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THE REACTION OF LEAD TETRAACETATE WITH ALICYCLIC ALCOHOLS—II[1,*]

PRIMARY ALCOHOLS CONTAINING A SIX-MEMBERED RING ATTACHED TO THE CARBINOL CARBON†

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Abstract—Cyclohexanemethanol, 1-methylcyclohexanemethanol and 2-tetrahydropyranmethanol were oxidized with lead tetraacetate, and in each case a different ratio of cyclization products (1,4-ethers) to β-fragmentation products (olefins, bridged saturated hydrocarbons, acetates and formates) was obtained. These relative product distributions are discussed in terms of conformational, steric (van der Waals) and electronic (resonance) effects.

AS REPORTED previously,[1] the lead tetraacetate reaction of cyclohexanol in refluxing benzene affords predominantly the corresponding acetate (32%) and unchanged alcohol (20%), accompanied by 5–7% of the oxidation product cyclohexanone, whereas cyclization to 1,4-epoxycyclohexane and β-fragmentation with opening of the ring proceeds in very low yields (0·8% and 1·5%, respectively). In order to permit 5-membered cyclic ether formation through homolytic 1,5-hydrogen transfer from the δ-carbon to the radical OH oxygen, controlled by a 6-membered ring transition state,[1,3,4] the distance between O and δ-C in the intermediate cyclohexyloxy radical should be about 2·5–2·7 Å.[3] This is possible only if the cyclohexane ring of cyclohexanol in the course of the reaction assumes the energetically unfavourable boat conformation in which, moreover, the OH oxygen with the nearby voluminous lead-triacetate residue, either bonded to oxygen in the form of alkoxy-lead(IV)-triacetate, R-OPb-$(OAc)_3$, or present in the form of a more or less fully developed radical pair, R–O··Pb$(OAc)_3$, suffers considerable hydrogen compression. Therefore, on conformational and steric grounds, the very low yield of 1,4-epoxycyclohexane (0·8%) obtained in the lead tetraacetate reaction of cyclohexanol is not unexpected. On the other hand, the fact that in this reaction cyclohexanol undergoes only a small amount of β-fragmentation (1·5%), involving αC—βC bond cleavage with ring opening (this being the sole possibility), and that this fragmentation yield corresponds

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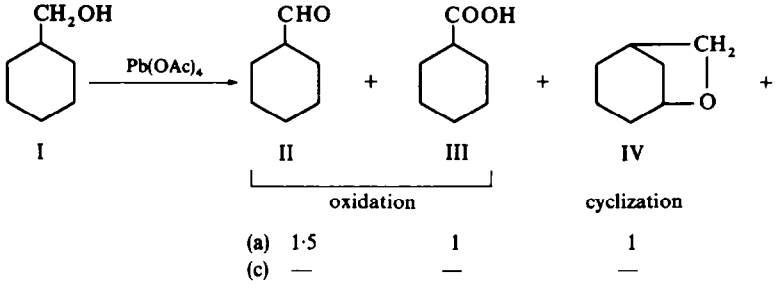
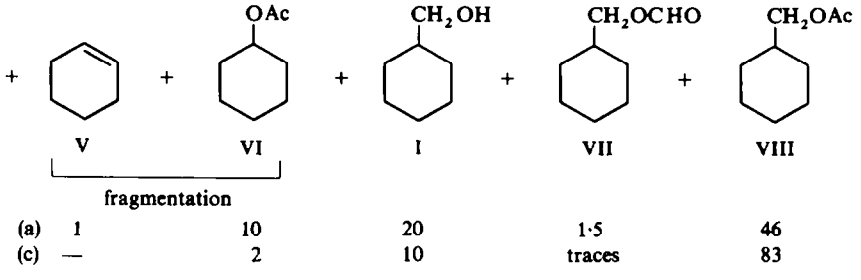
to the ease of fragmentation observed in the lead tetraacetate reaction of unbranched secondary aliphatic alcohols,[4,5] is also to be expected, since both systems (cyclic 6-membered and open-chain) are "constitutionally" similar (secondary alcohols affording initially, upon β-scission, a primary alkyl carbon radical) and with "strain-free" character (i.e. in the predominant stable conformations their total strain is similar and lies at an energy minimum).[6]

