was cooled to 0 °C. To the vigorously stirred solution was added dropwise a solution of *p*-nitrobenzenediazonium tetrafluoroborate[26] (0.59 g, 2.5 mmol) in water (30 mL). The mixture was stirred overnight at room temperature and evaporated to dryness in vacuo. The residue was extracted repeatedly with toluene, and the combined extracts were washed several times with deionized water and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was purified by chromatography on basic alumina with chloroform and chloroform/ethanol as eluents.

**Chromogenic cryptand 13**: 20% yield of a dark red semisolid; IR (film) 3354 (OH), 1095 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.30–3.00 (m, 12 H), 3.20–3.60 (m, 16 H), 6.67 (s, 2 H), 8.15 (AB q, 4 H), 8.60 (br s, 1 H). Anal. Calcd for $C_{26}H_{35}N_5O_8$: C, 57.24; H, 6.47. Found: C, 57.01; H, 6.63.

**Chromogenic cryptand 14**:[22] 48% yield of a red-brown semisolid; IR (neat) 3350 (OH), 1100 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.70–3.10 (m, 12 H), 3.50–3.90 (m, 16 H), 4.10–4.40 (m, 4 H), 7.42 (s, 2 H), 7.80–8.50 (m, 5 H). Anal. Calcd for $C_{28}H_{39}N_5O_9 \cdot H_2O$: C, 55.34; H, 6.80. Found: C, 55.20; H, 6.95.

**Chromogenic cryptand 15**: 54% yield of a dark red oil; IR (film) 3352 (OH), 1100 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.60–3.20 (m, 12 H), 3.35–4.40 (m, 24 H), 6.65 (s, 1 H), 7.40 (s, 2 H), 8.13 (AB q, 4 H). Anal. Calcd for $C_{30}H_{43}N_5O_{10} \cdot H_2O$: C, 55.29; H, 6.96. Found: C, 55.45; H, 7.18.

**Chromogenic cryptand 16**: 57% yield of a red-brown semisolid; IR (film) 3358 (OH), 1107 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.30–3.10 (m, 12 H), 3.20–3.90 (m, 28 H), 7.20–7.45 (m, 3 H), 8.15 (AB q, 4 H). Anal. Calcd for $C_{32}H_{47}N_5O_{11}$: C, 56.71; H, 6.99. Found: C, 56.54; H, 7.00.

**Chromogenic cryptand 17**: 65% yield of a red-brown glass; IR (film) 3400 (OH), 1135 and 1105 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.70–2.95 (m 12 H), 3.45–3.80 (m, 28 H), 4.69 (s, 4 H), 4.85 (br s, 1 H), 7.86 (s, 2 H), 8.13 (AB q, 4 H). Anal. Calcd for $C_{34}H_{51}N_5O_{11}$: C, 57.86, H, 7.28. Found: C, 57.74; H, 7.31.

**Cryptand Diamide 19.** Under argon, a solution (64 mL) of diacid chloride 18[24] (1.61 g, 5.00 mmol) in dry benzene and a solution (64 mL) of 1,13-diaza-24-crown-8[25] (1.75 g, 5.00 mmol) and triethylamine (1.88 mL, 13.6 mmol) in benzene were added simultaneously with two syringe pumps to 150 mL of vigorously stirred benzene at room temperature during 12 h. The reaction mixture was stirred overnight, the solvent was removed in vacuo, and the residue was chromatographed on alumina with chloroform/ethanol (49:1) as eluent to give diamide **19** (1.80 g, 60%) as a white, waxlike solid with mp 78–80 °C: IR (film) 1645 (C=O), 1110 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.30–3.85 (m, 30 H), 3.68 (s, 3 H), 4.00–4.20 (m, 6 H), 4.66 (AB q, 4 H), 7.12 (t, 1 H), 7.40 (d, 2 H). Anal. Calcd for $C_{29}H_{46}N_2O_{11} \cdot 0.5CHCl_3$: C, 53.82; H, 7.12. Found: C, 54.11; H, 6.88.

**Cryptand Sodium Phenolate 20.** A solution of diamide **19** (1.25 g, 2.10 mmol) in dry THF (15 mL) was added to a suspension of $LiAlH_4$ (0.66 g, 17.5 mmol) in THF (65 mL). The mixture was refluxed for 20 h and cooled and 5% aqueous NaOH was added. The inorganic solid was filtered and washed several times with THF. The solvent was removed in vacuo to afford 0.85 g (73%) of **20** as a pale green foam that was directly used in the preparation of **17** without additional purification.

