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THE REACTION OF LEAD TETRAACETATE WITH SOME ACYCLIC ALCOHOLS CONTAINING PHENYL GROUPS[1]

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Abstract—α-Substituted benzyl alcohols, 2-phenylethanol, 1,1-dimethyl-2-phenylethanol, 3-phenyl-1-propanol, 4-phenyl-1-butanol and 5-phenyl-1-pentanol have been subjected to the action of lead tetraacetate in nonpolar and polar solvents. The products obtained, i.e. carbonyl compounds corresponding to the starting alcohols, cyclic ethers and fragmentation carbonyl compounds and fragmentation acetates, and their relative distribution are discussed in terms of structural factors influencing the oxidation, cyclization and fragmentation processes.

It has recently been shown (Scheme 1) that when treated with lead tetraacetate in nonpolar solvents (such as benzene), unbranched primary and secondary aliphatic alcohols containing δ- (and ε-) methylene or methyl groups (I) chiefly undergo homolytic intramolecular cyclization (*cdd'*) to give 5-membered cyclic ethers VI (and small amounts of isomeric 6-membered tertahydropyrans VII),[3-8] whereas the second reaction, i.e. the fragmentation reaction (*cee'*), formulated as also proceeding homolytically *via* the same precursor as the cyclization reaction (*cdd'*), namely the transition state III,[5,9,10] and affording fragmentation carbonyl compounds IX and fragmentation acetates (or olefins) X, was observed to take place in low yield only in the case of secondary aliphatic alcohols (I).[4-6] Phase *d'* (Scheme 1) of the cyclization process was postulated[4,8,9] to occur by 1,5 (and 1,6) hydrogen transfer in the alkoxy radical V (Scheme 2), through a cyclic 6-membered (and 7-membered) transition state XI. According to available evidence, the last step in both the cyclization[4,9,11,12]

[1] Paper XII in the series *Reactions with lead tetraacetate.* For paper XI see A. Stojiljković, V. Andrejević and M. Lj. Mihailović, *Tetrahedron* **23**, 721 (1967).

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

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

[5] M. Lj. Mihailović, J. Bošnjak, Z. Maksimović, Ž. Čeković and Lj. Lorenc, *Tetrahedron* **22**, 955 (1966).

[6] M. Lj. Mihailović, R. I. Mamuzić, Lj. Žigić-Mamuzić, J. Bošnjak and Ž. Čeković, *Tetrahedron* **23**, 215 (1967).

[7] M. Lj. Mihailović and M. Miloradović, *Tetrahedron* **22**, 723 (1966).

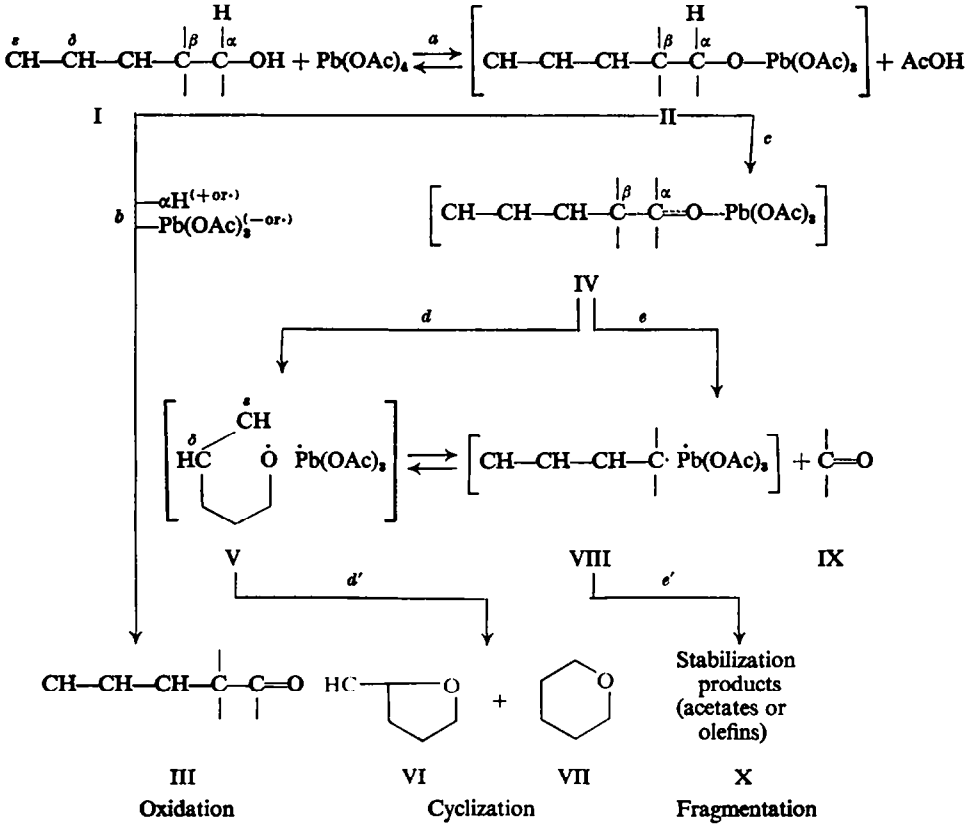
[8] R. E. Partch, *J. Org. Chem.* **30**, 2498 (1965).

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

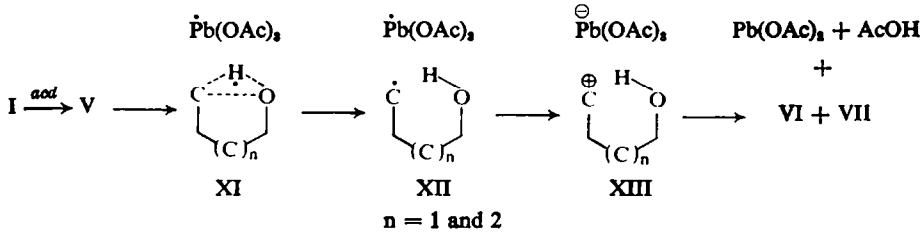
[10] K. Heusler, *Tetrahedron Letters* No. 52, 3975 (1964).

[11] D. Hauser, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **47**, 1883 (1964).

[12] M. Lj. Mihailović, Ž. Čeković and D. Jeremić, *Tetrahedron* **21**, 2813 (1965).



Scheme 1



Scheme 2

and fragmentation processes[4,13] may consist in the oxidation of the carbon radicals XII (Scheme 2) and VIII (Scheme 1) to the corresponding carbonium ions, by an one-electron transfer from carbon to lead in the respective radical pairs (XII and VIII).[14] The third reaction of interest, i.e. the oxidation of the alcohols I to the corresponding carbonyl compounds III (reaction *b*, Scheme 1), is of minor importance in nonpolar solvents,[3–10,12,15] but takes precedence over cyclic ether formation (*cdd'*) and fragmentation (*cee'*) with increasing polarity and basicity of the reaction medium (solvent and substrate);[5,8,10,12,15–17] therefore, this observation indicates that oxidation to carbonyl compounds III (reaction *b*) is favoured when heterolytic decomposition[18] of the initially formed alkoxy–lead acetate intermediate II may take place.[4,5,8,10,15]

In the present work we have studied the action of lead tetraacetate on various primary, secondary and tertiary acyclic alcohols containing Ph groups, with the purpose of determining the effect of structural factors on the yields of products formed by oxidation, cyclization and fragmentation processes.