We wish now to report results of the action of lead tetraacetate on some primary alcohols containing a 6-membered cyclohexane or 2-tetrahydropyran ring, in which the carbinol carbon (α-C) is attached to a tertiary or quaternary ring carbon (β-C) and which are capable of forming intramolecular (5-membered) 1,4-ethers in the stable chair conformations. The alcohols used were cyclohexanemethanol, 1-methyl-cyclohexanemethanol and 2-tetrahydropyranmethanol, and because of the above-mentioned structural features, they should undergo more readily β-fragmentation and cyclization than cyclohexanol. The products obtained from these alcohols and their yields are given in Schemes 1, 2 and 5. All reactions were performed with a 1:1 molar ratio of alcohol to lead tetraacetate until complete consumption of Pb(IV), in most cases in boiling benzene and in the presence of 1–1·5 molar equivalents of anhydrous calcium carbonate (runs a); in some reactions two molar equivalents of pyridine were added to benzene and these experiments were run at different temperatures (runs b); glacial acetic acid was also used as solvent, at 95–100° (runs c).

SCHEME 1

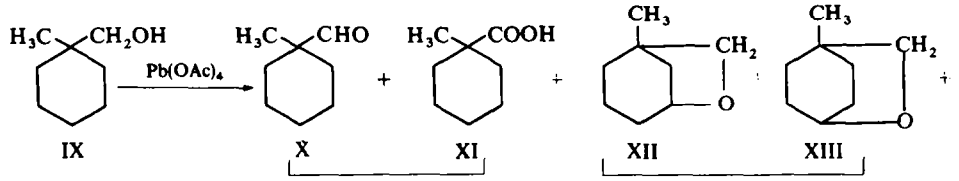
Lead tetraacetate reaction of cyclohexanemethanol (I)
(yields in %; run (a) in benzene at 80°; run (c) in glacial acetic acid at 95–100°)



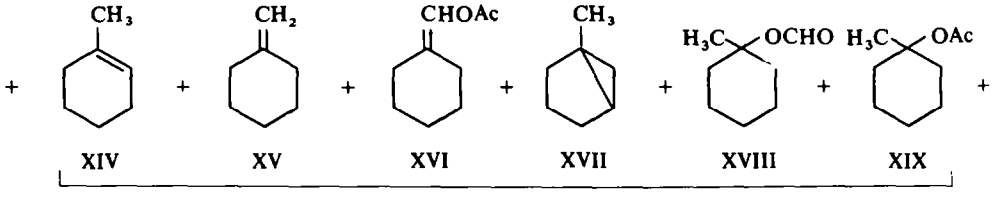


SCHEME 2

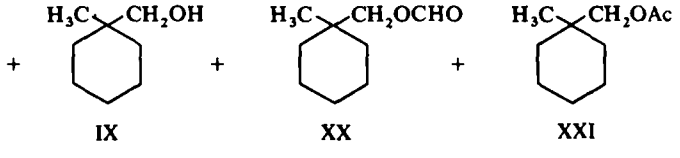
Lead tetraacetate reaction of 1-*methylcyclohexanemethanol* (IX)
(yields in %; run (a) in benzene at 80°; run (b) in benzene + pyridine (2 molar equivalents) at 18–80°; run (c) in glacial acetic acid at 95–100°)



