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LEAD TETRAACETATE OXIDATION OF SATURATED ALIPHATIC ALCOHOLS[1]—IV[2]

THE FORMATION OF SIX-MEMBERED CYCLIC ETHERS[3]

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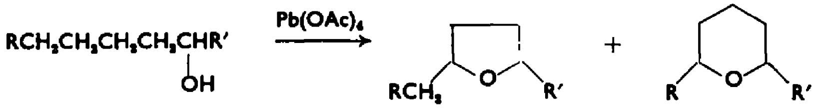
Abstract—The lead tetraacetate oxidation of saturated aliphatic alcohols, with structures which do not permit 1,5-cyclization, gave tetrahydropyran derivatives in yields not exceeding 16%. The formation of a small amount of the rearranged ether, 2-ethyl-2-methyltetrahydrofuran, from 4,4-dimethyl-1-pentanol indicates that the cyclization reaction proceeds *via* an intermediate with carbonium ion character.

Unbranched primary and secondary aliphatic alcohols (I) with δ- and ε-methylene groups react with lead tetraacetate in non-polar solvents to give as major products (33–50%) 2-alkyl- or/and 2,5-dialkyl-tetrahydrofurans (II), accompanied by small amounts (1–4%) of the isomeric six-membered cyclic ethers (III).[2,5]



I II III

This difference in reactivity between the secondary δ-hydrogen atoms and secondary ε-hydrogen atoms,[6] involved in 1,5- and 1,6-hydrogen transfer, respectively, was attributed[2] to different steric factors and probability conditions controlling the corresponding transition states (Va and Vb), through which the conversion of alkoxy radicals (IV) to the hydroxyalkyl carbon radicals (VI) is presumed to take place[7].

In the present work we have studied the action of lead tetraacetate on saturated aliphatic alcohols with structures permitting only ring closure to six-membered cyclic

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[1] Paper VII in the series *Reactions with lead tetraacetate.*

[2] For paper VI, part III, see M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, Lj. Lorenc and R. I. Mamuzić, *Tetrahedron* **21**, 2799 (1965).

[3] Presented at the XXXIV*th International Congress of Industrial Chemistry.* Belgrade, September 22–29 (1963).

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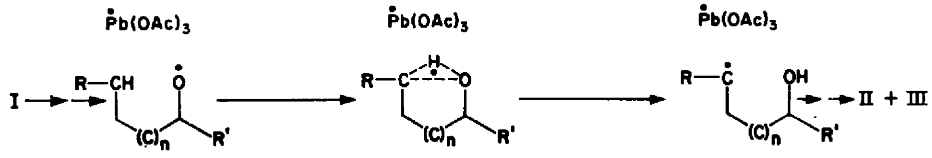
[5] V. M. Mićović, R. I. Mamuzić, D. Jeremić and M. Lj. Mihailović, *Tetrahedron Letters* No. 29, 2091 (1963); *Tetrahedron* **20**, 2279 (1964).

[6] Even when a tertiary hydrogen atom on a (non-activated) ε-methine group undergoes 1,6-abstraction, as shown on a 3α-hydroxy-5β-steroid, the yield of the corresponding six-membered cyclic ether was very low (0·4%). H. Immer, M. Lj. Mihailović, K. Schaffner, D. Arigoni and O. Jeger, *Experientia* **16**, 530 (1960); *Helv. Chim. Acta* **45**, 753 (1962).

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

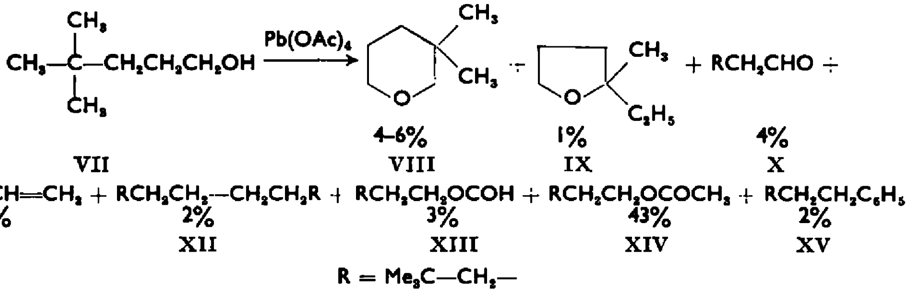


IV V VI

(a) n = 1; (b) n = 2

ethers (III), while the formation of tetrahydrofurans (II) was excluded in the normal reaction. The alcohols used were 4,4-dimethyl-1-pentanol and 4,4-dimethyl-1-hexanol.

