.[3] In polar media homolytic cyclization[33] was markedly suppressed whereas heterolytic carbonyl formation was noticeably enhanced (to be published).

[41] Criegee *et al.*[5] obtained comparable results with methanol, ethanol and 2-propanol.

and, on the other hand, polarizes this intermediate and aids in the elimination of the α-proton. Similarly, in excess of starting alcohol (in the absence of benzene) equilibrium (1) is also displaced to the side of the alkoxy lead triacetate (V), because of the large concentration of alcohol and probably, to a certain extent, because of removal by esterification of the formed acetic acid,[20] while the marked polar properties of the alcohol will, in addition, help in the heterolytic decomposition of the alkoxide (V). Moreover, the alkoxide (V) may further react with excess alcohol to give the dialkoxy lead diacetate (XI)[5,12]; decomposition of this intermediate *via* a cyclic-type transition state (6) to give the carbonyl compound (XII) and lead diacetate, with recovery of one molecule of alcohol (IV), would be assisted by the presence of the second alkoxy group attached to lead in XI.



XI XII IV

In glacial acetic acid, after 25 hr of heating at 60–65°, 1-propanol and 2-propanol give only traces of the corresponding carbonyl compound[42] (and some acetate). This unreactivity, already noted previously,[5,43] is understandable, since acetic acid lowers the concentration of the alkoxide (V) by displacing equilibrium (1) to the side of the starting alcohol and, the solvent being an acid, does not assist heterolytic decomposition of the complex lead alkoxide (V) in the sense of carbonyl formation.[44]

$$\begin{tikzcd}
 & CH_3CH_2CHO \arrow[r, "2\,IVa", "(7)"'] & CH_3CH_2CH(OCH_2CH_2CH_3)_2 \\
 & XIIa \arrow[d, "(8)"', "-H^{\cdot}"] & XIIIa \\
CH_3CH_2COOH & CH_3CH_2\dot{C}{=}O \arrow[l, "(9)"] \arrow[r, "V\ (or\ IX)", "(10)"'] & CH_3CH_2COOCH_2CH_2CH_3 \\
XVa & XIVa & XVIa
\end{tikzcd}$$

The presence of a small amount of propionic acid (XVa), observed as a product in the oxidation of 1-propanol (IVa) in benzene,[45] may be accounted for by assuming

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[42] Mosher *et al.*[11] reported that the lead tetraacetate oxidation of t-butylmethylcarbinol in glacial acetic acid afforded pinacolone (beside pinacolyl acetate and cleavage products) in a yield up to 9%, this yield decreasing with a larger amount of acetic acid (in accordance with the above discussion). However, the authors used relatively concentrated solutions, while in the present work a 1 : 17·5 molar ratio of alcohol to acetic acid was employed, the large excess of acid solvent preventing formation and decomposition of the intermediate lead alkoxide (V).

[43] N. J. Leonard and M. A. Rebenstorf, *J. Amer. Chem. Soc.* **67**, 49 (1945).

[44] The above discussion is valid for "slow" lead tetraacetate reactions, which require time and higher temp for the decomposition of the intermediate alkoxide (V) (e.g. conversion of alcohols to carbonyl compounds in non-polar solvents). In "fast" reactions, which generally occur at a low temp (e.g. glycol fission), the alkoxide (of type V) reacts immediately further on; therefore, although equilibrium (1) lies on the side of lead tetraacetate, small amounts of alcoholysis products are being constantly reformed and the reaction proceeds even in acetic acid.

[45] 1-Pentanol and other higher primary aliphatic alcohols also give in small amounts the corresponding acid and the esters of starting alcohol with this acid and formic acid (to be published).

autooxidation[46,47a] of the primarily formed propionaldehyde (XIIa), a process reported to be catalytically promoted by lead tetraacetate,[47a,48] i.e. by the liberated acetoxy or methyl radicals,[49] which will initiate the chain reaction (8) by abstraction of a hydrogen atom from the aldehyde (XIIa) to produce the oxoalkyl C-radical (XIVa). This transient radical, which is the active intermediate in the autooxidation of aldehyde to acid (9),[50] can also attack alkoxy lead triacetate (V), i.e. the corresponding alkoxy free radical (IXa) (10) to give 1-propyl propionate (XVIa),[51] another product isolated upon oxidation of 1-propanol (IVa) (Table 1).[45,52] Formates of the starting alcohols (XVII), found among the reaction products of 1-propanol and 2-propanol,[45] are probably formed in the same way, formaldehyde[53] arising from the autooxidation[46,47a] of methyl radicals.[54] This agrees with the fact that, in general, the yield of formates is higher the longer the reaction time necessary for complete consumption of lead tetraacetate.

Direct attack (11 and 13) of acetoxy or alkoxy radicals (IX) on the carbonyl compounds (XII), *via* a mechanism involving the enol form,[56] is undoubtedly in major part responsible for the formation of α-acetoxy (XVIII) and α-alkoxy carbonyl

[46] Cf., for example, E. S. Gould, *Mechanism and Structure in Organic Chemistry* pp. 705–714. (and Refs therein). H. Holt, New York (1959).

[47] W. A. Waters in H. Gilman's *Organic Chemistry* Vol. IV. [a] pp. 1138–1153; [b] pp. 1185–1189 (and Refs therein). J. Wiley, New York (1953).