(a)	0·3	1	1·5	0·2
(b)	2·5–6·5	—	traces	—
(c)	—	—	—	—



(a)	9·5	0·3	0·4	0·7	1·5	11
(b)	13–18	0·6	0·7	0·5	0–1·5	10–8·5
(c)	—	—	—	—	—	3·5



(a)	10	5·5	10
(b)	13–16	21–22	1–2
(c)	8	0·5	77

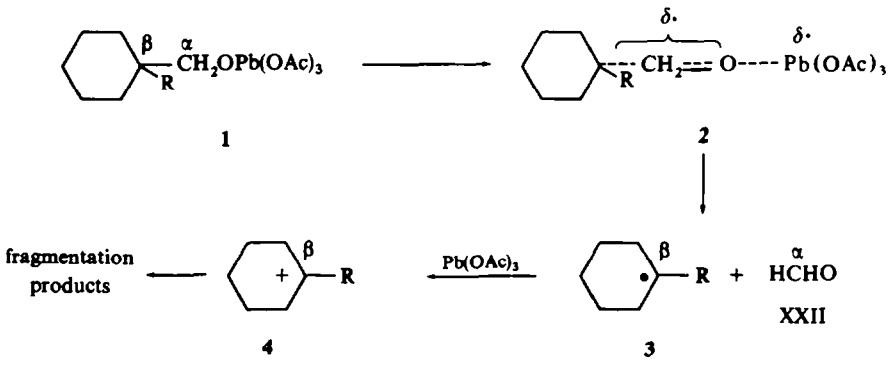
Alcohols with nonactivated β- *and* δ-*carbons.* As can be seen from Schemes 1 and 2 (runs 1), the total yield of fragmentation products (V + VI) obtained from cyclohexanemethanol (I) was 11%, whereas that of all the fragmentation products (XIV–XIX) isolated in the lead tetraacetate reaction of 1-methylcyclohexanemethanol (IX) was higher and amounted to about 23·5%.* These fragmentation yields correspond satisfactorily to those observed in the lead tetraacetate reactions of β-monomethyl substituted and β,β-dimethyl substituted primary aliphatic alcohols (reported 10% and 19%, respectively),[5] and are in agreement with the fact that ease of formation,

* The second fragmentation component, derived from the carbinol (α) carbon atom, i.e. formaldehyde (XXII, Scheme 3), was detected in all reactions (positive test with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid)).[8]

i.e. stability, increases from secondary to tertiary alkyl carbon radicals, and from secondary to tertiary carbonium ions; there is evidence that these species (Scheme 3), i.e. carbon radicals (**3**) and (upon further one-electron oxidation) the corresponding carbonium ions (**4**), are intermediates which are generated on the β-C atom fragment in the course of the lead tetraacetate fragmentation of alcohols (from the initially formed alkoxy-lead(IV)-acetate (**1**) and through a transition state of type (**2**) or the corresponding alkoxy radical).[1, 3–5, 7]

SCHEME 3

The fragmentation reaction



A: R = H; B: R = CH_3

The relative distribution of unsaturated fragmentation products obtained from 1-methylcyclohexanemethanol (IX, Scheme 2), i.e. the ratio of the more stable[9] 1-methylcyclohexene (XIV) to the less stable[9] methylenecyclohexane (XV) + its derivative cyclohexanecarboxaldehyde enolacetate (XVI), amounts to 93:7, and is consistent with a carbonium ion fragment (**4B**, Scheme 3) as precursor; namely, it was shown previously that dehydrations of 1-methylcyclohexanol which proceed through the corresponding 1-methylcyclohexyl cation (**4B**, Scheme 3) give a mixture of olefins (XIV + XV, Scheme 2) in which the more stable endocyclic product, 1-methylcyclohexene (XIV), is present in an amount of 95–97%.[10] The enolacetate of cyclohexanecarboxaldehyde (XVI, Scheme 2), isolated in 0·4% yield in the lead tetraacetate reaction of 1-methylcyclohexanemethanol (IX), is most probably formed by further attack of lead tetraacetate on the fragmentation product methylenecyclohexane (XV), since it is known that such a reaction between methylenecyclohexanes and lead tetraacetate affords the corresponding enolacetates.[11, 12]