**UV-Visible Spectroscopic Properties of Chromogenic Compounds 8–17 and Determination of Their p$K_a$ Values.** Chromogenic compounds **8–17** were dissolved in dioxane to make stock solutions of $1.0 \times 10^{-4}$ M. Solutions were made from 1.0 mL of the stock solution and 1.0 mL of 0.2 M HCl for the nonionized form (HL) and from 1.0 mL of the stock solution and 1.0 mL of 0.2 M tetramethylammonium hydroxide for the ionized form ($L^-$) and were scanned in a 1-cm pathlength cuvette from 700 to 300 nm with a Beckman DU-8 spectrophotometer. Molar absorptivities ($\epsilon$) at wavelength maxima ($\lambda_{max}$) were calculated according to Beer's law.

For the p$K_a$ determinations, absorbances were measured at the acid and base wavelength maxima of the chromogenic compounds in a zwitterionic buffer ((cyclohexylamino)ethanesulfonic acid (CHES)) at pH values equal to the p$K_a$ and the p$K_a \pm 0.5$ units.

**Responses to Sodium and Potassium.** The reagents for obtaining sodium and potassium responses consisted of $5.0 \times 10^{-5}$ M chromogenic compound in 50% (v/v) dioxane/water and an appropriate buffer (see Table II). Final concentration of sodium or potassium ions in each cuvette was $2 \times 10^{-2}$ M.

# *Notes*

## Unimportance of Steric Effects in Controlling the Stereochemistry of Base-Promoted, 1,2-Eliminations from *exo*-2-Bicyclo[2.2.1]heptyl Tosylate and Closely Related Compounds

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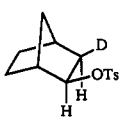
Greater facility of reactions involving the exo faces of bicyclo[2.2.1]heptyl compounds is usually attributed to greater steric hindrance by the 5,6-endo hydrogens to approach of the endo face than by the 7-syn hydrogen for exo attack.[3,4] Hydroboration, epoxidation, and many other reactions have been shown to be very sensitive to structural changes in this bicyclic ring system. For example, hydroboration of bicyclo[2.2.1]hept-2-ene gives solely the syn-exo adduct in contrast to only 22% of syn-exo addition for 7,7-dimethylbicyclo[2.2.1]hept-2-ene.[4]

The stereochemistry of base-promoted 1,2-elimination from bicyclo[2.2.1]heptyl compounds might be expected to be influenced by steric factors also.[3] As the base becomes bulkier, elimination involving base attack from the exo face should be accentuated. However, we have shown that the steric bulk of the base does not influence the level of preference for syn-exo 1,2-elimination from *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**1**) and chloride (**2**).[5] When the base was changed from potassium *tert*-butoxide to tri-2-norbornylmethoxide for reaction of **1** in triglyme (triethylene glycol dimethyl ether) in the presence of 18-crown-6, the percentage of syn-exo elimination ac-

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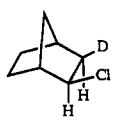


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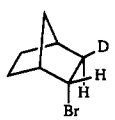


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(1) Texas Tech University.
(2) Pusan National University.
(3) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1970**, *92*, 200.
(4) Brown, H. C.; Kawakami, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 201.
(5) Bartsch, R. A.; Lee, J. G. *J. Org. Chem.* **1991**, *56*, 212.

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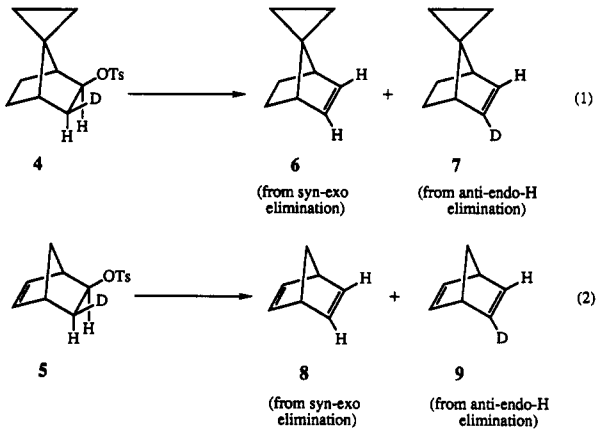
tually decreased from 94 to 88%. Thus, for a dramatic increase in steric requirements of the dissociated[6] alkoxide base, the relative proportion of syn–exo vs anti–endo H elimination failed to increase. The absence of a steric effect by the base was also noted in elimination from *exo*-3-deuterio-*endo*-2-bromobicyclo[2.2.1]heptane (3) for which the proportion of undeuterated bicyclo[2.2.1]hept-2-ene, the anti–exo H elimination product, remained essentially the same for dissociated *tert*-butoxide and tri-2-norbornylmethoxide.[7]

