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

METHYL- AND 4-*t*-BUTYL-CYCLOHEXANOLS—1

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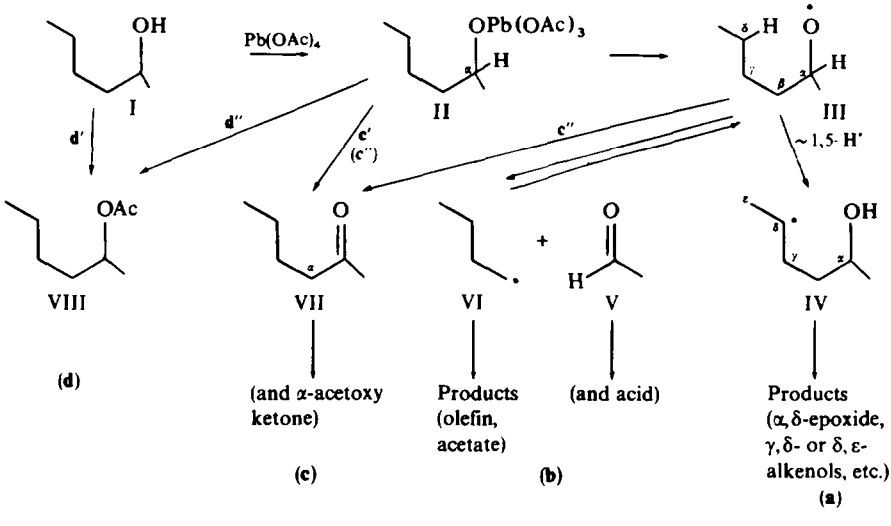
Abstract. In the reaction of lead tetraacetate (in refluxing benzene) with various isomeric and diastereomeric methylcyclohexanols and with *trans*- and *cis*-4-t-butylcyclohexanol (Table 1), it was found that the amount of intramolecular 1,5-hydrogen abstraction (**a**, Scheme 1) depends on the ease of attaining the cyclohexane conformation in which the hydroxylic oxygen and the hydrogen at the δ-carbon are in spatial proximity and suitably oriented, that the yield of β-fragmentation (**b**) is related to the stability of the intermediate open chain carbon radical fragment and to release of steric strain, and that oxidation to ketone (**c**) and acetate formation (**d**) appear to be controlled by factors similar to those which are known to be operative in the chromic acid oxidation and acetic anhydride acetylation of these alcohols.

IN THE present work cyclohexanol, 3,3-dimethylcyclohexanol, 4,4-dimethylcyclohexanol, and the diasteromers of 2-methyl-, 3-methyl-, 4-methyl-, 3,3,5-trimethyl- and 4-*t*-butyl-cyclohexanol were treated with one molar equivalent of lead tetraacetate in benzene (non-polar solvent) under thermal conditions, with the purpose of studying the effect of constitutional and steric (configurational and conformational) factors on intramolecular homolytic 1,5-hydrogen transfer (**a**, Scheme 1), β-fragmentation

SCHEME 1



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(**b**), oxidation to ketone (**c**) and acetate formation (**d**), namely on reactions which are known to occur when monohydroxylic alcohols are subjected to the action of lead tetraacetate in non-polar solvents.[3–5] The results obtained are presented in Table 1.

TABLE 1. PRODUCT DISTRIBUTION IN THE REACTION OF LEAD TETRAACETATE WITH CYCLOHEXANOL, METHYLCYCLOHEXANOLS AND 4-t-BUTYLCYCLOHEXANOLS (IN REFLUXING BENZENE)