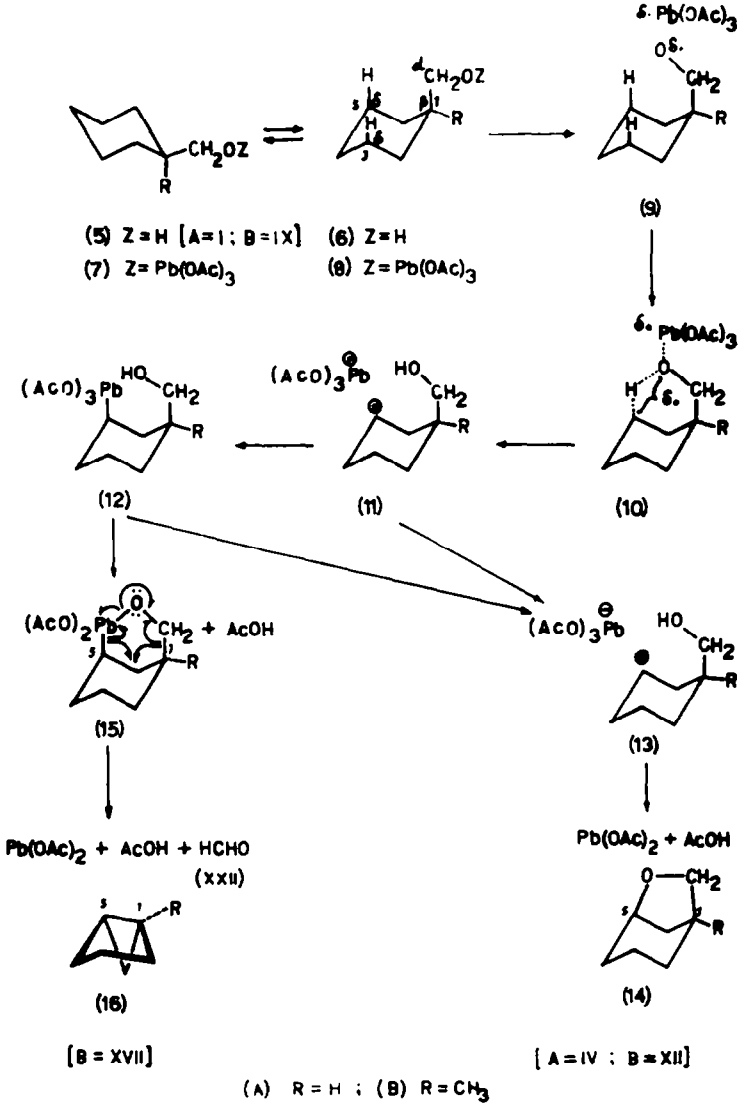
The formation of a small amount (0·7% yield) of the fused fragmentation product 1-methylbicyclo[3.1.0]hexane (XVII, Scheme 2) from 1-methylcyclohexanemethanol (IX) and lead tetraacetate is worthwhile mentioning,* since cyclopropane ring containing fragmentation hydrocarbons have not been observed previously in the lead tetraacetate reactions of alcohols, except in one case reported by Ourisson and

* It is possible that this bicyclic product (XVII) is initially formed in larger amounts but is subsequently cleaved by further attack of lead tetraacetate. Oxidative cleavage of similar systems, i.e. bicyclo[*n*.1.0]-alkanes, by lead tetraacetate has been reported previously.[14]

Lhomme.[13] However, the geometry of the substrates oxidized by these authors—the epimeric polycyclic alcohols longifolol and isolongifolol—was suitable for cyclopropane ring formation, and its was demonstrated that the fragmentation cyclopropane containing hydrocarbon was generated from the corresponding carbonium ion as precursor. In the present case, however, the steric requirements in the intermediate 1-methylcyclohexyl cation (4B, Scheme 3) for 1,3-bond formation leading to the fused cyclopropane compound (XVII, Scheme 2) are not particularly favourable, and therefore, although cyclopropane formation from poorly solvated cationic

SCHEME 4

Intramolecular formation of 1,4-*ethers* (14A = IV *and* 14B = XII) *and* 1-*methylbicyclo*[3.1.0]*hexane* (16B = XVII)



precursors (resulting from some terpene and aliphatic compounds) has been sporadically observed[14a,*] (but not in lead tetraacetate reactions of alcohols), an alternative pathway to 1-methylbicyclo[3.1.0]hexane (XVII), shown on Scheme 4, can also be envisaged, which would involve in the first stages the same steps (**6** → **8** → **9** → **10** → **11** → **12**) as those postulated for cyclic ether (**14**) formation.[1,3,4] In the organolead alcohol (**12**) the hydroxyl group of the methanol substituent, being suitably oriented, could react intramolecularly with the cyclohexyl–lead(IV)-triacetate moiety (in the same way as an alcohol reacts intermolecularly with lead tetraacetate) to give the corresponding internal 6-membered alkoxy-lead(IV)-derivative (**15**), which would eventually, via a series of simultaneous one-electron (or double-electron) transfers, collapse to the fused hydrocarbon (**16B** = XVII) and formaldehyde (XXII).