As can be seen from Table 1, benzyl alcohol, benzhydrol and α-methylbenzyl alcohol undergo in benzene solution mainly the oxidation reaction (*b* on Scheme 1) to give the corresponding carbonyl compounds and further oxidation products, i.e. benzoic acid (when benzaldehyde is the initially formed product)[19] and ω-acetoxyacetophenone (when acetophenone is the primarily produced carbonyl compound),[20] the yield of aldehyde and ketone being somewhat improved (and the reaction time shortened) when the lead tetraacetate reaction is performed in the presence of pyridine. α-Methylbenzyl alcohol in benzene (+ calcium carbonate) undergoes, in addition, fragmentation (*cee'*, Scheme 1) to the extent of 7·5% (Table 1); in this case β-scission involves a methyl group rather than a phenyl group[22] and furnishes benzaldehyde as the fragmentation carbonyl compound (which is further oxidized to benzoic acid),[19] probably because of the enhanced stability of the aromatic aldehyde compared to acetaldehyde (which would result from the departure of the phenyl group).[22] The lead tetraacetate fragmentation of the tertiary alcohol, α,α-dimethylbenzyl alcohol (in benzene), which cannot be converted to the corresponding carbonyl

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

[14] For further examples of the cyclization and fragmentation of alcohols (particularly in the steroid field) by means of lead tetraacetate, see Ref. 9 and R. Criegee, *Oxidations with Lead Tetraacetate*, in *Oxidations in Organic Chemistry* (edited by K. Wiberg) Part A; pp. 277–366. Academic Press, New York (1965), and Refs therein.

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

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

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

[18] R. Criegee, *Angew. Chem.* **70**, 173 (1958).

[19] Autooxidation of aldehydes to acids in the course of the reaction between lead tetraacetate and primary aliphatic alcohols has been observed previously.[4,15]

[20] The lead tetraacetate oxidation to the corresponding carbonyl compounds followed by α-acetoxylation was reported in the case of various primary and secondary alcohols.[4,15,21]

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

[22] The loss of an alkyl (Me) group rather than a Ph group was also observed in the β-cleavage of alkoxy radicals generated by thermolytic decomposition of t-dialkyl peroxides,[23] metal reductions of t-alkyl hydroperoxides[23] and photodecomposition of t-alkyl hypochlorites.[24]

[23] J. K. Kochi, *J. Am. Chem. Soc.* **84**, 1193 (1962).

[24] C. Walling and A. Padwa, *J. Am. Chem. Soc.* **85**, 1593 (1963).

Table 1. Product distribution in the reaction of lead tetraacetate with benzyl alcohol and α-substituted benzyl alcohols

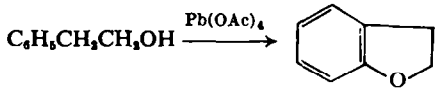
Alcohol $C_6H_5—C(R)(R')—OH$	Solvent (Bz = benzene, Py = pyridine)	Products (yields in %)		
		Oxidation	Fragmentation	Acetate of starting alcohol
Benzyl[a] R = R′ = H	Bz[b]	Benzaldehyde 51 Benzoic acid 18	—	11·5[c]
	Bz–Py (4*n*)[d]	Benzaldehyde 62·5 Benzoic acid 8	—	[e]
	Bz–Py (1:1)[f]	Benzaldehyde 70 Benzoic acid 3	—	[e]
Benzhydrol R = H, R′ = C_6H_5	Bz[b]	Benzophenone 80	—	7·5[g]
	Bz–Py (4*n*)[d]	Benzophenone 87	—	2·5[g]
α-Methylbenzyl R = H, R′ = CH_3	Bz[b]	Acetophenone 50 ω-Acetoxy-acetophenone 5	Benzoic acid 7·5	10[h]
	Bz–Py (4*n*)[d]	Acetophenone 65 ω-Acetoxy-acetophenone 1	—	3[h]
α,α-Dimethylbenzyl	Bz[b]	—	Acetophenone 3 ω-Acetoxy-acetophenone 17·5	8·5[i]
R = R′ = CH_3	Bz–Py (4*n*)[d]	—	Acetophenone 19·5 ω-Acetoxy-acetophenone 1·5	6·5[j]

[a] For this oxidation see also R. Criegee, L. Kraft and B. Rank, *Liebigs Ann.* **507**, 159 (1933), and E. Baer, *J. Am. Chem. Soc.* **62**, 1597 (1940). [b] One molar equivalent (with respect to lead tetraacetate) of anhydrous calcium carbonate was usually added to the reaction mixture. [c] In addition, 6% of benzyl alcohol and 5% of benzyl benzoate were also isolated. [d] Molar ratio of pyridine to lead tetraacetate = 4:1. [e] Not investigated. [f] Large excess of pyridine (Experimental). [g] About 5–7% of benzhydrol was recovered unchanged. [h] About 7·5–10% of starting alcohol was recovered unchanged. [i] In addition, 2% of isopropenylbenzene and 55% of unreacted starting alcohol were isolated from the reaction mixture. [j] More than 47% of α,α-dimethylbenzyl alcohol was recovered after the reaction.

derivative, also proceeds by loss of a methyl group[22] to give acetophenone (and its further acetoxylation product);[20] the amount of β-scission observed in this case (Table 1) is, however, larger than for α-methylbenzyl alcohol, a plausible explanation for this difference being that two of the factors influencing the fragmentation process—stability of the fragmentation carbonyl compound and relief of steric compression—are more favourable in the β-cleavage reaction of the tertiary α,α-dimethylbenzyl alcohol than in that of the secondary α-methylbenzyl alcohol. The reaction of α,α-dimethylbenzyl alcohol with lead tetraacetate in boiling benzene (until disappearance of tetravalent lead) was very slow and the amount of recovered alcohol was large (over 55%), probably, in part, because for steric reasons the equilibrium of the reversible

alcoholysis reaction (*a* in Scheme 1) is shifted to the left, thus retarding the initial formation of alkoxy–lead acetate (II); as a consequence, lead tetraacetate is consumed only slowly in the main reactions and is largely used in other, side-reactions (such as acetoxylation of the fragmentation ketone acetophenone, formation of acetic anhydride,[15] reaction with solvent,[15] etc.). The small amount of "dehydration" product of the starting alcohol, i.e. isopropenylbenzene (α-methylstyrene), is consistent with previously obtained information on the lead tetraacetate reactions of alcohols which proceed only slowly to completion.[12,15] In the presence of pyridine, the lead tetraacetate reaction of α,α-dimethylbenzyl alcohol was considerably faster, but the amount of fragmentation was not noticeably changed (Table 1).[25] This indicates that when oxidation of the starting alcohol to the corresponding carbonyl compound (reaction *b*, Scheme 1) is not possible (as in the case of tertiary alcohols), processes taking formally place through the transition state IV (Scheme 1), i.e. cyclization (*dd'*) and particularly fragmentation (*ee'*), occur in considerable amount even in polar (and basic) media,[26] naturally under the condition that other determining factors are also favourable for these reactions[4,9] (see also below the lead tetraacetate reaction of 1,1-dimethyl-2-phenylethanol).