Cyclohexanol (C_1–OH orientation)[c]		Yields (in %)[b] of products resulting from:				
		1,5-Hydrogen abstraction (**a**)[d]	β-Fragmentation (**b**)[e]	Oxidation to ketone (**c**)[f]		Formation of acetate (**d**)[f,h]
				Total yield	(ketone + α-acetoxy-ketones[g])	
1 cyclohexanol[7]	(eq)	0·8 (**14**)[i]	1·5	17·5	(9·5 + 8)	32
2 *trans*-2-methyl	(eq)	—	7 (+1·5)[j]	19	(12 + 7)	44
3 *cis*-2-methyl	(ax)	—	11 (+8)[k]	36	(25 + 11)	18
4 *cis*-3-methyl	(eq)	3 (**15**)[l]	1·5	16·5	(7·5 + 9)	40
5 *trans*-3-methyl	(ax)	—	2·7	33	(20 + 13)	24
6 *trans*-4-methyl	(eq)	0·8 (**16**)[m]	1·5	15·5	(6 + 9·5)	34
7 *cis*-4-methyl	(ax)	—	3	28	(18 + 10)	24
8 3,3-dimethyl	(eq)	9·5 (**17**)[i]	3	19·5	(13·5 + 6)	35
9 4,4-dimethyl	(eq)	—	2·5	21	(9 + 12)	31
10 *cis*-3,3,5-trimethyl	(eq)	—	2·5	23·5	(14 + 9·5)	59
11 *trans*-3,3,5-trimethyl	(ax)	55 (**18**)[i]	3·5	19	(13 + 6)	7
12 *trans*-4-t-butyl	(eq)	0·5 (**19**)[m] + 1·5 (**20**)[i]	1·5	14	(6 + 8)	40
13 *cis*-4-*t*-butyl	(ax)	—	2·5	30	(17 + 13)	21

[a] Using a 1:1 molar ratio of reactant.

[b] With the exception of β-fragmentation products[e] yields were in general obtained from gas-chromatograms (see Experimental).

[c] In the preferred chair form in which the methyl or *t*-butyl substituent at C-2, C-3, C-4 or C-5 is equatorial.

[d] See Schemes 1 and 2.

[e] Determined in the form of acid products of type **J** (Scheme 3) by titration with base (see Experimental).

[f] Of starting alcohol (Scheme 1).

[g] Further oxidation products of ketones, consisting of isomeric and/or stereoisomeric α-acetoxylated ketones.

[h] Starting alcohol was recovered in all runs in a yield of 12–40%.

[i] Of type **D** (Scheme 2).

[j] Of the epimeric *cis*-alcohol **3**, formed by reversible fragmentation (Scheme 3).

[k] Consisting of 5·7% of the epimeric *trans*-alcohol **2** and 2·3% of its acetate, formed by reversible β-fragmentation (Scheme 3).

[l] Of type **H** (Scheme 2).

[m] Of type **E** (Scheme 2).

(**a**) *Intramolecular* 1,5-*hydrogen abstraction*

In order to permit internal homolytic 1,5-hydrogen transfer from the δ-carbon to oxygen in the intermediate alkoxy radical (**a**, III→IV, Scheme 1), controlled by a 6-membered ring transition state,[3–5] and leading, in the case of the lead tetraacetate reaction, to tetrahydrofuran-type ethers (when the δ-carbon is primary or secondary)[3–5] and/or to olefinic (γ,δ- and δ,ε-) alcohols and derived products (when the δ-carbon is tertiary),[4–6] the optimal distance between δ-carbon and oxygen should be about

