200. Kinetic Isotope Effects and *exo/endo*-Face Selectivity in the Unimolecular Dehydrogenation of Norborneol Alkoxides in the Gas Phase

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Dedicated to Prof. *Tino Gäumann* on the occasion of his 65th birthday

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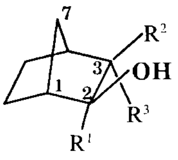
The study of specifically labeled alkoxides generated in the gas phase by deprotonation of epimeric norbernols demonstrates, beyond any doubt, that 'solvated' hydride ions are formed as intermediates in the course of enolate formation. Kinetic isotope effects and *exo/endo*-face selectivities for the dehydrogenation are discussed.

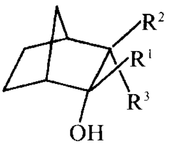
In a previous study [1], by using stereochemical criteria, unambiguous evidence was presented in favour of ion/molecule complexes ('solvated hydride ions') as intermediates in the course of enolate formation from alkoxide anions in the gas phase1). A concerted 1,2-elimination reaction could not account for the observed *stereo-unspecific* loss of molecular hydrogen from alkoxides of appropriately stereospecifically labeled isoborneols [1].

Here, we present further evidence for the operation of this mechanism by reporting the metastable-ion (MI) spectra of alkoxides generated by deprotonation of stereospecifically deuterated *exo*- and *endo*-norborneols (bicyclo[2.2.1]octan-2-ols; **1**–**10**). In addition, the kinetic isotope effect as well as the face-selectivity of dehydrogenation are reported.



exo

	R^1	R^2	R^3
1	H	H	H
2	H	D	H
3	H	H	D
4	D	H	H
5	H	D	D



endo

	R^1	R^2	R^3
6	H	H	H
7	H	D	H
8	H	H	D
9	D	H	H
10	H	D	D

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1) For further studies using other approaches and less direct criteria, see [2].

Experimental. – Compounds **1**–**10** were synthesized, purified, and fully characterized by standard laboratory procedures [3]. Alkoxides were generated by 70-eV electron-impact ionization of a mixture of the corresponding alcohol ($p \approx 10^{-4}$ Torr) and N_2O ($p \approx 10^{-5}$ Torr) [4] in the chemical-ionization source of a modified four-sector *BEBE ZAB-2F* mass spectrometer: emission current 50 μA; temp. of the ion-source *ca.* 200°. The alkoxides were mass-selected at an appropriate resolution by means of B(1)E(1), and the unimolecular dissociations (background pressure $p \approx 10^{-8}$ Torr), occurring in the field-free region between E(1) and B(2) were recorded by scanning of B(2). Averaging techniques were used to improve the signal-to-noise ratio.

Results and Discussion. – The findings reported in the *Table* permit the following conclusions to be drawn: *1*) the investigation of **4**, **5**, **9**, and **10** demonstrates that molecular hydrogen is generated exclusively from the positions C(2)/C(3) in a *formal* 1,2-elimination mode. In addition, the specific loss of HD from these precursors provides evidence that no exchange processes take place.

Table. *Unimolecular Losses of H_2 and HD from Deprotonated* exo/endo-*Norborneols* **1**–**10**[a])

Alkoxide precursor	H_2	HD
1	100	
2	58±1	42±1
3	60±1	40±1
4		100
5		100
6	100	
7	54±1	46±1
8	60±1	40±1
9		100
10		100

[a]) Intensitites are given in ΣH_2, HD = 100%. The loss of H_2 is the only metastable-ion process observed for deprotonated *exo*/*endo*-norborneols. In the MI spectra of the doubly-deuterated isotopomers **5** and **10**, elimination of D_2 is not observed.

2) However, the dehydrogenation cannot be described in terms of a concerted mechanism (*Scheme: Path* ⓐ). This follows directly from the data of **2**, **3**, **7**, and **8**. If this were to happen, the alkoxides of **2** and **8** should undergo specific loss of H_2, while **3** and **7** should give rise to the exclusive elimination of HD. This is not observed. Rather, the alkoxides formed from these four isotopomers undergo eliminations of either H_2 and HD. Thus, a multi-step reaction is operative (*Scheme: Path* ⓑ). The study of **4** and **9** indicates that the configuration at C(2) is insignificant. This finding constitutes further evidence for the operation of a multi-step process in the course of which the stereocentre at C(2) is destroyed.