The lead tetraacetate reactions of 2-phenylethanol (XIV, Scheme 3) and its disubstituted derivative, 1,1-dimethyl-2-phenylethanol (XXII, Scheme 4), in boiling benzene (+ calcium carbonate), proceed in considerable part by the fragmentation process *cee'* (Scheme 1), to produce in both cases, as one of the β-cleavage products,



+ C_6H_5CHO + C_6H_5COOH +

	XIV	XV	XVI	XVII
Solvent[a]	Bz (at 80°)	0·5%	5%	2%
	Bz—Py(4*n*) (at 80°)	0·3%	2%	—
	Py (at 80°)	—	2%	—
	Py (at 17°)	—	4%	—

+ $C_6H_5CH_2OAc$ + $C_6H_5CH_2CHO$ + $C_6H_5CH_2CH_2OH$ + $C_6H_5CH_2CH_2OAc$ + $C_6H_5CHCHR_1$ (OR$_2$)

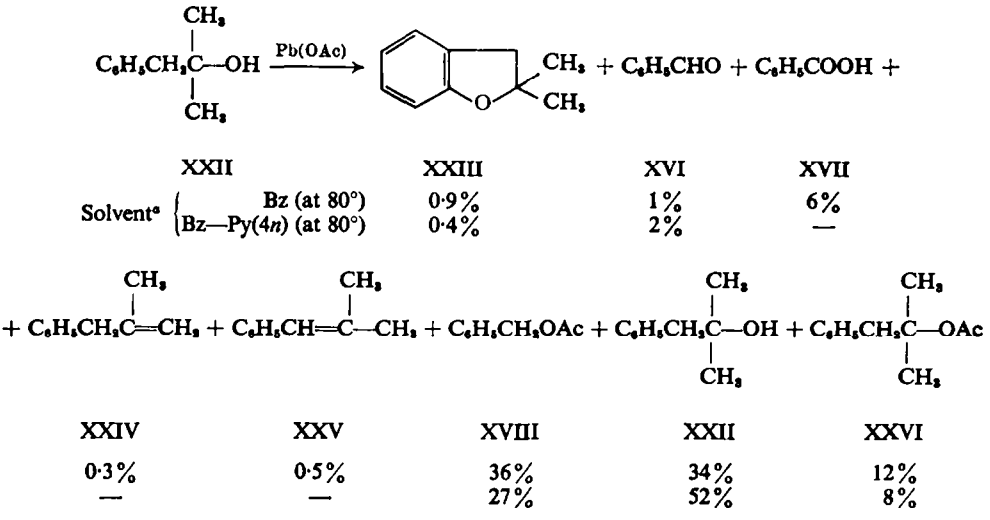
XVIII	XIX	XIV	XX	XXI
18%	—	10%	42%	(a) R_1 = HOH
21%	5%	11·5%	21%	or
19%	6·5%	17%	9%	HOAc
11%	16%	18%	10%	(b) R_1 = 0

Scheme 3

[a] See remarks *b* and *d* in Table 1 (and Experimental)

[25] The only difference being that in the presence of pyridine (fast reaction) the yield of primarily formed acetophenone was considerably higher and that of subsequently produced ω-acetoxyacetophenone considerably lower, compared to the respective yields of the same products obtained when benzene alone (or benzene + calcium carbonate) was used as solvent (slow reaction).

[26] Usually, in the lead tetraacetate reactions of primary and secondary alcohols, by increasing the proportion of base in the solvent system benzene–pyridine, the yields of cyclic ether formation (*cdd'*, Scheme 1) and fragmentation (*cee'*, Scheme 1) decrease, whereas the yield of oxidation to the corresponding carbonyl compounds (*b*, Scheme 1) increases.[5,10]



Scheme 4

[a] See remarks *b* and *d* in Table 1 (and Experimental)

benzyl acetate (XVIII); this may be accounted for by the resonance stabilization of the initially formed benzyl radical[9,23,24] and/or benzyl cation.[4] The tertiary 1,1-dimethyl-2-phenylethanol (XXII, Scheme 4) undergoes fragmentation to a larger extent than the primary 2-phenylethanol (XIV, Scheme 3), as evident from the respective yields of benzyl acetate (XVIII) given in Schemes 3 and 4, presumably as the result of the enhanced stability of acetone, which is the fragmentation carbonyl compound of the tertiary alcohol XXII (Scheme 4), compared to formaldehyde, which represents the fragmentation carbonyl component of the primary alcohol XIV (Scheme 3). The tendency toward fragmentation *via* benzyl radical or/and benzyl cation formation is so strong, that even in polar and basic solvent systems (benzene + pyridine at 80°, pyridine alone at 80° or room temperature) these two alcohols (XIV and XXII) afford benzyl acetate (XVIII) in an amount comparable to or only slightly lower than that obtained in the nonpolar solvent benzene[26] (Schemes 3 and 4). On the other hand, under these conditions, the yield of phenylacetaldehyde (XIX, Scheme 3), which is produced from 2-phenylethanol (XIV) by the oxidation reaction (*b*, Scheme 1), was lower than is usual in such cases. This may be due to the fact that even in the presence of pyridine the oxidation reaction is suppressed in favour of fragmentation and/or that the initially formed phenylacetaldehyde (XIX) is further acetoxylated by lead tetraacetate in the course of the reaction to furnish the acetate of phenylglycolaldehyde (XXIb, R_2 = Ac; Scheme 3) (see below).[27] Benzaldehyde (XVI), which was isolated from the lead tetraacetate reactions of both alcohols XIV and XXII in a yield ranging up to about 7% (Schemes 3 and 4) (taking into account also benzoic acid (XVII) which is produced by further oxidation of benzaldehyde[19]),

[27] It is well known that a C—H bond adjacent to an aromatic ring is activated toward lead tetraacetate and usually undergoes substitution by an acetoxy group, in acetic acid or benzene solution (see Ref. 14*b*, pp. 312–316).

represents formally also a β-cleavage product of the starting alcohols, but cannot arise from the fragmentation process according to path *cee'* (Scheme 1).[28] However, it might be formed by further lead tetraacetate α-acetoxylation of the primarily produced benzyl acetate (XVIII),[29,30] followed by hydrolysis of the resulting α,α-diacetoxytoluene,[31] and/or by lead tetraacetate acetoxylation of the starting alcohols (XIV and XXII) or their acetates (XX and XXVI) (and by acetoxylation of phenylacetaldehyde XIX in the reaction of 2-phenylethanol XIV) on the methylene group adjacent to the benzene ring,[27] followed by hydrolysis and usual lead tetraacetate 1,2-diol cleavage.[32] Moon and Lodge,[29] who also treated 2-phenylethanol (XIV) with lead tetraacetate and obtained (using benzene as solvent) as reaction products benzaldehyde (XVI), benzyl acetate (XVIII), unchanged starting alcohol and 2-phenylethyl acetate (XX), have reported that benzyl acetate upon oxidation with lead tetraacetate in refluxing benzene was converted in low yield (2%) to benzaldehyde; on the other hand, in the present work, it was found that the high-boiling fraction of the reaction mixture obtained from the lead tetraacetate reaction of 2-phenylethanol (XIV, Scheme 3), upon acid hydrolysis and lead tetraacetate treatment in the cold, gave some benzaldehyde, this result suggesting the presence of 2-phenyl-1,2-ethanediol (XXIa, $R_2 = H$; Scheme 3) and/or phenylglycolaldehyde (XXIb, $R_2 = H$; Scheme 3).[33] Thus, it appears that both above proposed pathways leading to the cleavage product benzaldehyde (XVI) are operative in the case of the lead tetraacetate reaction of 2-phenylethanol (XIV, Scheme 3) and 1,1-dimethyl-2-phenylethanol (XXII, Scheme 4).[33] Similarly to the tertiary alcohol α,α-dimethylbenzyl alcohol (Table 1), 1,1-dimethyl-2-phenylethanol (XXII) gave also in low yields (Scheme 4) the corresponding "dehydration" products (when benzene was used as solvent), i.e. 2-methyl-3-phenyl-1-propene (XXIV) and 2-methyl-1-phenyl-1-propene (XXV),[12,15] while a considerable amount of unreacted starting alcohol was recovered from the reaction mixture.