2.5–2.7 Å[3,4] with a suitable orientation of the C_δ—H bond (with respect to oxygen). Whereas for alcohols **7**, **9** and **13** (having an *a,e* or *e,a* orientation of substituents at C-1 and C-4 in the chair conformation) this is not possible even in the energetically unfavourable flexible (boat or twist-boat) conformation of type **A** (Scheme 2), since there is no flagpole hydrogen at C-4, in all other cyclohexanols the flexible form (of type **B** and **C**) would allow 1,5-hydrogen abstraction from the ring C-4 carbon atom. However, only cyclohexanol (**1**), *trans*-4-methyl- (**6**) and *trans*-4-*t*-butylcyclohexanol (**12**) underwent such an internal 1,5-hydrogen rearrangement to a small extent, resulting in the formation (Table 1) of the 1,4-epoxides **14** and, probably, **20*** (of type **D**, Scheme 2) from **1**[7] (secondary δ-carbon) and **12** (tertiary δ-carbon), respectively, and of the 4-alkyl-3-cyclohexen-1-ols **16** and **19** (of type **E**) from **6** and **12** (tertiary δ-carbons), respectively, in approximately 1–2% yield.† For these three cyclohexanols, which have no substituents at C-2 and C-3, the free energy difference at 80° (refluxing benzene) between the stable chair conformer (1,4-*e,e*) and the flexible form of type **C** (Scheme 2) should be similar and probably somewhat over 4 kcal/mole.‡ In alcohols **2**, **3** and **5**, which do not undergo 1,5-hydrogen shift when treated with lead tetraacetate, the free energy difference between the preferred chair form and the flexible form must be higher, because of eclipsing or near-eclipsing of the methyl group at C-2 or C-3 with a hydrogen at the adjacent carbon in the boat or twist-boat conformation of type **B** (Scheme 2).§ This is also true for alcohols **4**, **8**, **10** and **11** (which did not give 1,4-epoxides of type **D**), but here 1,5-hydrogen abstraction (**a**, III → IV, Scheme 1) can also involve the methyl group at C-3 in a chair conformation of the cyclohexane ring, such as **G** (Scheme 2). Alcohols **4**, **8** and **11** did actually react with lead tetraacetate in this way to give the corresponding 6-oxabicyclo[3.2.1]-octane products of type **H** in 3% (**15**), 9·5% (**17**) and 55% (**18**) yield, respectively (Table 1 and Scheme 2),‖ while with alcohol **10** no such cyclization (to **H**) could be observed. This difference in yield of ether products (of type **H**) is consistent with the free energy difference (in the reacting substrate) between the chair conformation of type **F**, which is usually more stable (however, see below) but structually unsuitable for internal 1,5-H shift, and the chair form of type **G** in which intramolecular 1,5-H transfer followed by cyclization can occur (i.e. in which both the oxygen at C-1 and a methyl group at C-3 are *syn*-axial), the values for $\Delta G°$ (at 80°), for the inversion chair **F** ⇄ chair **G**, calculated from reported conformational energies and 1,3-diaxial group interactions,[12] being approximately 3·4 kcal/mole for **4**, 1·7 kcal/mole for **8**, −1·8

* The identification of 1-*t*-butyl-7-oxabicyclo[2.2.1]heptane (**20**) is tentative and based on its IR spectrum (bands in the 930–1050 cm^{-1} region) and combined gas chromatography-mass spectrometry analysis [*m/e* = M, 154; M − CH_3, 139; M − $(CH_3)_3C$, 97; $(CH_3)_3C$, 57].

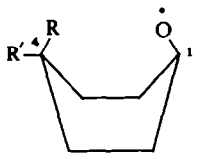
† Twist-boat conformations for *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate, with the 4-*t*-butyl group in the twist-equatorial and the 1-tosyloxy group in the twist-axial orientation (as in **C**, Scheme 2), have been proposed to rationalize the results of some solvolysis reactions.[8]

‡ Estimated on the basis of the value 3·6 kcal/mole for $\Delta G°$ at 80° for the transformation chair form ⇄ flexible form in cyclohexane itself,[9,10] and taking into account the van der Waals interaction between the twist-axial oxygen at C-1 and the twist-axial hydrogen at C-4[9,10] in the flexible conformation of type **C** (Scheme 2).

§ However, under drastic conditions, such flexible forms (as **B**) can be attained, for example by passing 2-methylcyclohexane-1,4-diol over alumina at 250–320°, whereby *exo*- and *endo*-2-methyl-1,4-epoxycyclohexane were formed in 24·5% and 5·5% yield, respectively.[11]

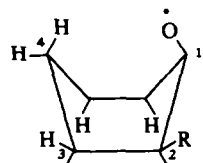
‖ For NMR spectra of these ether products (**15**, **17** and **18**) see Table 2 (Experimental part).

