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THE REACTION OF LEAD TETRAACETATE WITH ALICYCLIC ALCOHOLS—I[1,2]

CYCLOALKANOLS

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Abstract—Secondary cycloalkanols, containing 4- to 16-membered rings, have been treated with lead tetraacetate in refluxing benzene. It was found that the ease of oxidation to the corresponding ketones follows the reactivity order of reactions of alicyclic compounds involving an $sp^3 \rightarrow sp^2$ ring carbon hybridization change, and that the amount of β-fragmentation resulting in opening of the ring is in accord with the total strain associated with carbocyclic rings. The yield of intramolecular ether formation appears to depend upon ring size and conformational factors in the transition state; it increases from cyclohexanol to cyclooctanol, drops sharply for cyclododecanol and reaches the highest value with cyclohexadecanol. The major ether obtained in the case of cyclodecanol was *trans*-1,2-epoxycyclodecane.

INTRODUCTION

THREE major types of reactions (Scheme 1) may occur when monohydroxylic alcohols (I) are treated with lead tetraacetate in nonpolar solvents (such as benzene or cyclohexane), namely (*ab*) oxidation to the corresponding carbonyl compounds (III) (when the starting alcohols are primary or secondary),[2,3–13] this process being considerably enhanced in the presence of pyridine as base,[6,8–10,12] and therefore probably in most cases associated with the removal of a proton from the α-carbinol C atom and heterolytic cleavage of the O—Pb bond in the intermediate alkoxy-lead(IV)-acetate (II);[2,4,6–10,14] (*acdd'*) intramolecular ring closure leading usually to 5-membered cyclic ethers (VI) and less readily to 6-membered tetrahydropyran ethers (VII);[2,4,5,7,8,10–13,15–19] and (*acee'*) cleavage of the bond between the α-carbinol C atom and the β-C atom, with formation of a carbonyl containing fragment (IX) and fragmentation products (usually acetates X*a* and/or olefins X*b*) derived from the initially produced alkyl carbon radical fragment (VIII).[2,4,5,7,8,10,13,18,20–23] Both cyclization and β-fragmentation have been formulated[2,4a,7,8,10] (Scheme 1) as proceeding in the first stages by homolytic decomposition (*c*) of the primarily formed alkoxy-lead(IV)-acetate (II) and *via* a common transition state with alkoxy radical character (IV) or a more or less fully developed alkoxy radical (V),† which subsequently collapses either to intramolecular cyclic ethers (VI and VII) or/and to fragmentation products (VIII and IX), in dependence on structural features

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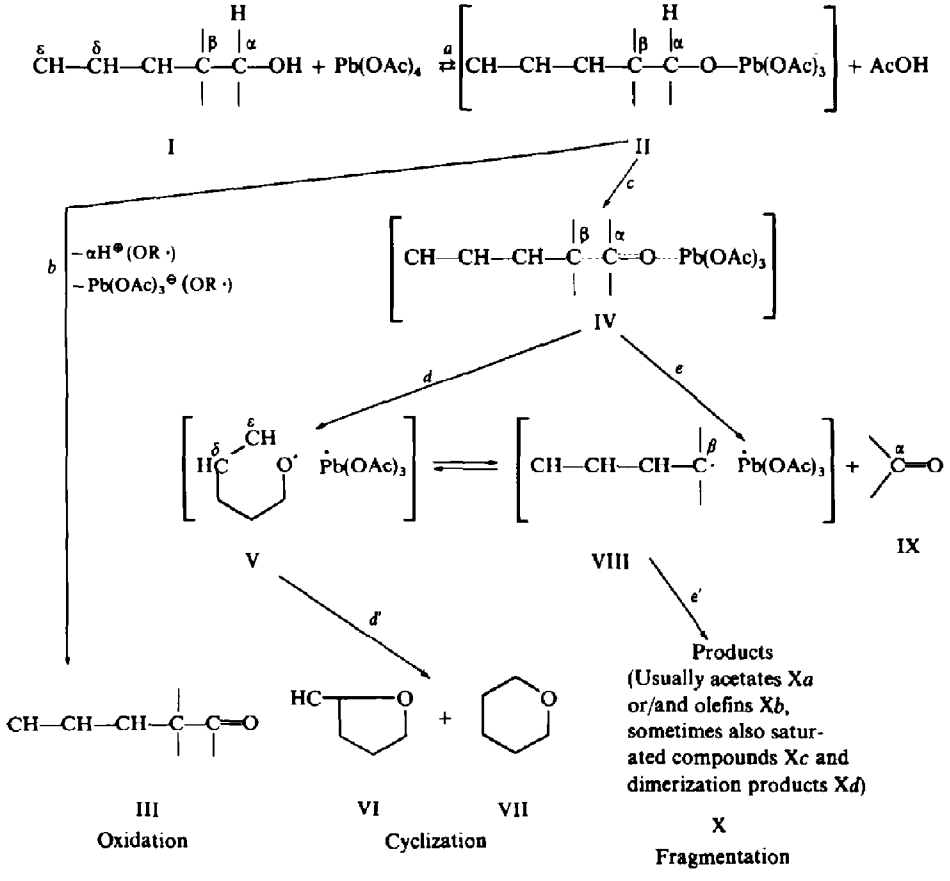
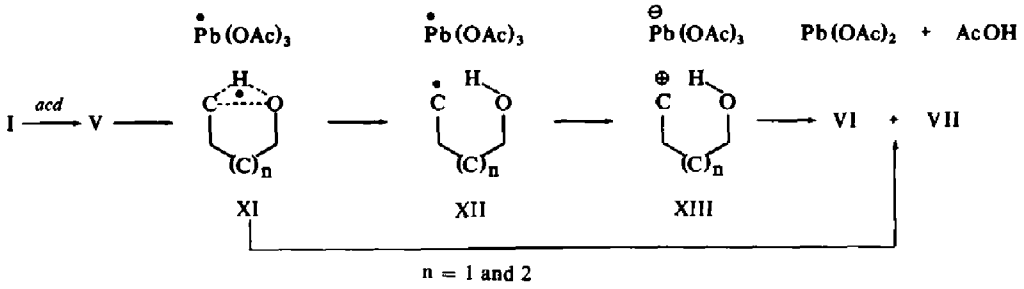
† Additional evidence for the occurrence of radical mechanisms in the lead tetraacetate reaction of alcohols, involving alkoxy radicals (of type V) as intermediates, was recently presented by Starnes.[24]