In contrast to 2-phenylethanol (XIV, Scheme 3) and 1,1-dimethyl-2-phenylethanol (XXII, Scheme 4), which with lead tetraacetate in boiling benzene gave only very low yields of the corresponding 5-membered cyclic ethers, i.e. 2,3-dihydrobenzofuran (coumaran) (XV, Scheme 3) and 2,2-dimethyl-2,3-dihydrobenzofuran (2,2-dimethylcoumaran) (XXIII, Scheme 4), respectively, 3-phenyl-1-propanol (XXVII, Scheme 5) undergoes (in boiling benzene) more readily cyclization and affords 3,4-dihydro-2*H*-1-benzopyran (chroman) (XXVIII) in about 13% yield. As expected, when the lead tetraacetate reaction of 3-phenyl-1-propanol was performed in benzene-pyridine,

[28] As shown by Kochi,[23] and Walling and Padwa,[24] tertiary α,α-dialkylbenzyloxy radicals undergo β-scission only by loss of the benzyl group.

[29] S. Moon and J. M. Lodge, *J. Org. Chem.* **29**, 3453 (1964).

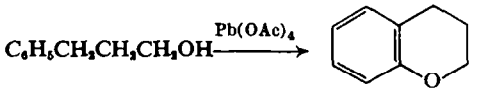
[30] W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.* **82**, 5342 (1960), have shown that lead tetraacetate (in boiling acetic acid) acetoxylates in the α-position the alcoholic component of aliphatic esters.

[31] During the oxidation reaction or in the course of the working up procedure.

[32] *Cf.* C. A. Bunton, *Glycol Cleavage and Related Reactions*, in *Oxidations in Organic Chemistry* (Edited by K. Wiberg) Part A; pp. 398–405. Academic Press, New York (1965).

[33] Naturally, in the lead tetraacetate reaction of the tertiary alcohol 1,1-dimethyl-2-phenylethanol (XXII, Scheme 4), the formation of 1,2-hydroxycarbonyl acetate compound of type XXIb (Scheme 3) is not possible, and fragmentation to benzaldehyde (XVI) by this sequence can only take place through a 1,2-diol acetate corresponding to XXIa (on Scheme 3).

cyclic ether formation (XXVIII) was suppressed in favour of the oxidation process leading to 3-phenylpropionaldehyde (XXIX) (which is partly further converted to the corresponding acid XXX[19]).[26,34]



	XXVII	XXVIII	XXIX
Solvent[a]	Bz (at 80°)	12·5%	2·5%
	Bz—Py(4*n*) (at 80°)	3%	27%

	XXX	XXXI	XXXII
+ $C_6H_5CH_2CH_2COOH$ + $C_6H_5CH_4CH_4CH_2OH$ + $C_6H_5CH_2CH_2CH_2OAc$	7%	11%	41%
	3%	15·5%	15%

Scheme 5

[a] See remarks *b* and *d* in Table 1 (and Experimental)

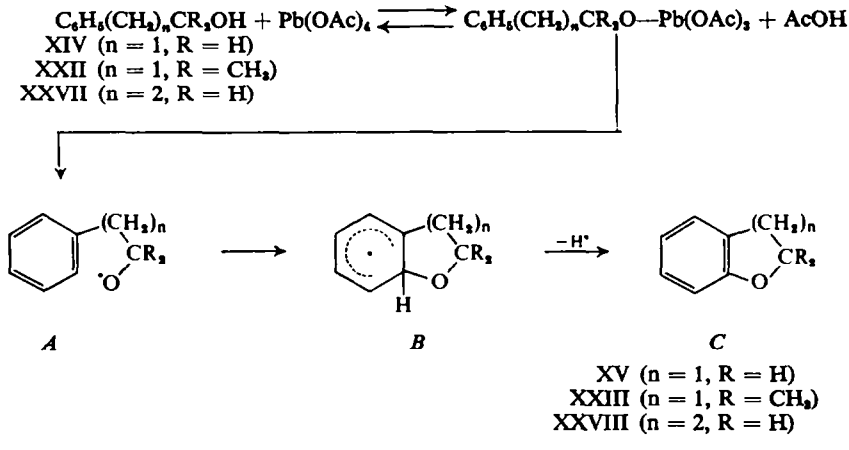
The considerably higher yield of 6-membered chroman (XXVIII, Scheme 5) compared to the yields of the 5-membered coumarans XV (Scheme 3) and XXIII (Scheme 4), is contrary to the results obtained with simple aliphatic alcohols (I, Schemes 1 and 2), which, upon treatment with lead tetraacetate in refluxing benzene, afford as major cyclization products the corresponding tetrahydrofuran ethers (VI, Schemes 1 and 2) and only small amounts of isomeric 6-membered tetrahydropyrans (VII, Schemes 1 and 2).[3–8] If the sequence in Scheme 2, which involves homolytic hydrogen transfer from carbon to oxygen, were operative for the above described lead tetraacetate cyclizations of ω-phenyl-1-alkanols, 2-phenylethanols would be expected to cyclize at least as readily as 3-phenyl-1-propanol, since tetrahydrofuran formation (VI), proceeding through a cyclic 6-membered transition state XI (n = 1), is perferred to tetrahydropyran formation (VII), which requires a 7-membered cyclic transition structure XI (n = 2).[4,12] Therefore, it appears that the mechanism in Scheme 2 cannot be valid in these cases, and the formation of coumarans XV (Scheme 3) and XXIII (Scheme 4) and of chroman XXVIII (Scheme 5) should be probably rationalized as a radical intramolecular *o*-alkoxylation (Scheme 6), proceeding *via* a σ-complex-type intermediate or transition state *B*,[7,35,36] since according to such a sequence, the formation of a 6-membered cyclic ether *C* (n = 2), involving a 6-membered intermediate structure *B* (n = 2), would be favoured over the formation of a 5-membered cyclic ether *C* (n = 1), which takes place through a sterically more strained 5-membered intermediate structure *B* (n = 1).[37]

[34] In this and other lead tetraacetate reactions part of the produced aldehyde is usually present in the form of its acetal with the starting alcohol.[4,12,15]

[35] Similarly to free-radical intramolecular *o*-acylation; *cf.* W. Urry, D. J. Trecker and H. D. Hartzler, *J. Org. Chem.* **29**, 1663 (1964).

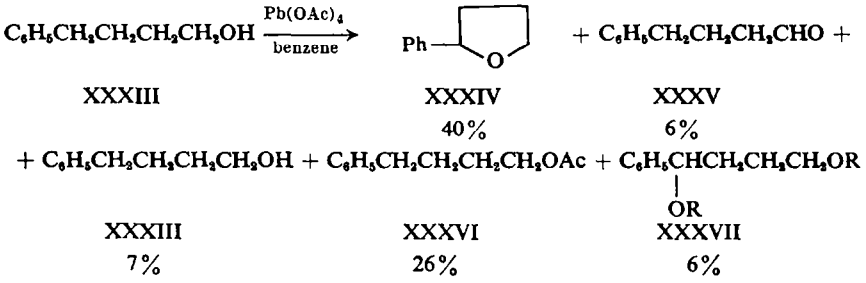
[36] Step $B \rightarrow C$ in Scheme 6 might take place through an intermediate cationic species corresponding to *B*.

