# A Novel 1,4-Hydride-shift–Substitution Reaction

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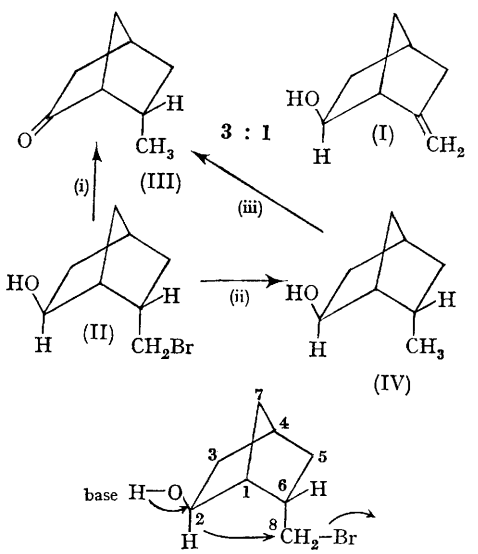
WE report two reactions, one a novel 1,4-hydride shift–substitution, encountered in the preparation of 6-methylene-2-*exo*-norbornanol (I).

Hydroboration of the Diels–Alder mixture of 5-bromomethylnorbornene gave a viscous product (70%) from which a crystalline material, formulated as *endo*-6-bromomethyl-*exo*-2-norbornanol (II), $C_8H_{13}BrO$,† m.p. 74·5—75·5°, slowly separated. The stereochemical formulation of this product can in part be established from the n.m.r. spectral data. The high-field one-proton resonance ($J \simeq 11{\cdot}0$, 4·5, and 3·0 Hz) can be attributed to the *endo*-5-proton shielded by an adjacent *endo*-bromomethyl substituent.[1] The *exo*-assignment for the hydroxyl group is consistent with the observed magnitude of the n.m.r. coupling of the carbinol proton,[2] $\tau$ 5·93 (br d, $J \simeq 6{\cdot}0$ Hz) and the very high *exo* specificity for the hydroboration of norbornene.[3] The relationship of the *exo*-hydroxyl and the *endo*-bromomethyl substituents as 2,6 follows from the conversion of (II) into the known alcohol (IV).

Reaction of the crystalline hydroboration product (II) with potassium t-butoxide in refluxing t-butyl alcohol overnight gave, in addition to some unreacted (II), a 3:1 two-component mixture consisting of 6-*endo*-methyl-2-norbornanone[4] (III), $C_8H_{12}O$, m.p. 45·5—47·0°; $\nu_{CCl_4}$ 1750 cm.$^{-1}$ (C=O); $\tau_{CCl_4}$ 9·07 (3H, d, $J$ 5·5 Hz, $CHCH_3$) and the expected alcohol (I), $C_8H_{12}O$, $\nu_{CCl_4}$ 3300 (OH), and 880 (=$CH_2$) cm.$^{-1}$; $\tau_{CCl_4}$ 5·10, 5·34 (1H each, br s, =$CH_2$), and 6·25 (1H, br d, $J$ *ca.* 6 Hz, C*H*OH), respectively. The ketone (III) proved identical with an authentic sample prepared by the lithium aluminium hydride reduction of (II) to 6-*endo*-methyl-2-*exo*-norbornanol[4] (IV), $C_8H_{14}O$, m.p. ~25°, $\tau_{CCl_4}$ 5·99 (1H, br d, $J$ *ca.* 6·0 Hz, C*H*OH), 7·0 (1H, sh s, OH), and 9·07 (3H, d, $J$ *ca.* 6·0 Hz, $CHCH_3$), followed by a Jones oxidation.




Reagents: (i) t-BuOK–t-BuOH,Δ; (ii) $LiAlH_4$, tetrahydrofuran, reflux; (iii) $CrO_3$, $H_2SO_4$.

The formation of ketone (III) can best be rationalized by a base-promoted intramolecular *endo*-C(2)-hydride displacement of bromide ion from C(8) as shown. The possibility that the hydride displacement is an intermolecular process cannot be discounted although the stereochemistry of (II) would seem ideally suited for the intramolecular pathway proposed. The proposed 1,4-hydride transfer with substitution appears unique.

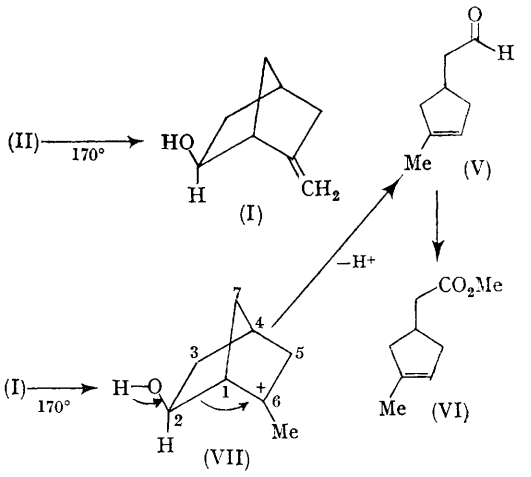
The driving force for this novel pathway must be associated with the steric hindrance to t-butoxide attack at the *exo*-C(6)-hydrogen to bring about the dehydrobromination to produce alcohol (I). This is supported by the observation that (II) upon treatment with refluxing alcoholic potassium hydroxide gave (I) with less than 5% of the ketone product. On the other hand (III) was produced almost exclusively from the reaction of (II) with sodium hydride in refluxing tetrahydrofuran by the mechanism shown.

Treatment of (II) with refluxing collidine (~170°, 30 min.) gave a product consisting of two major components in about equal amounts. The product of longer chromatographic retention time proved to be the alcohol (I) while the earlier component was established as 3-methylcyclopenten-3-ylacetaldehyde (V), $\nu_{CCl_4}$ 3040 (=CH), 2710 (–CHO), and 1725 (C=O) cm.$^{-1}$; $\tau_{CCl_4}$ = 0·03(1H, t, $J \simeq 2{\cdot}0$ Hz, CHO), 4·78 (1H, br s, =C–H) and 8·32 (3H, broadened s, –Me). The latter product was readily oxidized by air and gave

† All compounds assigned a molecular formula gave satisfactory carbon and hydrogen analysis; melting points are uncorrected.

an orange 2,4-dinitrophenylhydrazone, $C_{14}H_{16}N_4O_4$, m.p. 108·7—109·8°. The identity of aldehyde (V) was determined by oxidation with silver oxide and conversion of the resulting acid with diazomethane to the methyl ester (VI), $C_9H_{14}O_2$, identical in all respects with an authentic sample prepared by the Arndt–Eistert procedure from 1-methylcyclopent-ene-4-carboxylic acid.[5]

A reasonable mechanism for this fragmentation involves electrophilic attack of collidine hydrobromide on alcohol (I) under the forcing conditions to generate the norbornyl cation (VII). Cleavage of the C(1)–C(2) bond and a proton loss results in the formation of aldehyde (V). A similar mechanism has been proposed to explain the isomerization of α-pinene oxide to campholenic aldehyde.[6] The proposed isomerization of (I) to (V) was convincingly established by the observation that the reaction of collidine hydrobromide and alcohol (I) (30 min., 170°) showed a significant portion of the aldehyde product. Collidine alone produced no detectable isomerization. Presumably, the driving force toward the fragmentation path resides in the generation of a very favourable leaving group, the conjugate acid of a carbonyl. Under solvolytic conditions similar ring-opening reactions of the norbornyl cation have not been observed.

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