Intramolecular cyclic ether formation is not favoured in the lead tetraacetate reaction of cyclohexanemethanol (I, Scheme 1) and 1-methylcyclohexanemethanol (IX, Scheme 2), as evident from the very low yields of 6-oxabicyclo[3.2.1]octane (IV, Scheme 1; 1%), and of 1-methyl-6-oxabicyclo[3.2.1]octane (XII, Scheme 2; 1·5%) + 4-methyl-2-oxabicyclo[2.2.2]octane (XIII, Scheme 2; 0·2%), respectively, and from comparison of these yields with those of tetrahydrofuran ethers obtained in the lead tetraacetate reaction of "constitutionally" similar primary aliphatic alcohols with a tertiary β-carbon (e.g. $CH_3CH_2CH_2CH(CH_3)CH_2OH$) and quaternary β-carbon (e.g. $CH_3CH_2CH_2C(CH_3)_2CH_2OH$), which amounted to 36% and 17%, respectively.[5] (As mentioned above, fragmentation yields are comparable in both series.)

The amount of 1,4-ether (IV, Scheme 1) formed from cyclohexanemethanol (I) was somewhat lower than the amount of 1,4-ether (XII, Scheme 2) obtained from 1-methylcyclohexanemethanol (IX), although the opposite might be expected on grounds of previous observations that in a series of similar alcohols those which undergo less β-fragmentation usually afford more 5-membered cyclic ethers.[5] In the presence case, however, this small difference might be explained by the fact, illustrated on Scheme 4, that in order to permit homolytic 1,5-hydrogen transfer from the δ-carbon to oxygen in the intermediate, more or less fully developed, alkoxy radical (**9**), the distance $\delta C \cdots O$ must be in the range 2·5–2·7 Å,[3] which is possible only if the CH_2OC substituent assumes an axial orientation (as in **6**, **8** and **9**). In the unsubstituted cyclohexanemethanol (I) the predominant chair conformation in equilibrium is the one (**5A**) in which the CH_2OH group is equatorial, and therefore before cyclization it must change into the energetically unfavourable (less stable) chair conformation (**6A**) in which the CH_2OH substituent is axial. In the case of 1-methylcyclohexanemethanol (IX), however, both substituents on C-1 (CH_3 and CH_2OH) have similar conformational energies,[6,15] and the equilibrium mixture of chair conformers (**5B** ⇄ **6B**) should therefore contain about 50% (or somewhat more) of the conformation required for intramolecular cyclization, in which CH_2OH is axial (**6B**). Nevertheless, even in these chair conformations (**6**) with an axial CH_2OZ group (either in cyclohexanemethanol (I) or 1-methylcyclohexanemethanol (IX)), cyclic 1,4-ether formation will be hindered and proceed in low yield, since generation of the δ-carbon radical (**11**) via the transition state (**10**) requires a highly unfavourable (because of strong van der

* To our knowledge there are no reports in the literature, so far, on the conversion of common cyclohexyl cations to bicyclo[3.1.0]hexanes.

Waals 1,3-interactions) *endo* orientation of the hydroxyl oxygen atom together with the nearby voluminous lead-triacetate residue (as in **9**). This oxygen will therefore have the tendency to relieve strain, i.e. to attain the *exo* orientation, by rotation of the CH_2OZ group around the αC—βC bond (as in **8**) or, better, to convert to the equatorial position by inversion of the cyclohexane ring (**8** → **7**), in which cases 1,5-hydrogen transfer (**10**) leading to intramolecular 1,4-ether formation is not possible. On the other hand, the fragmentation reaction (Scheme 3) via the cyclohexyl β-carbon radical (**3**) and cation (**4**) is not limited to the axial position of the CH_2OZ group (**6** and **8**, Scheme 4) but may proceed as well when this substituent is equatorial (**5** and **7**, Scheme 4); therefore, this is an additional factor which favours β-fragmentation over intramolecular cyclization.

The 6-membered cyclic 1,5-ether, i.e. 4-methyl-2-oxabicyclo[2.2.2]octane (XIII, Scheme 2), was isolated only in traces (0·2%),* which is not unexpected, since usually tetrahydropyran ether formation is not favoured in lead tetraacetate oxidations of alcohols;[4,16] moreover, in the present case, the molecule of the reacting 1-methylcyclohexanemethanol (IX, Scheme 2) must convert to the unstable flexible conformation in order to allow this kind of cyclization (homolytic 1,6-hydrogen transfer, 7-membered ring transition state).