[37] The somewhat higher yield of 2,2-dimethylcoumaran XXIII (Scheme 4) compared to the yield of the unsubstituted coumaran XV (Scheme 3), might be the result of the *gem*-dimethyl effect,[38] which facilitates cyclization of the α,α-disubstituted alkoxy radical ($A \rightarrow B$, R = CH_3, n = 1; Scheme 6) by decreasing the free energy of ring closure (i.e. by reducing the internal angle C—C—O, decreasing the enthalpy and increasing the entropy of cyclization).

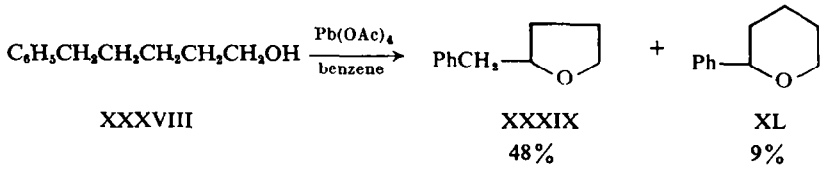


Scheme 6

The reaction of 4-phenyl-1-butanol (XXXIII) with lead tetraacetate in refluxing benzene afforded, as expected, predominantly the corresponding cyclization product, i.e. 2-phenyltetrahydrofuran (XXXIV). That attack of the reagent (by acetoxylation) takes place also on the methylene group adjacent to the benzene ring was demonstrated by isolating, upon acid hydrolysis of the high-boiling residue, some 1-phenyl-1,4-butanediol (XXXVII, R = H).



5-Phenyl-1-pentanol (XXXVIII) reacted readily with lead tetraacetate (in boiling benzene) to give as major product (in 48% yield) 2-benzyltetrahydrofuran (XXXIX), whereas the corresponding isomeric 6-membered 2-phenyltetrahydropyran (XL) was isolated in 9% yield. Although here the amount of tetrahydropyran ether (XL) is larger than in the case of simple aliphatic alcohols,[3-8] it is considerably less compared to the yield of 6-membered cyclic ethers obtained in the lead tetraacetate reaction of



[3-8] *Cf.* E. L. Eliel, *Stereochemistry of Carbon Compounds* pp. 197–198. McGraw-Hill, New York (1962), and Refs therein; E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* pp. 191–192. Interscience, New York (1965), and Refs therein.

some acyclic hydroxy ethers,[7] indicating that an ether oxygen is more efficient than a Ph group in activating an adjacent ε-C—H bond and thus facilitating 1,6-hydrogen transfer in the corresponding alkoxy radical (V, n = 2; Schemes 1 and 2).[39]

The acetate esters of the starting alcohols were formed, usually in considerable amount, in all lead tetraacetate reactions of alcohols, while the corresponding formate esters were produced (in lower yield) particularly in reactions which proceed slowly to completion. Possible pathways leading to these products have been discussed previously.[6,8,15,29,40]

EXPERIMENTAL[41]

B.ps and m.ps are uncorrected. Analytical and preparative gas chromatography was run on a Perkin–Elmer instrument, Model 116-E, equipped with a thermistor detector; the columns (2 m × 4 mm, 4 m × 6 mm, 7 m × 8 mm) consisted of Apiezon L adsorbed on Celite or Chromosorb P (30–40%); the temperature of the columns, the sensitivity of the detector and the press and flow rate of the carrier gas (dry H_2) were adjusted according to the fractions which were analyzed. IR spectra were recorded on a Perkin–Elmer Infracord, Model 137. For fractional distillations well isolated, modified semimicro Vigreux and Widmer columns were used.

The preparation of lead tetraacetate, drying of the reagents and the lead tetraacetate oxidations in benzene, benzene–pyridine or pyridine alone were carried out as described previously.[42,43] If not stated otherwise, the oxidations were performed under reflux at 80° (temp of the reaction mixture), using (a) for reactions in *benzene*–$CaCO_3$: *n* moles of alcohol, (*n* + 2–5% excess) moles $Pb(OAc)_4$, (*n* + 5% excess) moles anh. $CaCO_3$ and *n*·1000–*n*·1500 ml dry benzene; (b) for reactions in *benzene–pyridine* (4n): *n* moles of alcohol, (*n* + 2–5% excess) moles $Pb(OAc)_4$, 4·*n* moles dry pyridine and *n*·1000–*n*·1500 ml dry benzene; (c) for reactions in *benzene–pyridine* (1:1): *n* moles of alcohol, (*n* + 2–5% excess) moles $Pb(OAc)_4$, *n*·600 ml dry pyridine and *n*·600 ml dry benzene; (d) for reactions in *pyridine* (at 80° or room temp): the same amounts of alcohol and $Pb(OAc)_4$ as above and *n*·1200 ml dry pyridine.

The neutral products from the benzene–ether extract (neutral part), upon separation by distillation and gas chromatography, were identified and characterized on the basis of their physical properties (b.ps, refractive indices, retention times, IR spectra, m.ps of solid derivatives), which were usually compared with those of authentic compounds synthesized by independent routes (acetates of the starting alcohols, fragmentation acetates, carbonyl compounds corresponding to the starting alcohols and fragmentation carbonyl compounds were prepared, for comparison purposes, according to usual procedures). Carbonyl compounds were characterized (and if necessary quantitatively determined) by conversion to the corresponding 2,4-dinitrophenylhydrazones.[44] The acid components were isolated from the $NaHCO_3$-washings (acid part), upon acidification and ether extraction.

Benzyl alcohol

(a) *In benzene*–$CaCO_3$. The reaction with 0·02 moles (2·16 g) benzyl alcohol was completed after refluxing for 15–20 min, and afforded, from the neutral part, 50·6% benzaldehyde,[45] 6·2% unchanged benzyl alcohol, 11·5% benzyl acetate[45] and 5·2% benzyl benzoate,[45,46] From the acid part benzoic acid[45] was obtained in 18·4% yield.

[39] The activating influence of an ether function (and a phenyl group) on 1,6-ring closure of hydroxy-ethers by means of lead tetraacetate is discussed in Ref. 7.

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

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

[42] For oxidations in benzene see Ref. 4.

[43] For oxidations in benzene–pyridine and pyridine alone see Refs. 12, 15, 16.

[44] Houben-Weyl, *Methoden der organischen Chemie* (Edited by E. Müller) 4th Edition, Vol. II, p. 457. Georg Thieme Verlag, Stuttgart (1953).

[45] *Cf.* A. I. Vogel, *Practical Organic Chemistry* (Third Edition). Longmans Green, London (1961); R. L. Shriner, R. C. Fuson and C. Y. Curtin, *The Systematic Identification of Organic Compounds* (5th Edition). J. Wiley, New York (1964).

[46] T. J. Thompson and G. J. Leuck, *J. Am. Chem. Soc.* **44**, 2894 (1922).

(b) *In benzene–pyridine* (4n). This oxidation (reaction time 12 min), with 0·02 moles benzyl alcohol, gave 62·5% benzaldehyde and 8·2% benzoic acid.

(c) *In benzene–pyridine* (1:1). From this oxidation (0·02 moles benzyl alcohol; reaction time 7 min), benzaldehyde and benzoic acid were obtained in 70·3% and 3% yield, respectively.

Benzhydrol

(a) *In benzene–*$CaCO_3$. The reaction with 0·05 moles (9·2 g) of benzhydrol was completed in 5·5 hr. From the neutral part distillate (7·3 g), b.p. 170–172° at 17–19 mm, and from the residue of the distillation (1·25 g), benzophenone was isolated (in the form of its 2,4-dinitrophenylhydrazone,[44] m.p. and mixed m.p. 237–238°[45]) in a total yield of 80·2% (7·25 g). According to the saponification value of the distillate and residue, benzhydryl acetate was present in 7·5% yield, while 5% of benzhydrol was recovered unchanged.