of the substrate. Details of the postulated reaction pathways, following the production of an alkoxy radical (V) and leading to cyclic ethers (VI and VII, phase *d'*, Scheme 1),[4a, 7–9, 12, 17, 18] and those following the formation of the alkyl carbon radical fragment (VIII) and giving rise to the final fragmentation products (X, phase *e'*, Scheme 1),[4a, 5, 7, 18, 20] are shown in Schemes 2A and 2B, respectively.

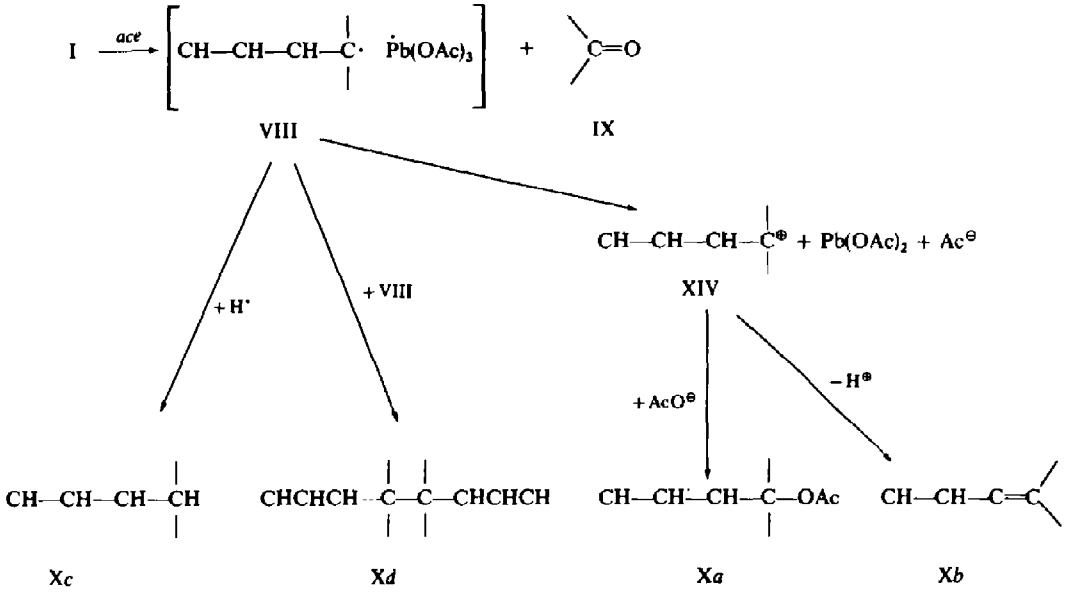


SCHEME 1

In the present work we have studied the action of lead tetraacetate in refluxing benzene (nonpolar solvent) on secondary cycloalkanols containing 4 to 16 ring C atoms, with the purpose of determining the effect of ring size and related factors (strain, conformation, flexibility) on the yields of products formed by the above-described oxidation, cyclization and β-fragmentation processes (Scheme 1). The results obtained are summarized in Table 1 and Fig. 1.



A. Cyclization (phase *d'* of Scheme 1)



B. Fragmentation (phase *e'* of Scheme 1)

SCHEME 2

RESULTS AND DISCUSSION

Oxidation reaction (cycloalkanone formation). Direct oxidation (Scheme 1, *ab*) of saturated primary and secondary alcohols (I) to the corresponding aldehydes and ketones (III), occurs generally in fairly low yield when the lead tetraacetate reaction is performed in nonpolar media (benzene or cyclohexane).[4, 5, 7, 8, 10, 12, 13, 15–23] Even when ring closure (*acdd'*) to 5-membered and/or 6-membered cyclic ethers (VI and VII) is very slow or not feasible and fragmentation (*acee'*) to VIII (i.e. X) and IX is not favoured, carbonyl compound (III) formation (*ab*) does not increase

TABLE 1. PRODUCT DISTRIBUTION IN THE REACTION OF LEAD TETRAACETATE WITH SECONDARY CYCLOALKANOLS (IN BENZENE AT 80°)

Alcohol	Products (yields in %)[a]			
	Oxidation	Cyclization	β-Fragmentation	Acetate
	(cycloalkanone)[b,c]	(intramolecular oxido compounds)	(open-chain ω- and (ω-1)-acetoxy-aldehydes)[d]	(of starting alcohol)[e]
Cyclobutanol	3·5	None	15[f]	25
Cyclopentanol	8[g]	None	4[h]	26
Cyclohexanol	5·5[i]	0·8[j]	1·5[k]	32[l]
Cycloheptanol	10[m]	15[n,o]	3[k]	38[o]
Cyclooctanol	28[p,q]	36[n,s]	3·5[k]	15[s]
Cyclodecanol	41	27·5[t]	u	21·5
Cyclododecanol	33	8·5[v]	u	30[w]
Cyclohexadecanol	15	45[x]	u	26[w]

[a] Yields were in general obtained from gas-chromatographic analysis and/or separation by column chromatography (Experimental).

[b] Corresponding to the starting alcohol.

[c] And α-acetoxylated cycloalkanone.

[d] And/or, as the result of further oxidation, the corresponding acids, either free or esterified with the starting alcohol.

[e] Starting alcohol was recovered in all runs, in a yield of 9–25%.

[f] Consisting of 6·5% 4-acetoxybutyraldehyde, 5·5% 3-acetoxybutyraldehyde and 3% octane-1,8-dial (as such or as further oxidation products;[4] see Experimental).