[48] A. Robertson and W. A. Waters, *Trans. Faraday Soc.* **42**, 201 (1946); *J. Chem. Soc.* 492 (1947); W. A. Waters, *Trans. Faraday Soc.* **42**, 184 (1946).

[49] Methyl radicals (together with CO_2) are generated by collapse of acetoxy radicals. The formation of methyl radicals was proposed[36,47b] to account for the methylation reactions of lead tetraacetate. See L. F. Fieser and C. Chang, *J. Amer. Chem. Soc.* **64**, 2043 (1942), and other related papers.[7]

[50] When the lead tetraacetate oxidation was carried out in an O_2-free atmosphere, propionic acid (XVa) and α-acetoxy-propionic acid (XIXa) are not found among the reaction products.

[51] Because the concentration of starting alcohol or of the intermediate alkoxide (V) is much larger than that of the aldehyde (XIIa) during the lead tetraacetate oxidation of 1-propanol (IVa) in benzene, this pathway (10) leading to ester (XVIa) appears to be preferred over the two-step chain mechanism in which the oxoalkyl C-radical (XIVa) would attack the aldehyde (XIIa) with addition to the oxygen of the carbonyl function and stabilization of the newly formed radical by abstraction of hydrogen from compounds present in the reaction mixture. For the latter mechanism see W. H. Urry, D. J. Trecker and H. D. Hartzler, *J. Org. Chem.* **29**, 1663 (1964), and Refs therein.

[52] This ester (XVIa) may have also been produced by direct esterification of 1-propanol with formed propionic acid. Another possibility leading to the same ester (XVIa) consists in the oxidation of the hemiacetal of propionaldehyde and 1-propanol, the corresponding acetal (XIIIa) being one of the actually isolated reaction products (Table 1). Cf. W. A. Mosher and D. M. Preiss, *J. Amer. Chem. Soc.* **75**, 5605 (1953).

[53] The presence of traces of formaldehyde was detected in all the lead tetraacetate oxidations of alcohols investigated, and in reactions of various other compounds with the same reagent.[36]

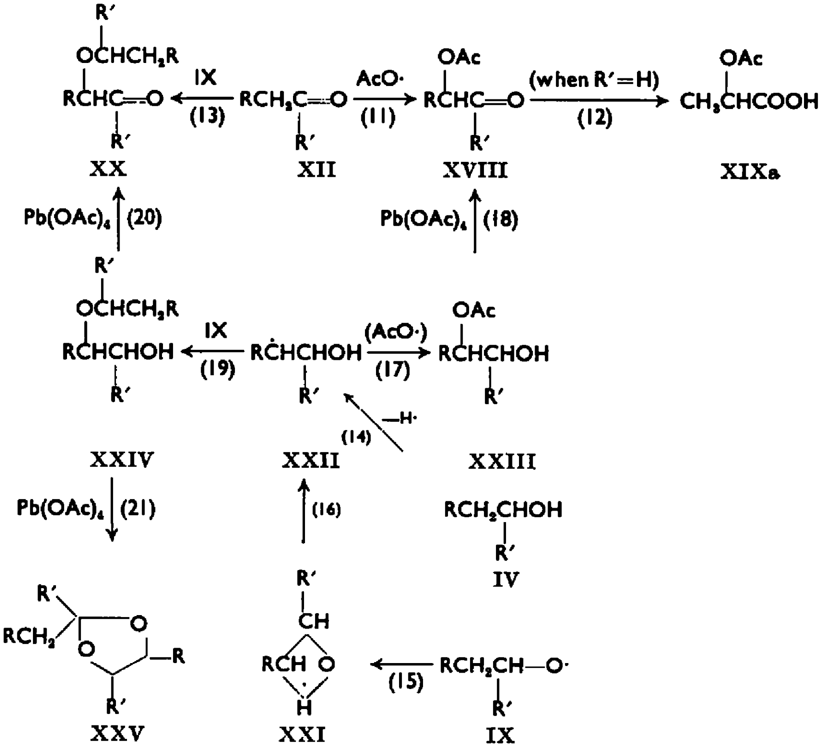
[54] Formaldehyde may also be formed by fragmentation of 2-propanol (IVb) to methyl radicals and subsequent oxidation, or directly by fragmentation of 1-propanol (IVa).[1,33,55] However, other products resulting from such fragmentation processes (such as methyl acetate and acetaldehyde from 2-propanol, and ethyl acetate or ethylene from 1-propanol) were not detected, although it has been demonstrated on other examples that secondary aliphatic alcohols with normal alkyl chains (but not primary alcohols) do undergo to a small extent fragmentation when subjected to the action of lead tetraacetate.

[55] D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **47**, 1961 (1964).