SCHEME 2



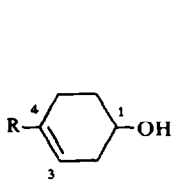
A

7: R = Me, R′ = H
9: R = R′ = Me
13: R = Me_3C, R′ = H



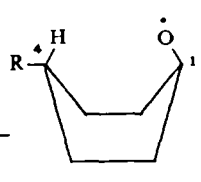
B

2: R = R″ = H, R′ = Me
3: R = Me, R′ = R″ = H
5: R = R′ = H, R″ = Me



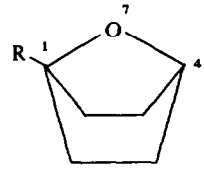
E

—
16:
19:



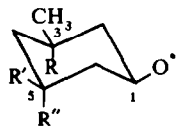
C

1: R = H
6: R = Me
12: R = Me_3C

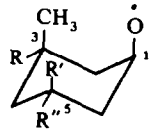


D

14
—
20

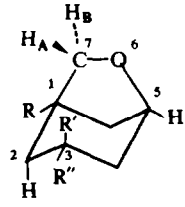


F



G

4; R = R′ = R″ = H
8: R = Me, R′ = R″ = H
11: R = R″ = Me, R′ = H
10: R = R′ = Me, R″ = H



H

15
17
18
—

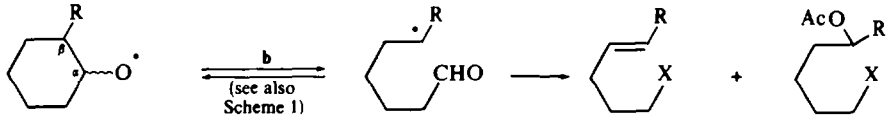
kcal/mole for **11** (i.e. the preferred chair form of this alcohol is **G** and already appropriate for internal 1,5-H migration, hence the good yield of ether product **18**), and 6·2 kcal/mole for **10** (which does not cyclize).

(**b**) β-*Fragmentation.* Homolytic α,β-carbon-carbon bond cleavage in the intermediate alkoxy radicals derived from cyclohexanols (III ⇄ V–VI, Scheme 3; see also **b**, Scheme 1) results in opening of the ring and affords, in the lead tetraacetate reaction, as final products a mixture of olefinic and unsaturated aldehydes (**I**, Scheme 3) and corresponding acids (**J**, Scheme 3).

As shown in Table 1, the yield of β-fragmentation when β-unsubstituted cyclohexanols are used as substrates is low (about 1·5–3·5%), and corresponds to the amount of β-cleavage observed in the lead tetraacetate reaction of aliphatic β-unsubstituted

secondary alcohols,[4,7,13,14] since in both cases the reacting systems are of comparable stability and the resulting fragmentation carbon radicals are primary (V–VI, R = H, Scheme 3; VI, Scheme 1).[3–5] However, with β-monosubstituted alcohols, such as the diasteromeric *trans*- and *cis*-2-methylcyclohexanols **2** and **3**, β-fragmentation proceeds to a larger extent (up to 11%), due to the intermediate formation of more stable secondary carbon radicals (V–VI, R = Me, Scheme 3).[3–5,14]

SCHEME 3



III R = H or Me V–VI I X = CHO J: X = COOH

Moreover, both of these alcohols (**2** and **3**) undergo also *reversible* β-*fragmentation*[1,3–5] (**3** more than **2**, see Table 1), i.e. α,β-bond cleavage in III (R = Me, Scheme 3) followed by intramolecular recombination of the carbonyl moiety with the carbon radical site in V–VI, to give back the alkoxy radical III, but now as a mixture of diastereomers with starting and opposite stereochemistry. This was established by detecting *cis*-2-methylcyclohexanol **3** (1·5%) among the products formed from the *trans*-epimer **2**, and *trans*-2-methylcyclohexanol **2** (5·7%) and its acetate (2·3%) in the reaction mixture obtained from the *cis*-epimer **3**, whereby the fact that reversible β-fragmentation is more favoured in the *cis*-alcohol **3** than in the *trans*-diastereomer **2** is consistent with the relative stabilities of these two epimers in their preferred chair conformation (**3**, OH-axial, being less stable than **2**, OH-equatorial).* To our knowledge, these are the only examples of reversible β-fragmentation in the lead tetraacetate reaction of alcohols which cannot undergo (via alkoxy radicals) 1,5-hydrogen abstraction (leading to ether ring closure), and resulting in the formation of the diastereomer of the starting alcohol.†

It should also be noted that in all cases listed in Table 1 the upper limit of β-fragmentation was observed with alcohols containing an axial hydroxyl group (**3**, **5**, **7**, **11**, **13**) or axial alkyl group (**8**–**11**), probably because here opening of the cyclohexane ring is associated with more release of steric strain (i.e. *syn*-axial interactions) than in substrates having only equatorial substitutents.