[g] Consisting of 5·5% cyclopentanone and 2·5% α-acetoxycyclopentanone.

[h] Consisting of about 2% 5-acetoxyvaleraldehyde and 2% 4-acetoxyvaleraldehyde (and further oxidation products;[4] see Experimental).

[i] Consisting of 4% cyclohexanone and 1·5% α-acetoxycyclohexanone.

[j] 1,4-Epoxycyclohexane.

[k] The ω- and (ω-1)-acetoxy fragmentation products were not separated.

[l] Previously reported[28] yield, 38%.

[m] Consisting of 8% cycloheptanone and 2% α-acetoxycycloheptanone.

[n] 1,4-Epoxycycloheptane.

[o] Previously reported[28] yield, about 4% of 1,4-epoxycycloheptane and 28% cycloheptyl acetate.

[p] Consisting of 23% cyclooctanone and 5% α-acetoxycyclooctanone.

[q] Previously reported yields (of cyclooctanone only), 4%,[28] and 6%.[29]

[r] Consisting of 35·2% of 1,4-epoxycyclooctane and 0·8% of 1,5-epoxycyclooctane.

[s] Previously reported yields, 22·5%[28] and 30%[29] of 1,4-oxide (as the sole ether); 29%[28] and 17%[29] of cyclooctyl acetate.

[t] Mixture of several intramolecular ethers, the major component being *trans*-1,2-epoxycyclodecane (~12%).

[u] Not determined.

[v] Mixture of three intramolecular ethers.

[w] In addition, the corresponding *cis*- and *trans*-cycloalkenes were isolated in 2–3% yield.

[x] Only one ether, possibly 1,4-epoxycyclohexadecane.

accordingly and rarely exceeds 15–20%,[2,6–8,12,25,*] except in those cases[26] when the conversion of an alcohol function to a CO group results in considerable energy gain associated with release of steric compression,[27] whereby the yields of ketones obtained are much higher.

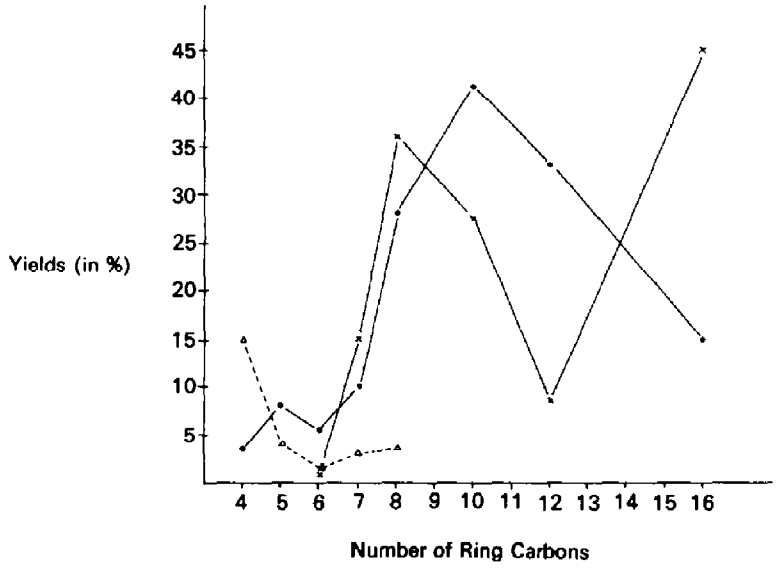


FIG. 1 Effect of ring size on the yields of cycloalkanone formation (●), intramolecular ether formation (×) and β-fragmentation with ring opening (△), in the lead tetraacetate reaction of cycloalkanols (in benzene at 80°)

The ease of carbonyl compound formation from secondary cycloalkanols and lead tetraacetate in refluxing benzene, as reflected (in Table 1 and Fig. 1) by the yields of the respective cycloalkanones and α-acetoxylated cycloalkanones,† parallels the trend observed in the rate constants for various S_N1 (and radical) reactions of alicyclic compounds involving a change of hybridization of the reacting ring C atom from sp^3 to sp^2, either in the transition state or in the final product.[31–33] As expected, the highest yield of ketone was obtained from cyclodecanol (Table 1), since in this case the conversion of the carbinol C atom to a keto-carbonyl C atom is associated with

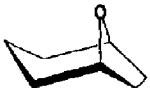
* For that reason and for the fact that oxidation of alcohols (I) with lead tetraacetate to the corresponding carbonyl compounds (III) is greatly enhanced by the addition of pyridine as base, it was suggested that this process (Scheme 1, *ab*) involves in major part an ionic-type decomposition of the initially formed alkoxy-lead (IV)-acetate II (see Introduction).

† The action of lead tetraacetate on cyclohexanol, cycloheptanol and cyclooctanol has been previously reported by other authors.[28,29] However, according to their results it appears that no ketone was obtained from cyclohexanol,[28] that in the case of cycloheptanol the corresponding ketone was not separated from unreacted alcohol,[28] and that cyclooctanol afforded only 4–6% of cyclooctanone.[28,29] These low yields, with respect to our own results (Table 1), could be due to a different quality of lead tetraacetate,[8,10,30] and also to the fact that upon prolonged reaction a considerable amount of initially formed ketone was converted to the corresponding α-monoacetoxy and α,α′-diacetoxy derivatives (see text below), which were not investigated. The difference in yield of other products (see below) may be due, in part, to the same reasons.

considerable relief of bond angle strain and decrease in ("transannular" non-bonded) van der Waals compression (due to the change of carbon coordination number from 4 to 3 ($sp^3 \rightarrow sp^2$) involving removal of an α-hydrogen).[31-35] However, it is possible that part of the cyclodecanone obtained from cyclodecanol is not produced by the direct oxidation pathway (Scheme 1, *ab*), but rather by a process involving transannular hydrogen shifts.[36] Cyclohexadecanol afforded the corresponding ketone in about 15% yield, which is only slightly more than the amount (5–10%) of ketone usually obtained in the lead tetraacetate reaction of secondary aliphatic alcohols with unbranched alkyl groups.[7,13] It should be noted that in addition to the unsubstituted cycloalkanone, some corresponding α-acetoxy-ketone was also formed in most cases (Table 1). This is not unexpected, since it is known that carbonyl compounds can be α-acetoxylated by means of lead tetraacetate.[2,4b,6,7,*]