[56] K. Ichikawa and Y. Yamaguchi, *J. Chem. Soc. Japan* **73**, 415 (1952); W. K. Cavill and D. H. Solomon, *J. Chem. Soc.* 4426 (1955). See also R. C. Fuson, E. W. Maynert, T.-L. Tan, E. R. Trumbull and F. W. Wassmundt, *J. Amer. Chem. Soc.* **79**, 1938 (1957); H. B. Henbest, D. N. Jones and G. P. Slater, *J. Chem. Soc.* 4472 (1961), and Ref. 7 and 15.

compounds (XX), which are isolated upon oxidation of 1-propanol (IVa) and 2-propanol (IVb) in benzene solution (Table 1),[57] and which can undergo further oxidation (12), when possible, to acids such as XIXa. α-Acetoxylation of ketones with lead tetraacetate in acetic acid or benzene is a well known reaction,[7,56,58,59] and it was also recently reported that simple aliphatic aldehydes (including propionaldehyde) can be acetoxylated by the same reagent in acetic acid solution.[60]

In the present work acetone was oxidized with lead tetraacetate in boiling benzene to give 21% of monoacetoxy derivative (XVIIIb) and 10% of α,α'-diacetoxyacetone,[61] and propionaldehyde, under the same conditions, affords in low yields 1-propyl propionate (XVIa),[62] α-acetoxypropionaldehyde (XVIIIa),[60] propionic acid (XVa) and α-acetoxypropionic acid (XIXa),[50] beside other unidentified material.



(c) *Novel reactions*

An alternate but less favoured pathway leading to α-substituted carbonyl compounds (XVIII and XX) consists in subsequent lead tetraacetate oxidation (18 and

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[57] Oxidation to ketone followed by α-acetoxylation was also observed in the case of 6β-hydroxy-3α,5α-cycloandrostan-17-one.[14]

[58] O. Dimroth and R. Schweizer, *Ber. Dtsch. Chem. Ges.* **56**, 1375 (1923); E. Detilleux and J. Jadot, *Bull. Soc. Roy. Sci., Liège* **11-12**, 366 (1955).

[59] Cf. R. Criegee in *Neuere Methoden der Präparativen Organischen Chemie* pp. 21–38. Verlag Chemie, Berlin (1944); L. F. Fieser and M. Fieser, *Steroide* Verlag Chemie, Weinheim (1961).

[60] J.-J. Riehl, *C.R. Acad. Sci. Paris* **250**, 4174 (1960).

[61] The same products are also obtained upon lead tetraacetate oxidation of acetone in acetic acid solution.[58]

[62] Probably formed by attack of the intermediate oxoalkyl C-radical (XIVa) on propionaldehyde.[51]

20) of the corresponding, primarily produced, β-acetoxy (XXIII) and β-alkoxy alcohols (XXIV). The formation of these alcohols may be envisaged as first involving either intermolecular hydrogen abstraction (14) from starting alcohol (IV) or alkoxide (V),[63] by radicals present in the solution, or an intramolecular 1,3 hydrogen abstraction (15) by the electron deficient oxygen in the alkoxy radical (IX),[63,64] to give (16), *via* a cyclic four-membered transition state (XXI),[65] the hydroxyalkyl C-radical (XXII),[66] which then further reacts (17 and 19) with species acting as sources of acetoxy and alkoxy radicals. Although β-alkoxy alcohols (XXIV) may be further heterolytically oxidized (20) to the corresponding carbonyl compounds (XX), they should preferably if not exclusively undergo homolytic 1,5 cyclization (21), by interaction with lead tetraacetate, to give 2-substituted 4-methyl-1,3-dioxolanes (XXV), similar to the facile formation of tetrahydrofuran derivatives from simple aliphatic alcohols with sufficiently long alkyl chains.[2] That this reaction course is valid follows from the fact that 1-isopropoxy-2-propanol (XXIVb) and 2,2,4-trimethyl-1,3-dioxolane (XXVb) are actually isolated from the lead tetraacetate oxidation of 2-propanol (IVb), and that 2-ethyl-4-methyl-1,3-dioxolane (XXVa) is found among the oxidation products of 1-propanol (IVa) (Table 1).[67] Dioxolane formation has not been observed so far in lead tetraacetate oxidations of alcohols.

The formation of deoxygenated saturated dimeric products, i.e. hexane (XXVIa) from 1-propanol (IVa) and 2,3-dimethylbutane (XXVIb) from 2-propanol (IVb),[68] isolated in small yields upon lead tetraacetate oxidation in benzene (Table 1), as well as the formation of the previously described monomeric structures obtained from some steroid alcohols,[1,69] was formally represented[1] as procedeing *via* alkyl radicals of the type $RCH_2\dot{C}HR'$, produced from the lead alkoxide (V). However, since the energy requirements for homolytic C—O bond cleavage in the alkoxide (V) are unfavourable (as compared to O—Pb bond cleavage (4)) and since with such small concentrations of alkyl radicals, under the reaction conditions employed, the probability for coupling of two alkyl radicals would be extremely low,[70] it appears that the

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[63] Cf. H. E. De La Mare and F. F. Rust, *J. Amer. Chem. Soc.* **81**, 2691 (1959).

[64] Similarly to the postulated 1,5 hydrogen shift from carbon to oxygen preceding the cyclization step in the lead tetraacetate oxidation of alcohols with structures permitting the formation of tetrahydrofuran derivatives.[1,33]

[65] A direct 1,3 hydrogen shift from carbon to carbon was proposed to account for the observed isomerization in boiling CCl_4 of the primarily formed α-^{14}C-labelled propyl radical. See O. A. Reutov in *Congress Lectures Presented at the* XIXth *International Congress of Pure and Applied Chemistry*, pp. 205–211. Butterworths, London (1963).

