isotropic temperature factors, hydrogen atomic parameters, all bond lengths and angles, all torsion angles, 2-fold axis calculation for **3**, powder spectrum indexation and lattice parameters refinement from powder the diffractogram of **3**, least-squares mean plane calculation in **3**·LiNCS and calculated, observed, and unobserved structure factors for **2**, **3**, and **3**·LiNCS are available as supplementary material.

X-ray Powder Diffraction Analysis and Lattice Parameter Refinement. The X-ray powder spectrum of **3** was measured to check that the loose crystalline powder of **3** was homogeneous and shared the same crystal structure as found in the hand-picked single crystal. The crystalline powder sample of **3** used for ^{13}C CPMAS solid-state NMR was given additional grinding with a mortar and pestle to get a finer powder for the X-ray powder diffraction experiment. The finely ground powder was loaded in the cavity of a sample holder. The flat blade of a spatula and a glass slide were used to compress gently but firmly the powder and to slice off surplus powder. A new loose layer of powder was deposited and the previous steps repeated.

The sample was measured on a Rigaku D/max-B automated XRD instrument operating in the θ:θ geometry. Diffraction data were obtained using Cu Kα radiation ($\lambda(K\bar{\alpha})$ = 1.541 78 Å). The diffractometer was equipped with a diffracted beam monochromator, a scintillation detector and solid-state counting electronics. The following slit arrangement was used for data collection: divergent slits, 1°; receiving slits, 0.15°; and Soller slits, 1°. The spectral range 5° to 75° (2θ) was measured at 2°/min. The diffractogram of **3** was smoothed and positions of the peak maxima were obtained using manual and computerized searches.

Materials. Synthetic details for the preparation of these systems have been reported elsewhere.[18]

^{13}C CPMAS Spectra. All spectra were recorded at 45.3 MHz using a Bruker CXP-180 NMR instrument via methods described earlier.[13,20]

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Supplementary Material Available: X-ray data for **2**, **3**, and **3**·LiSCN (25 pages); table of structure factors (33 pages). Ordering information is given on any current masthead page.

Stereochemistry of Base-Promoted 1,2-Elimination from *exo*-2-Bicyclo[2.2.1]heptyl Tosylate and Choride

Richard A. Bartsch*,[1] and Jong Gun Lee[2]

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, and Department of Chemistry, Pusan National University, Pusan 609-735, Korea

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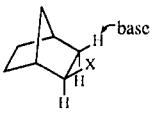
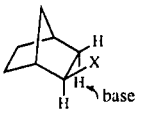
Elimination reactions of *exo*-2-bicyclo[2.2.1]heptyl tosylate and chloride and their exo-3-deuterated analogues are studied in base–solvent systems that induce clean bimolecular 1,2-eliminations. The relative propensities for competitive syn-exo and anti-endo-H elimination modes are assessed from nonkinetically determined deuterium isotope effects and the deuterium content in the bicyclo[2.2.1]hept-2-ene formed from the deuterated substrates. The competitition between syn-exo and anti-endo-H elimination is influenced by base association, which stabilizes the syn elimination transition state. Potential steric hindrance by oversized dissociated bases has no effect on the elimination stereochemistry.

Introduction

Due to the rigidity of the bicyclo[2.2.1]heptane ring system, studies of base-promoted 1,2-eliminations from 2-monosubstituted and 2,3-disubstituted norbornanes have provided fundamental information concerning the stereochemistry of bimolecular elimination reactions.[3,4] For base-promoted eliminations from exo-2-substituted bicyclo[2.2.1]heptanes, two reaction stereochemistries are possible. Attack of the base on the 3-exo hydrogen as shown in **1** gives syn-exo elimination. Alternatively, base attack on the 3-endo hydrogen as depicted in **2** produces anti-endo-H elimination in which the dihedral angle between the β-hydrogen and the leaving group is much smaller than the optimal dihedral angle of 180° for anti elimination.[5]



1
(syn-exo)



2
(anti-endo-H)

Specific incorporation of deuterium at either the 3-exo or 3-endo position allows these two elimination modes to be differentiated. When Kwart, Takeshita, and Nyce[6] reacted *endo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate with potassium 3-methyl-3-pentoxide in *p*-cymene at 130 °C, a ratio of 2-deuteriobicyclo[2.2.1]hept-2-ene to bicyclo[2.2.1]-hept-2-ene of 2.2 was obtained. Thus some preference for the syn-exo pathway **1** over anti-endo-H elimination **2** was observed. In a later study conducted by Brown and Liu,[7] the ratio of syn-exo/anti-endo-H

(1) Texas Tech University.
(2) Pusan National University.
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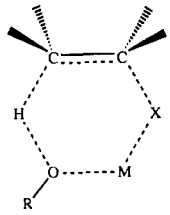
elimination was estimated to be ≥49 for reaction of *exo*-3-deuterio-*exo*-3-bicyclo[2.2.1]heptyl tosylate with sodium 2-cyclohexylcyclohexoxide in triglyme at 80 °C. Pronounced favoring of syn-exo over anti-endo-H elimination was also noted for a halogen leaving group.[6] Thus reaction of *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl bromide with potassium 3-methyl-3-pentoxide in 3-methyl-3-pentanol at 130 °C gave 94% of bicyclo[2.2.1]hept-2-ene and 6% of 2-deuteriobicyclo[2.2.1]hept-2-ene.

