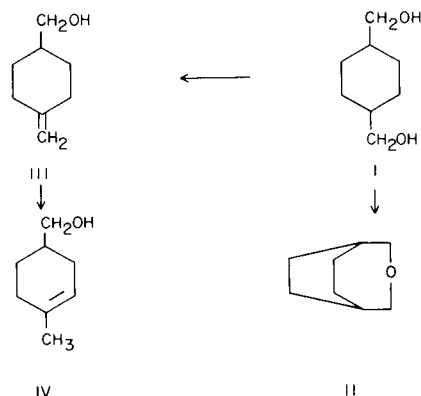


Synthesis of 3-Oxabicyclo[3.2.2]nonane

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Unsuccessful attempts to prepare 3-oxabicyclo[3.2.2]nonane (II) by the alkaline hydrolysis of the dimethanesulfonate of 1,4-cyclohexanedimethanol (I) and by batch distillation of 1,4-cyclohexanedimethanol (I) from an equal weight of alumina (2) are reported in the literature. Recently, we prepared compound II in 81% yield by passing the vaporized diol (I) diluted by nitrogen, over an alkaline alumina at 325°. The by-products of the reaction were primarily 4-methylenecyclohexanemethanol (III) plus a smaller amount of 4-methyl-3-cyclohexene-1-methanol (IV). The indicated reactions are consistent with established mechanisms for the dehydration of alcohols (3).



In the preliminary work a catalyst of pure, neutral alumina (Harshaw Chemical Co., AL0104) was used to obtain the desired product in 95% yield, but the conversion of I was low. By examining models of II, we concluded that it could exist only in the *cis* boat configuration. However, the diol (I) was available as a mixture of *trans* (72%) and *cis* (28%) isomers. We, therefore, sought a catalyst that would first cause isomerization of the *trans* diol to the *cis* diol, then dehydration of the *cis* diol to II, the desired product. Alkaline materials are known to catalyze this *trans/cis* isomerization (4); hence, an alkaline alumina (Alcoa F-1)

was chosen as the catalyst for this reaction even though basic materials are known to inhibit the vapor-phase dehydration of alcohols (5).

Product II is a white solid with a camphor-like odor. It melts at 168-171° and sublimes rapidly at its melting point. The structural identity of II was confirmed by infrared and n.m.r. spectra and elemental analyses. The identities of III and IV were confirmed by comparing their properties to those reported by Haggis and Owens (6) and Mousseron, Mousseron-Canet and Granier (7) respectively.

EXPERIMENTAL

The melting point was determined in a sealed capillary tube in an oil bath apparatus. The n.m.r. spectrum was determined in deuteriochloroform solution at 60 Mc with a Varian A-60 spectrometer; chemical shifts are reported in p.p.m. relative to tetramethylsilane as an internal standard.

The vapor-phase catalytic reactor was fabricated from Pyrex glass. The catalyst, 40 ml. of 30 X 50 mesh gamma alumina which contained 0.8% alkali calculated as sodium oxide (Alcoa F-1), was placed in three consecutive tubular sections of equal volume. The first section was a spiral-shaped tube (5 mm. o.d.), the second section was a straight tube (10 mm. o.d.), and the third section was a straight tube (25 mm. o.d.). To permit a compact configuration that could be easily submerged in a liquid, the first section was coiled around the second and third sections, and the entire apparatus was submerged in a Wood's metal bath maintained at 325°.

Nitrogen and diol I (144 g.) in a mole ratio of 3:1 respectively, were passed through the reactor at a space velocity of 422 hours⁻¹ (calculated at S. T. P.). Diol I was a mixture of *trans* (72%) and *cis* (28%) isomers. The reaction period was approximately 5.3 hours. The crude product was crystallized from a 90/10 mixture of ethylene glycol and water to remove the hydrophilic by-products, washed with water to remove the glycol, dissolved in petroleum ether and azeotropically distilled to remove the water. The product was recrystallized from petroleum ether and then dried at room temperature to produce 102 g. (81%) of white crystalline solid, m.p. 168-171°.

The infrared spectrum of II exhibited strong absorptions at 1137 cm⁻¹ (assigned to the -CH₂-O-CH₂-) and 1453 cm⁻¹ (assigned to the -CH₂-). The n.m.r. spectrum of II consisted of two regions of absorption: a singlet at δ 1.74 with an area equivalent to ten hydrogens per molecule (assigned to the cyclohexane ring hydrogens), and a doublet at 3.70 with an area equivalent to four hydrogens per molecule (assigned to OCH₂ group). Splitting of

the latter peak was caused by the adjacent tertiary hydrogen.

Anal. Calcd. for $C_8H_{14}O$: C, 76.21; H, 11.10. Found: C, 76.14; H, 11.03.

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