(b) *In benzene–pyridine* (4n). This reaction, with 0·05 moles (9·2 g) of benzhydrol, lasted 60 min. The distillate (7·0 g), b.p. 170–172° at 18–19 mm, m.p. 49°, consisted of pure benzophenone[45] (IR spectrum identical with that of an authentic product); a further 0·9 g of the same ketone was also isolated (as the 2,4-dinitrophenylhydrazone)[44] from the distillation residue (1·6 g), bringing the total yield of benzophenone to 86·8% (7·9 g). According to the saponification value of the distillation residue, benzhydryl acetate was present in about 2·5% yield, while 6·5% of benzhydrol remained unchanged.

α-Methylbenzyl alcohol

(a) *In benzene–*$CaCO_3$. The oxidation of 0·1 mole (12·2 g) α-methylbenzyl alcohol was completed in 2 hr. From the neutral part distillate (8·5 g), b.p. 89–92° at 17 mm, 50% (6 g) of acetophenone was isolated by quantitative conversion[44] to its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238–239.[45] From the distillation residue, in the same way,[44] there was obtained 5·2% (0·93 g) of ω-acetoxyacetophenone in the form of its 2,4-*dinitrophenylhydrazone*, m.p. 171–174°, undepressed by the presence of the same derivative of authentic ω-acetoxyacetophenone (see below). In addition, by gas-chromatographic separation of the distillate and residue, unchanged α-methylbenzyl alcohol (7·5% yield) and its acetate[47] (10·3% yield) were identified on the basis of their IR spectra.

From the acid part, by acidification of the $NaHCO_3$ extract, benzoic acid, m.p. 121°,[45] was isolated in 7·5% yield (0·92 g).

(b) *In benzene–pyridine* (4n). From this oxidation (0·1 mole alcohol; reaction time 20 min), in the same way as above, the following products were obtained: 65% (7·8 g) acetophenone (as its 2,4-dinitrophenylhydrazone), 0·7% (0·12 g) ω-acetoxyacetophenone (in the form of its 2,4-*dinitrophenylhydrazone*), 3·4% (0·56 g) α-methylbenzyl alcohol acetate and about 10% of unchanged starting alcohol.

ω-*Acetoxyacetophenone*. This product was prepared by the usual oxidation of acetophenone (12 g, 0·1 mole) with $Pb(OAc)_4$ (44·3 g, 0·1 mole) in 80 ml benzene. The reaction was completed after stirring and heating to reflux for 9·5 hr. The usual working up procedure afforded 8 g (49%) of ω-acetoxyacetophenone, b.p. 110–114° at 2 mm.[48] Its 2,4-*dinitrophenylhydrazone*, upon crystallizafrom benzene, melted at 173–174° (Found: N, 15·8 and 15·6. $C_{16}H_{14}O_6N_4$ requires: N, 15·6%.)

α,α-Dimethylbenzyl alcohol

(a) *In benzene–*$CaCO_3$. The reaction with 0·1 mole (13·6 g) of α,α-dimethylbenzyl alcohol was completed after refluxing for 55 hr. From the neutral part distillate (10·4 g), b.p. 95–97° at 18–19 mm, 2·9% (0·35 g) of acetophenone was isolated in the form of its 2,4-dinitrophenylhydrazone,[44] m.p. 237–238°.[45] By the same method,[44] 17·5% (3·12 g) of ω-acetoxyacetophenone, in the form of its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 171–173° (see α-methylbenzyl alcohol), was obtained from the distillation residue (3·6 g). By gas-chromatographic separation (and saponification value determination) of the distillate and residue, it was found that the reaction mixture contained also 2·1% of isopropenylbenzene (α-methylstyrene), identical with a commercial product (Fluka, b.p. 161–163°, n_D^{20} 1·5372),[49] 55% of unchanged starting alcohol, and 8·5% of the corresponding α,α-*dimethylbenzyl alcohol acetate* (see below).

(b) *In benzene–pyridine* (4n). The products of this oxidation (0·1 mole α,α-dimethylbenzy

[47] *Cf.* J. Marshall, *J. Chem. Soc.* **107**, 523 (1915) (b.p. 222° or 105–108° at 15 mm).

[48] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.* 4426 (1955).

[49] See, for example, G. B. Bachman and H. M. Hellman, *J. Am. Chem. Soc.* **70**, 1772 (1948).

alcohol; reaction time 25 min) were determined and identified as above (a), and consisted of 19·5% (2·34 g) of acetophenone, 1·5% (0·26 g) of ω-acetoxyacetophenone, 47·3% of unchanged α,α-dimethylbenzyl alcohol and 6·5% of its *acetate*.

α,α-Dimethylbenzyl alcohol acetate. Acetyl chloride (9·4 g, 0·12 moles) was slowly added to a soln of 13·6 g (0·10 moles) α,α-dimethylbenzyl alcohol and 15·7 g (0·13 moles) freshly distilled N,N-dimethylaniline in 55 ml anh. diethyl ether, at such a rate as to maintain gentle reflux. After refluxing for another 2·5 hr, the mixture was cooled to room temp, treated with water (55 ml) to dissolve the ppt, and the layers were then separated. The aqueous soln was extracted with ether, the combined ethereal extracts and original ethereal layer washed with 10% H_2SO_4aq and H_2O, and dried ($MgSO_4$). The twice distilled product was chromatographed on neutral Al_2O_3 (activity II) and afforded, upon elution with petroleum ether (b.p. 40–60°), pure *α,α-dimethylbenzyl alcohol acetate* in 44% yield (7·8 g), b.p. 93–94° at 10 mm, n_D^{20} 1·4970. (Found: C, 74·2; H, 7·9. $C_{11}H_{14}O_2$ requires: C, 74·1; H, 7·9%.)

2-Phenylethanol

(a) *In benzene–*$CaCO_3$. The oxidation of 12·2 g (0·1 mole) 2-phenylethanol was completed in 10 hr. The products from the neutral part were fractionated (over a temp range of 68–108° at 14 mm and 100–120° at 6 mm), and each fraction was subjected to preparative gas chromatography (temp 150°, flow rate 120 ml/min). The following products were separated and characterized: 2,3-dihydrobenzofuran (coumaran) in 0·52% yield (identical with a synthetic product,[50] b.p. 79–81° at 16 mm, n_D^{20} 1·5509; picrate, m.p. 75–76° [50–52]), benzaldehyde[45] in 4·7% yield, unchanged 2-phenylethanol in 10·1% yield, 2-phenylethyl formate[53] in 5·4% yield, benzyl acetate[45] in 18·3% yield and 2-phenylethyl acetate[45] in 42% yield. Distillation residue, 1·9 g.

From the acid part, upon acidification of the $NaHCO_3$ washings, benzoic acid[45] was obtained in 1·7% yield.

(b) *In benzene–pyridine* (4n). This oxidation (0·1 mole 2-phenylethanol; reaction time 50–60 min) afforded 0·3% of 2,3-dihydrobenzofuran, 2·3% benzaldehyde, 5·1% phenylacetaldehyde (in agreement with the synthetic aldehyde,[54] b.p. 87–89° at 18 mm), 11·5% unchanged 2-phenylethanol, 0·6% 2-phenylethyl formate,[53] 21·3% benzyl acetate and 21% 2-phenylethyl acetate. Distillation residue, 2·9 g.