When two molar equivalents of pyridine were added to benzene (Scheme 2, run b), the lead tetraacetate reaction of 1-methylcyclohexanemethanol (IX) (at different temperatures varying from 18 to 80°) afforded a somewhat higher yield of corresponding aldehyde (X) and fragmentation products (XIV–XIX).[17] It should be noted that under these conditions the amount of unsaturated hydrocarbon fragments (XIV–XVI), relative to the fragmentation acetate (XIX), was slightly larger, probably because pyridine catalyzes proton elimination from the intermediate carbonium ion fragment (**4B**, Scheme 3) and, at the same time, binds acetic acid and thus prevents its addition to the same carbonium ion.

The formate esters of the starting alcohols (VII, Scheme 1, runs a and c; XX, Scheme 2, runs a, b and c) and the fragmentation formate ester XVIII (Scheme 2) are formed from formic acid (or/and the radical H—Ċ=O), which arises as further oxidation product of the carbonyl fragment formaldehyde (XXII, Scheme 3).[18,4] In the presence of pyridine (Scheme 2, run b), the yield of 1-methylcyclohexanemethanol formate (XX) was considerably increased (from 5·5 to 21–22%), probably because pyridine, by neutralizing the acetic acid formed in the course of the reaction, prevents polymerization of formaldehyde.† In glacial acetic acid as solvent, both cyclohexanemethanol (I, Scheme 1, run c) and 1-methylcyclohexanemethanol (IX, Scheme 2, run c) afforded as major product the corresponding acetates (VIII and XXI, respectively), whereas other products were either absent (oxidation and cylization products) or formed only in small amounts (the fragmentation acetates VI and XIX, respectively).

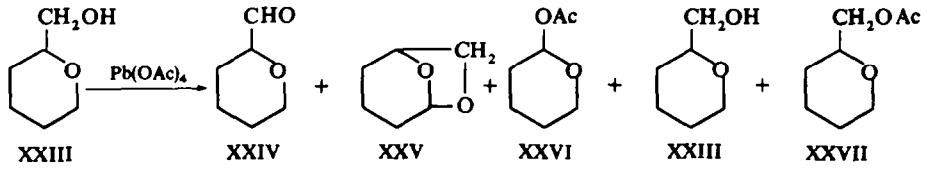
* The structure of this reaction product (XIII, Scheme 2) is only tentative, and was assigned solely (because of trace amounts) on the basis of its IR spectrum, which shows C—O stretching vibrations characteristic for cyclic ethers (in the region 985–1150 cm^{-1}) and does not contain bands corresponding to other functional groups (but is different from the IR spectrum of the isomeric 1,4-ether XII).

† A substantial amount of solid polymeric product derived from formaldehyde was formed during the lead tetraacetate oxidation of cyclohexanemethanol (I, Scheme 1) and 1-methylcyclohexanemethanol (IX, Scheme 2) in benzene alone (runs a), whereas in the presence of pyridine (Scheme 2, run b) the formation of polymeric material from formaldehyde was not observed.

Alcohol with activated β- *and* δ-*carbons.* When tetrahydropyran-2-methanol (XXIII) was oxidized in refluxing benzene with lead tetraacetate, the products shown on Scheme 5 were obtained. Although tetrahydropyran-2-methanol (XXIII, Scheme 5)

SCHEME 5

Lead tetraacetate reaction of tetrahydropyran-2-methanol (XXIII)
(yields in %; in benzene (+$CaCO_3$) at 80°)



resembles formally cyclohexanemethanol (I, Scheme 1), it undergoes both cyclization, i.e. formation of the 1,4-ether 6,8-dioxabicyclo[3.2.1]octane (XXV, Scheme 5), and β-fragmentation, i.e. formation of 2-acetocytetrahydropyran (XXVI, Scheme 5), in considerably higher yields.* These results confirm our previous experience[19] that in alkoxy- and aryloxy-alkanols the ether oxygen enhances intramolecular cyclic ether formation when it is adjacent to a δ-C—H (or ε-C—H) bond and also facilitates β-fragmentation when it is directly attached to a β-carbon, probably in both cases as the result of resonance stabilization of the intermediate δ- (or ε-) carbon radical and β-carbon radical, respectively (—Ċ—Ö ↔ —C⊖—Ö⊕—) and/or the corresponding, subsequently produced, carbonium ions (—C⊕—Ö— ↔ —C=Ö⊕—).