[66] The fact that the corresponding epoxide is not isolated indicates that stabilization of the hydroxyalkyl C-radicals (XXII), eventually upon oxidation to the carbonium ions,[33] does not occur in this case by cyclization to ethylene oxides, probably because of unfavourable energetic conditions related to steric strain in the transition state leading to three-membered cyclic oxides.

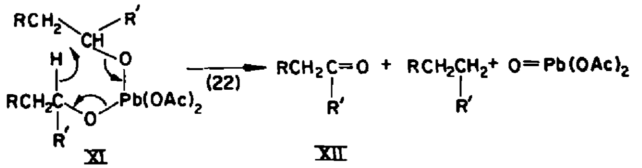
[67] 2-Propoxy-1-propanol (XXIVa) and 1-isopropoxy-2-propanol (XXIVb) reacted in separate runs with lead tetraacetate in benzene solution to give the corresponding dioxolanes (XXV) (to be published).

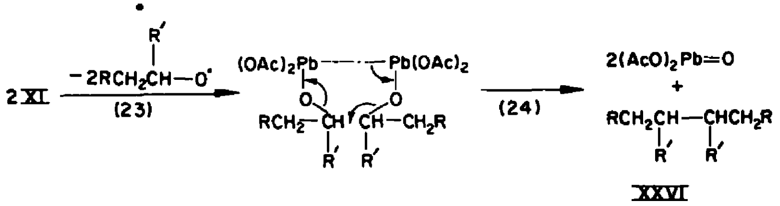
[68] Similar dimerization and dehydration products are also isolated from lead tetraacetate oxidation of 4,4-dimethyl-1-pentanol (unpublished result).

[69] M. Lj. Mihailović, M. Stefanović, Lj. Lorenc and M. Gašić, *Tetrahedron Letters* No. 28, 1867 (1964).

[70] Cf. J. Smid, A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.* **78**, 3315 (1956); M. Matsuoka, P. S. Dixon, A. P. Stefani and M. Szwarc, *Proc. Chem. Soc.* 304 (1962); J. N. Bradley, *J. Chem. Phys.* **35**, 748 (1961); J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Chem. Kinetics* **1**, 107 (1961).

monomer[1,69] and dimer (XXVI)[68] are generated by other routes.[71] Thus, the monomer might possibly be produced by a type of oxido-reduction process (22) involving dialkoxy lead diacetate (XI) as an intermediate, which could decompose to the monomeric derivative and corresponding carbonyl compound (XII) (with formation of O=Pb(OAc)$_2$), and the dimer (XXVI) might originate from a complex in which both residues are held together before coupling occurs, e.g. by decomposition of a product of the type shown in equation (24).[72] This intermediate could arise from dialkoxy lead diacetate (XI), by loss of an alkoxy group followed by dimerization (23).[73] However, further evidence is necessary in order to devise a satisfactory mechanism for this novel and unexpected mode of reaction of lead tetraacetate with alcohols.





The formation of dehydration products, i.e. propene (XXVII) from 1-propanol (IVa) and 2-propanol (IVb),[68] and similar unsaturated compounds from some steroid alcohols,[1,69] upon lead tetraacetate oxidation in benzene solution, may be envisaged either as resulting from a Lewis acid-type action of lead tetraacetate on the starting alcohol (IV) or/and as a direct elimination reaction (25) taking place in the lead alkoxide (V).[74,75]

The presence of a small amount of rearranged acetate, i.e. 2-propyl acetate

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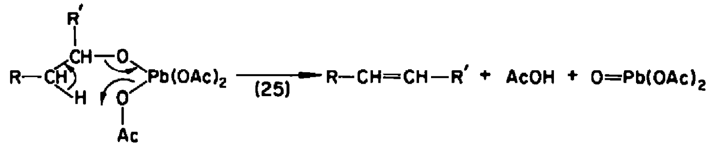
[71] If, however, any alkyl radicals are formed, the reaction leading to dimers (XXVI) would not result from a recombination process involving free radicals which lose their indentity, but rather from a "cage" recombination involving two alkyl radicals formed from a single molecule of some intermediate product.[70]

[72] These possibilities were suggested by Dr. J. Kalvoda and Dr. K. Heusler.

[73] Compounds of the type R_6Pb_2 have been described. See L. C. Willemsens, *Organolead Chemistry*, International Lead Zinc Research Organization, New York (1964).

[74] No olefin or other stabilization products of the corresponding carbonium ion are found upon prolonged heating of 1-propanol and 2-propanol in benzene with lead diacetate, lead dioxide, acetic acid or $CaCO_3$, or their various combinations, thus indicating that these reagents, which are present or formed in the course of the lead tetraacetate oxidations, are not involved (eventually as electrophilic catalysts) in the formation of electron deficient alkyl species or their rearrangement products.

[75] If free alkyl radicals are produced (however, *vide supra*),[71] the olefinic compound (XXVII) could arise either from a "cage" disproportionation process,[70] together with the corresponding monomer,[1,69] or more probably by oxidation of the carbon radical to carbonium ion,[33,37,76] followed by loss of a proton, eventually after rearrangement to a more stable alkyl cation.