Cyclization reaction (intramolecular ether formation). When treated with lead tetraacetate cyclobutanol and cyclopentanol do not yield intramolecular ethers, since the initially produced 4- and 5-membered cycloalkoxy radicals (of type V, Schemes 1 and 2A), cannot undergo—across the shorter atom chain—a homolytic 1,5-hydrogen transfer from carbon to oxygen *via* the respective 6-membered cyclic transition states (of type X, $n = 1$; Scheme 2A), a process which appears to be a favoured prerequisite for intramolecular ether formation from alcohols with nonactivated C—H bonds and lead tetraacetate.[6,7,†] The structure of cyclohexanol permits 1,5-hydrogen transfer in the corresponding alkoxy radical, controlled by a 6-membered ring transition state, but because of the energetically unfavourable boat conformation which the cyclohexane ring must assume in such a process the yield of 1,4-epoxycyclohexane (XV), isolated upon treatment of cyclohexanol with lead tetraacetate, was very low—under 1% (see Table 1).‡§

XV (0·8%)



XVI (15%)

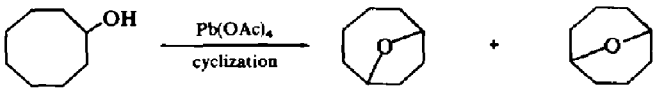
* When cyclohexanol was treated with lead tetraacetate at 80° in benzene in the presence of pyridine (5:1 molar ratio of pyridine to lead tetraacetate), in pyridine alone (at 80–100°), and in the absence of any solvent (excess cyclohexanol at about 80°), the yield of cyclohexanone increased to 62, 63 and 90%, respectively (and no 1,4-epoxycyclohexane could be detected).[8] These results provide further support that carbonyl compound formation from a monohydric alochol and lead tetraacetate (Scheme 1, *ab*) is essentially a heterolytic process (see also text above).

† And also for other radical-type reactions involving intramolecular hydrogen transfer from carbon to oxygen in the intermediate alkoxy radical, such as the photochemically induced rearrangements of hypochlorites,[37] nitrites,[38] and hypoiodites,[4a] or intramolecular hydrogen abstraction from carbon by the nitrogen radical-cation in the Hofmann-Löffler-Freitag reaction.[39]

‡ Probably for that reason, Cope *et al.* did not report the formation of any 1,4-oxido-compound from cyclohexanol and lead tetraacetate.[28]

§ This finding is similar to the result reported for the photolysis of cyclohexyl nitrite (which also gives rise to the corresponding alkoxy radical).[38,40,41]

As one goes from cyclohexanol to cycloheptanol and to cyclooctanol (XVII), ring flexibility increases and the possible conformations in the 6-membered* cyclic transition states (of type XI, n = 1; Scheme 2A) and corresponding intramolecular ether products (XVI and XVIII, respectively) become more and more favourable,[32,33,42] resulting in an appreciable increase in yield (Table 1 and Fig. 1), which amounts to 15% for 1,4-epoxycycloheptane† (XVI) and to over 35% for 1,4-epoxycyclooctane‡ (XVIII).§ Although cyclooctanol (XVII) can also form a 1,5-ether (XIX), the yield of this cyclization product (XIX) was only about 0·8%,‖ approxi-



XVII XVIII (36%) XIX (0·8%)

mating the amount of 6-membered tetrahydropyrane ethers which are obtained in the lead tetraacetate reaction of unbranced secondary aliphatic alcohols.[7,8] This result indicates that in the case of cyclooctanol (XVII), similarly to acyclic alcohols, the main prerequisite for intramolecular hydrogen transfer from carbon to oxygen in the corresponding alkoxy radical is a cyclic 6-membered* transition state (of type XI, n = 1; Scheme 2A), involving transannular attack at the 4-position of the ring and leading to a tetrahydrofurane-type* 1,4-ether (XVIII), and that "proximity effects",[31,35] which might be expected to increase the ease (and yield) of the tetrahydropyrane-type* 1,5-epoxycyclooctane (XIX) formation,** do not seem to be operative in the case of cyclooctyloxy radicals generated from cyclooctanol and lead tetracetate.†† However, as reported by Cope *et al.*[28] the tertiary alcohol 1-methylcyclooctanol (XX), upon interaction with lead tetraacetate, affords as major cyclization product (in about 18% yield), the corresponding 1,5-epoxy-compound (XXII),

* Viewed along the shorter atom chain.

† The yield of 1,4-epoxycycloheptane (XVI) reported by Cope *et al.*[28] was only about 4–5%. (See footnote† on page 4951).

‡ In previous lead tetraacetate oxidations of cyclooctanol (XVII) 1,4-epoxycyclooctane (XVIII) was obtained in 22·5%[28] and 30% yield,[29] whereas the formation of the corresponding 1,5-oxido-compound (XIX) was not observed. (See footnote† on page 4951).

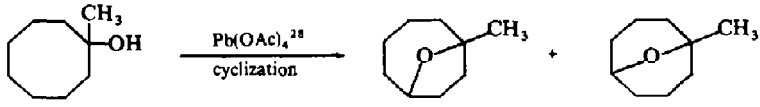
§ The yield of rearrangement involving abstraction of a hydrogen atom from the 4-position (i.e. homolytic 1,5-hydrogen shift) in the intermediate cycloalkoxy radicals was about 21% for the photolysis of both cycloheptyl nitrite and cyclooctyl nitrite.[38,41] In the latter case no product of attack at the 5-position was observed. (See also next footnote.)

‖ In previous lead tetraacetate oxidations of cyclooctanol,[28,29] the formation of the corresponding 1,5-oxide (XIX) was not observed. (See also the preceding footnote.)