To further probe the potential for steric interactions in elimination from bicyclo[2.2.1]heptyl compounds, additional modifications in substrate structure have now been made. We have synthesized 7,7-dimethylene-*exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (4) and *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]hept-5-enyl tosylate (5) and investigated their elimination reactions (eqs 1 and 2). For




4, syn–exo elimination should be disfavored compared with 1 by reduced access to the exo face due to the 7-syn methylene group. For 5, anti–endo H elimination should be accentuated compared with 1 by removal of the 5,6-endo hydrogens which would reduce the steric requirement for base attack on the endo face.[8]

Tosylates 4 and 5 were synthesized by adaptations of known synthetic procedures. Reaction of cyclopentadiene with NaH and 1,2-dichloroethane gave spiro[4.2]hepta-2,4-diene, which underwent a Diels–Alder reaction with 1,2-dibromoethene at 180 °C to provide 5,6-dibromo-7,7-dimethylenebicyclo[2.2.1]hept-2-ene. This alkene was hydrogenated over W-4 Raney nickel catalyst, and the resulting 1,2-dibromo-7,7-dimethylenebicyclo[2.2.1]heptane was debrominated with Zn–Cu couple to form 7,7-dimethylenebicyclo[2.2.1]hept-2-ene (6). Oxymercuration of 6 and bicyclo[2.2.1]hepta-2,5-diene (8) gave oxymercurials from stereospecific syn addition[10] with consistent $^1$H NMR spectra.[10,11] The oxymercurials were reacted with sodium amalgam and NaOD in $D_2O$[11] to give the corresponding *exo*-3-deuterated alcohols with consistent $^1$H NMR spectra[11] that were converted into the corresponding tosylates by a standard method.[12a]

**Table I. Elimination Products from Reactions of Tosylates 1, 4, and 5 with Potassium Alkoxides in Triglyme at 60 °C[a]**

| tosylate | RO⁻ of ROK | equimolar 18-crown-6 present | hydrocarbon product yield (%) | undeuterated 1,2-elimination product[b] (%) |
|---|---|---|---|---|
| 1 | *tert*-butoxide | yes | 60.1[c] | 90.0[c] |
| 4 | *tert*-butoxide | yes | 63.9[d] | 93.4 |
| 5 | *tert*-butoxide | yes | 10.4[e] | 88.0 |
| 1 | tri-2-norbornyl-methoxide | yes | 53.9[c] | 81.0[c] |
| 4 | tri-2-norbornyl-methoxide | yes | 67.2[d] | 80.3 |
| 5 | tri-2-norbornyl-methoxide | yes | 12.9[e] | 85.6 |
| 1[f] | *tert*-butoxide | no | ND[c,g] | 93.2[c] |
| 4[f] | *tert*-butoxide | no | ND[g] | 100.0 |

[a] Reaction of 0.125 M tosylate with 0.25 M ROK and 0.25 M 18-crown-6 for 3.0 h. [b] Remaining percentage is deuterated 1,2-elimination product. [c] Data from ref 5. [d] Total hydrocarbon products contained >98% of 1,2-elimination products. [e] Total hydrocarbon products contained 94–97% of 1,2-elimination products. [f] Reaction of 0.125 M tosylate and 0.25 M ROK for 7.0 h at 80 °C. [g] Not determined.

The combination of a potassium tertiary alkoxide in triglyme in the presence of 1 equiv of 18-crown-6 has been shown to be an effective base–solvent system for promoting clean bimolecular eliminations from a bicyclic tosylate that is very prone to solvolytic rearrangement.[13] Such base–solvent systems were utilized successfully to study the stereochemistry of elimination from both *exo*- and *endo*-2-bicyclo[2.2.1]heptyl halides and arenesulfonates.[5,7]

Suppression of solvolytic elimination from 4 and 5 was demonstrated by the absence of hydrocarbons when these tosylates were heated with 2,6-lutidine[14] in triglyme at 80 °C for 5.0 h.[15] Reaction of 4 with potassium *tert*-butoxide and tri-2-norbornylmethoxide in triglyme in the presence of equimolar 18-crown-6 at 60 °C for 3.0 h[15] gave 64 and 67% conversions to hydrocarbon products, respectively (Table I). Under the same conditions, 5 gave only 10–13% conversions to hydrocarbon products (Table I). Presumably, the lower conversion of 5 to hydrocarbon products during the specific reaction period reflects a reduced rate of formation of the more strained bicyclo[2.2.1]hepta-2,5-diene. Of the total hydrocarbon products formed from 4 and 5, less than 2 and 6%, respectively, were products of rearrangement. Thus, appropriate reaction conditions were established that could be used to probe the stereochemistry of 1,2-eliminations from 4 and 5 by dissociated alkoxide bases.[6]