In these investigations, hydrocarbon, alcoholic, or ethereal solvents of low polarity were utilized to suppress solvolysis reactions of the *exo*-2-bicyclo[2.2.1]heptyl tosylate and bromide. In such solvents, association of alkali metal alkoxide bases (formation of ion pairs and/or aggregates of ion pairs) has an important influence upon competitive syn and anti elimination processes.[8,9] The transition state for syn elimination is stabilized by the interactions shown in **3**, where X is the leaving group and



3

M is the metal cation. Due to geometric limitations, no comparable stabilization of the anti elimination transition state may be realized. In earlier work,[10] we reported preliminary evidence that the propensity for syn-exo elimination from *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate induced by sodium 2-cyclohexylcyclohexoxide in triglyme at 80 °C was markedly diminished in the presence of 18-crown-6.

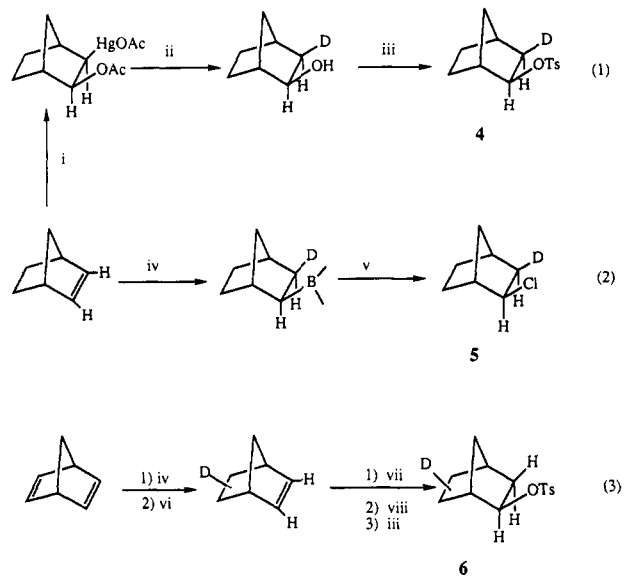
We now report determination of the stereochemistries of elimination from *exo*-2-bicyclo[2.2.1]heptyl tosylate and chloride by dissociated alkoxide bases in solvent systems that provide clean bimolecular eliminations. By a combination of nonkinetically determined deuterium isotope effects and the deuterium content of the bicyclo[2.2.1]-hept-2-ene formed from *exo*-3-deuterio-*exo*-2-bicyclo-[2.2.1]heptyl tosylate, the relative propensities for syn-exo and anti-endo-H elimination are assessed.

Results and Discussion

Synthesis of Deuterated Substrates. By the methods summarized in Scheme I, *exo*-3-deuterio-*exo*-2-bicyclo-[2.2.1]heptyl tosylate (**4**) and chloride (**5**) and 5(6)-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**6**) were prepared.

Stereospecific syn addition[11-13] of mercuric acetate to bicyclo[2.2.1]hept-2-ene in acetic acid gave the acetoxymercurio acetate, which was reductively demercurated with sodium amalgam in alkaline deuterium oxide to provide *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptanol (eq 1). Although reduction with sodium amalgam[12] in deuterium oxide is less convenient than that with sodium borodeuteride,[13] it is absolutely stereospecific.[12,14] The deuterated alcohol was converted into the deuterated tosylate **4** in the usual fashion. Reaction of bicyclo[2.2.1]hept-2-ene with externally generated deuteroborane followed by chlorination with *N*-chloropiperidine[15] gave *exo*-3-deuterio-*exo*-2-chlorobicyclo[2.2.1]heptane (**5**) (eq 2). The deuterated tosylate **4** and chloride **5** showed well-separated doublets for their endo-2 protons in the ^{1}H NMR spectra, which is consistent with stereospecific deuteration at the exo-3 position.[12]

Scheme I[a]



[a] (i) $Hg(OAc)_2$, AcOH; (ii) Na(Hg)–D_2O; (iii) TsCl, pyridine; (iv) B_2D_6; (v) *N*-chloropiperidine; (vi) propionic acid-*d*; (vii) B_2H_6; (viii) H_2O_2–NaOH.

The 5(6)-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**6**), which was used in the deuterium isotope effect measurement by competitive reactions, was prepared by incomplete hydroboration of bicyclo[2.2.1]hepta-2,5-diene followed by reaction with propropionic acid-*d* to give 5(6)-deuteriobicyclo[2.2.1]hept-2-ene[16] (eq 3). The deuterated bicyclic alkene was hydroborated and the borane adduct was oxidized with alkaline hydrogen peroxide to give 5(6)-deuterio-*exo*-2-bicyclo[2.2.1]heptanol, which was converted into deuterated tosylate **6**.

