Alumina-catalyzed Rearrangements of α-Methyltetrahydrofurfuryl Alcohol, 5-Methyltetrahydrofurfuryl Alcohol, 2-Methyl-2,3-dihydropyran, and 6-Methyl-2,3-dihydropyran

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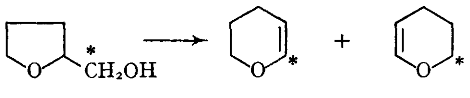
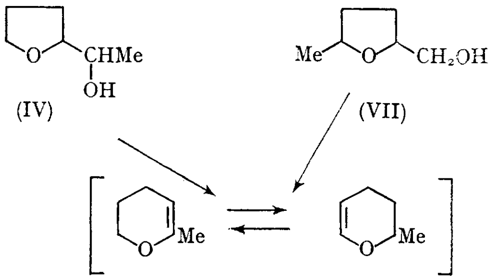
WHEN tetrahydrofurfuryl alcohol (I), labelled in the exocyclic methylene group with carbon-14, is passed over a bed of alumina at 350°, 2,3-dihydropyran (II and III) is formed in which both the 2- and 6-positions are radioactive.[1] This scrambling could come about as the result of a reversible double-bond transfer in 2,3-dihydropyran from one side of the molecule to the other.[2] If so, α-methyltetrahydrofurfuryl alcohol (IV) over alumina might be predicted to give a mixture of 6-methyl-2,3-dihydropyran (V) and 2-methyl-2,3-dihydropyran (VI). We have confirmed this prediction. α-Methyltetrahydrofurfuryl alcohol (IV), prepared by a two-stage reduction of 2-acetylfuran and passed over alumina, gives a mixture, which as analyzed by gas–liquid chromatography, contains both isomeric dihydropyrans (V) and (VI). Thus, the earlier report[3] that α-methyltetrahydrofurfuryl alcohol (IV) over hot alumina gives only 6-methyl-2,3-dihydropyran (V) must be revised. In an analogous way, 5-methyltetrahydrofurfuryl alcohol (VII) on exposure to alumina has already been shown to give the same two products, (V) and (VI)[4,5] and we have confirmed this finding.

Proof that 2-methyl- and 6-methyl-dihydropyran are interconvertible would bolster our interpretation of the origin of these two products in the alumina-catalyzed dehydration–rearrangement of tetrahydrofurfuryl alcohols (IV) and (VII). Such proof was obtained by showing that passing either 6-methyldihydropyran (V)[6] or 2-methyldihydropyran (VI)[7] over hot alumina produces a mixture containing both compounds. Gas–liquid chromatography served conveniently to demonstrate the homogeneity of starting materials as well as the



(I) (II) (III)



(IV) (VII) (V) (VI)

presence of both isomers in the products. Earlier experiments designed to demonstrate the conversion of such a compound as 2-methyldihydropyran (VI) into 6-methyldihydropyran (V) failed to give positive results.[4] Possibly the nature of the alumina is important here.

The equilibrium constant for the (V)–(VI) interconversion has now been determined as close to 0·6 at 346 ± 5°c. On the assumption that the two dihydropyrans have the same entropies, the enthalpy difference may be calculated to be +0·6 kcal. per mole. Note that compound (V), with a trisubstituted double bond, is more stable than compound (VI), with a disubstituted double bond. The relative stability is, accordingly, in the same direction as the relative resonance stabilization in 2-methylbut-2-ene and but-2-ene.[8]

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