** Such effects have been shown to influence the course of the Hofmann–Löffler–Freitag reaction of N-chloro-N-methylcyclooctylamine, which gives a product resulting only from abstraction of an H atom from the 5-position of the cyclooctane ring in the intermediate nitrogen radical-cation.[43]

†† Nor in the case of cyclooctyloxy radicals produced by photolysis of cyclooctyl nitrite (Barton reaction).[41,38] (See footnote § on this page).

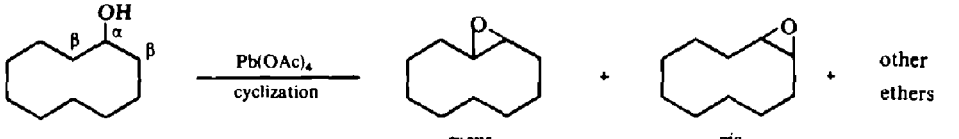
whereas the isomeric 1,4-ether (XXI) is obtained in only 6% yield.[44] A pronounced proximity effect, involving attack on hydrogen at the 5-position, has also been observed in the photolysis of 1-methylcyclooctyl hypochlorite.[45] These results would



XX XXI (6%) XXII (18%)

suggest that the 1-Me group changes appreciably the geometry of the cyclooctane ring in the reacting tertiary 1-methylcyclooctyloxy radical* and thus, by influencing on stereoelectronic and steric factors, decreases the activation energy of the 7-membered† cyclic transition state (of type XI, n = 2; Scheme 2A) necessary for 1,5-ether formation by way of ε-hydrogen abstraction.

Cyclodecanol (XXIII) also undergoes intramolecular ether formation to a considerable extent (27·5%; Table 1), but here *several* oxido-compounds were isolated, the major product (about 12%) being *trans*-epoxycyclodecane (XXIV), accompanied by a small amount (about 1%) of the *cis*-isomer (XXV).[36] This appears to be the *first case of oxirane ring formation from an alcohol and lead tetraacetate*, and it might possibly occur, as the result of proximity effects, by a transannular hydrogen shift from a remote carbon to oxygen in the intermediate cyclodecalyloxy radical (of type V, Schemes 1 and 2A) followed by a second transannular transfer of an H atom from the β-carbon (C2) to the radicalic carbon in the so-produced hydroxy-carbon-alkyl radical (of type XII, Scheme 2A), or preferably by a similar transannular hydride ion shift in the corresponding hydroxy-carbonium ion (of type XIII, Scheme 2A).[36]



XXIII *trans* XXIV (12%) *cis*- XXV (~1%) (14–15%)

In the case of cyclododecanol, the activation energy of the cyclic transition state (of type XI, Scheme 2A) necessary for intramolecular ether formation must be considerably higher, probably as the result of unfavourable conformational factors,‡ since cyclization amounts to only 8·5% (Table 1, Fig. 1); three ethers are formed in this process, and they all appear to be unrearranged cyclic oxido-compounds containing only α-CH groups.[36]

* As compared to the unsubstituted secondary cyclooctyloxy radical discussed above.

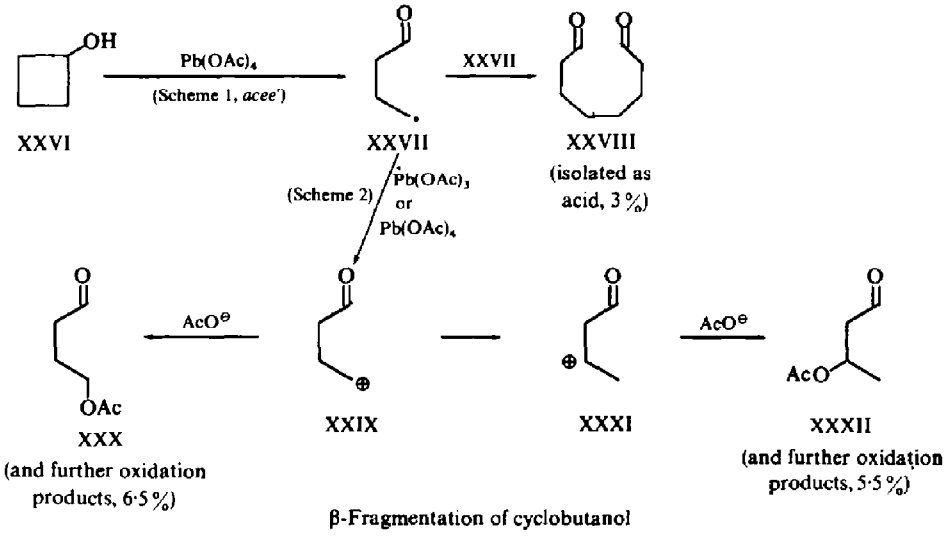
† See footnote * on p. 4953.

‡ In S_N2 reactions of cyclic compounds the rate minimum corresponds to the 12-membered ring,[31] and has been ascribed to difficulties in achieving collinearity of the entering and leaving groups.[31,32] This collinearity factor or some similar effect, which would depend on the possible conformations in the transition states, may be also of (some) importance (in addition to steric effects) in the intramolecular formation of cyclic ethers from alcohols and lead tetraacetate.[4a,7]

Intramolecular cyclic ether formation from cyclohexadecanol and lead tetraacetate parallels the cyclization reaction of secondary aliphatic alcohols, such as 2-octanol,[7] whereby only one normal oxido-product (with two α-CH groups) is formed in 45% yield (probably the 1,4-ether).