V XXVII

(VIb), among the reaction products of 1-propanol (IVa), suggests that in the 1-propanol–lead tetraacetate complex or in the propoxy lead triacetate (Va) the 1-propyl residue, prior to olefin formation, should have some sort of primary carbonium ion character,[76] in order to account for the 1,2-hydride shift followed by addition of an acetate ion to the newly formed, more stable, carbonium ion,[77] the 1,2-hydride shift and acetate ion addition possibly taking place by a concerted process.[78]

The isolation of small amounts of the corresponding alkyl benzenes (XXVIII), upon lead tetraacetate oxidation of 1-propanol (IVa) and 2-propanol (IVb) in benzene (Table 1), indicates that the alcohol–lead tetraacetate complex, alkoxide (V) or some other active intermediate can react with solvent (benzene), probably by a Friedel-Crafts type reaction.

(d) *Solvent reactions*

Toluene, benzyl acetate, phenyl acetate and biphenyl are found in almost every lead tetraacetate oxidation of alcohols in boiling benzene, their yields being higher when the consumption of lead tetraacetate is slow. Toluene must be formed by the attack of methyl radicals on benzene (as solvent),[49] and the subsequent acetoxylation of toluene by means of lead tetraacetate would then produce benzyl acetate.[79,80] The presence of biphenyl indicates that phenyl radicals are formed from benzene in the course of the reaction.[82]

EXPERIMENTAL[83]

B.ps and m.ps are uncorrected. Gas chromatography was carried out on a Perkin–Elmer instrument model 154-D, equipped with thermistor detectors. The columns (2 m × 4 mm, 4 m × 6 mm,

[76] J. K. Kochi, *Tetrahedron* **18**, 483 (1962); *J. Amer. Chem. Soc.* **85**, 1958 (1963); C. Walling and A. Zavitsas, *Ibid.* **85**, 2084 (1963); G. Sosnovsky and S.-O. Lawesson, *Angew. Chem.* **76**, 218 (1964), and references in these papers.

[77] Similar stabilization of primarily formed secondary carbonium ions to tertiary carbonium ions by a Wagner-Meerwein type rearrangement, followed by loss of a proton from an adjacent carbon atom. are observed in the lead tetraacetate oxidation of benzpinacolyl alcohol in acetic acid[11] and of isoborneol in benzene,[28] tetraphenylethylene and camphene, respectively, being the final rearranged products.

[78] See Ref 65, pp. 211–222.

[79] L. F. Fieser, R. C. Clapp and W. H. Daudt, *J. Amer. Chem. Soc.* **64**, 2052 (1942), reported that benzyl acetate was obtained in the reaction between lead tetraacetate and benzene in acetic acid, but they did not observe the formation of toluene or phenyl acetate.

[80] Acetoxylation of toluene with lead tetraacetate leading to benzyl acetate has been described, and can be preformed in acetic acid or in benzene solution.[58,81]

[81] G. W. Cavill and D. H. Solomon, *J. Chem. Soc.* 3943 (1954).

[82] After this work was completed, R. E. Partch, *Tetrahedron Letters* No. 41, 3071 (1964) and K. Heusler, *Ibid* No. 52, 3975 (1964), have reported similar observations concerning the yields of carbonyl compounds obtained by the lead tetraacetate oxidation of alcohols in non-polar solvents and in the presence of pyridine.

[83] We thank Mrs. R. Tasovac and Miss R. Dimitrijević, from the Microanalytical Laboratory of our Department, for the elemental microanalyses they carried out.

6 m × 8 mm) consisted of polyethylene glycol, polypropylene glycol or Apiezon adsorbed on Chromosorb or Celite 545 (60–80 mesh), and were operated at temp ranging from 40 to 170°, with H_2 (100–200 ml/min) as carrier gas. IR spectra were recorded on a Perkin–Elmer spectrophotometer model 13-U or Infracord model 137, and NMR spectra were registered on a Varian A-60 spectrometer. For distillations a Todd fractionating column, a semimicro spinning-band column and micro-Vigreux columns were used.

Starting alcohols were high-purity grade commercial products, dried before use by refluxing over Mg turnings. The purity of each alcohol was checked by means of gas chromatography.

Lead tetraacetate oxidations were carried out as described previously,[2] in carefully dried round-bottomed flasks equipped with an ice-cooled spiral-type condenser and magnetic stirrer (and, when necessary, with a dropping funnel). The end of the reaction was indicated by a negative starch-iodide test, or by the nonformation of dark-brown lead dioxide upon addition of water to one or two drops of the reaction solution. Gaseous propene, formed in the oxidation of 1-propanol and 2-propanol in benzene, was passed into a trap connected to the top of the condenser, which contained an ice-cooled 10% solution of Br_2 in CCl_4. The amounts of lead tetraacetate used in different runs (values in grams and moles given below) are based on a product of 100% purity.