Base–Solvent Systems for Clean 1,2-Eliminations. Previous investigations of the stereochemistry of bimolecular eliminations from *exo*-2-bicyclo[2.2.1]heptyl tosylate and bromide were complicated by concomitant formation of hydrocarbon products through solvolytic elimination processes.[6] Use of solvents with low polarities helped to suppress the complicating unimolecular reactions. Appropriate base–solvent combinations for inducing clean bimolecular eliminations from *exo*-2-bicyclo[2.2.1]heptyl tosylate and chloride were suggested by results of a study of base-promoted eliminations from *endo*-2-bicyclo-[2.2.1]heptyl halides and arenesulfonates.[17] In that study, clean bimolecular eliminations were achieved with dissociated alkoxide ion bases (free alkoxides and/or solvent-separated ion pairs produced from equivalent amounts of

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(14) In the earlier study,[10] the *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptanol precursor to the corresponding tosylate was prepared by sodium borodeuteride reduction of the mercuric acetate adduct of bicyclo-[2.2.1]hept-2-ene. The ^{1}H NMR peak for the endo 2-proton[12] of the *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptanol prepared in this manner indicated that not all of the deuterium was in the exo 3-position.
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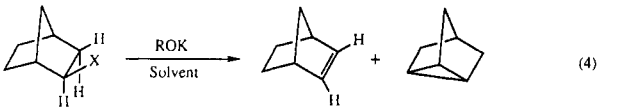
Table I. Elimination Products from Reactions of ROK with *exo*-2-Bicyclo[2.2.1]heptyl Tosylate and Chloride and Their *exo*-3-Deuterio Analogues in the Presence of Equimolar 18-Crown-6 in Triglyme

entry	leaving group	exo-3 atom	RO^- of ROK	total hydrocarbon yield, %	relative proportions in hydrocarbon product, %[a] 9	11	10	12
1[b]	OTs	H	isopropoxide	30.5	99.79		0.21	
2[b]	OTs	D	isopropoxide	35.1	86.03	13.51		0.46
3[b]	OTs	H	*tert*-butoxide	62.3	99.41		0.59	
4[b]	OTs	D	*tert*-butoxide	61.9	88.98	9.95		1.07
5[b,c]	OTs	H	*tert*-butoxide	43.8	99.66		0.34	
6[b,c]	OTs	D	*tert*-butoxide	36.8	90.96	8.82		0.72
7[b]	OTs	H	tricyclohexylmethoxide	57.4	99.67		0.33	
8[b]	OTs	D	tricyclohexylmethoxide	54.5	85.77	13.61		0.62
9[b]	OTs	H	tri(2-norbornyl)methoxide	56.8	99.49		0.51	
10[b]	OTs	D	tri(2-norbornyl)methoxide	53.9	80.23	18.91		0.86
11[d]	OTs	H	2-cyclohexylcyclohexoxide	57.5	96.83		3.17	
12[d]	OTs	D	2-cyclohexylcyclohexoxide	60.8	78.01	16.32		5.67
13[e]	OTs	D	*tert*-butoxide	ND[f]	93.20	6.80		ND[f]
14[g]	Cl	D	isopropoxide	72.2	93.90	6.10		>0.05
15[g]	Cl	D	*tert*-butoxide	83.1	93.80	6.20		>0.05
16[g]	Cl	D	tricyclohexylmethoxide	84.6	94.00	6.00		>0.05
17[h]	Cl	D	*tert*-butoxide	70.1	99.78	0.22		>0.05

[a] Uncertainty is ±0.05%. [b] Reaction at 60 °C for 3.0 h. [c] Solvent was *tert*-butylbenzene. [d] The sodium alkoxide was used to allow for comparison with earlier reports.[7,10] Reaction at 80 °C for 3.0 h. [e] Reaction at 80 °C for 7.0 h in the absence of 18-crown-6. [f] Not determined. [g] Reaction at 90 °C for 3.0 h. [h] Reaction at 110 °C for 7.0 h in the absence of 18-crown-6.

a potassium alkoxide and 18-crown-6) in triglyme (triethyleneglycol dimethyl ether) or *p*-cymene (4-isopropyltoluene).

Reactions of *exo*-2-bicyclo[2.2.1]heptyl tosylate (**7**) with potassium alkoxide bases in the presence of equimolar 18-crown-6 were conducted at 60 °C in triglyme. Use of this high boiling solvent allowed a slow sweep of nitrogen to carry the hydrocarbon products, bicyclo[2.2.1]hept-2-ene (**9**) and nortricyclene (**10**) (eq 4), from the reaction vessel into a chilled receiver for analysis by gas chromatography. Results are recorded in Table I (entries 1, 3, 7, and 9).



7 (X=OTs)
8 (X=Cl)

9 **10**

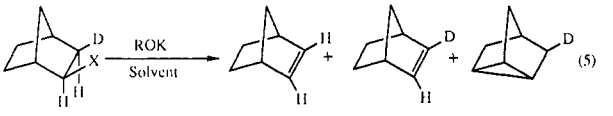
Conversions to **9** + **10** after 3.0 h were 30–62%, and the relative proportion of nortricyclene in the hydrogen products was less than 1.0%. Conversions to hydrocarbon products were considerably higher with tertiary alkoxide bases than for a secondary alkoxide base (compare entries 3, 7, 9, and 11 with 1). Complete suppression of solvolytic elimination was demonstrated by the absence of hydrocarbon products when **7** was heated at 90 °C for 6.0 h in triglyme in the presence of 2,6-lutidine.