β-Fragmentation reaction (with ring opening). As can be seen from Table 1 and Fig. 1, the yield of fragmentation reaction (of type *acee'*, Scheme 1), involving opening of the alicyclic ring by way of α,β-carbon–carbon bond cleavage, decreases from cyclobutanol to cyclohexanol, when it reaches a minimum value corresponding to the amount of β-scission observed in the lead tetraacetate reaction of "strain-free" secondary aliphatic alcohols, such as 2-octanol;[7] with cycloheptanol and cyclooctanol the yield of fragmentation products increases again slightly. This order of ease of fragmentation of cycloalkanols (based on yield data) is in accord with the total strain associated with carbocyclic rings of various size,[33] and parallels, in general lines, the ease of β-scission with ring opening of cycloalkoxy radicals generated photolytically or thermally from the corresponding hypochlorites[46] or nitrite esters,[40,38] thus indicating that relief of strain by way of ring opening (in cyclic oxy radicals) is yet another factor which influences the rate of the lead tetraacetate β-fragmentation reaction of alcohols. It should be noted that Jeger *et al.*,[47] and Fried and Brown[48] have recently reported that hydroxyl containing 4-membered rings incorporated in fused polycyclic systems undergo to a considerable extent the ring opening fragmentation reaction, when subjected to the action of lead tetraacetate.

That the lead tetraacetate fragmentation of alcohols proceeds as shown on Schemes 1 (*cee'*) and 2B, i.e. through the initial formation of a carbon radical fragment (of type VIII), is supported, as illustrated in Scheme 3, by the isolation, from cyclobutanol (XXVI) and lead tetraacetate (Table 1), of the dimerization product XXVIII, in about 3% yield (actually obtained in the form of its dicarboxylic—suberic—acid),* whereas further one-electron oxidation of the carbon radical fragment XXVIII



β-Fragmentation of cyclobutanol

SCHEME 3

* For details of isolated fragmentation products see Experimental.

(Scheme 3) to the corresponding carbon cation XXIX, in the course of the reaction, is supported by the formation of both the unrearranged primary acetate XXX and the rearranged secondary acetate XXXII (actually these acetoxy-aldehydes XXX and XXXII undergo, in major part, further oxidation, to give the corresponding acetoxy acids or their esters with starting alcohol[6]).[7,*] Similar unrearranged and rearranged fragmentation products were also observed in the lead tetraacetate reaction of cyclopentanol (Table 1).*

Beside the products from the above-described three oxidation processes, unreacted alcohol and its acetate were always obtained in various amounts (Table 1), and in the case of cyclodecanol and cyclododecanol, 2–3% of the corresponding *cis*- and *trans*-cycloalkenes were also isolated. The possible formation paths of these products were discussed elsewhere.[6–8, 11–13, 21]

EXPERIMENTAL†

M.ps and b.ps are uncorrected. Gas chromatography: Perkin–Elmer instrument, Model 116-E, equipped with a thermistor detector; the columns (2 m × 4 mm, 6 m × 8 mm) consisted of 1,2,3-tris-(2-cyanoethoxy)propane (TCEP) or Apiezon L adsorbed on Chromosorb P or Celite (30–40%); the temp 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 analysed. IR spectra: Perkin-Elmer Infracord, Models 137B and 337. NMR spectra: Varian A-60A spectrometer.

The preparation of lead tetraacetate, drying of the reagents and the lead tetraacetate oxidations in benzene were carried out as described previously.[7] If not stated otherwise, the oxidations were performed under reflux at 80°, using n moles of alcohol, (n + 5–10% excess) moles $Pb(OAc)_4$, (n + 5–10% excess) moles anhd. $CaCO_3$ and $n \cdot 1000$–$n \cdot 1500$ ml dry benzene. The neutral products from the benzene ether extract (neutral part),[7] upon separation (by distillation, column chromatography and gas chromatography) where characterized and identified on the basis of their elemental analyses and physical properties (b.ps, m.ps, retention times, refractive indices, IR spectra, NMR spectra, mass spectra, m.ps of solid derivatives), which were usually compared, when possible, with those of authentic compounds synthesized by independent routes. The yields of products were in most cases determined from gas chromatograms (planimetrically); carbonyl compounds were, if necessary, also estimated quantitatively by conversion to 2,4-dinitrophenylhydrazones,[49] or, when not otherwise possible, from intensity measurements of IR absorption bands (base line method).[50] The acid components were isolated from the $NaHCO_3$-washings (acid part),[7] upon acidification and ether extraction.

Cyclobutanol. The oxidation of 0·1 mole (7·2 g) of cyclobutanol[51] (b.p. 123–125°, n_D^{25} 1·4330[51,52]) was completed after 6 hr. Upon fractional distillation of the neutral part (at 760, 40 and 13 mm), the various fractions (4·7 g) were subjected to preparative gas chromatography, affording: 3·5% cyclobutanone (identical with the synthetic ketone,[51] b.p. 98–99°, n_D^{25} 1·4180[51,53,54]); 16·8% recovered cyclobutanol; 25·2% cyclobutyl acetate (in agreement with an authentic specimen, b.p. 130–132°, n_D^{25} 1·4165,[55,56] prepared from cyclobutanol and acetyl chloride in pyridine); 1·1% 4-acetoxybutyraldehyde (2-acetoxytetrahydrofuran) (compared with the product, b.p. 85–86° at 11 mm, n_D^{25} 1·4240,[57] obtained by cleavage of 1,2,3-pentanetriol 5-acetate with $Pb(OAc)_4$ in ether[57]). The residue (3·1 g) from the distillation of the neutral part was hydrolysed with 20% H_2SO_4 aq (stirring and heating at 80° for 3 hr), and the mixture was continuously extracted with ether. The ethereal layer was washed with sat $NaHCO_3$ aq (until neutral), dried and subjected to gas chromatography, affording 11% of cyclobutanol (but no cyclobutanone) and 5·3% γ-butyrolactone (compared with a commercial (Fluka) product, b.p. 83–84° at 11 mm). The combined $NaHCO_3$-washings were acidified with mineral acid, continuously extracted with ether, and the dried ethereal layer treated with diazomethane. Gas chromatography of the resulting soln showed the presence of 3-hydroxybutyric acid methyl ester in 3·9% yield (based on starting cyclobutanol) (in agree-

* See preceding footnote.

† We thank Mrs. R. Tasovac, from the Microanalytical Laboratory of our Department, for the elemental microanalyses.

ment with a synthetic specimen, b.p. 67–68° at 13 mm, n_D^{25} 1·4180,[58] prepared by Pt hydrogenation of methyl acetoacetate).