Oxidation of 1*-propanol* (IVa) *and* 2*-propanol* (IVb)

In benzene. Lead tetraacetate (466 g; 1·05 moles), dried *in vacuo* over P_2O_5 and KOH, and 120 g (1·2 moles) of anhydrous $CaCO_3$ (dried *in vacuo* over P_2O_5) in 2000 ml of thiophene-free benzene (dried over Na) were heated to reflux for 30 min with stirring. Upon cooling, 60 g (one mole) 1-propanol (IVa) or 2-propanol (IVb) was added and the mixture heated under reflux with stirring until completion of the reaction, i.e. disappearance of lead tetraacetate (25–32 hr).[84] The flask was then cooled for 6 hr at 5°, the clear solution was decanted and the solid residue extracted with several portions of boiling benzene. The benzene extracts were combined with the original solution, dried over $CaSO_4$ and fractionated up to 93° (Part A). The remaining solution was washed with $NaHCO_3$aq until neutral, the aqueous layer was continuously extracted with ether, the ether extracted was combined with the main organic solution, dried and fractionated (Part B). The $NaHCO_3$aq was carefully acidified with HCl, continuously extracted with ether, dried and finally subjected to fractional distillation (Part C). Excess of unreacted Br_2 in CCl_4, in the trap connected to the reflux condenser of the original reaction flask (see above), was reduced with 10% $Na_2S_2O_3$aq, the CCl_4 solution was neutralized with sat. $NaHCO_3$aq, dried and fractionated (Part D).

The fractions from parts A, B, C and D were analysed and further separated, if necessary, by gas chromatography;[85] all the individual products obtained were again purified by gas chromatography and identified by elemental analysis[86] and by comparison of their chemical and physical properties[87] (b.ps,[89] refractive indices, gas chromatographic retention times, IR spectra and NMR spectra) with those of authentic reference compounds, either commercially available or synthesized by independent routes.

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[84] The mixture usually became at first dark-brown but at the end of the reaction the precipitate was almost colourless.

[85] Yields calculated planimetrically from gas chromatograms were obtained by using various appropriate internal standards and comparison product mixtures of known concentrations.[17]

[86] Most of the compounds isolated in these oxidations were well-known products. They all gave correct elemental analyses for C and H.

[87] If not stated otherwise the m.ps, b.ps and refractive indices of products and their derivatives were compared with those reported in the literature.[88]

[88] [a] J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds.* Elsevier, Amsterdam (1950); [b] A. I. Vogel, *Practical Organic Chemistry* (Third Ed.). Longmans Green, London (1961); [c] A. I. Vogel, *J. Chem. Soc.* 624 (1948); [d] A. I. Vogel, *Ibid,* 616 (1948); [e] R. L. Shriner, R. C. Fuson and D. Y. Curtin. *The Systematic Indentification of Organic Compounds* (Fourth Ed.). J. Wiley, New York (1957).

[89] B.ps of most products, paricularly of those isolated by gas chromatography were determined by micro-methods. Cf. N. D. Cheronis, *Micro- and Semimicro Methods, Technique of Organic Chemistry* (A. Weissberger, Editor-in-chief) Vol. VI, pp. 190–192. Interscience, New York (1954).

Oxidation of 1-propanol (IVa)

The following products were obtained (yields given in Table 1).

From part A. Hexane; 1-propyl formate; 2-propyl acetate.

From part B. Unreacted 1-propanol; 1-propyl acetate; toluene; 2-ethyl-4-methyl-1,3-dioxolane, b.p. 114–118°,[90] n_D^{20} 1·4055,[90a] (Found: C, 61·8; H, 10·5. Calc. for $C_6H_{12}O_2$: C, 62·0; H, 10·4%), was identical with an authentic sample prepared from propionaldehyde and propane-1,2-diol,[90] and upon acid hydrolysis afforded the same aldehyde and diol; 1-propyl propionate, b.p. 120–122°, n_D^{20} 1·3925,[88c] was identical with the ester prepared by treating 1-propanol with N-bromosuccinimide in CCl_4;[91] 1-propylbenzene; 2-acetoxypropionaldehyde[92] (Found: C, 51·8; H, 6·9. Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9%), semicarbazone, m.p. 161–162°;[93] 1,1-dipropoxypropane,[94] n_D^{20} 1·4068,[94,95] which upon acid hydrolysis gave propionaldehyde and 1-propanol; phenyl acetate; benzyl acetate; biphenyl.

From part C. Acetic acid; propionic acid; 2-acetoxypropionic acid, b.p. 88–90° at 1 mm, n_D^{20} 1·4262[96] (Found: C, 45·2; H, 6·2. Calc. for $C_5H_8O_4$: C, 45·4; H, 6·1%).

From part D: 1,2-Dibromopropane, b.p. 140–142°, n_D^{20} 1·5190.[97]

Oxidation of 2-propanol (IVb)

The following products were obtained (yields given in Table 1).

From part A. Acetone ; 2,3-dimethylbutane; 2-propyl formate; recovered 2-propanol; 2-propyl acetate.

From part B. 2,2,4-Trimethyl-1,3-dioxolane,[98] b.p. 97–101°, n_D^{20} 1·3978[99] (Found: C, 61·7; H, 10·6. Calc. for $C_6H_{12}O_2$: C, 62·0; H, 10·4%), was hydrolysed by acid to acetone and propane-1,2-diol: toluene; 1-isopropoxy-2-propanol, b.p. 136–139°, n_D^{20} 1·4082[100] (Found: C, 60·9; H, 11·9. Calc. for $C_6H_{14}O_2$: C, 61·0; H, 11·9%); 1-isopropoxy-2-propanone, b.p. 139–141°,[101] 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. (with a synthetic product[101]) 142–143°;[101] 2-propylbenzene; 1-acetoxy-2-propanone, n_D^{20} 1·4151[60,102] (Found: C, 52·0; H, 7·0. Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9%), 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 114–115°;[60,103] 2-propyl phenyl ether; phenyl acetate; benzyl acetate; biphenyl.

