

AN ALKALI INDUCED 1,4-HYDRIDE SHIFT IN endo-TRICYCLO[5.2.1.0^{2,6}]DECYL KETOLS

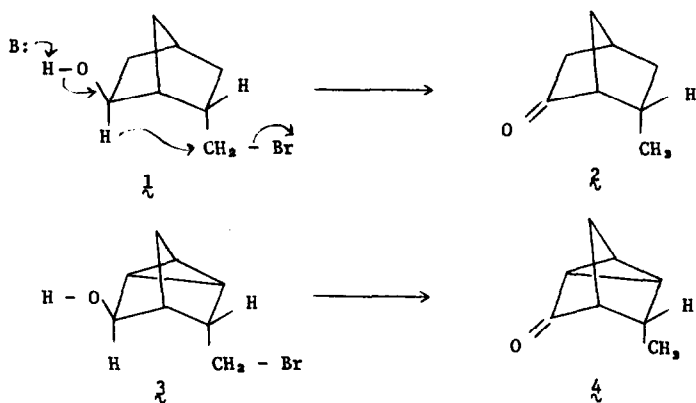
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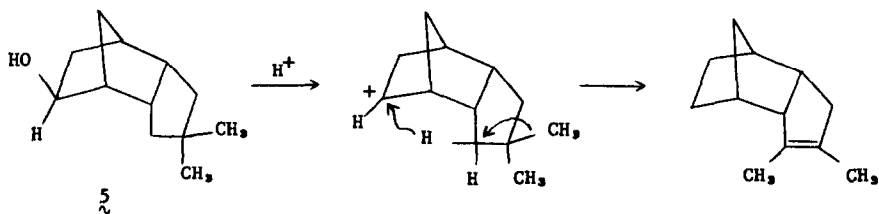
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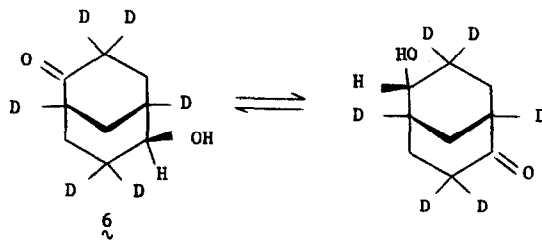
The most common types of intramolecular hydride shifts are of order 1,2; 1,3; and 1,5. Reports of 1,4-hydride shifts are extremely rare.¹ Base induced 1,4-shifts have been proposed for the formation of $\overset{2}{\sim}$ from $\overset{1}{\sim}$ ² and the closely related formation of $\overset{4}{\sim}$ from $\overset{3}{\sim}$.³ An intramolecular



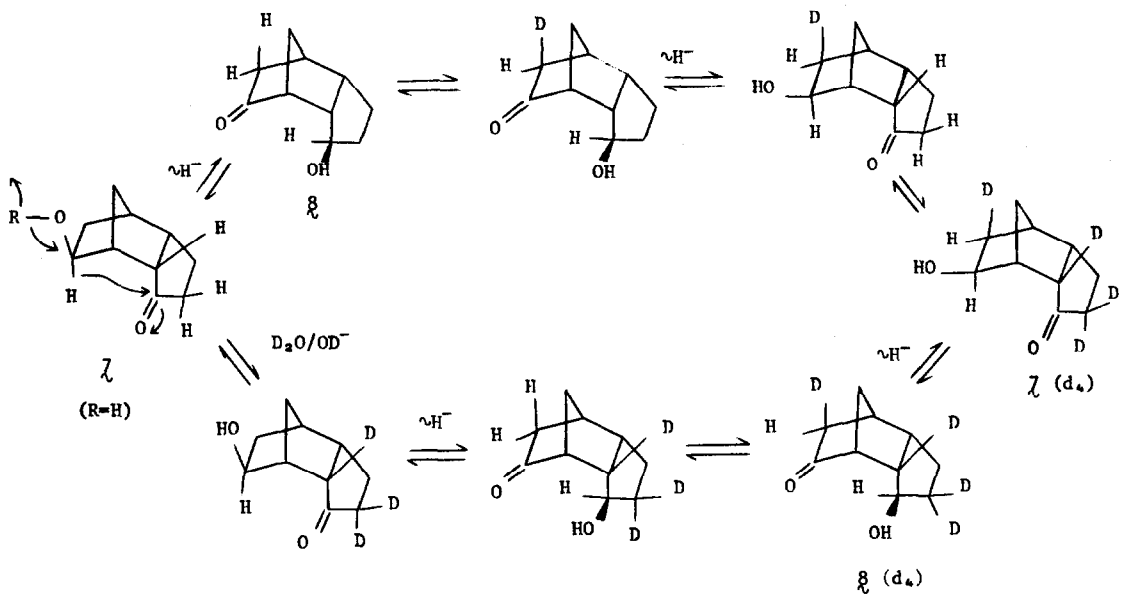
1,4-hydride shift has also been proposed in the acid catalyzed dehydration of $\overset{5}{\sim}$,⁴ and only recently Parker and Stevenson⁵ have confirmed an alkali induced transannular 1,5-hydride shift by



