Reaction of Lead Tetra-acetate with 2-Cyclohexylethanol and 3-Cyclohexyl-, 3-Cyclohex-1-enyl-, and 3-Cyclohexylidene-propan-1-ol

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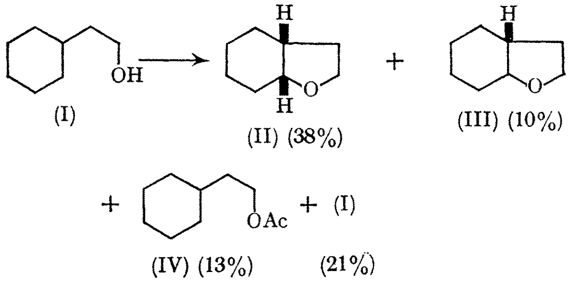
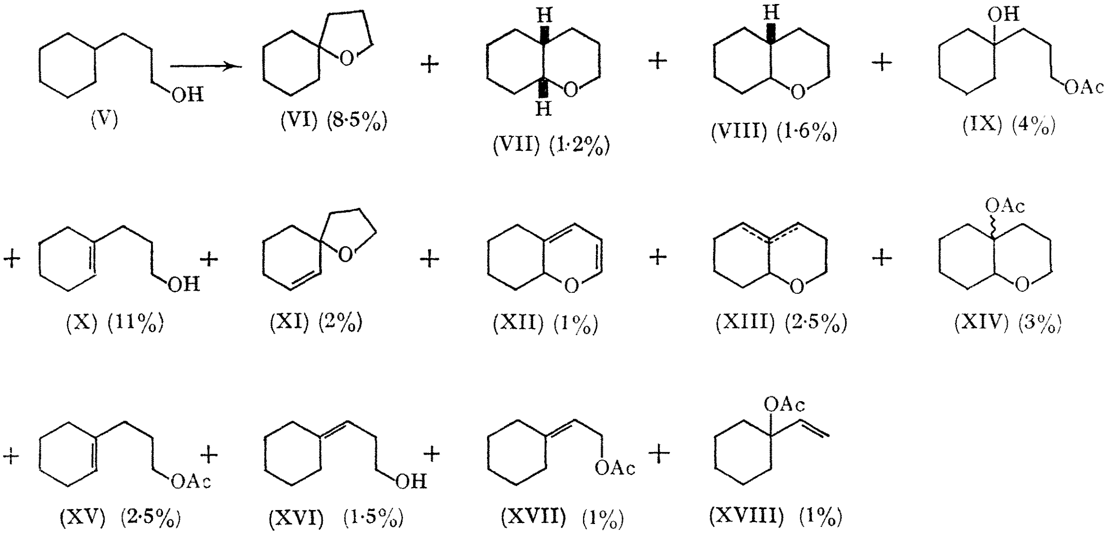
TREATMENT of 2-cyclohexylethanol (I); in benzene with lead tetra-acetate (1 mol.) gave the expected intramolecular *cis*-(II) and *trans*-ethers (III), and the acetate (IV).†



SCHEME 1

Under identical conditions 3-cyclohexylpropanol (V) gave a complex mixture of products (Scheme 2) together with 3-cyclohexylpropan-1-al (1%), unchanged (V) (36%), and the corresponding formate (2%) and acetate (4%).



SCHEME 2

According to the proposed mechanism for intramolecular cyclization of alcohols by means of lead tetra-acetate,[1,2] the saturated cyclic ethers [(VI)—(VIII)] are normal oxidation products, formed by homolytic 1,5- and 1,6-hydrogen transfer (from the δ- and ε-carbon to oxygen) in the intermediate alkoxy-radical and oxidation of the resulting δ-[(XIX), Scheme 3] and ε-carbon radicals (XX) to the carbonium ions (XXI) or (XXII), followed by ring closure. However, the tertiary, δ-carbonium ion [(XXI) Scheme 3] is relatively stable and can undergo other reactions, *e.g.* addition of an acetate ion [to give (IX)] or β-proton elimination [to give the unsaturated alcohols (X) and (XVI)]. These can then react further with lead tetra-acetate to give (XI)–(XV) and (XVII)—(XVIII).[3]

This was confirmed by the action of lead tetra-acetate on alcohols (X) and (XVI) (prepared by independent syntheses). 3-(Cyclohex-1-enyl)-propan-1-ol (X) gave, besides the corresponding aldehyde and acetate (XV), the bicyclic ethers (XI)–(XIV) in 8, 7, 9, and 9% yield, respectively (resulting from initial addition of oxygen to one of the unsaturated carbons in the intermediate alkoxy-radical[3]), whereas 3-cyclohexylidenepropan-1-ol (XVI) gave, in addition to the corresponding acetate, only the two β-fragmentation acetates (XVII) (unrearranged, 23%) and (XVIII) (rearranged 19%), from cleavage of the α-C–β-C bond and intermediate formation of the resonance-stabilized allyl radical and cation[1,2,4,5].

These results and others[2,3] indicate that the intermediate formation of secondary (or primary) δ-carbonium ions [as with 2-cyclohexylethanol (I)] leads almost exclusively to five-membered cyclic ethers; a more stable tertiary δ-carbonium ion [*e.g.* as with 3-cyclohexylpropan-1-ol (V)] gives only reduced yields of tetrahydrofurans since it undergoes further reactions as well.

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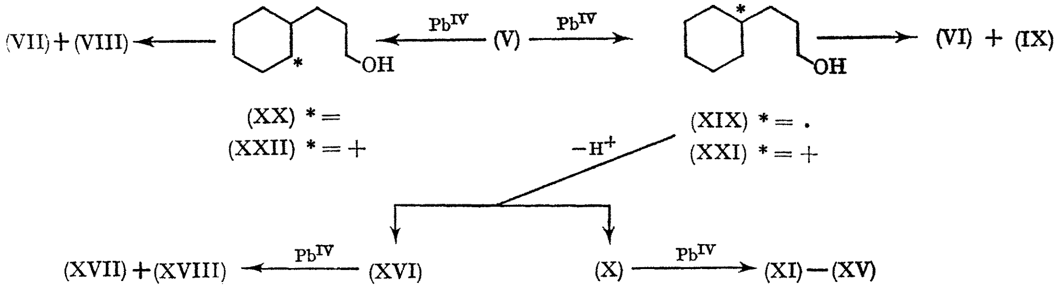
† Products were isolated by gas chromatography. Their structures were deduced from i.r., n.m.r. and mass spectra, and usually confirmed by independent syntheses.



SCHEME 3

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