(d) *In pyridine at* 80°. 2-Phenylethanol (6·1 g, 0·05 moles) was oxidized in 62 ml dry pyridine at 80° (reaction time 5 min). Obtained: 2% benzaldehyde, 6·5% phenylacetaldehyde, 17·2% unchanged 2-phenylethanol, 19·3% benzyl acetate and 8·8% 2-phenylethyl acetate. Distillation residue, about 2 g.

(d′) *In pyridine at room temperature.* The same oxidation was repeated, but 2-phenylethanol (0·05 moles) was added dropwise, with stirring, to an ice-cooled soln of 0·05 moles (+2% excess) $Pb(OAc)_4$ in dry pyridine (62 ml), so that the temp of the reaction mixture did not exceed 15–17° (reaction time 1·5 hr). Obtained: 3·7% benzaldehyde, 15·8% phenylacetaldehyde[54] (2,4-dinitrophenylhydrazone,[45] m.p. and mixed m.p. 120–121°), 18·2% unchanged starting alcohol, 11·3% benzyl acetate and 10% 2-phenylethyl acetate. Distillation residue, about 2 g.

The half-solid distillation residues from all the above described oxidations, when hydrolysed with a 20% HCl in MeOH–H_2O (1:1), afforded a mixture in which benzoic acid, 2-phenylethanol, benzaldehyde and phenylacetaldehyde were detected, thus indicating the presence (in the original reaction mixture) of higher esters and acetals. In addition, the same hydrolysis mixture afforded some 1-phenyl-1,2-ethanediol, m.p. 64–66°, which was identical with a synthetic product, m.p. 66–68°,[55] prepared by LAH reduction of mandelic acid.[56]

[50] G. Chateluz, *Ann. Chim. Paris* (12) **4**, 505 (1949); G. Baddeley, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.* 2455 (1956).

[51] J. I. Jones and A. S. Lindsey, *J. Chem. Soc.* 1836 (1950); G. Wittig and G. Kolb, *Chem. Ber.* **93**, 1469 (1960).

[52] G. Baddeley and M. A. Vickars, *J. Chem. Soc.* 4665 (1958).

[53] According to its IR spectrum.

[54] K. W. Rosenmund and F. Zetzsche, *Ber. Dtsch. Chem. Ges.* **54**, 425 (1921).

[55] Th. Zincke, *Liebigs Ann.* **216**, 294 (1882); H. Adkins and H. R. Billica, *J. Am. Chem. Soc.* **70**, 3121 (1948).

[56] See, for example, S. P. Bakshi and E. E. Turner, *J. Chem. Soc.* 168 (1961).

1,1-*Dimethyl-2-phenylethanol*

(a) *In benzene–*$CaCO_3$. The reaction with 0·1 mole (15 g) of 1,1-dimethyl-2-phenylethanol was completed after refluxing for 27 hr. Gas-chromatographic separation (at 160°, flow rate 275 ml/min) of the neutral part distillate (first fraction (10·2 g), b.p. 80–97° at 18 mm; second fraction (0·5 g), b.p. 100–107° at 18 mm) and of the residue (0·5 g) afforded 0·3% 2-methyl-3-phenyl-1-propene (in agreement with an authentic sample,[57] b.p. 66–68° at 18 mm, n_D^{20} 1·5077[57,58]), 0·5% 2-methyl-1-phenyl-1-propene (identical with the synthetic product,[57] b.p. 76–77° at 18 mm, n_D^{20} 1·5368[57,58]), 0·9% 2,2-dimethyl-2,3-dihydrobenzofuran (2,2-dimethylcoumaran) (which corresponds to the synthetic ether,[59] b.p. 81–82° at 18 mm, n_D^{20} 1·5183[51,58]), 1·2% benzaldehyde,[45] 35·7% benzyl acetate,[45] 33·8% unchanged starting alcohol and 11·7% 1,1-*dimethyl-2-phenylethanol acetate* (identical with an authentic acetate; see below).

From the acid part, by acidification of the $NaHCO_3$ washings, benzoic acid was isolated in 5·8% yield.

(b) *In benzene–pyridine* (4n). This oxidation (with 0·1 mole alcohol; reaction time 80 min), after preparative gas chromatography of the distillation fractions and residue (as described in (a)), afforded 0·4% 2,2-dimethyl-2,3-dihydrobenzofuran, 2·1% benzaldehyde, 26·6% benzyl acetate, 52·1% unchanged alcohol and 7·8% 1,1-*dimethyl-2-phenylethanol acetate*.

1,1-*Dimethyl-2-phenylethanol acetate*. This ester was prepared from the parent alcohol (7·5 g, 0·05 moles) as described for α,α-dimethylbenzyl alcohol acetate. Chromatography of the distilled product on neutral Al_2O_3 (activity II) and elution with pet. ether (b.p. 40–60°) afforded pure 1,1-*dimethyl-2-phenylethanol acetate* (3·9 g, 40·6%), b.p. 102–103° at 10 mm, n_D^{20} 1·4912. (Found: C, 75·1; H, 8·3. $C_{12}H_{16}O_2$ requires: C, 75·0; H, 8·4%.)

3-*Phenyl*-1-*propanol*

(a) *In benzene–*$CaCO_3$. The oxidation of 0·1 mole (13·6 g) 3-phenyl-1-propanol was completed after refluxing for 15·5 hr. Gas chromatography (at 170°, flow rate 275 ml/min) of the neutral part distillate (12 g), which consisted of 4 fractions boiling between 110° and 175° at 18 mm, afforded 12·5% 3,4-dihydro-2*H*-1-benzopyran (chroman) (which agrees in its properties with an authentic product,[50,60] b.p. 95–97° at 18 mm, n_D^{20} 1·5476), 2·5% 3-phenylpropionaldehyde (identical with a synthetic specimen,[61] b.p. 109–112° at 18 mm[61,62]), 2·5% 3-phenyl-1-propyl formate,[53] 11·3% recovered starting alcohol, 41·1% 3-phenyl-1-propyl acetate (corresponding to the acetate prepared directly from the starting alcohol[62]). Distillation residue, 1·5 g (not investigated).

From the acid part, upon acidification of the $NaHCO_3$ washings, 3-phenylpropionic acid, m.p. 48° (from H_2O),[45] was isolated in 7·4% yield (1·1 g). (Found: C, 71·7; H, 6·8. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%.)