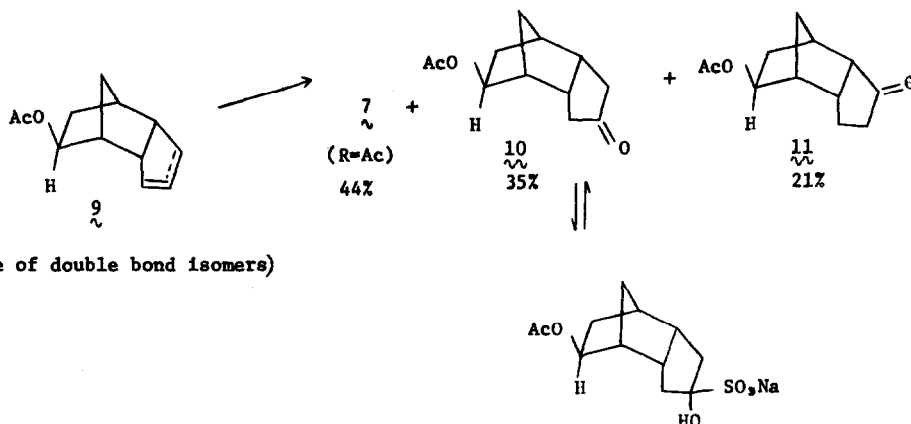
incorporation of six deuterium atoms when $\underline{6}$ was treated with sodium in D_2O -dioxane.



In the current study we have found that keto alcohol $\underline{7}$ ($R=H$) incorporates up to four deuterium atoms under similar conditions. An intramolecular 1,4-hydride shift is proposed to account for this observation.



Compound $\underline{7}$ ($R=Ac$) along with keto acetates $\underline{10}$ and $\underline{11}$ was prepared by hydroboration-oxidation of acetate $\underline{9}$, followed by chromic acid oxidation in situ.⁶ It was found that $\underline{10}$ quantitatively



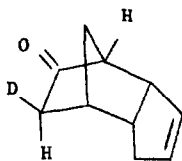
(mixture of double bond isomers)

forms a bisulfite addition complex while the keto acetates **7** and **11** are completely unreactive toward the reagent. By this route an efficient separation of **7** and **11** from **10** is effected.^{7,8}

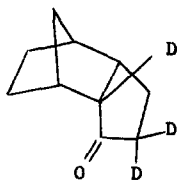
The deuterium exchange was attempted with a mixture of 68% **7** (R=Ac) and 32% **11** using NaOD in 50% THF-D₂O. Hydrolysis of the acetates was complete within 90 min. at room temperature, and no further change was evident in the glpc trace during the next 48 hours. The reaction mixture was then heated to 60° and almost immediately a third component appeared in the glpc trace coinciding with the disappearance of the keto alcohol **7** (R=H). No change in the relative amount of ketol **11** was detected. After 24 hours the mixture was isolated. Mass spectral analysis indicated products containing approximately 53% d₄ species and 47% d₃, and on the assumption that ketol **11** is all d₃, ketol **7** (R=H) is approximately 78% d₄.

The progress of the exchange was also followed by infrared and nmr spectroscopy. The presence of an equilibrating mixture of keto alcohols **7** and **8** was indicated in the infrared by the broadening and finally the splitting of the carbonyl stretching absorbance into a doublet. A similar phenomenon was observed in the nmr spectrum for the downfield secondary protons in **7** and **8**.

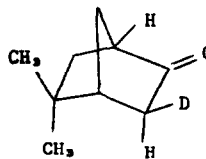
That only four deuterium atoms should be incorporated was verified by deuteration of **12** and **13** under the exchange conditions. The incorporation of only one deuterium in **12** is consistent



12



13



14

with results obtained in similar compounds,⁹ most notably isofenone (14)¹⁰ in which neither the bridgehead nor the endo hydrogen undergoes exchange.

When reacted with NaOD in D₂O-THF keto acetate 10 was found to incorporate up to five deuterium atoms, an observation consistent with an intramolecular 1,5-hydride shift.

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