4,4-Dimethyl-1-pentanol (VIII) reacts very slowly with an equimolar amount of lead tetraacetate in boiling benzene and in the presence of calcium carbonate, and even after 30 hr, the oxidizing agent was not completely consumed. The products isolated from the reaction mixture by fractional distillation and gas-chromatographic separation, and their yields, are shown in Scheme 1. In addition, about 8–10% of unreacted starting alcohol (VII) was recovered.

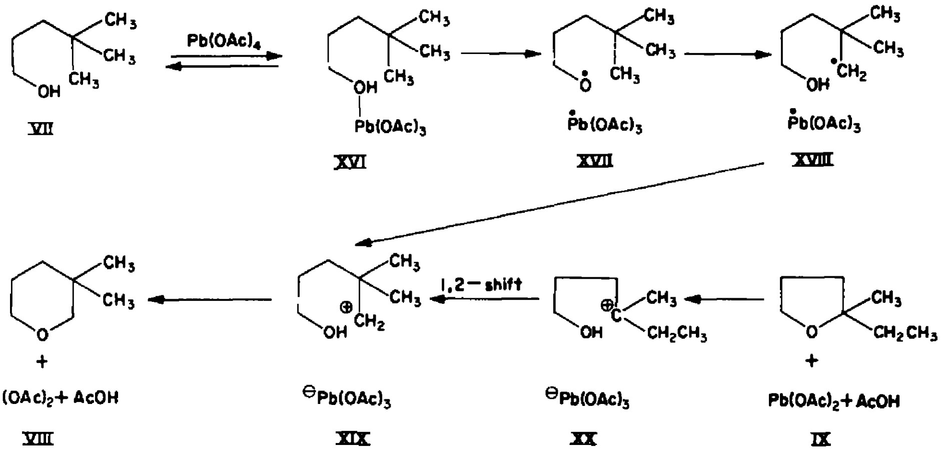


Scheme 1

The structures of the cyclic ether (IX), olefin (XI), saturated hydrocarbon (XII) and 1-phenyl-4,4-dimethylpentane (XV), which are all known compounds (Experimental), were confirmed by comparing their physical properties (b.ps, refractive indices, gas-chromatographic retention times, IR and NMR spectra) with those of the corresponding authentic products, synthesized as reported in the literature. The remaining reaction products are new compounds; 3,3-dimethyltetrahydropyran (VIII) is identical with the ether prepared by cyclization involving acid dehydration of 2,2-dimethyl-1,5-pentanediol; 4,4-dimethylpentanal (X) was isolated and characterized in the form of its 2,4-dinitrophenylhydrazone; the identity of the acetate (XIV) was established by comparison with an authentic sample, obtained by esterification of the starting alcohol (VII); structure assignment of the formate ester (XIII) was made on the basis of its IR spectrum.

As expected the yield of 3,3-dimethyltetrahydropyran (VIII) does not exceed 6%. However in analogous systems, such as 1-pentanol, 2-hexanol, 3-heptanol, 4-octanol and 5-nonanol, in which tetrahydropyran formation must also involve primary ε-hydrogen atoms, but which, in addition, can undergo the preferred 1,5-cyclization to tetrahydrofurans (II), the corresponding six-membered cyclic ethers (III) are either not produced or only present in traces.[2] In the case of 4,4-dimethyl-1-pentanol (VII) 1,6-cyclization does occur on account of the long reaction time, i.e. of the impossibility of tetrahydrofuran formation, and of the increased statistical probability of one of the primary ε-hydrogen atoms (from the terminal methyl groups) being abstracted by the oxygen in the alkoxy radical IV (IV → VI).

The isolation of the rearranged product, 2-ethyl-2-methyl-tetrahydrofuran (IX), is of particular interest. Since the evidence available indicates that alkyl radicals do not undergo 1,2-hydrogen or 1,2-alkyl shifts,[8] it is necessary to assume that the hydroxyalkyl carbon radical (XVIII, Scheme 2), generated from the alkoxy radical (XVII) upon 1,6-hydrogen transfer, is transformed to a primary carbonium ion (XIX), by a one-electron oxidation process (probably involving radical and ion pairs[9]). This primary, neopentyl-type carbonium ion (XIX) can either undergo cyclization to the normal reaction product, i.e. the tetrahydropyran derivative (VIII), or else it can rearrange by a 1,2-methyl shift to the more stable tertiary carbonium ion (XX), which will then furnish the five-membered cyclic ether (IX).



