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THERMAL AND CATALYSED HOMO- 1,5 -HYDROGEN SHIFTS

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The caged oxetanes (1, a-d)≠ were prepared by the route previously described.[1] These oxetanes underwent cleavage to the olefinic alcohols (2, a-d; > 70%) on treatment, in ethanol free chloroform, with a catalytic amount of 45% hydrogen bromide in acetic acid for a few minutes at room temperature. These alcohols had characteristic nmr spectra (C_6D_6) with H_a occurring at ca. τ 6.2 and the geminal vinylic protons at ca. τ 5.2, $J \sim 5.5$ Hz. The strained olefinic alcohols (2, a-d) have favourable geometry for a homo-[1,5] -sigmatropic hydrogen shift (or a retro oxy-ene reaction) which would also result in considerable release of strain. On heating to 180° the alcohols smoothly rearranged (2 → 3), in untreated glassware, to a mixture of the endo- and exo-cyclic olefins (3 and 4) in high yield (> 85%). A related rearrangement of (-)-7-epichrysanthenol to (+)-(IR)-l-formyl-2,2,4-trimethylcyclohex-3-ene was recently observed on attempted g.l.c. purification of the former compound.[2]

Formally the same rearrangement (2 → 3) occurs at a lower temperature, ca. 120°, in the presence of a catalytic amount of $Rh_2Cl_2(CO)_4$. We have no evidence to suggest that this latter effect is other than acid catalysis. The ability of rhodium to form metal hydrides in the presence of alcohols is well known[3], and more recently the formation of Bronsted acids has been observed in systems containing $Rh_2Cl_2(CO)_4$ and alcohols.[4] The yields of (3) and (4) in the presence of $Rh_2Cl_2(CO)_4$ are lower (ca. 50%) and the loss of material presumably occurs by acid catalysed side reactions.

The unsubstituted alcohol (2a) does not give any exo-cyclic olefin but instead a mixture of endo-(3a) and exo-aldehydes (5) is obtained from both the thermal and catalysed reactions, with (3a) predominating (ca 4:1). The nmr peak for the proton on the endo-aldehyde group [3a; τ (C_6D_6) 0.57] is at slightly higher field than the corresponding peak in [5; τ (C_6D_6) 0.53]. The alcohols (2b and c) give mixtures of (3) and (4) in which (3) predominates under both sets of conditions, e.g. (2c) gives 55% (3c) and 34% (4c) at 180° and a ca. 4:3 mixture of (3c) and (4c) in the presence of $Rh_2Cl_2(CO)_4$ at 120°; [(3c), τ (C_6D_6) 0.68, C<u>H</u>O, and (4c) τ (C_6D_6) 0.72, C<u>H</u>O].

≠ All new compounds gave satisfactory analytical and spectral data

The rearrangements were terminated when (2) could no longer be detected (nmr) and consequently the equilibrium compositions are not known as yet. In contrast to (2, a-c) the olefinic alcohol (2d) rearranged to a single isomer [3d; τ (C_6D_6) 0.69 C$\underline{H}$O] under both sets of conditions.

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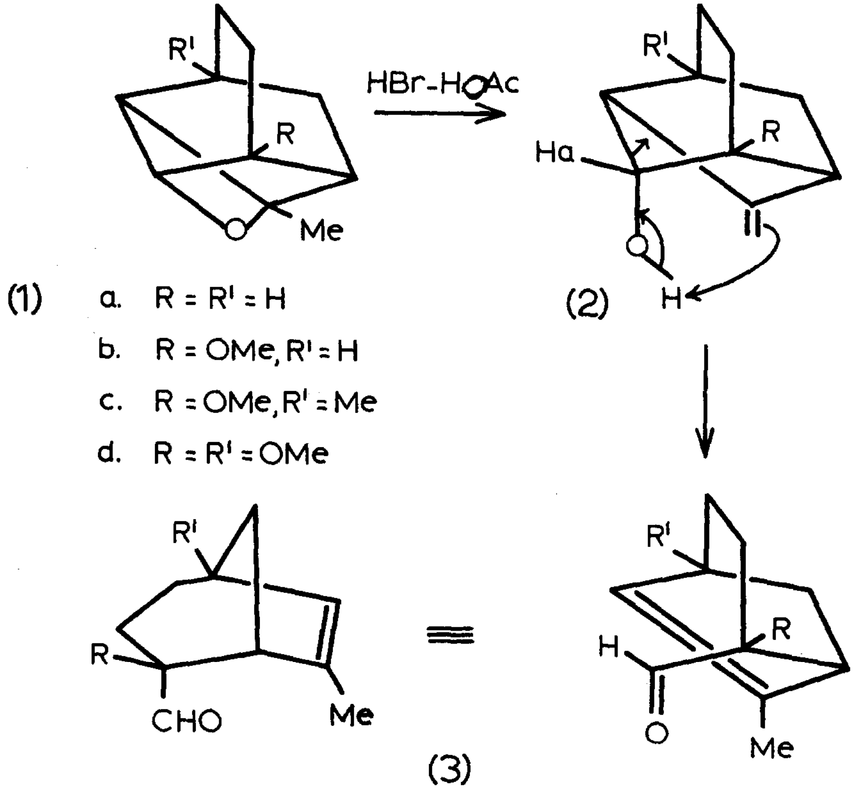
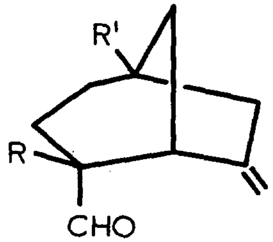
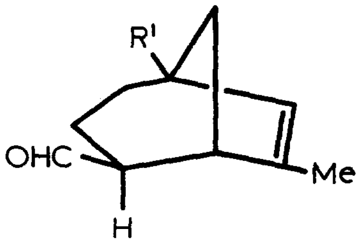




(4)



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