Hydrocarbon products from reactions 4 and 5 with potassium alkoxides in triglyme in the presence of 18-crown-6 were analyzed by GC–MS to determine the deuterium content of the 1,2-elimination products (Table I). The relative percentage of undeuterated alkene reflects the proportion of syn–exo elimination[16] (eqs 1 and 2). Reported[5] yields of hydrocarbon products and relative percentages of undeuterated bicyclo[2.2.1]hept-2-ene formed in eliminations from *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]-heptyl tosylate (1) with dissociated *tert*-butoxide and

(6) Free ions or solvent-separated ion pairs produced by addition of 1 equiv of 18-crown-6 to the potassium alkoxide.
(7) Bartsch, R. A.; Lee, J. G. *J. Org. Chem.* **1990**, *55*, 5247.
(8) A striking effect for similar structural variation upon the rate of a reaction that involves 3-exo and 3-endo hydrogens in bicyclo[2.2.1]-heptyl compounds has been reported by Tidwell.[9] Relative rates of deuterium exchange of the 3-exo vs 3-endo hydrogen by NaOD in $D_2O$ for bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (camphor), and bicyclo[2.2.1]hept-5-en-2-one under identical conditions were 715:1, 21.4:1, and 122:1, respectively.
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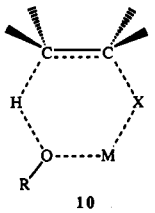
(15) A slow stream of nitrogen was used to sweep hydrocarbon products from the reaction vessel into a cold trap. At the conclusion of the reaction period, the cold trap was separated, pentane and an internal standard were added to the cold trap, and the pentane solution was removed and stored in a refrigerator until analysis by GC or GC–MS.[5,7]
(16) The percentages of syn–exo elimination from 4 and 5 may not be used to calculate directly the syn–exo/anti–endo H ratios since formation of the syn–exo product is retarded by the primary deuterium isotope effect.

tri-2-norbornylmethoxide in triglyme under the same reaction conditions are also included in Table I for comparison.

According to the steric theory,[3] elimination reactions from 4 and 5 should exhibit a diminished preference for syn–exo elimination compared with 1 (vide supra). However, for 1,2-eliminations from 1, 4, and 5 promoted by dissociated *tert*-butoxide, the relative percentages of syn–exo product are 90, 93, and 88%, respectively (Table I). Hence, there is no appreciable variation in the percentage of exo–syn elimination product for these three substrates. For the sterically more demanding dissociated base tri-2-norbornylmethoxide, the relative percentages of exo–syn elimination product from 1, 4, and 5 are 81, 80, and 86%, respectively (Table I). Thus, there is no appreciable variation in the relative percentages of syn–exo elimination product and no decrease in the proportion of syn–exo elimination for 4 and 5 with respect to 1 as would be predicted by the steric theory.

For a given substrate 4 or 5, an increase in the relative percentage of syn–exo elimination would be anticipated from the steric theory when the highly ramified base tri-2-norbornylmethoxide replaces *tert*-butoxide. Once again, the results are contrary to the predictions of the steric theory since for 4 the relative percentages of syn–exo product drops from 93 to 81% and for 5 it remains essentially unchanged as the spatial demands of the base are increased markedly (Table I).

Association of metal alkoxide bases in solvents of low polarity has been shown to have a pronounced effect on competitive syn and anti 1,2-elimination processes.[17,18] Base association favors syn elimination via transition states 10 in which both the β-hydrogen and the leaving group

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interact with the base species. Similar interactions are not possible in the anti elimination transition state for geometrical reasons. In eliminations from *exo*-2-bicyclo[2.2.1]heptyl halides and arenesulfonates by associated alkoxide bases,[19] syn–exo elimination involving transition state 10 might be sensitive to steric interactions caused by the introduction of 7-syn substituents.[20] In apparent agreement, Brown and Liu[3] reported that the relative percentage of >98% undeuterated 1,2-elimination product obtained by reaction of 1 with sodium 2-cyclohexylcyclohexoxide in triglyme at 80 °C was reduced to 95% for elimination from 7,7-dimethyl-*exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (11). The elimination stereochemistry was determined by integrating the areas of the olefinic protons and the bridgehead protons on 60-MHz $^1$H NMR spectra.