Scheme 2

Although evidence has been advanced[10] that in the lead tetraacetate cyclization of alcohols involving δ-hydrogen atoms, the δ-methine group affords intermediate species (of type XIX) with a more pronounced carbonium ion character than δ-methylene or δ-methyl groups, the formation of the rearranged cyclic ether (IX) from 4,4-dimethyl-1-pentanol (VII) strongly suggests that a primary hydroxylalkyl carbon radical (XVIII) can also be oxidized to an intermediate which has sufficiently marked carbonium ion properties (XIX) to undergo, prior to cyclization, rearrangement *via* 1,2-alkyl anion shifts (XIX → XX → IX).

Other interesting features of the lead tetraacetate oxidation of 4,4-dimethyl-1-pentanol (VII) are: (a) the formation of the "dehydration" product of the starting alcohol, i.e. 4,4-dimethyl-1-pentene (XI), and the formation of 1-phenyl-4,4-dimethylpentane (XV), both compounds probably arising from an intermediate acting as

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[8] *Cf.* C. Walling, *Free Radical Rearrangements* in *Molecular Rearrangements* (Edited by P. de Mayo) Part One, pp. 416–423. Interscience, New York (1963).

[9] Carbonium ion intermediates similar to XIX have been postulated to account for the formation of tetrahydrofurans from alcohols, in which one or both of the reacting centres (i.e. the carbinol carbon atom and the δ-carbon atom) are not fixed.[6,7]

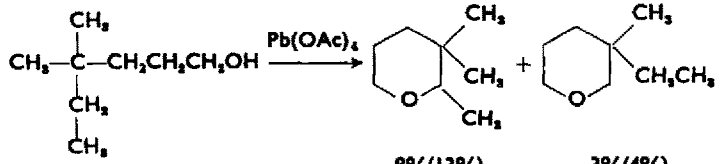
[10] D. Hauser, K. Schaffner and O. Jeger, *Helv. Chim. Acta* 47, 1883 (1964).

source of potential or actual carbonium ions of the type Me$_3$CCH$_2$CH$_2$CH$_2^{\oplus}$;[11,12] (b) the isolation of the "dimeric" hydrocarbon, 2,2,9,9-tetramethyldecane (XII), formally produced from the alkoxy lead triacetate XVI (Scheme 2) by rupture of the C—O bond and subsequent recombination.[11,12] Products similar to XI, XII and XV (and the corresponding monomers) also may be observed in other cases, particularly when cyclization of the alcohol is not possible and when the reaction proceeds slowly to completion (until disappearance of tetravalent lead).[12]

The esters (XIII and XIV) of the starting alcohol were expected products, since acetates are always (and formates usually) formed in the lead tetraacetate oxidation of aliphatic alcohols, their yields increasing (particularly that of acetates) with an increase in the duration of the reaction (i.e. in the time necessary for complete consumption of lead tetraacetate).[2,12]

The yield (free aldehyde + acetal[13]) of 4,4-dimethylpentanal (X) is, as expected, low (4%), since as recently demonstrated[12,14,15] the formation of carbonyl compounds from alcohols by means of lead tetraacetate proceeds by heterolytic cleavage of the O—Pb bond in the alkoxy lead triacetate (of type XVI, Scheme 2) with the elimination of an α-proton, and is not favoured in non-polar solvents. When the lead tetraacetate oxidation of 4,4-dimethyl-1-pentanol (VII) is carried out in the presence of two molar equivalents of pyridine (thus increasing the polarity and basicity of the solvent), the yield of the aldehyde (X) is increased to 19% and the reaction completed in 20 minutes (the yield of VIII was 2·5%, of IX about 1% and of VII + XIV 22%).

The oxidation of 4,4-dimethyl-1-hexanol (XXI) with an equimolar amount of lead tetraacetate in boiling benzene and in the presence of calcium carbonate is faster than the oxidation of 4,4-dimethyl-1-pentanol (VII), the reaction being complete after 12 hr. The products and their yields are given in Scheme 3. In addition, 5–7% of unreacted alcohol was recovered from the reaction mixture.



8%(13%) 3%(4%)

XXI XXII XXIII

+ RCH$_2$CHO + RCH=CH$_2$ + RCH$_2$CH$_2$OCOH + RCH$_2$CH$_2$OCOCH$_3$

3%(5%) 3%(—) 2%(1%) 22%(16%)

XXIV XXV XXVI XXVII

R = Me$_2$EtC—CH$_2$—

Scheme 3

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[11] Products such as XI, XII and XV (Scheme 1) were not observed when 4,4-dimethyl-1-pentanol (VII) was heated in benzene with lead dioxide, calcium carbonate or acetic acid, or with their various combinations.