For eliminations from **7** induced by potassium *tert*-butoxide in the presence of 18-crown-6 in *tert*-butylbenzene instead of triglyme, the yield of **9** + **10** dropped from 62 to 44%, but the relative percentage of nortricyclene in the hydrocarbon products remained very low (compare entries 3 and 5).

The reaction of **7** with sodium 2-cyclohexylcyclohexoxide and 18-crown-6 in triglyme was also conducted (entry 11) to allow for comparison with previous studies.[7,10] For this base–solvent combination, the yield of **9** + **10** was 58% and the relative proportion of nortricyclene in the hydrocarbon products exceeded 3%.

Exploratory investigation of the reactions of *exo*-2-bicyclo[2.2.1]heptyl chloride (**8**) with tertiary potassium alkoxides in the presence of 18-crown-6 in triglyme revealed that a higher reaction temperature of 90 °C was required. Also it was noted that the relative proportion of nortricyclene in the hydrocarbon products was very low (>0.05%). The absence of hydrocarbon products when **8** was heated with 2,6-lutidine in triglyme at 110 °C for 6.0 h demonstrated the total suppression of solvolytic elimination.

Products for Base-Promoted Eliminations from *exo*-3-Deuterio-*exo*-2-bicyclo[2.2.1]heptyl Tosylate (4) and Chloride (5). For bimolecular eliminations from **4** and **5**, syn-exo elimination produces bicyclo[2.2.1]hept-2-ene (**9**) and anti-endo-H elimination yields 2-deuteriobicyclo[2.2.1]hept-2-ene (**11**) (eq 5). Hydrocarbon yields



4 (X=OTs)
5 (X=Cl)

9 (from syn-exo elimination) **11** (from anti-endo-H elimination) **12** (from 1,3-elimination)

and the relative proportions of **9**, **11**, and *exo*-3-deuterionortricyclene (**12**) in the hydrocarbon products formed in reactions of dissociated alkoxide ion bases with deuterated tosylate **4** in triglyme or *tert*-butylbenzene at 60 °C for 3.0 h are recorded in Table I (entries 2, 4, 6, 8, 10, and 12). The relative proportion of syn-exo elimination product **9** varies from 78 to 91%, which establishes a pronounced favoring for syn-exo vs anti-endo-H elimination from **4**. However, the relative proportions of **9** and **11** may not be used to calculate syn-exo/anti-endo-H elimination rate ratios directly since the formation of **9** is suppressed by the deuterium isotope effect.

Compared with the relative proportions of nortricyclene formed from the corresponding undeuterated substrate **7** under the same conditions, the relative proportions of *exo*-3-deuterionortricyclene (**12**) are approximately doubled for eliminations from the deuterated tosylate **4**. Formation of **9**, but not **12**, from **4** is retarded by a deuterium isotope effect. Brown and Liu[7] also noted an increase in nortricyclene formation in reaction of deuterated tosylate **4** with sodium 2-cyclohexylcyclohexoxide in triglyme (no crown ether present) compared with elimination from the undeuterated substrate **7**.

The relative proportions of 1,2-elimination products **9** and **11** formed by reaction of deuterated tosylate **4** with potassium *tert*-butoxide in triglyme in the absence of 18-

Table II. Relative Proportions of Syn-exo vs Anti-endo-H Elimination from Dehydrotosylation of *exo*-2-Bicyclo[2.2.1]heptyl Tosylate Promoted by Alkoxides in the Presence of Equimolar 18-Crown-6 in Triglyme at 60 °C

entry	RO⁻ M⁺		k_H/k_D[a] for syn-exo elimination	corrected percentage of syn-exo elimination, %[b]	syn-exo / anti-endo-H
	M⁺	RO⁻			
1	K	isopropoxide	2.2	93.3	13.9
2	K	*tert*-butoxide	1.8	94.2	16.2
3[c]	K	*tert*-butoxide	2.1	95.6	21.7
4	K	tricyclohexylmethoxide	1.9	92.3	12.0
5	K	tri(2-norbornyl)methoxide	1.7	87.8	7.2
6[d]	Na	2-cyclohexylcyclohexoxide	1.8	89.5	8.6
7[e]	K	*tert*-butoxide	3.43[f]	96.5	49

[a] Calculated from hydrocarbon product proportions. See text. [b] Percent of syn-exo elimination after correction for the deuterium isotope effect in eliminations from *exo*-2-bicyclo[2.2.1]heptyl tosylate. The difference from 100% is the percentage of corrected anti-endo-H product. [c] Solvent was *tert*-butylbenzene. [d] Reaction at 80 °C. [e] Reaction at 80 °C in the absence of 18-crown-6. [f] From ref 20.

crown-6 at 80 °C for 7.0 h are also recorded in Table I (entry 13). The higher reaction temperature and longer reaction time were required for the less reactive, associated base.