The acid part, upon acidification of the $NaHCO_3$-washings, extraction with ether, removal of the solvent and acetic acid from the organic layer, treatment of the residue, dissolved in ether, with diazomethane in ether, and gas chromatography of the resulting soln, afforded 1·6% of 3-acetoxybutyric acid methyl ester (compared with an authentic sample, b.p. 82–84° at 13 mm, n_D^{25} 1·4129,[58,59] obtained by treating 3-hydroxybutyric acid methyl ester with acetyl chloride in pyridine), and 3·2% suberic acid dimethyl ester (in agreement with a synthetic specimen, b.p. 133–134° at 13 mm,[60] prepared from suberic acid and diazomethane).

Cyclopentanol. The oxidation of 0·1 mole (8·6 g) commercial (Fluka) cyclopentanol was completed upon refluxing for 11 hr. Fractional distillation (at 25 mm and 11 mm) of the neutral part (6·9 g), followed by gas chromatography of the various fractions, afforded: 5·5% cyclopentanone[53,61] (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 144–145°[61]); 1·7% cyclopentyl formate (in agreement with the authentic ester, b.p. 137–139°[62]); 25·2% unchanged cyclopentanol; 26% cyclopentyl acetate (authentic acetate, b.p. 152–153°,[61,62] was prepared from cyclopentanol and acetic anhydride[55,56]); 2·3% α-acetoxycyclopentanone (compared with the product, b.p. 116–117° at 15 mm,[63,64] obtained by α-acetoxylation of cyclopentanone with $Pb(OAc)_4$[63]).

The residue (1·6 g) from the distillation of the neutral part was hydrolysed with 20% H_2SO_4 aq (3 hr at 100°) and the mixture was extracted with ether. The ethereal layer was neutralized by washing with sat $NaHCO_3$ aq, dried and gas chromatographed, affording 4·6% cyclopentanol (but no cyclopentanone), 1·8% γ-valerolactone (in agreement with an authentic specimen, b.p. 84–86° at 11 mm, n_D^{25} 1·4308[65,66]), and 2·1% δ-valerolactone (corresponding to a synthetic sample, b.p. 111–113° at 11 mm[66,67]).

Cyclohexanol. The oxidation of 0·1 mole (10·0 g) of cyclohexanol (commercial Fluka product) was completed in 13 hr. Gas chromatography of the various fractions (9 g) obtained by fractional distillation *in vacuo* of the neutral part, afforded: 0·82% 1,4-epoxycyclohexane (in agreement with 7-oxabicyclo-[2.2.1]heptane, b.p. 120–122°, prepared by passing *trans*-1,4-hexanediol over activated alumina at 280°[68]); 3·9% cyclohexanone[53,61] (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 160–161°[61]); 2% cyclohexyl formate (in agreement with the synthetic formate, b.p. 160–161°[62]); 20% unchanged cyclohexanol; 31·7% cyclohexyl acetate (authentic product, b.p. 172–174°,[61,62] from cyclohexanol and acetic anhydride); 1·5% α-acetoxycyclohexanone (corresponding to the synthetic keto-acetate, b.p. 122–124° at 15 mm, m.p. 40–41° (light petroleum),[63,69,70] prepared by treating cyclohexanone with $Pb(OAc)_4$ in benzene[70]). Gas chromatography of the acid-hydrolyzed distillation residue (~1·5 g) of the neutral part (see above cyclopentanol) showed the presence of about 1·2–1·5% of cyclohexanol, but no cyclohexanone.

Cycloheptanol. The oxidation of 0·1 mole (11·4 g) of (commercial Fluka) cycloheptanol (b.p. 183–183·5°[52,71]) was completed in 12·5 hr. Gas chromatography of the various fractions (amounting to 10·9 g) obtained upon distillation *in vacuo* of the neutral part, afforded: 15·3% 1,4-epoxycycloheptane (see below); 7·9% cycloheptanone[53,61,72–74] (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 146–147°[61,72–74]); 2·2% cycloheptyl formate (on the basis of its IR spectrum); 14·5% unchanged cycloheptanol; 38·2% cycloheptyl acetate (in agreement with an authentic acetate, b.p. 83–84° at 13 mm,[56,75] prepared from cycloheptanol and acetic anhydride in pyridine at room temp); 1·9% α-acetoxycycloheptanone (corresponding to the synthetic keto-acetate, b.p. 125–127° at 13 mm,[76] prepared from cycloheptanone and $Pb(OAc)_4$ in refluxing benzene). Gas chromatography of the acid-hydrolyzed distillation residue (1·2 g) of the neutral part (see above cyclopentanol) showed the presence of about 2·8% cycloheptanol, but no cycloheptanone.

The combined crude reaction products (neutral part) of two above-described $Pb(OAc)_4$ oxidations of cycloheptanol were reduced with LAH in diethyl ether (until disappearance of keto-carbonyl and ester-carbonyl groups), and the resulting mixture was fractionally distilled. A sample of the first fraction, (2·2 g, 10%), b.p. 60–65° at 28 mm, was further purified by gas chromatography (TCEP at 125°) to give 1,4-epoxycycloheptane, m.p. 45–47°.[28,*†] (Found: C, 74·8; H, 10·8. Calc. for $C_7H_{12}O$: C, 75·0; H, 10·8%).

Cyclooctanol. The oxidation of 0·1 mole (12·8 g) of (commercial Fluka) cyclooctanol (b.p. 101–102° at 16 mm[52,71,75]) in refluxing benzene was completed after 8 hr. Gas chromatography of the fractions (amounting to 12·2 g) obtained upon distillation *in vacuo* (at 15 mm and 4 mm) of the neutral part, afforded:

* See footnote † on page 4953.

† Cope *et al.*[28] have proved the structure of 1,4-epoxycycloheptane by conversion (with acetic anhydride and boron trifluoride etherate) to *trans*-1,4-cycloheptanediol.