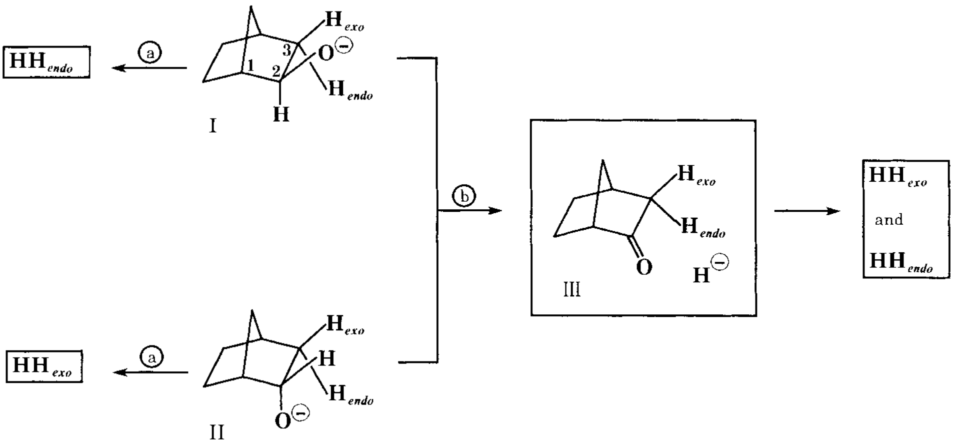
3) The data for **2**, **3**, **7**, and **8** permit to estimate both the kinetic isotope effect k_H/k_D and the *exo*/*endo*-face selectivity for the intracomplex reaction of the 'solvated' hydride ion **III** with the H-atoms attached to C(3). For the former, we arrive at $1.1 < k_H/k_D < 1.5$; these values should be compared with $k_H/k_D = 1.6$ for the collision-induced dehydrogenation of $CH_2DCH_2O^-$ [2c]. For the *exo*/*endo*-face selectivity, we estimate a value of < 1.1; thus, the approach from the *exo*-face is slightly favoured. While this finding is in line with condensed-phase data on the base-catalyzed homo-enolization of bicyclic ketones [5], we should like to recall that in the dehydrogenation of borneol alkoxides (in which the H-atoms at C(7) are replaced by two Me groups) no face-selectivity has been observed [1].

4) The slight preference for an *exo*-attack in the present system is, however, not reflected in the kinetic-energy release, $T_{(0.5)}$, associated with the dehydrogenation of borneol alkoxides. We observe for the alkoxides generated from **2**, **3**, **7**, and **8** that – irrespective of the precursor – loss of H_2 gives rise to $T_{(0.5)} = 0.66 \pm 0.03$ eV; the elimination of HD from these four precursors is associated with a slightly larger value ($T_{(0.5)} = 0.83 \pm 0.04$ eV). Common to the losses of H_2 and HD is the peak-shape, in that a 'flat-topped' signal is observed [6].

5) Finally, the charge-reversal (CR) [7] mass spectra of the enolates generated by dehydrogenation of norborneol alkoxides are nearly identical with the CR spectra generated by fluorodesilylation [8] of the trimethylsilyl ether of the corresponding enol. These spectra are available upon request from the principal author.

We have also considered several mechanistic variants of other multi-step processes as an alternative to the reaction depicted in the *Scheme*. Most conceivable are those in which **I** or **II** undergo *reversible* cleavage of either C(1)–C(2) or C(2)–C(3) bonds; this, in principle, would also bring about loss of stereospecificity. We discard this possibility on two grounds: *i*) based on the work of *Brauman* and coworkers [2f] and *DePuy* and *Bierbaum* [9], a relative order of leaving-group propensity Ph > H > *t*-Bu > Me > i-Pr > Et from alkoxides was established. Thus, in the present case, formation of a 'solvated' hydride ion **III** is favoured over the generation of a secondary or primary carbanion, *i.e.* cleavage of the C(1)–C(2) or C(2)–C(3) bond. *ii*) While base-induced cage-opening reactions of polycyclic alkoxides are known to exist in solution [10], the reactions are by and large confined to the *irreversible* ring-opening of *three*- and *four*-membered rings. However, these structural units are not present in our model system. Thus, we conclude that the results described here further support our view that stereochemical criteria serve as an ideal probe to unravel crucial mechanistic features of ionic fragmentation processes,

Scheme



and provide compelling evidence for the existence of ion/neutral complexes ('solvated hydride ions') as intermediates in the dehydrogenation of alkoxides.

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