From part C. Acetic acid.

From part D. 1,2-Dibromopropane, b.p. 140–142°, n_D^{20} 1·5192.[97]

[90] [a] A. Noshay and C. Price, *J. Org. Chem.* **23**, 647 (1958); [b] E. Augdahl and O. Hassel, *Acta Chem. Scand.* **9**, 172 (1955).

[91] V. M. Mićović, R. I. Mamuzić and Lj. Mihailović, *Glasnik hem. društva* (Beograd) **22**, 443 (1957).

[92] Identical with an authentic product. A. M. Pujot, J. Boileau and C. Fréjacques, *Bull. Soc. Chim. Fr.* 974 (1955).

[93] J. U. Nef, *Liebigs Ann.* **335**, 247 (1904); H. Adkins and G. Krsek, *J. Amer. Chem. Soc.* **71**, 3051 (1949).

[94] Identical with an authentic product (b.p. 160–162°, n_D^{20} 1·4063) obtained from propionaldehyde (one mole) and 1-propanol (2 moles) in the presence of anhydrous $CaCl_2$. See W. Herold and K. L. Wolf, *Z. für physik. Chem.* [B] **12**, 182 (1931).

[95] H. W. Post, *J. Org. Chem.* **5**, 244 (1940).

[96] Cf. E. M. Filachione and C. H. Fisher, *Ind. Eng. Chem.* **36**, 472 (1944); B. T. Gillis, *J. Org. Chem.* **24**, 1027 (1959); E. B. Reid and G. H. Denny, Jr., *J. Amer. Chem. Soc.* **81**, 4632 (1959).

[97] See, for example M. S. Kharasch, J. G. McNab and M. C. McNab, *J. Amer. Chem. Soc.* **57**, 2463 (1935); K. Sisido and Y. Takeda, *J. Org. Chem.* **26**, 2301 (1961).

[98] Identical with a synthetic product prepared from acetone and propane-1,2-diol, according to the procedure of C. S. Rondestvedt, Jr., *J. Org. Chem.* **26**, 2247 (1961).

[99] J. Böeseken and P. H. Hermans, *Rec. trav. chim. Pays-Bas* **42**, 1104 (1923); P. Salomaa and A. Kankaanperä, *Acta Chem. Scand.* **15**, 871 (1961).

[100] H. C. Chitwood and B. T. Freure, *J. Amer. Chem. Soc.* **68**, 680 (1946); V. S. Abramov and E. N. Nikolaeva, *Zh. Obsh. Khim.* **20**, 100 (1950); S. M. Gurvich, *J. Gen. Chem. USSR* **25**, 1667 (1955).

[101] H. R. Henze, V. B. Duff, W. H. Matthews, Jr., J. W. Melton and E. O. Forman, *J. Amer. Chem.* Soc. **64**, 1222 (1942); R. A. Barnes and W. M. Budde, *Ibid*, **68**, 2339 (1946).

[102] G. F. Hennion and W. S. Murray, *J. Amer. Chem. Soc.* **64**, 1220 (1942).

[103] H. Reich and B. K. Samuels, *J. Org. Chem.* **21**, 68 (1956).

In benzene in the presence of pyridine. The starting alcohol (1·20 g; 0·02 mole), powdered lead tetraacetate (8·9 g; 0·02 mole) and 6·4 g (0·08 mole)[81] anhydrous pyridine (dried and distilled over $Ba(OH)_2$) in 20 ml of dry benzene were heated to boiling, with stirring. The reaction, which was at first exothermic, was completed in 5 min (negative starch-iodide test). The mixture was cooled for 3 hr at 5°, the solution was decanted and the solid residue in the flask washed twice with a little cold benzene. The washings and the original solution were combined, dried, fractionated and the fractions subjected to preparative gas chromatography.

Propionaldehyde, 1-propyl acetate and acetic anhydride (from 1-propanol), and acetone, 2-propyl acetate and acetic anhydride (from 2-propanol) were identified by comparison of their retention times and IR spectra with those of authentic reference samples. In addition, the carbonyl compounds were characterized by conversion to the corresponding 2,4-dinitrophenylhydrazones.[88b,e] Products and yields are listed in Table 2, runs 9 and 10.

In pyridine alone. The same amounts of alcohol and lead tetraacetate (as above) in 20 ml of anhydrous pyridine were heated with stirring. The strongly exothermic reaction was completed in a few min (disappearance of tetravalent Pb). Anhydrous ether (20 ml) was added to the mixture in order to precipitate lead diacetate. After standing for 3 hr at 5° the clear solution was decanted and the solid residue washed with ether. The ether–pyridine solution was dried, fractionated and the products isolated by gas chromatography and identified as above. Results are given in Table 2, runs 11 and 12.