35·2% of 1,4-epoxycyclooctane[28,29,*] (IR and NMR spectra identical with those of an authentic sample, b.p. 82–84° at 30 mm, m.p. 31°[77,78]); 0·8% of 1,5-epoxycyclooctane* (IR and NMR spectra identical with those of an authentic product, b.p. 81° at 30 mm, m.p. 52–54°[78,79]); 23% cyclooctanone (in agreement with authentic cyclooctanone, m.p. 43–44°[53,71,74,80]); 8·2% unchanged cyclooctanol; 14·8% cyclooctyl acetate (corresponding to the authentic acetate, b.p. 98–100° at 13 mm,[75,81] prepared from cyclooctanol and acetic anhydride in pyridine at room temp); 5·2% α-acetoxy-cyclooctanone.[80] Gas chromatography of the acid-hydrolyzed distillation residue (1·8 g) of the neutral part (see above cyclopentanol) showed the presence of about 3·4% cyclooctanol (but no cyclooctanone).

Cyclodecanol. This alcohols, b.p. 124–126° at 13 mm, m.p. 42°,[75,82,83] was prepared by LAH reduction of cyclodecanone,† b.p. 106–108° at 13 mm, m.p. 24–25°.[53,74,82,83] The oxidation of 0·1 mole (15·6 g) of cyclodecanol was completed in 10·5 hr. An aliquot of the crude reaction mixture—neutral part (16·3 g) was subjected to analytical and preparative gas chromatography on an Apiezon L column at 180°, and afforded: about 27·4% of a mixture of cyclic ethers (according to IR and NMR spectra); 40·9% of cyclodecanone (see above; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 163–164°[74,80,84]); 21·5% cyclodecyl acetate (IR spectrum and NMR spectrum identical with those of an authentic acetate, b.p. 122–124° at 13 mm, n_D^{20} 1·4685,[75,81,85] prepared from cyclodecanol and acetic anhydride in pyridine at room temp).

The remainder of the crude neutral part (15·0 g) was reduced with LAH in diethyl ether (until disappearance of keto-carbonyl and acetate–carbonyl groups) and the products obtained (9·8 g) were separated by chromatography on a column of Al_2O_3 (neutral, activity II). The mixture of cyclic ethers (4·1 g), eluted with pet. ether (b.p. 40–60°), was further separated by gas chromatography on TCEP at 140°. The first fraction was a mixture of *cis*- and *trans*-cyclodecenes (2·4% based on starting alcohol), whose IR and NMR spectra were identical with those of authentic products.[82,83,86,87] The next several components appeared to be all ethers (according to IR and NMR spectal data).[36] The last two compounds consisted of *trans*-1,2-epoxycyclodecane (11·8% yield based on starting cyclodecanol) and *cis*-1,2-epoxycyclodecane (about 1% yield based on starting alcohol), whose IR and NMR spectra, and retention times, were in agreement with those of authentic 1,2-oxides,[82,86] prepared by epoxidation (with perbenzoic acid) of the corresponding *trans*- and *cis*-cyclodecenes.[82,86]

It should be noted that such a separation of ether products from the crude reaction mixture, involving LAH reduction, is possible since it was found (in separate experiments) that *trans*- and *cis*-1,2-epoxycyclodecanes, contrary to most 1,2-epoxides, were *not* attacked or only very slowly by LAH in diethyl ether at room temp. This behaviour of 1,2-epoxycyclodecanes toward LAH was already previously described and discussed by Westen.[88]

Cyclododecanol. The oxidation of this alcohol† (0·05 moles, 9·2 g), m.p. 80°,[75] was completed in 16 hr. Gas chromatography of an aliquot of the crude reaction mixture (neutral part, 9·2 g) on Appiezon L at 180° showed the presence of 8·5% of ether compounds, 32·8% of cyclododecanone (in agreement with authentic cyclododecanone, m.p. 60–61°[53,74,84,89]), 29·1% of cyclododecyl acetate (corresponding to the authentic acetate, b.p. 145–147° at 13 mm,[75,87] prepared from cyclododecanol and acetic anhydride in pyridine at room temp). The remainder of the crude neutral part (7·8 g) was reduced with LAH in anhyd diethyl ether (until disappearance of keto-carbonyl and acetate–carbonyl groups) to afford 6·7 g of reduction products. This mixture (6·5 g) was chromatographed on Al_2O_3 (neutral, activity II), and the products (0·6 g) eluted with pet. ether (b.p. 40–60°) were subjected to gas chromatography on TCEP at 150°, to give 2–3%§ of a mixture of *cis*- and *trans*-cyclododecene,[87,90,91] and three more compounds, which are all saturated ethers with no other functional groups in their molecules (according to elemental analysis, IR, NMR and mass spectra).[36]

Cyclohexadecanol. The oxidation of 0·04 moles (9·6 g) of cyclohexadecanol,† m.p. 79–80°,[75] was completed upon refluxing for 8·5 hr. Quantitative IR measurements of the crude neutral part (9·7 g) showed the presence of about 15% cyclohexadecanone, whereas saponification value determination[61] gave an average yield of 26·3% of cyclohexadecyl acetate.[75] The crude neutral part (7 g) was reduced with LAH (until

* See footnote ‡ on page 4953.

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§ Yield based on starting alcohol.

disappearance of keto-carbonyl and ester-carbonyl groups) and the reduction products were separated by column chromatography on Al_2O_3 (neutral, activity II). The fraction (3·1 g) eluted with pet. ether (b.p. 40–60°) consisted (according to gas chromatography) of only one compound of mol wt 238 (mass spectrum), corresponding to 1,*x*-*epoxycyclohexadecane* (*x* probably = 4), m.p. 26–27°, obtained in 45% yield; NMR spectrum, δ = 3·84 (broad singlet, two $\underline{H}-\overset{|}{C}-O-$ α-protons). (Found: C, 80·6; H, 12·7. $C_{16}H_{30}O$ requires: C, 80·6; H, 12·7%).

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