Reduction of ring size of the starting alcohol alters the course of the reaction to eliminate bicyclic 1,4-ether formation. Hence, tetrahydrofuran-2-methanol (XXVIII) upon reaction with lead tetracetate in refluxing benzene (+$CaCO_3$) yields: tetrahydrofuraldehyde (XXIX, 10–12%), 2-acetoxytetrahydrofuran (XXX, 12–17%), unchanged tetrahydrofuran-2-methanol (XXVIII, 30%) and tetrahydrofuran-2-methanol acetate (XXXI, 25%). The lack of formation of the intramolecular 5-membered 1,4-ether 2,7-dioxabicyclo[2.2.1]heptane, even though the δ-carbon is adjacent to an ether oxygen atom, is most likely due to a high energy in the hydrogen transfer transition state (since in the 5-membered tetrahydrofuran ring the CH_2OZ substituent and hydrogen in positions 2 and 5, respectively, are quasiaxial and therefore the distance δC···O in the intermediate alkoxy radical is larger than the required 2·5–2·7 Å[3]), as well as to the great ring strain in the desired and unknown product.

* A test to measure the susceptibility of the bicyclic dioxolane (XXV, Scheme 5) to decomposition when in contact with lead tetraacetate (in refluxing benzene), showed that no noticeable amounts of volatile components were formed corresponding to dioxolane cleavage.

EXPERIMENTAL*

M.ps and b.ps are uncorrected. Gas chromatography: Perkin–Elmer instrument Model 116-E, equipped with a thermistor detector; the columns (4 m × 8 mm, 6 m × 8 mm) consisted of Apiezon L, β,β'-oxidopropionitrile or Carbowax adsorbed on Chromosorb P (30–40%), and of SE-30 Silicone adsorbed on firebrick; the temp of the columns, the sensitivity of the detector, and press and flow rate of the carrier gas (H_2 or He) were adjusted according to the fractions which were analysed. IR spectra: Perkin–Elmer Infracord Model 137B. NMR spectra: Varian A-60A spectrometer. For fractional distillations well isolated, modified semimicro Vigreux and Widmer columns were used.

Starting materials. Cyclohexanemethanol (I), XXIII and XXVIII were of commercial origin, dried and purified by distillation prior to use; their purity was always checked by gas chromatography. Compound IX, b.p. 96–97° at 21 mm,[20] was prepared by conversion of cycloheptanol to XI, b.p. 135–136° at 22 mm, m.p. 39°[20a] (by the HCOOH—H_2SO_4 method[20a]), followed by LAH reduction.

Lead tetraacetate reactions. The preparation of lead tetraacetate, drying of the reagents and solvents, and the lead tetraacetate oxidations in benzene–$CaCO_3$ at 80° and in benzene–pyridine (2 molar equivts per one molar equivt of $Pb(OAc)_4$) at 18°, 50° or 80°, were carried out as described previously.[1,4,16–18] When glacial AcOH was used as solvent at 95–100° (*n*.1000–*n*.1500 ml AcOH for *n* moles of alcohol), after completion of the reaction, ice-cold water was added (*n*.1000–*n*.1500 ml) to the mixture, the aqueous layer was extracted several times with ether, the ethereal layers were combined with the original organic layer and washed with water and $NaHCO_3$aq until neutral. In all reactions a 1:1 molar ratio of alcohol to $Pb(OAc)_4$ was used. With 0·1 mole of alcohol the reaction times (until complete consumption of tetravalent Pb) were as follows. In benzene–$CaCO_3$ (at 80°): compound I—13·5 hr; IX—3·5–4 hr; XXIII—5 hr; XXVIII—7·5 hr. In benzene–pyridine: compound IX, at 18°—25 hr, at 50°—3·5 hr, at 80–90°—10 min. In AcOH at 95–100°: compound I—25–30 hr; IX—18–20 hr.

