

A FURTHER EXAMPLE OF A "1,4-HYDRIDE-SHIFT-SUBSTITUTION REACTION"

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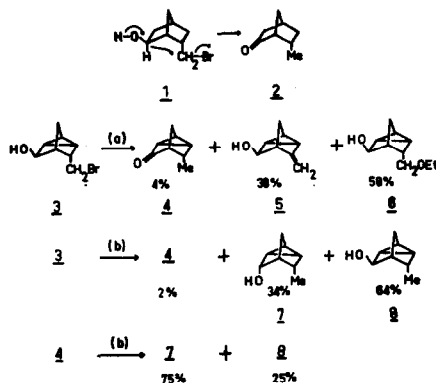
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Gwynn and Skillern¹ have recently noted that basic treatment of endo-6-bromomethylnorbornan-exo-2-ol 1 can give rise to ketone 2 depending on basic conditions. For example, NaH/THF reacts with 1 to yield 2 almost exclusively. This conversion was rationalized in terms of a novel intramolecular 1,4-hydride-shift-substitution reaction (shown schematically in the accompanying chart) although the possibility of an intermolecular pathway was not discounted. We have now found that the structurally related bromohydrin 3 undergoes a similar transformation to give 4. Since 3 possesses the same pertinent stereochemical features as 1, the observation of this same type of conversion lends further support to the proposed intramolecular pathway.

Compound 3 in refluxing EtOH/KOH gave a mixture of three components: the expected elimination product 5 as well as the expected displacement product 6 and the methylnortricyclanone 4. The pmr spectrum of olefin 5 showed signals (τ -scale, relative to TMS) at 5.43, 5.49 (s, 2H, =CH₂); 6.22 (br tr, 1H, CHOH); 6.47 (s, 1H, OH); 7.97 (br m, 1H); 8.1 to 8.7 (br m, 5H). The infrared spectrum of 5 displayed characteristic absorption at 3616 (OH stretching), 3073 (olefinic and cyclopropyl C-H stretching), 1673 (C=C stretching) and 860 cm⁻¹ (=CH₂ deformation mode and nortricyclene skeleton²). The pmr spectrum of the ethyl ether 6 showed signals at 6.01 (br tr, 1H, CHOH); 6.61 (quart, J = 7 Hz, CCH₂CH₃) and 6.72 (d, J = 7 Hz, CHCH₂O), total 4H; 7.01 (s, 1H, OH); 8.08 (br m, 3H); 8.85 (tr, J = 7 Hz, CH₃CH₂O, superimposed on br m, 7H). The infrared spectrum of 6 showed characteristic absorption at 3624 (OH stretching), 3072 (cyclopropyl C-H stretching), and 841 cm⁻¹ (nortricyclene skeleton). The minor component 4 was shown to be identical (vpc R_t and ir) to the ketone prepared from 3 via debromination and subsequent oxidation.³

Treatment of 3 with NaH/THF gave a mixture of ketone 4 (identified by vpc peak enhancement only) and the diastereomeric alcohols 7 and 8.³ It is known that enolizable ketones (such as 2) react with NaH to form the enolate anion rather than undergo hydride attack of the



Conditions:- (a) KOH/EtOH, reflux, 24 hr. (b) NaH/THF, reflux, 50 hr.

carbonyl carbon.⁴ With non-enolizable ketones (such as 4) the latter process occurs. On the basis of these observations it would appear that 3 undergoes 1,4-hydride-shift-substitution to yield 4 which, in contrast to 2, suffers carbonyl reduction under these conditions giving 7 and 8. In support of this, ketone 4 was found to give 7 and 8 (and 2% reactant 4) under identical conditions. However, the proportions of 7 (75%) and 8 (25%) were markedly different from the proportions resulting from identical treatment of 3 and is therefore not consistent with a single pathway for reaction of 3 involving 1,4-hydride-shift-substitution and subsequent carbonyl reduction. We feel therefore that 3 undergoes two competing reactions: one involving direct NaH debromination of 3 to give 8 directly and the other involving 1,4-hydride-shift-substitution to give 7 and 8 via ketone 4. The product distribution suggest that these two pathways compete to roughly equal extents.

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REFERENCES

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