(b) *In benzene–pyridine* (4n). This oxidation (0·1 mole alcohol; reaction time 60 min) was performed as above. Gas chromatography of the neutral part distillate (9·5 g) afforded 2·8% chroman, 26·7% of 3-phenylpropionaldehyde,[61,63] 0·9% 3-phenyl-1-propyl formate, 15·5% unchanged alcohol and 15·4% 3-phenyl-1-propyl acetate. A similar yield (24·2%) of 3-phenylpropionaldehyde was obtained by its quantitative precipitation[44] (from the distillate) in the form of 2,4-dinitrophenylhydrazone, m.p. 158° (from EtOH).[61,64] (Found: C, 57·6; H, 4·5; N, 17·6. Calc. for $C_{15}H_{14}N_4O_4$: C, 57·3; H, 4·5; N, 17·8%.) The distillation residue (2·5 g) was hydrolysed by refluxing for 2 hr with 40 ml 2N HClaq in 40 ml MeOH. Upon addition of 20 ml H_2O, MeOH and H_2O were removed by distillation until the volume of the remaining solution amounted to 15–20 ml. The distillate was neutralized with $NaHCO_3$aq and extracted with ether. This ether layer was dried and evaporated, and from the residue, by the 2,4-dinitrophenylhydrazine method,[44] 3-phenylpropionaldehyde was identified

[57] C. Rüchardt, *Chem. Ber.* **94**, 2599 (1961).
[58] W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.* **66**, 1438 (1944).
[59] Q. R. Bartz, R. F. Müller and R. Adams, *J. Am. Chem. Soc.* **57**, 371 (1935).
[60] R. E. Rindfusz, *J. Am. Chem. Soc.* **41**, 665 (1919); P. Maitte, *Ann. Chim. Paris* (12) **9**, 431 (1954); R. Huisgen, H. König and A. R. Lepley, *Chem. Ber.* **93**, 1496 (1960).
[61] M. Stiles and A. J. Sisti, *J. Org. Chem.* **25**, 1691 (1960).
[62] E. Fischer and E. Hoffa, *Ber. Dtsch. Chem. Ges.* **31**, 1992 (1898).
[63] L. Rügheimer, *Liebigs Ann.* **172**, 128 (1874).
[64] M. F. Ansell and M. E. Selleck, *J. Chem. Soc.* 1238 (1956).

in about 4% yield (based on total starting alcohol). The soln remaining upon distillation of MeOH and H_2O (15–20 ml) was treated with 20 ml 15% KOHaq and extracted with ether. Gas chromatography of this extract showed the presence of 3-phenyl-1-propanol in about 10% yield (based on total starting alcohol). These results indicate that the original distillation residue (2·5 g) contains probably some acetal of the starting alcohol with the corresponding aldehyde.

From the acid part, 3-phenylpropionic acid, m.p. 48° (H_2O),[45] was isolated in 2·6% yield.

4-Phenyl-1-butanol

This alcohol, b.p. 138–140° at 14 mm, n_D^{25} 1·5183,[65–67] was prepared in 66% yield by the usual LAH reduction of 4-phenylbutyric acid (commercial, Fluka).

(a) *In benzene–*$CaCO_3$. The $Pb(OAc)_4$ oxidation of 0·1 mole (15 g) alcohol was completed after refluxing for 60 min. By fractional distillation, the neutral part was separated into 4 fractions (total amount 11·5 g), boiling in the range 85–128° at 8 mm, and residue (2·3 g). Preparative gas chromatography of the distillate (at 205°, flow rate 300 ml/min) afforded 40·3% of 2-phenyltetrahydrofuran (identical with the authentic cyclic ether, b.p. 94–96° at 8 mm, n_D^{25} 1·5279,[67–69] prepared by cyclization[69] of 1-phenyl-1,4-butanediol), 6·2% of 4-phenylbutyraldehyde (corresponding to the authentic aldehyde,[70] semicarbazone, m.p. 105–106°), 6·8% of unchanged starting alcohol and 25·7% of 4-phenyl-1-butyl acetate (in agreement with a synthetic product, b.p. 130–132° at 14 mm, n_D^{23} 1·4958[71]).

Acid hydrolysis of the distillation residue (2·3 g), as described for 3-phenyl-1-propanol, afforded, after removal (under reduced press) of MeOH, H_2O and other distillable products, a solid material (1 g; 6% based on total starting alcohol), m.p. 66–67° (from benzene–hexane), which corresponds to 1-phenyl-1,4-butanediol, m.p. 67–68°,[69] prepared by LAH reduction of methyl β-benzoylpropionate.

5-Phenyl-1-pentanol

γ-Benzoylbutyric acid[72] was reduced with Zn–Hg in conc. HCl[73] to 5-phenylvaleric acid, m.p. 58–59°,[74] which, upon LAH reduction, afforded 5-phenyl-1-pentanol, b.p. 148–150° at 14 mm,[65,75] in 81% yield.

(a) *In benzene–*$CaCO_3$. The $Pb(OAc)_4$ oxidation of 0·1 mole (16·4 g) alcohol was completed after refluxing for 120 min. Preparative gas chromatography (at 180°, flow rate 300 ml/min) of the neutral part distillate (11 g), which consisted of 2 fractions boiling in the range 115–160° at 14 mm, and of the residue (4·2 g), afforded as major product, in 47·8% yield, 2-benzyltetrahydrofuran, n_D^{25} 1·5196 (lit.[75,76] n_D^{17} 1·5228, n_D^{11} 1·5242). (Found: C, 81·6; H, 8·8. Calc. for $C_{11}H_{14}O$: C, 81·4; H, 8·7%). The isomeric 6-membered cyclic ether, 2-phenyltetrahydropyran, was detected in 8·9% yield, and was identical with an authentic product, b.p. 115° at 14 mm, n_D^{25} 1·5248,[76–78] which was independently

[65] J. von Braun, *Ber. Dtsch. Chem. Ges.* **44,** 2867 (1912).
[66] G. M. Badger and R. W. L. Kimber, *J. Chem. Soc.* 2455 (1958).
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[68] H. Normant, *C.R. Acad. Sci. Paris* **226,** 1734 (1948).
[69] R. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.* **78,** 6079 (1956); see also V. G. Bukharov and T. E. Pozdnyakova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 135 (1961).
[70] J. von Braun, *Ber. Dtsch. Chem. Ges.* **67,** 218 (1934); M. H. Durand, *Bull. Soc. Chim. Fr.* 2396 (1961).
[71] R. Heck and S. Winstein, *J. Am. Chem. Soc.* **79,** 3105 (1957).
[72] L. F. Somerville and C. F. H. Allen, *Org. Syntheses*, Coll. Vol. **2,** 82 (1948).
[73] A. B. Hornfeldt and S. Gronowitz, *Arkiv Kemi* **21,** 239 (1963).
[74] *Cf.* A. Ali, R. D. Desai, R. F. Hunter and S. M. M. Muhammad, *J. Chem. Soc.* 1013 (1937); J. T. Plati, W. H. Strain and S. L. Warren, *J. Am. Chem. Soc.* **65,** 1273 (1943).
[75] R. Paul, *C.R. Acad. Sci. Paris* **202,** 1444 (1936); *Bull. Soc. Chim. Fr.* (5) **5,** 1053 (1938). See also F. F. Blicke and B. A. Brown, *J. Org. Chem.* **26,** 3685 (1961).
[76] R. Paul, *C.R. Acad. Sci. Paris* **206,** 1028 (1938); *Bull. Soc. Chim.Fr.* (5) **6,** 331 (1939).
[77] R. Paul, *C.R. Acad. Sci. Paris.* **198,** 1246 (1934); *Bull.Soc. Chim. Fr.* (5) **2,** 311 (1935); C. W. Smith, D. G. Norton and S. A. Ballard, *J. Am. Chem. Soc.* **73,** 5273 (1951); N. I. Shuikin, I. F. Belskii, R. A. Karakhanov, B. Kozma and M. Bartok, *Izv. Akad. Nauk SSSR, Ser. Khim.* 747 (1964).
[78] C. Crisan, *Ann. Chim. (Paris)* (13) **1,** 436 (1956).

prepared in 60·4% yield by H_3PO_4-dehydration[78] of 1-phenyl-1,5-pentanediol, b.p. 170° at 5 mm (this diol being obtained in 72·2% yield by LAH reduction of ethyl γ-benzoylbutyrate, b.p. 182–184° at 14 mm[79]). In addition, the oxidation mixture was shown to contain 20% of unreacted 5-phenyl-1-pentanol and 8·5% of its acetate.[65]

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