Identification of products. Reaction products were separated and isolated by gas chromatography, and their yields (usually an average of 2 or 3 runs) were determined planimetrically from gas chromatograms (with necessary corrections using different standards). The isolated products were identified and characterized on the basis of their IR and NMR spectra (sometimes also elemental analysis and refraction index or m.p.) and by comparison of these spectral data and retention times with those of authentic compounds. The formate esters of XVIII and XX were characterized on the basis of the C—O stretching vibrations in their IR spectra.[21] In some cases carbonyl compounds (aldehydes) were also estimated quantitatively and identified by conversion to 2,4-dinitrophenylhydrazones.[22]

Of commercial origin were compounds II, III, V, XIV, XV and XXIX. The acid XI was an intermediate in the synthesis of the starting alcohol IX (see above). Compounds VI, b.p. 172–173°,[23] VII, b.p. 70–72° at 15 mm,[24] VIII, b.p. 76–77° at 15 mm,[25] XIX, b.p. 67–68° at 15 mm,[26] XXVII, b.p. 96–97° at 15 mm,[27] XXXI, b.p. 194–196°,[28] were prepared according to usual procedures. Compound XXVI, b.p. 73–74° at 10 mm, n_D^{20} 1·4369, was prepared by addition of AcOH to commercial 2,3-dihydro-4*H*-pyran,[29] and XXX, b.p. 71° at 15 mm, n_D^{20} 1·4300, from THF and t-butyl peracetate under photolytic conditions.[30]

The aldehyde X,[20b,31] which is formed in the $Pb(OAc)_4$ oxidation of IX, was also isolated from the reaction mixture in the form[22] of its 2,4-dinitrophenylhydrazone, m.p. 153–154° (from EtOH).[31] (Found: C, 55·1; H, 5·9; N, 18·5. Calc. for $C_{14}H_{18}O_4N_4$: C, 54·9; H, 5·9; N, 18·3%). Compound XXIV, b.p. 152–154°,[32] was obtained by $Pb(OAc)_4$ (or CrO_3) oxidation of XXIII in pyridine at room temp.[33]

Compound XVII, b.p. 92–93°, n_D^{20} 1·4328, was prepared in about 50% yield from 1-methylcyclopentene, methylene iodide and Zn–Cu couple in ether,[34] and compound IV, m.p. 96–97°,[35] was obtained by cyclization of *cis*-3-hydroxymethylcyclohexanol† by means of benzenesulphonyl chloride in pyridine.[36] Compound XXV, b.p. 69–71° at 40 mm, m.p. 49–50°,[37] was prepared by acid catalyzed cyclization of commercial 3,4-dihydro-2*H*-pyran-2-methanol.

1-*Methylcyclohexanemethanol acetate* (XXI) was not previously reported in the literature. It was prepared by refluxing for 2 hr 2·56 g (0·02 moles) IX and 2·25 g (0·22 moles) Ac_2O in 4 ml pyridine, adding water and ether to the cooled mixture, washing the ethereal layer successively with water, 2N HClaq, water, $NaHCO_3$aq and water, and drying. Distillation afforded 2 g (60%) of acetate XXI, b.p. 100° at 20 mm, n_D^{22} 1·4472. (Found: C, 70·9; H, 10·4. $C_{10}H_{18}O_2$ requires: C, 70·6; H, 10·6%).

* We thank Dr. D. Jeremić for measurements and discussion of IR and NMR spectra, and Mrs. R. Tasovac for the elemental microanalyses.

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Cyclohexanecarboxaldehyde enolacetate (XVI) was prepared by heating for 1·5 hr at 160–165° a mixture of 8·4 g (0·075 moles) of II, 13 ml Ac_2O and 2·65 g anhyd, freshly fused AcOK. After working up as usual, distillation afforded 6·5 g (55·5%) of the enol-acetate XVI, b.p. 90–91° at 15 mm, n_D^{20} 1·4700. (Found: C, 70·1; H, 9·3. $C_9H_{14}O_2$ requires: C, 70·1; H, 9·1%).

1-*Methyl-6-oxabicyclo*[3.2.1]*octane* (XII), isolated by gas chromatography from the reaction mixture which was obtained upon $Pb(OAc)_4$ oxidation of IX, had the following constants: n_D^{26} 1·4454; IR(film): ν_{max} 995 and 1028 cm^{-1}; NMR(CCl_4): 4·22 δ (1H, tr, H—C(—O—)—), 3·65 δ (H_A) and 3·35 δ (H_B) (2H, AB-qu, H_2C(—O—)—), 1·2–2·0 δ (8H, complex absorption, H_2C-ring protons), 1·02 δ (3H, s, H_3C—). (Found: C, 75·8; H, 11·3. $C_8H_{14}O$ requires: C, 76·1; H, 11·2%).

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