(c) *Oxidation to ketone.* As shown on Table 1, the yield of ketonic products (i.e. ketones of the starting alcohols and the corresponding α-acetoxy-ketones‡) formed in

* A similar ratio of reversible β-fragmentation, as reflected by the relative amounts of diastereomeric cyclic ether products, was also observed in the lead tetraacetate reaction of *trans*- and *cis*-2-butylcyclohexanol.[1]

† In all other cases reported so far,[1,3–5] reversible β-fragmentation was followed by internal 1,5-hydrogen transfer (Scheme 1, III ⇄ V + VI ⇄ III′ → IV′) and ring closure, affording as final products cyclic ethers which were isomeric or/and stereoisomeric with intramolecular ethers formed in the direct cyclization process (Scheme 1, III → IV → ether).

‡ α-Acetoxy-ketones are formed by further action of lead tetraacetate on the ketone products (VII, Scheme 1). The constitution and stereochemistry of α-acetoxy-ketones obtained from alcohols **1**–**13** and directly from the corresponding ketones (by means of lead tetraacetate) will be described in a forthcoming communication.

the lead tetraacetate reaction (**c**, Scheme 1) did not exceed 36%.* this being consistent with previous observations that in non-polar media the lead tetraacetate oxidation of alcohols to the corresponding carbonyl compounds is not particularly favoured, even when other competing processes (1,5-hydrogen abstraction **a** and/or β-fragmentation **b**) are slow or not feasible.[3-5,7,13] However, two points are here of interest and in general agreement with data resulting from the study of chromic acid oxidation of methyl- and *t*-butyl-cyclohexanols:[15,16] (1) In all diastereomeric *cis-trans* pairs, the alcohol with an axial hydroxyl group gives higher yield of ketonic products than the equatorial epimer; (2) the order of ease of ketone formation (based on yield data from Table 1) follows qualitatively the sequence found for oxidation rates with chromic acid. These results support the view that the lead tetraacetate oxidation of alcohols to the corresponding carbonyl products VII (**c**, Scheme 1) is predominantly a process involving heterolytic decomposition of the intermediate alkoxy-lead(IV)-acetate complex II (**c'**, i.e. $-H^+$ and $-Pb(OAc)_3^-$) and that homolytic α-hydrogen eliminations from II and/or III (**c''**, involving $-H^\cdot$) are of minor importance.[3-5]

(**d**) *Acetate formation.* Whatever the mode of O-acetylation (**d**, Scheme 1) of starting alcohols in the lead tetraacetate reaction may be [formation of VIII either by direct esterification of I (**d'**) and/or via II (**d''**)],[4,5,17] data in Table 1 show (1) that the ease of acetate formation (as reflected by product yield) corresponds in general lines to the relative rates of esterification of these alkyl-cyclohexanols with acetic anhydride (in pyridine),[18-20] and (2) that in all cases an alcohol with equatorial hydroxyl is more reactive to esterification than its axial epimer, which also agrees with the results of direct O-acetylation with acetic anhydride.[18-20]

In conclusion it can be said that although lead tetraacetate in refluxing benzene reacts with various methyl- and 4-*t*-butyl-cyclohexanols in a complex way involving several parallel and competing reaction sequences, each of the individual processes described above is qualitatively subjected to similar structural and steric (i.e. energetic) requirements which have been previously shown to control the reactivity of such cyclohexane systems in other simple chemical transformations of known mechanistic course.

EXPERIMENTAL

B. ps and m. ps are uncorrected. Gas chromatography: Perkin–Elmer instrument, Model 116-E (thermistor detector) and Varian Aerograph instrument, Model A-700 (thermistor detector) for preparative separations; Varian Aerograph instrument, Series 1200 (flame-ionization detector) for analytical purposes; the columns consisted of Carbowax 20M, 1,2,3-tris(2-cyanoethoxy)propane (TCEP), Apiezon L or polyethylene glycol 4000, as stationary phases, adsorbed on Chromosorb P or Celite, as solid supports; carrier gas—dry H_2. IR spectra: Perkin–Elmer Infracord instruments, Models 137B and 337. NMR spectra: Varian spectrometers A-60A (60 MHz) and HA-100-D (100 MHz); $CDCl_3$ or CCl_4 solutions and TMS as internal standard were used (chemical shift values given in δ units). Fractional distillations were performed on a Podbielniak spinning band column and on well isolated, modified semi-micro Vigreux columns.