[12] For a more detailed discussion on the possible pathways leading to products of these types see M. Lj. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović and Lj. Lorenc, *Tetrahedron* **21**, 1395 (1965), and Refs therein.

[13] The acetal (of X and VII) was not actually isolated but its presence was inferred[8,12] from spectral data of the high-boiling fraction, which, moreover, upon acid hydrolysis and treatment with 2,4-dinitrophenylhydrazine gave the same solid derivative as that obtained from the free aldehyde (X).

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

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

The structure of 2,3,3-trimethyltetrahydropyran (XXII) was deduced from its IR spectrum (ν_{max} in cm^{-1}: the bands at 1385 and 1364 suggest the presence of the 3,3-*gem*-dimethyl group, the attachment to a quaternary carbon atom being confirmed by the skeletal vibrations at 1189 and 1174; the band at 1377 corresponds to the 2-methyl group; ether band at 1101) and NMR spectrum at 60 Mc/s (Fig. 1). The singlets at 0·79 and 0·88 ppm correspond to the quaternary 3,3-*gem*-dimethyl grouping and the doublet centered at 0·97 ppm ($J \sim$ 6·5 c/s) to the tertiary 2-methyl group; the signals in the region 2·8–4·0 ppm are produced by the 2- and 5-protons, the tertiary 2-proton being responsible for the quartet centered at 3·05 ppm ($J \sim$ 6·5 c/s).

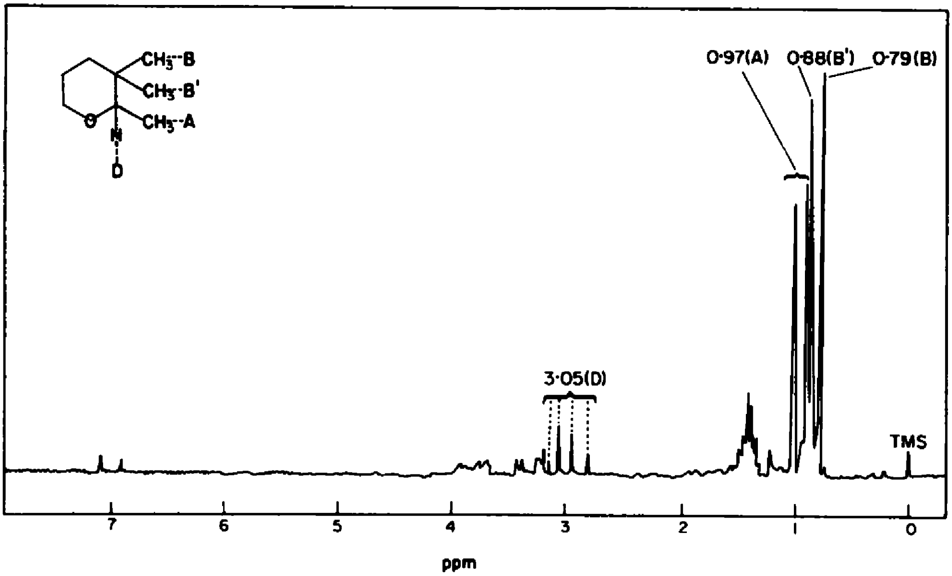

FIG. 1. NMR spectrum of 2,3,3-trimethyltetrahydropyran (XXII), at 60 Mc/s relative to TMS, 0·00 ppm.

The IR spectrum of the other isomeric cyclic ether (ether band at 1095 cm^{-1}) has peaks of lower intensity at 1383 and 1374 cm^{-1} (isolated methyl groups) and does not show skeletal vibrations characteristic of *geminal* methyl groups. Moreover, it differs from the IR spectra of the possible rearrangement products, i.e. 2,2-diethyltetrahydrofuran[16] and 2-isopropyl-2-methyltetrahydrofuran.[17] Therefore, the structure of this cyclic ether should correspond to 3-ethyl-3-methyltetrahydropyran (XXIII).

The structures of 4,4-dimethyl-1-hexene (XXV) and of the unreported acetate (XXVII) were confirmed by syntheses, while those of 4,4-dimethylhexanal (XXIV) and the formate ester (XXVI) were deduced from their IR spectra.

