[1,3] Shifts of Potassium Alkoxides: the Bicyclo[3.2.0]heptene–Norbornene Transformation

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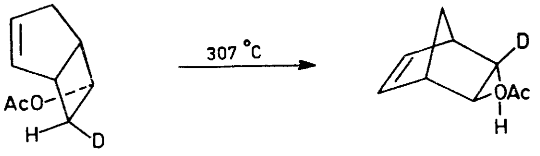
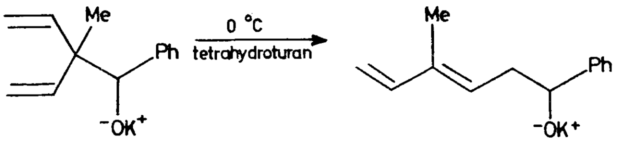
Summary *exo*-Bicyclo[3.2.0]hept-2-en-7-ol can be isomerized to *exo*-norbornenol on treatment with potassium hydride in tetrahydrofuran at room temperature.

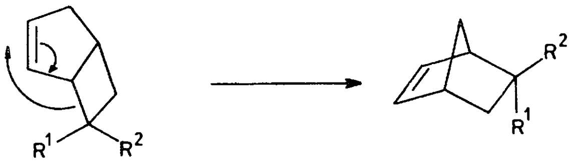
Of all the [1,3] sigmatropic shifts of hydrocarbons[1] perhaps the best known is the classic case reported by Berson[2] (**1**) → (**2**). The reaction was shown to be concerted, with inversion of configuration of the migrating group. The recent report by Evans[3] that oxy-Cope [3,3] sigmatropic rearrangements are strongly accelerated for potassium salts prompted us[4] to investigate the effect of a potassium alkoxide substituent on a [1,3] sigmatropic[5] shift. Although dramatic accelerations were observed for isomerizations of potassium salts such as (**3**) → (**4**), the mechanism of such reactions remains unclear. These formal [1,3] sigmatropic shifts can be considered 'reverse Grignard-type' reactions. Indeed in the case of (**3**) → (**4**) crossover products have been observed, although this and analogous reactions[6] have been observed in protic solvents, hardly a suitable environment for an allyl anion. In the course of exploratory studies on the mechanism of such alkoxide accelerated shifts, we have prepared the *exo*-(**5**) and *endo*-alcohols (**6**) *via* the recently reported method of Fleming.[7] Compound (**5**) isomerized (as the potassium salt) to a mixture of 67% (**7**), 8% (**8**), and 25% (**5**) (by g.l.c.) after 3 h at room temperature. Under the same conditions the *endo*-alcohol (**6**) was stable.† This result is consistent with a concerted mechanism.[8] The *exo*-substituted compound isomerizes with (mainly) inversion at C-7 whereas the *endo*-substituted isomer (**6**) does not react, since the clockwise rotation about C-6—C-7 required by a concerted isomerization would force the alkoxide substituent into the cyclopentane ring. Under more vigorous conditions (refluxing tetrahydrofuran or in the presence of the macrocyclic polyether 18-crown-6) compound (**6**) does isomerize yielding (**7**) and (**8**) in a 6:1 ratio. This again is consistent with the results of Berson who found that *endo*-substituted bicyclo[3.2.0]heptenes isomerize with retention. A concerted mechanism still may not be operating here since the thermodynamic ratio of (**7**):(**8**) is close to 6:1.



(1) (2)



(3) (4)



(5); $R^1 = H, R^2 = OH$ (7); $R^1 = H, R^2 = OH$

(6); $R^1 = OH, R^2 = H$ (8); $R^1 = OH, R^2 = H$

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† The norbornenols (**7**) and (**8**) are stable under the reaction conditions.

These results do show however that many well known thermal rearrangements may be accelerated by alkoxide substituents on the C–C bond undergoing cleavage in the reaction. Further examples of this process have been observed and will be reported elsewhere.

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[5] Throughout this discussion the term 'sigmatropic shift' is used to indicate the overall bonding change and not to imply a concerted mechanism (R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970).

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[8] J. A. Berson, *Accounts Chem. Res.*, 1972, **5**, 406.