Starting materials. Cyclohexanol, 2- and 3-methylcyclohexanol, *trans*-4-methyl- and *cis*-4-methylcyclohexanol were of commercial (Fluka) origin; they were purified by fractional distillation and/or gas chromatography, and the *cis-trans* mixtures of 2- and 3-methylcyclohexanol were separated into the pure dias-

* Differences in yields of ketonic (and other) products obtained from the same substrate (*e.g.* cyclohexanol),[7] which were observed in several cases of repeated lead tetraacetate oxidations,[7] are probably due to a different quality of lead tetraacetate[7] (and also, possibly, to somewhat different reaction conditions). Therefore, in the present work, all the reactions listed in Table 1 were carried out under identical conditions (see Experimental) and with the same lead tetraacetate.

tereomers by preparative gas chromatography and other reported procedures,[19,21] to afford, in all cases, compounds with correct physical constants.[16,19-22] Literature methods were used for the preparation of the following alcohols: 3,3-dimethylcyclohexanol (from dimedone, H_2/PtO_2 in AcOH),[19,23] b.p. 83–85° at 15 mm;[19,20,23,23] 4,4-dimethylcyclohexanol (from methyl vinyl ketone and isobutyraldehyde,[19] via 4,4-dimethyl-2-cyclohexen-1-one, H_2/PtO_2[19,25]), b.p. 80–81° at 13 mm;[19,24] *cis*-3,3,5-trimethylcyclohexanol (from isophorone, H_2/Ni,[26] followed by acid phthalate separation[27]), m.p. 37–38°;[26-28] *trans*-3,3,5-trimethylcyclohexanol (from isophorone, H_2/PtO_2 in AcOH),[27] m.p. 57–58°;[26-28] *trans*-4-*t*-butylcyclohexanol (by mixed hydride reduction of 4-*t*-butylcyclohexanone),[29,30] m.p. 80–81°;[20,28-31] *cis*-4-*t*-butylcyclohexanol (by reduction of 4-*t*-butylcyclohexanone with $IrCl_4$–HCl-trimethyl phosphite in 2-propanol),[32] m.p. 82–83°.[20,28,31,32]

Lead tetraacetate reactions. The oxidations in refluxing benzene were carried out as described previously,[4,13] using *n* moles of alcohol, *n* (+5% excess) moles $Pb(OAc)_4$, *n* (+5% excess) moles anhd $CaCO_3$, and $n \cdot 1500$–$n \cdot 2000$ ml dry (thiophene-free) benzene. Upon working up,[4,13] the benzene-ether extract ("neutral part") contained all the neutral products, while the $NaHCO_3$-washings ("acid part") contained acid products (J, Scheme 3) resulting from further oxidation of the β-fragmentation aldehydes I. Since oxidation of I to J takes place readily in the presence of air, acids J were also formed in the "neutral part" on standing. In order to obtain reliable results on the yield of the β-fragmentation reaction, in repeated lead tetraacetate reactions (with 0·1 mole of alcohol), the products in the "neutral part", after removal of solvents, were dissolved in dioxane (150–200 ml), treated with $AgNO_3$ (8·5 g) in 40 ml water and NaOH (15 g) in 40 ml

TABLE 2. SPECTRAL DATA OF THE BICYCLIC ETHERS **15**, **17** AND **18** OF TYPE **H** (SCHEME 2)

Ether **H** (Scheme 2)	IR (cm^{-1})	NMR[a] (shift – δ, *J* – Hz)			
		H—C_5—O	H_A, H_B > C_7—O	Me—C_1	Me—C_3
15[b] (R = R′ = R″ = H)	1100, 1070, 1050, 985, 932, 905	4·19, t	3.70, m	—	—
17[c] (R = Me, R′ = R″ = H)	1140, 1067, 1030, 992, 920, 910	4·22, t	3·67, d (H_A) 3·34, d (H_B) J_{AB} = 7·5	1·03, s	—
18[d] (R = R′ = Me, R″ = H)	1135, 1032, 998, 987, 918	4·32, t	3·72, d (H_A) 3·42, q (H_B)[e] J_{AB} = 7·5	1·03, s	0·91, d