4,4-Dimethyl-1-hexanol (XXI) can give two six-membered cyclic ethers, the formation of 2,3,3-trimethyltetrahydropyran (XXII) involving 1,6-transfer of a secondary ε-hydrogen atom, and that of 3-ethyl-3-methyltetrahydropyran (XXIII) involving 1,6-abstraction of a primary ε-hydrogen atom. As expected from our results of the 1,5-cyclization of aliphatic alcohols to tetrahydrofuran derivatives,[2] the yield of ether XXII

[16] J. Colonge and P. Garnier, *Bull. Soc. Chim. Fr.* 432 (1948).

[17] R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.* 520 (1950); T. A. Favorskaya, N. V. Shcherbinskaya and E. S. Golovacheva, *Zhr. Obshch. Khim.* 23, 1878 (1953).

(8 %) is higher than that of ether XXIII (3 %), the reactivity (i.e. ease of intramolecular 1,6-hydrogen transfer) per ε-hydrogen being in the order: secondary > primary, 8:1.

It should be noted that the yields of the unsaturated hydrocarbon (XXV) and acetate (XXVII) are considerably lower than the yields of the corresponding analogous products (XI and XIV, Scheme 1) obtained from 4,4-dimethyl-1-pentanol (VII), undoubtedly because in the case of 4,4-dimethyl-1-hexanol (XXI) the time required for complete consumption of lead tetraacetate is shorter, i.e. because the cyclization reaction proceeds more readily.

When the lead tetraacetate oxidation of 4,4-dimethyl-1-hexanol (XXI) is performed in the presence of catalytic amounts of benzoyl peroxide (Scheme 3, yields of products given in parentheses), the reaction is much faster (5 hr) and the yields of tetrahydropyran derivatives are improved, particularly the yield of 2,3,3-trimethyltetrahydropyran (XXII), which is increased to 13 %.[6] This is in agreement with the homolytic character of the first stages of the cyclization process (Scheme 2). At the same time, the yield of the acetate (XXVII) decreases and the olefin (XXV) was not detected among the reaction products.

From these results and those obtained previously,[2,5] it may be concluded, first, that in the cyclization of aliphatic alcohols to tetrahydropyran derivatives by means of lead tetraacetate, an ε-methylene group (secondary hydrogens) involved in ring closure is more reactive than an ε-methyl group (primary hydrogens), probably because of polar and stability factors operating in the various stages of this process (Scheme 2),[2] and, secondly, that the formation of six-membered cyclic ethers from saturated aliphatic alcohols not containing activated centres is considerably less favoured than cyclization to tetrahydrofuran derivatives, even in cases where five-membered cyclic ethers cannot be produced, probably because the transition states (V) which control the transfer of a hydrogen atom from ε- and δ-carbon to oxygen (IV → VI) differ in their free energies of activation.

EXPERIMENTAL[18]

B.ps and m.ps are uncorrected. Analytical and preparative gas chromatography, and fractional distillations were carried out as described previously.[2,12] IR spectra were registered on a Perkin–Elmer Infracord, Model 137. NMR spectra were recorded on a Varian A-60 spectrometer at 60 Mc/s, in CCl_4 solution, using tetramethylsilane as internal standard.

Starting alcohols

4,4-Dimethyl-1-pentanol (VII), b.p. 158–160°, n_D^{23} 1·4205 (lit.[19] b.p. 158° at 737 mm, n_D^{20} 1·4202), was prepared[19] starting from t-butylmagnesium chloride and allyl bromide, *via* 4,4-dimethyl-1-pentene, 1-bromo-4,4-dimethylpentane and oxidation of the corresponding Grignard compound.

4,4-Dimethyl-1-hexanol (XXI), b.p. 86–87° at 15 mm, n_D^{20} 1·4339 (lit.[20] b.p. 95–98° at 21 mm, $n_D^{20.1}$ 1·4351), was obtained in a similar way,[20] from t-amylmagnesium chloride and allyl bromide, *via* 4,4-dimethyl-1-hexene,[21] 1-bromo-4,4-dimethylhexane and oxygen oxidation of the corresponding Grignard derivative.

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

[19] F. C. Whitmore and A. H. Homeyer, *J. Amer. Chem. Soc.* **55**, 4555 (1933).

[20] E. M. Gutman and W. J. Hickinbottom, *J. Chem. Soc.* 3344 (1951).

[21] A. L. Liberman and B. A. Kazanskii, *C.R. Acad. Sci., SSSR* **40**, 353 (1943); *Chem. Abstr.* **38**, 6271 (1944).

The purity of both alcohols was checked by gas chromatography.