Lead tetraacetate oxidations in excess of starting alcohol

For the quantitative determination of carbonyl compounds. The starting alcohol (10 ml) and 2·22 g (0·005 mole) of powdered lead tetraacetate were mixed at room temp and heated, with stirring, to the desired temp or shaken at room temp in sealed tubes. After the reaction was completed, the stirred mixture was quickly cooled in ice water to room temp and the separated lead diacetate dissolved by the addition of water (40 ml). The formed carbonyl compound was converted to the *p*-nitrophenylhydrazone by treating the aqueous solution with *p*-nitrophenylhydrazine (0·005 mole + 20% excess) dissolved in 50 ml of 50% aqueous acetic acid. After standing overnight the precipitate was filtered off, washed with dil. acetic acid and dried to constant weight. The yields of *p*-nitrophenylhydrazones[104] obtained from the oxidation of various alcohols are shown on Table 2, runs 1–4 and 6–8.[105]

For the preparative separation of the reaction products by gas chromatography. The starting alcohol (20 ml) and powdered lead tetraacetate (8·9 g; 0·02 mole) were heated to the desired temp, with stirring.[106] After the reaction was completed, the mixture was treated with an equal volume of anhydrous ether (to precipitate lead diacetate), cooled in ice (2 hr) and the precipitate separated by centrifuging. The solid was washed with cold ether (20 ml) and the combined filtrates, after drying, were directly subjected to gas chromatography, the isolated products being identified by their physical properties (as described above).[107] Products and yields are listed on Table 2, runs 2,4 and 5.[108]

Lead tetraacetate oxidation of acetone and propionaldehyde

The carbonyl compound (8·7 g; 0·15 mole) and lead tetraacetate (73 g; 0·15 mole + 10% excess) in 150 ml of benzene were stirred and heated under reflux until the reaction was completed (17–20 hr).[84] The mixture was cooled to room temp, treated with 100 ml of ether and allowed to stand for 3 hr at 5°. The solution was decanted and the solid precipitate was extracted twice with ether. The benzene–ether solution was washed with water (saturated with NaCl) and sat. $NaHCO_3$aq. The first

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[104] In view of obtaining accurate results, the conversion yields to *p*-nitrophenylhydrazones were also determined, under the same conditions, with authentic and pure carbonyl compounds.

[105] Yields are based on lead tetraacteate.

[106] Alternatively, the starting alcohol can be first heated and then treated in portions with powdered lead tetraacetate, each following portion being added after the disappearance of the yellow colour produced by the preceding portion. The yields of products are not markedly changed by this modification, which facilitates stirring of the reaction mixture.

[107] 1,1-Diethoxyethane (acetal) abtained from EtOH (Table 2, run 2) was compared with an authentic sample (b.p. 102–103°, n_D^{20} 1·3818 [88b,e], prepared according to H. Adkins and B. H. Nissen, *Org. Syntheses* Coll. Vol. 1, 1 (1948).

aqueous washing and the bicarbonate washing were cautiously combined, made weakly alkaline with solid $NaHCO_3$ (with cooling), filtered from the precipitated lead salt and continuously extracted with ether. The ethereal extract and the original benzene–ether solution were combined, washed with a little water (NaCl-saturated), dried and fractionated (Neutral fraction).

In the case of propionaldehyde, the aqueous alkaline solution, after extraction with ether, was carefully acidified with HCl and continuously extracted with ether. After drying and evaporation of the solvent, the residue was fractionally distilled (Acid fraction).

Oxidation of acetone. The neutral fraction afforded 3·7 g (21·3% yield) of 1-acetoxy-2-propanone, b.p. 74–75·5° at 18 mm, n_D^{20} 1·4152[60,102] (Found: C, 51·6; H, 7·0. Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9%); 2,4-dinitrophenylhydrazone, m.p. 115°.[60,108] The solid residue was recrystallized from light petroleum–ether to give 2·7 g (10·3% yield) of 1,3-diacetoxy-2-propanone, m.p. 46–47°[108] (undepressed by an authentic sample[108a]) (Found: C, 48·2; H, 5·7. Calc. for $C_7H_{10}O_5$: C, 48·3; H, 5·8%).[109]

Oxidation of propionaldehyde. The neutral fraction afforded 0·17 g (1% yield) 1-propyl propionate, n_D^{20} 1·3930[88c] (IR spectrum agreed with that of an authentic product[91]); 1·7 g (10% yield) of 2-acetoxypropionaldehyde,[110] b.p. 58–60° at 18 mm,[60,92,93] n_D^{20} 1·4108[93b] (Found: C, 51·8; H, 6·8. Calc. for $C_5H_8O_3$: C, 51·7; H, 6·9%); semicarbazone, m.p. 162–163°.[93] The acid fraction gave, beside acetic acid, 0·6 g (5·5% yield) propionic acid (*p*-bromophenacyl ester, m.p. and mixed m.p. 63°[88d]) and 0·65 g (3·3% yield) 2-acetoxypropionic acid, n_D^{20} 1·4269[96] (Found: C, 45·3; H, 5·9. Calc. for $C_5H_8O_4$: C, 45·4; H, 6·1%).

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[108] F. Weygand, V. Schmied-Kowarzik, A. Wacker and W. Rupp, *Chem. Ber.* **83**, 460 (1950); E. R. Clark and J. G. B. Howes. *J. Chem. Soc.* 1152 (1956).

[109] The same products were obtained by performing the lead tetraacetate oxidation of acetone in glacial acetic acid.[58]

[110] This compound was also formed, in much shorter time, by oxidizing propionaldehyde in glacial acetic acid at 80°.[60]