[a] s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet.
[b] IR—CCl_4, NMR (60 MHz)—CCl_4.
[c] IR—film, NMR (60 MHz)—CCl_4.
[d] IR—film, NMR (100 MHz)—$CDCl_3$.
[e] Double resonance has shown that the H_B proton at C-7 in **18** (see **H**, Scheme 2) is coupled (^4J = 2·5 Hz) via long range "W" coupling[41] to the axial proton at C-4 (δ ~ 1·14).

water, and the resulting mixture containing Ag_2O was stirred at room temp. for 15 hr. It was then filtered off, the precipitate washed with aqueous NaOH and the combined alkaline filtrates evaporated. Upon addition of water (100 ml) and extraction with ether, the aqueous layer was acidified (conc HCl-H_2O 1:1) and extracted with ether. The ethereal layer was combined with the ethereal extract of the acidified original $NaHCO_3$-washings ("acid part", see above), dried and evaporated. Acetic acid and remaining HCl were removed by repeated addition of dry benzene and evaporation. The amount of β-fragmentation acid(s) (J, Scheme 3) was determined by titration of the residue with NaOH.[33]

Identification of products. Reaction products were separated and isolated by gas chromatography, and their yields were determined planimetrically from gas chromatograms. They were identified and characterized on the basis of their IR and NMR spectra (and, if necessary, elemental microanalysis) and, in most cases, by comparison of these spectral data and gas chromatographic retention times with those of authentic compounds.

With the exception of 3,3-dimethylcyclohexanone, b.p. 78–80° at 15 mm,[24] and 4,4-dimethylcyclohexanone, m.p. 39–41°,[24,25] which were prepared by chromic acid oxidation of the corresponding alcohols,[34] all other ketones (VII) used for comparison purposes were of commercial (Fluka) origin. Further oxidation products (of ketones), i.e. α-acetoxy ketones, were separated and compared with products obtained in separate lead tetraacetate oxidations of the corresponding ketones.*

Acetates of starting alcohols (VIII)[21,35] were obtained by the usual Ac_2O-pyridine or Ac_2O-AcOK method, and compared with esters formed in the lead tetraacetate reactions.

7-Oxabicyclo[2.2.1]heptane (**14**, R = H, Scheme 2) obtained from **1**[7] was identical with the cyclodehydration product of *trans*-1,4-cyclohexanediol.[11,36] 4-Methyl-3-cyclohexen-1-ol (**16**, R = Me, Scheme 2) from **6**, and 4-*t*-butyl-3-cyclohexen-1-ol (**19**, R = Me_3C, Scheme 2) from **12**, had spectral data in agreement with those of synthetic products prepared from *p*-methoxytoluene[37] and *p*-*t*-butylanisole,[38] respectively.

6-Oxabicyclo[3.2.1]heptane[39] (**15**, R = R′ = R″ = H, Scheme 2) from **4**† (Found: C, 74·75; H, 10·92. Calc. for $C_7H_{12}O$: C, 74·95; H, 10·78%), 1-methyl-6-oxabicyclo[3.2.1]heptane (**17**, R = Me, R′ = R″ = H, Scheme 2) from **8**† (Found: C, 75·90; H, 11·06. Calc. for $C_8H_{14}O$: C, 76·14; H, 11·18%), and *1,3-dimethyl-6-oxabicyclo*[3.2.1]*heptane* (**18**, R = R′ = Me, R″ = H, Scheme 2) from **11**, n_D^{24} 1·4512 (Found: C, 77·25; H, 11·50. $C_9H_{16}O$ requires: C, 77·09; H, 11·50%), had spectral data shown on Table 2.

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* Results of these ketone acetoxylations will be discussed elsewhere.

† The epoxides **15** and **17** were also produced in low yield (1–1·5%) in the lead tetraacetate reaction of cyclohexanemethanol and 1-methylcyclohexanemethanol, respectively.[40]

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