The hydrocarbon yields and relative proportions of 1,2-elimination products **9** and **11** formed by reactions of deuterated chloride **5** with dissociated secondary and tertiary alkoxide bases in triglyme at 90 °C for 3.0 h and with potassium *tert*-butoxide in the absence of 18-crown-6 in triglyme at 110 °C for 7.0 h are presented in Table I (entries 14–16 and 17, respectively). In all cases, the yield of *exo*-3-deuterionortricyclene (**12**) was very low (>0.05%). The proportion of syn-exo elimination product **9** formed from deuterated chloride **5** is even higher than that obtained from deuterated tosylate **4** with the same base–solvent system (compare entries 14 and 2, 15 and 4, and 16 and 8 in Table I).

For reactions of both the deuterated tosylate **4** and chloride **5** with potassium *tert*-butoxide, the relative proportion of anti-endo-H elimination product **11** is higher in the presence of 18-crown-6 (compare entries 3 and 13 and entries 15 and 17 in Table I). The crown ether disrupts base association and facilitation of syn-exo elimination through the transition state **3**.[8-10] Hence the relative proportion of syn elimination product **9** decreases in the presence of 18-crown-6.

Quantitative Syn-exo/Anti-endo-H Rate Ratios for Bimolecular 1,2-Eliminations from *exo*-2-Bicyclo-[2.2.1]heptyl Tosylate. If the primary deuterium isotope effect values for formation of syn elimination product **9** from deuterated tosylate **4** and chloride **5** were known, then syn-exo/anti-endo-H rate ratios could be calculated from the relative proportions of **9** and **11**. By a control experiment (vide supra), it was demonstrated that the formation of nortricyclene in reactions of *exo*-2-bicyclo-[2.2.1]heptyl tosylate (**7**) with dissociated alkoxide bases does not result from unimolecular solvolytic elimination. Instead, the most probable mechanism for nortricyclene formation is concerted, bimolecular, 1,3-elimination. Hence, bicyclo[2.2.1]hept-2-ene and nortricyclene are formed from **7** by parallel, bimolecular elimination processes. Although the proportion of nortricyclene formed in reactions of **7** with dissociated bases is small, it may be precisely measured by gas chromatography.

The larger amount of *exo*-3-deuterionortricyclene (**12**) formed from the deuterated tosylate **4** than nortricyclene (**10**) from tosylate **7** is due to retardation of the syn-exo bimolecular elimination process by a primary deuterium isotope effect. If the simplifying approximation is made that all of the 1,2-elimination product results from syn-exo elimination,[18] the deuterium isotope effect for that elimination process may be calculated from the relative proportions of hydrocarbon products:

$$\frac{k_H}{k_D} = \frac{\text{12 from 4}}{\text{10 from 7}} \times \frac{\text{\% 9 from 7}}{\text{\% (9 + 11) from 4}} \qquad (6)$$

Calculated k_H/k_D values for syn-exo eliminations from *exo*-2-bicyclo[2.2.1]heptyl tosylate induced by dissociated alkoxide bases are presented in Table II (entries 1–6). For reactions conducted in the presence of 18-crown-6, k_H/k_D values of 1.7–2.2 are calculated for syn-exo dehydrotosylation promoted by potassium isopropoxide, *tert*-butoxide, tricyclohexylmethoxide, and tri(2-norbornyl)methoxide and sodium 2-cyclohexylcyclohexoxide in triglyme (entries 1, 2, and 4–6, respectively) and for potassium *tert*-butoxide in *tert*-butylbenzene (entry 3).

The deuterium isotope effect for reaction with dissociated *tert*-butoxide was determined by an alternative method to demonstrate the validity of this method for assessing the syn-exo elimination deuterium isotope effect values. The incomplete reaction of equimolar 5(6)-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**6**) and *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**4**) with potassium *tert*-butoxide in triglyme at 60 °C for 30 min gave a less than 10% yield of 1,2-elimination products, which were 61.7% deuterated. With adjustment for the isotopic purities of **6** and **4**, the percentage of deuterated bicyclo[2.2.1]hept-2-ene is calculated to be 61.8% when k_H/k_D is 1.90 in close agreement with the observed values.[19] A k_H/k_D value of 1.9 agrees very favorably with that of 1.8, which is given in Table II (entry 2).

With both the deuterium isotope effect for syn-exo elimination from *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**4**) and the deuterium content of the 1,2-elimination product mixture, relative proportions of **9** and **11** obtained in reactions of **4** with a dissociated alkoxide base may be corrected and the relative rates of syn-exo and anti-endo-H elimination calculated. Results are given in Table II (entries 1–6). The k_H/k_D value for reaction of **4** with potassium *tert*-butoxide in triglyme in the absence of crown ether has been determined kinetically in Kwart, Gaffney, and Wilk.[20] Using this value of 3.43 and our measurements of the deuterium content of the 1,2-elimination products obtained under these conditions (Table I, entry 13), the syn-exo/anti-endo-H ratio for reaction of **4** with an associated alkoxide base is calculated (Table II, entry 7).