Lead tetraacetate oxidations

The preparation of lead tetraacetete, drying of the reagents and benzene, and the general procedure for the oxidations were described previously.[2,12] When the reaction was interrupted before lead tetraacetate was completely consumed, the combined organic filtrates (benzene solution, separated from insoluble lead diacetate by filtration, and benzene washings), prior to extraction with 5–10% $NaHCO_3$aq, were treated with 10% KIaq and the liberated I_2 was reduced by washing with 10% $Na_2S_2O_3$aq. When the oxidation was carried out in the presence of 0·2 mole (+10% excess) pyridine (dried before use by distillation over KOH), per 0·1 mole of lead tetraacetate and alcohol, the addition of $CaCO_3$ was omitted. And, upon completion of the reaction, the combined organic filtrates (benzene solution and benzene washings) were successively washed with sat. NaClaq, dil. HCl, saturated $NaHCO_3$aq and sat. NaClaq. In general, all the aqueous layers were re-extracted with diethyl ether, since some of the reaction products (particularly cyclic ethers) were partially soluble in water.

The reaction products, obtained by gas-chromatographic separation, were identified by elemental analysis and spectral data (or conversion to solid derivatives) and, in most cases, by comparison of their physical properties (b.ps, refractive indices, gas-chromatographic retention times, IR and NMR spectra) with those of reference compounds, synthesized by independent routes. The yields of products are given in Schemes 1 and 3.

4,4-*Dimethyl*-1-*pentanol* (VII).

(a) *In the presence of calcium carbonate.* The oxidation of 11·6 g (0·1 mole) of VII with 0·1 mole (+2–5% excess) lead tetraacetate in 110 ml benzene and in the presence of 0·1 mole (+10–20% excess) $CaCO_3$ was interrupted after 30 hr heating under reflux. Gas-chromatographic separation of the fractions obtained by distillation afforded the following products (yields given in Scheme 1).

From the benzene fraction: 4,4-dimethyl-1-pentene (XI),[22] n_D^{20} 1·3922.

From the fraction, b.p. 110–130°: 3,3-*dimethyltetrahydropyran* (VIII),[22] n_D^{20} 1·4250. (Found: C, 73·3; H, 12·3. $C_7H_{14}O$ requires: C, 73·6; H, 12·4%); 2-ethyl-2-methyltetrahydrofuran (IX),[22] n_D^{20} 1·4200. (Found: C, 73·2; H, 12·2. Calc. for $C_7H_{14}O$: C, 73·6; H, 12·4%); 4,4-*dimethylpentanal* (X), 2,4-*dinitrophenylhydrazone*, m.p. 103–104° (undepressed by the dinitrophenylhydrazone of the aldehyde obtained from the oxidation of VII in the presence of pyridine; see below).

From the fraction, b.p. 70–90° at 13 mm: 4,4-*dimethyl*-1-*pentyl formate* (XIII), identified by its IR spectrum; 4,4-*dimethyl*-1-*pentyl acetate* (XIV).[22] n_D^{20} 1·4130. (Found: C, 68·6; H, 11·6. $C_9H_{18}O_2$ requires: C, 68·3; H, 11·5%); 2,2,9,9-tetramethyldecane (XII)[22]. (Found: C, 84·6; H, 15·3. Calc. for $C_{14}H_{30}$: C, 84·7; H, 15·3%.)

From the fraction boiling above 90° at 13 mm: 1-phenyl-4,4-dimethylpentane (XII)[22]. (Found: C, 88·3; H, 11·6. Calc. for $C_{13}H_{20}$: C, 88·6; H, 11·4%.)

(b) *In the presence of pyridine.* The oxidation, which was completed in 20 min heating under reflux, was carried out as in (a), but without $CaCO_3$ and in the presence of 0·2 mole (+10% excess) dry pyridine. The following products were obtained: 3,3-dimethyltetrahydropyran (VIII) in 2·5% yield; 2-ethyl-2-methyl-tetrahydrofuran (IX) in 1% yield; 4,4-dimethylpentanal (X) in 19% yield;[23] recovered alcohol (VII) + 4,4-dimethyl-1-pentyl acetate (XIV) in 22% yield. The aldehyde (X) was converted to 4,4-*dimethylpentanal* 2,4-*dinitrophenylhydrazone*,[24] which was recrystallized 4 times from EtOH, m.p. 103–104°, (Found: C, 53·3; H, 6·3; N, 19·1. $C_{13}H_{18}N_4O_4$ requires: C, 53·1; H, 6·2; N, 19·0%.)

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[22] Identical with an authentic product (see below *Syntheses of Reaction Products*).

[23] This yield represents the total yield of aldehyde. The low-boiling fraction (b.p. 112–135°) contained 15% of free aldehyde (X), while the residue (boiling over 80° at 13 mm), which probably contained the acetal of X and starting alcohol (VII),[18] upon mild acid (H_2SO_4) hydrolysis and quantitative conversion to the 2,4-dinitrophenylhydrazone,[24] gave another 4% of aldehyde (X).

[24] E. Müller (Editor-in-chief), *Methoden der Organischen Chemie* (Houben-Weyl) Vol. II (Fourth Edition), p. 457. Georg Thieme Verlag, Stuttgart (1953).

4,4-Dimethyl-1-hexanol (XXI)

(a) *In the presence of calcium carbonate.* The oxidation of 13 g (0·1 mole) XXI with 0·1 mole (+5% excess) lead tetraacetate in 120 ml benzene and in the presence of 0·1 mole (+10–20% excess) $CaCO_3$ was completed after 12 hr heating under reflux. The following products were obtained (yields given in Scheme 3).

From the fraction, b.p. 38–42° at 18 mm: *2,3,3-trimethyltetrahydropyran* (XXII), b.p. 39–40° at 18 mm, n_D^{21} 1·4355. (Found: C, 75·1; H, 12·4, $C_8H_{16}O$ requires: C, 74·9; H, 12·6%), structure assignment was based on the IR spectrum and NMR spectrum (Fig. 1), which are discussed above; *3-ethyl-3-methyltetrahydropyran* (XXIII), b.p. 40–42° at 18 mm. (Found: C, 74·7; H, 12·5. $C_8H_{16}O$ requires: 74·9; H, 12·6%), structure assignment was based on the IR spectrum, which is discussed above; *4,4-dimethylhexanal* (XXIV). (Found: C, 74·8; H, 12·6. $C_8H_{16}O$ requires: C, 74·9 H, 12·6%), was characterized by its IR spectrum.

From the fraction, b.p. 70–93° at 19 mm: *4,4-dimethyl-1-hexyl formate* (XXVI), structure assignment based on the IR spectrum; *4,4-dimethyl-1-hexyl acetate* (XXVII),[22] n_D^{20} 1·4238. (Found: C, 69·5; H, 11·6. $C_{10}H_{20}O_2$ requires: C, 69·7; H, 11·7%.)

4,4-Dimethyl-1-hexene (XXV),[23] (Found: C, 85·4; H, 13·3. Calc. for C_8H_{16}: C, 85·6; H, 13·4%), was isolated in part from the benzene fraction and in part from the fraction, b.p. 38–42° at 18 mm (the first drops).

(b) *In the presence of benzoyl peroxide.* The above oxidation (a) was repeated with the addition of 0·05 g benzoyl peroxide. After 5 hr heating under reflux, lead tetraacetate was completely consumed. The distribution of products, isolated by fractional distillation and gas chromatography, is shown on Scheme 3 (yields given in parenthesis).

Syntheses of Reaction Products

Unsaturated hydrocarbons (XI, XXV and XV)

4,4-Dimethyl-1-pentene (XI), b.p. 71°, n_D^{20} 1·3917 (lit.[19] b.p. 72·4° at 760 mm, n_D^{20} 1·3911–1·3918), was prepared by reaction of allyl bromide with t-butylmagnesium chloride in ether.[19] *4,4-Dimethyl-1-hexene* (XXV), b.p. 103–104°, n_D^{20} 1·4102 (lit.[21] b.p. 106·4° at 742 mm, n_D^{20} 1·4106), was prepared in a similar way, from allyl bromide and t-amylmagnesium chloride.[21] Both compounds gave correct elemental analyses for C and H. *1-Phenyl-4,4-dimethylpentane* (XV), b.p. 118–120° at 12 mm, n_D^{20} 1·4822 (lit.[25] b.p. 228°, n_D^{20} 1·4832). (Found: C, 88·4; H, 11·4. Calc, for $C_{13}H_{20}$: C, 88·6; H, 11·4%), was prepared[25] by the Huang-Minlon modification of the Wolff-Kishner reduction of benzylpinacolone.