Effect of Base Association. Comparison of the syn-exo/anti-endo-H elimination ratio for reaction of **4** with potassium *tert*-butoxide in triglyme in the absence and

(18) This assumption introduces an error of 5–10% into the calculated k_H/k_D value.

(19) For k_H/k_D values of 1.80 and 2.00, the calculated percentages of deuterated bicyclo[2.2.1]hept-2-ene, are 60.9 and 64.5, respectively.

(20) Kwart, H.; Gaffney, A. H.; Wilk, K. A. *J. Chem. Soc., Perkin Trans. II* **1984**, 565.

presence of 18-crown-6 is revealing (Table II, entries 2 and 7, respectively). In the absence of 18-crown-6, the base is associated (ion pairs and/or aggregates of ion pairs) and an overwhelming propensity for syn-exo elimination is noted (syn-exo/anti-endo-H = 49). However, when the dissociated base (free alkoxide or solvent-separated ion pairs) is produced by the presence of 18-crown-6, the ratio plummets to 16. Similarly Brown and Liu[7] reported a syn-exo/anti-endo-H ratio of ≥49 for eliminations from 4 induced by sodium 2-cyclohexylhexoxide in triglyme at 80 °C. In the presence of 18-crown-6, the ratio drops to 9 (Table II, entry 6). Once again, base association is demonstrated to have an important influence upon competitive syn and anti elimination processes.[8,9] With the associated base, the transition state for syn-exo elimination is stablized by the interactions depicted in 3, which are not possible in the anti-endo-H elimination transition state for geometrical reasons. Further evidence for appreciable differences between syn-exo elimination transition states involving associated[21] and dissociated alkoxides is provided by a change in the primary deuterium isotope effect value from 3.4 to 1.8 when 18-crown-6 is present in reactions of 4 with potassium *tert*-butoxide in triglyme.

For reactions of 4 with potassium *tert*-butoxide in the presence of 18-crown-6, the syn-exo/anti-endo-H elimination ratio is enhanced somewhat when the solvent is changed from triglyme to *tert*-butylbenzene (Table II, entries 2 and 3, respectively). This may indicate that equimolar 18-crown-6 is insufficient to completely disrupt association of potassium *tert*-butoxide in the extremely nonpolar hydrocarbon solvent.

Effect of Base Size. For eliminations from *exo*-2-bicyclo[2.2.1]heptyl tosylate with dissociated alkoxides in triglyme, the syn-exo/anti-endo-H elimination ratios are in the range of 7–16 (Table II, entries 1, 2, and 4–6). This represents a strong favoring of the syn-exo elimination process. Brown and Liu have proposed that preferential syn-exo elimination results from base attack at the sterically less hindered 3-exo hydrogen.[7] If this hypothesis is correct, the relative propensity for syn-exo elimination should be enhanced when the base size is increased.

For reactions of 4 with dissociated alkoxide bases in triglyme, the syn-exo/anti-endo-H ratios for isopropoxide, *tert*-butoxide, tricyclohexylmethoxide, and tri(2-norbornyl)methoxide are 13.9, 16.2, 12.0, and 7.2, respectively. These ratios clearly show that there is no correlation of base size and the relative propensity for syn-exo elimination. In fact, the syn-exo/anti-endo-H ratio is found to be lowest for tri(2-norbornyl)methoxide, an extremely ramified dissociated base. This contradicts the steric proposal of elimination stereochemistry as advanced by Brown and Liu.[7]

Conclusions

Base–solvent combinations have been developed that promote clean 1,2-eliminations from *exo*-2-bicyclo[2.2.1]-heptyl tosylate and chloride. The stereochemistry of eliminations from *exo*-3-deuterio-*endo*-2-bicyclo[2.2.1]-heptyl tosylate has been determined for reactions with dissociated alkoxide bases in triglyme. The observed syn-exo/anti-endo-H elimination ratios of 7–16 show a clear preference for syn-exo elimination. However, there is no correlation between base size and the relative propensity for syn-exo dehydrotosylation. Association of potassium *tert*-butoxide base in triglyme substantially influences the elimination stereochemistry by facilitating syn-exo elimination.

Experimental Section

General Methods. All melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded on Varian EM-360 and XL-100 instruments with $CDCl_3$ as the solvent and TMS as the internal standard unless specified otherwise. For analysis of the hydrocarbon reaction products, an Antek Model 400 gas chromatograph was utilized. GC-MS analysis was conducted with a Varian Aerograph Series 2700 gas chromatograph interfaced with a MAT-311 mass spectrometer that had a Varian 620-I data system.

Bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.1]hepta-2,5-diene, 18-crown-6, 40% NaOD in D_2O (99+ atom % D), $NaBD_4$ (98 atom % D), and BH_3·THF were purchased from Aldrich and used as received. Triglyme and *tert*-butylbenzene were purchased from Aldrich and distilled from $LiAlH_4$. Propionic acid-*d* was prepared by a reported procedure.[16] Sodium amalgam (2%) was prepared by a reported method.[22]

Procedures for solvolysis studies, preparation of base–solvent solutions, conduct of the elimination reactions, and isolation and analysis of the hydrocarbon products are the same as those described previously.[17]

***exo*-2-Acetoxy-*exo*-3-(acetoxymercurio)bicyclo[2.2.1]-heptane.** $Hg(OAc)_2$ (34.3 g, 0.10 mol) and bicyclo[2.2.1]hept-2-ene (4.90 g, 0.050 mol) in 600 mL of glacial AcOH and stirred at room temperature for 15 h, and the AcOH was distilled under reduced pressure. CCl_4 (10 mL) was added to the syrupy residue, and all volatile solvents were vacuum distilled. The white residue was recrystallized from benzene–heptane to give 35.4 g (80%) of the hygroscopic title compound, mp 128–130 °C: ^{1}H NMR (CD_3SOCD_3) δ 1.05–1.90 (m, 6 H), 1.92 (s, 3 H), 2.01 (s, 3 H), 2.35 (s, 1 H), 2.52 (d, J = 7.1, 2.5 Hz, 1 H), 2.70 (s, 1 H), 4.78 (d, J = 7.1, 1 H).

***exo*-2-Deuterio-*exo*-2-bicyclo[2.2.1]heptyl Tosylate (4).** A reported method for reduction of oxymercurials with sodium amalgam in NaOD–D_2O[12] was modified for this substrate. *exo*-2-Acetoxy-*exo*-3-(acetoxymercurio)bicyclo[2.2.1]heptane (12.8 g, 31 mmol), freshly prepared 2% sodium amalgam (47 g), and 20 mL of 2 N NaOD–D_2O in a 100-mL round-bottomed flask tightly stoppered with a rubber septum was stirred vigorously at room temperature. Periodically the pressure developed was relieved with a syringe needle. After 24 h, a second portion of 2% sodium amalgam (30 g) was added and stirring was continued for an additional 48 h. A small amount of $CHCl_3$ was added, and the mercury and insoluble salts were filtered with a glass wool pad and were washed with additional $CHCl_3$. The combined $CHCl_3$ layers were washed with H_2O and dried over $MgSO_4$. Evaporation of the $CHCl_3$ solution in vacuo gave crude *exo*-3-deuterio-*exo*-bicyclo[2.2.1]heptan-2-ol (mp 116–117 °C), which was reacted with tosyl chloride in pyridine according to a general procedure[22b] to give a 50% yield (based on the oxymercurial) of deuterated tosylate 4, mp 53 °C (lit.[23] mp 52.5–53.5 °C). ^{1}H NMR ($CDCl_3$): δ 0.85–1.75 (m, 8 H), 2.28 (m, 2 H), 2.44 (s, 3 H), 4.42 (d, J = 6.6 Hz, 1 H), 7.54 (q, 4 H).

***exo*-2-Bicyclo[2.2.1]heptyl Tosylate (7).** By use of 2 N aqueous NaOH instead of NaOD–D_2O in the procedure given above, crude *exo*-2-bicyclo[2.2.1]heptanol (mp 115.5–117 °C) was obtained and converted to tosylate 7 with mp 53 °C in 57% overall yield from the oxymercurial.

5(6)-Deuteriobicyclo[2.2.1]hept-2-ene. A reported procedure[16] was modified. A 1-L, two-necked flask equipped with an addition funnel and condenser was flame dried while being flushed with nitrogen. Freshly distilled bicyclo[2.2.1]hepta-2,5-diene (54.2 g, 0.60 mol) dissolved in 300 mL of dry THF was introduced into the flask. With the addition funnel, 57.3 mL of 2.04 M BH_3·THF (0.35 mol) was slowly added with cooling. After 2 h at room temperature, volatile components were removed by distillation under reduced pressure and the foamy residue was maintained at 50 °C/1 Torr to remove traces of bicyclo[2.2.1]hepta-2,5-diene.

(21) A nonplanar transition state for syn-exo elimination from 4 has been proposed for associated alkoxide bases.[20]

(22) Fieser, L. F.; Fieser, M. *Reagents in Organic Synthesis*, Vol 1; Wiley: New York, 1967; (a) p 1030, (b) p 1180.
(23) Kwart, H.; Takeshida, T. *J. Org. Chem.* **1963**, *28*, 670.

Propionic acid-*d* (65 mL) was added and the mixture was slowly heated to 150 °C. After 5 h, fractions with bp <145 °C were collected and washed with 10% $NaHCO_3$ and with H_2O. The crude product was dried over $MgSO_4$ and fractionally distilled to give 13.0 g (39.5%) of the title compound with bp 94 °C/680 Torr. GC-MS analysis showed 90.5% deuterium incorporation.

5(6)-Deuterio-*exo*-2-bicyclo[2.2.1]heptyl Tosylate (6). The 5(6)-deuteriobicyclo[2.2.1]hept-2-ene was hydroborated and oxidized with H_2O_2 according to Brown's procedure.[24] The crude alcohol was reacted with tosyl chloride in pyridine[22b] to give a 37.5% yield (overall from the alkene) of **6**, mp 35.5 °C.

***exo*-3-Deuterio-*exo*-2-chlorobicyclo[2.2.1]heptane (5).** To 21.3 g (0.25 mol) of freshly distilled pyridine in 80 mL of cold water were added 20.2 (0.25 mol) of concentrated HCl and 200 mL of Et_2O. The mixture was cooled to 5 °C and Chlorox (445 g, 0.31 mol of sodium hypochlorite) was added at such a rate that the temperature did not exceed 15 °C. After stirring for 1 h at room temp, the layers were separated, and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined Et_2O layers were washed with 25 mL of 8% H_2SO_4 and 25 mL of 5% NaOH before being dried over $CaCl_2$.

Bicyclo[2.2.1]hept-2-ene (19.8 g, 0.21 mol) was deuteroborated[24] with externally generated B_2D_6 (from $NaBD_4$ and $BF_3{\cdot}Et_2O$) in 350 mL of Et_2O. The slight excess of B_2D_6 was destroyed by adding a small amount of H_2O. To the reaction mixture was added 25 mL of piperidine followed by the *N*-chloropiperidine in Et_2O solution prepared above. The resulting solution was stirred at room temperature for 4 days under nitrogen and poured into a separatory funnel partially filled with crushed ice. HCl (9 N, 100 mL) was added and the mixture was extracted with Et_2O. Sodium bisulfite solution (38 g in 100 mL of H_2O) was added to destroy the excess *N*-chloropipiridine and the Et_2O layer was separated and washed with 0.2 N HCl (2 × 250 mL) and once with dilute aqueous Na_2CO_3. After drying over Na_2SO_4, the solution was concentrated at atmorpheric pressure. The residual liquid was distilled under vacuum to give 7.4 g (27%) of **5** as the main fraction, bp 66.5–67 °C/15 Torr (lit.[25] bp 84–88 °C/76 Torr). ^1H NMR ($CDCl_3$): δ 1.0–2.0 (m, 7 H), 2.40 (s, 2 H), 3.93 (d, J = 7.2 Hz, 1 H).

***exo*-2-Chlorobicyclo[2.2.1]heptane (8).** Using the same procedure, 15.1 g (57%) of **8** with bp 66.5–67 °C/15 Torr was obtained from 18.8 g (0.20 mol) of bicyclo[2.2.1]hept-2-ene.

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"Spin–Charge Exchange" in Allodial Radical Ions, a Novel Intramolecular Single Electron Transfer Equilibrium

Manuel Ballester,* Isabel Pascual, Juan Riera, and Juan Castañer

Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC), Jordi Girona, 18-24, 08034 Barcelona, Spain

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The intramolecular single-electron transfer in radical anions and radical cations, constituted by two identical triphenylmethyl moieties, has been studied. The preparation of the radical ions has been effected by mixing the corresponding stable diions (tetra-*n*-butylammonium or hexachloroantimonate salts) and chemically inert diradicals: by partial oxidation of the dianion salts with iodine (radical anions) and by partial oxidation of the diradicals with $SbCl_5$ (radical cations). The ESR ^{13}C hyperfine coupling constants and linewidths and UV–vis absorptivity spectra afford compelling evidence for a rapid spin–charge exchange equilibrium:

$$(C_6Cl_5)_2\overset{\bullet}{C}\text{-}C_6Cl_4\text{-}Sp\text{-}C_6Cl_4\text{-}\overset{*}{C}(C_6Cl_5)_2 \rightleftharpoons (C_6Cl_5)_2\overset{*}{C}\text{-}C_6Cl_4\text{-}Sp\text{-}C_6Cl_4\text{-}\overset{\bullet}{C}(C_6Cl_5)_2$$

(Sp = none, CH_2CH_2, C≡C. * = –, +). Relevant structural aspects, such as steric inhibition of resonance, electron paths, and counterion involvement, are discussed. The synthesis and isolation of related disalts from the corresponding diradicals are also described.

Introduction

The trivalent carbon radicals of the perchlorotriphenylmethyl (PTM) series posses a chemical inertness and a thermal stability much greater than those of the overwhelming majority of tetravalent carbon compounds and materials.[1-3] In fact, their half-lives in solution, in the air, are of the order of 100 years, and they withstand harsh chemicals (H_2SO_4, HNO_3, NO, NO_2, Cl_2, Br_2, etc.) and temperatures up to 300 °C in the air. The unique inertness of such radicals is due to molecular overcrowding by their chlorine substituents which shield effectively their would be normal reaction sites.

Therefore, these inert free radicals (IFRs) are quite appropriate for the study of reactions involving radicals and nonradical species, as single-electron transfers between radicals and ions, particularly those between inert 4-X-tetradecachlorotriphenylmethyl radicals (X-PTM•) and low reactivity, stable 4-Y-tetradecachlorotriphenylmethyl anions (Y-PTM:⁻). This process, which has recently been investigated (Scheme I),[4] leads to SET equilibria, the equilibration rates of which are unusually slow mainly

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