Saturated hydrocarbon (XII)

2,2,9,9-Tetramethyldecane (XII), b.p. 95–96° at 13 mm, n_D^{20} 1·4243 (lit.[20] b.p. 93° at 10 mm, n_D^{20} 1·4250). (Found: C, 84·5; H, 15·1. Calc. for $C_{14}H_{30}$: C, 84·7; H, 15·3%), was prepared by treating the Grignard compound of 1-bromo-4,4-dimethylpentane[19,20] with dry AgBr in ether.[20]

Acetates (XIV and XXVII)

These esters were prepared by gently refluxing (2 hr) 0·05 mole alcohol (VII or XXI) with 0·05 mole acetic anhydride and 0·7 ml pyridine. The cooled mixture was washed successively with dil. HCl, 5% $NaHCO_3$aq and water, then dried ($CaSO_4$) and distilled *in vacuo*. *4,4-Dimethyl-1-pentyl acetate* (XIV) was obtained in 84% yield from VII, b.p. 70–71° at 16 mm, n_D^{20} 1·4138. (Found 68·5; H, 11·6. $C_9H_{18}O_2$ requires: C, 68·3; H, 11·5%.) *4,4-Dimethyl-1-hexyl acetate* (XXVII) was obtained in 77% yield from XXI, b.p. 88–89° at 15 mm, n_D^{21} 1·4230. (Found: C, 69·6; H, 11·6 $C_{10}H_{20}O_2$ requires: C, 69·7; H, 11·7%.)

Cyclic ethers (VIII *and* IX)

3,3-Dimethyltetrahydropyran (VIII). Diethyl 2,2-dimethylglutarate[26] (24 g, 0·11 mole) in 150 ml dry ether was slowly added, through a dropping funnel, to a stirred suspension of 5·23 g (0·11 mole +

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[25] E. Berliner and F. Berliner, *J. Amer. Chem. Soc.* **72**, 222 (1950).

[26] This ester, b.p. 118–120° at 12 mm, was prepared in 94% yield by esterification[27] of 2,2-dimethylglutaric acid with ethanol, using toluene as solvent and conc. H_2SO_4 as acid catalyst.

[27] V. M. Mitchovitch, *Bull. Soc. Chim. Fr.* [5] 4, 1661 (1937).

24% excess) LAH in 300 ml ether, at a rate to produce gentle refluxing of the mixture. Upon addition, heating and stirring were continued for another hr. The cooled mixture (0°) was carefully treated (dropwise) with acetone (10 ml) and then with water (5 ml), 15% NaOHaq (5 ml) and water (5 ml). After stirring for 45 min, the granular precipitate was separated by filtration and extracted (in a Soxhlet apparatus) with ether. The original ethereal filtrate and ethereal extract were combined, dried (K_2CO_3) and fractionated. 2,2-Dimethyl-1,5-pentanediol, b.p. 137–139° at 14 mm (lit.[28] b.p. 134° at 10 mm) was obtained in 65·5% yield (9·5 g).

This diol (9·0 g, 0·068 mole) and 1 g phosphoric acid (86%; sp.gr. 1·7) were placed in a distillation flask and slowly heated to 180°, when products started to distill. After 2 hr at 200° the reaction was complete. The layers in the distillate were separated, the lower aqueous layer was extracted with ether, the ethereal extract combined with the original upper layer, and washed with 5% $NaHCO_3$aq and with sat. NaClaq. After drying (K_2CO_3) and removal of solvent, the residue was distilled over Na and afforded 4·5 g (58%) 3,3-*dimethyltetrahydropyran* (VIII), b.p. 115–116°, n_D^{20} 1·4259. (Found: C, 73·4; H, 12·3. $C_7H_{14}O$ requires: C, 73·6; H, 12·4%.)

2-*Ethyl-2-methyltetrahydrofuran* (IX). This cyclic ether was prepared[16] from allylethylmethylcarbinol, *via* 2-ethyl-2-methyl-4-bromotetrahydrofuran and 2-ethyl-2-methyl-2,5-dihydrofuran. Hydrogenation of the dihydrofuran with Raney Ni (in water at 30–40 atm and 40°) afforded 2-ethyl-2-methyltetrahydrofuran (IX), b.p. 118°, n_D^{25} 1·4170 (lit.[16] b.p. 119°, n_D^{15} 1·4218). (Found: C, 73·2; H, 12·2. Calc. for $C_7H_{14}O$: C, 73·6; H, 12·4%.)

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[28] L. Bouveault and G. Blanc, *C.R. Acad. Sci. Paris* **137**, 329 (1903); *Bull. Soc. Chim. Fr.* [3] **31**, 1203 (1904); see also E. Chabley, *C.R. Acad. Sci. Paris* **156**, 1022 (1913).