In an earlier study,[5] we determined that the relative percentage of undeuterated 1,2-elimination product obtained from reaction of 1 with potassium *tert*-butoxide in triglyme for 7.0 h at 80 °C was 93%. In the present investigation, it was not possible to determine the stereochemistry of 1,2-elimination from 5 induced by associated *tert*-butoxide due to the sluggish bimolecular reaction that allowed solvolytic processes to become important. However, for 4 reaction with potassium *tert*-butoxide in triglyme for 7.0 h at 80 °C gave the 1,2-elimination product that contained only the undeuterated alkene 6. Thus, the relative proportion of syn–exo elimination actually increased when a 7-syn methylene group was introduced instead of decreasing as would be predicted if steric interactions of the associated base and a 7-syn substituent were important.

Reasons for the disparity of this result and that obtained by Brown and Liu[3] could be due to the sterically more demanding 7-syn substituent and associated base species employed in the earlier work. However, the difference could also arise from the use of a less precise method for deuterium analysis (integration of 60-MHz $^1$H NMR absorptions[3]). Since the synthetic methods utilized by Brown and Liu for the preparation of 1 and 11 were not specified, it is also possible less than complete stereospecificity was obtained in the deuterium incorporation step.[11]

In conclusion, the results of this study fail to support the proposed steric control of stereochemistry in 1,2-eliminations from bicyclo[2.2.1]heptyl compounds by either dissociated or associated potassium alkoxide bases.

## 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. For analysis of the hydrocarbon reaction products, an Antek Model 400 gas chromatograph was utilized. GC–MS 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. Elemental analysis was performed by Desert Analytics of Tucson, Az.

Bicyclo[2.2.1]hepta-2,5-diene, 1,2-dibromoethene (mixture of *E* and *Z* isomers), 1,2-dichloroethane, dicyclopentadiene, 40% NaOD in $D_2O$ (99+ atom % D), and other organic and inorganic reagents were purchased from Aldrich and used as received. Triglyme was purchased from Aldrich and distilled from $LiAlH_4$. Sodium amalgam (2%) was prepared by a reported method.[12b]

**Spiro[4.2]hepta-2,4-diene.** The procedure of Wilcox and Craig[22] was modified. NaH (80.0 g, 60% dispersion in mineral oil, 2.00 mol) was suspended in dry THF (470 mL), and freshly distilled cyclopentadiene[23] (66.1 g, 1.00 mol) was slowly added. After 20 min, 99.0 g (1.00 mol) of 1,2-dichloroethane was slowly added and the reaction mixture was stirred at room temperature for 8 h. Wet THF was carefully added to destroy the residual NaH, and the mixture was poured into ice and water in a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with pentane (150 mL). The organic layer and pentane extract were combined and washed twice with 0.5 N HCl and twice with $H_2O$ and dried ($MgSO_4$). The pentane was distilled by use of a steam bath, and the residue was carefully fractionated to give 59.0 g (83%) of the title compound as a colorless liquid, bp 107–109 °C (680 Torr) (lit.[24] bp 113 °C (737 Torr)). $^1$H NMR ($CDCl_3$): δ 1.50 (s, 4 H), 6.50 (d of m, 4 H).

**5,6-Dibromo-7,7-dimethylenebicyclo[2.2.1]hept-2-ene.** A solution of spiro[4.2]hepta-2,4-diene (39.0 g, 0.35 mol) and 1,2-dibromoethene (87.0 g, 0.47 mol) was divided into four equal portions and sealed in four Pyrex tubes (18 × 25 × 300 mm). The tubes were heated at 180 °C for 24 h, cooled, and opened, and the combined contents were distilled. Fractions boiling at 120–160 °C were combined and dissolved in a small amount of hot 95% EtOH. The solid (21.0 g, 18%) that formed on cooling had mp 75 °C (lit.[23] mp 75 °C). $^1$H NMR ($CDCl_3$): δ 0.56 (s, 4 H), 2.67

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(20) A nonplanar transition state has been proposed for syn–exo elimination from 1 induced by associated alkoxide bases.[21]
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(24) Alder, K.; Ache, H. J.; Flock, F. H. *Chem. Ber.* **1960**, *93*, 1888.

(m, 2 H), 4.65 (t, $J$ = 2 Hz, 2 H), 6.41 (t, $J$ = 1.9 Hz, 2 H).

**1,2-Dibromo-7,7-dimethylenebicyclo[2.2.1]heptane.** Catalytic hydrogenation was carried out with a Parr low-pressure hydrogenator under 75 psi initial pressure. A solution of 5,6-dibromo-7,7-dimethylenebicyclo[2.2.1]hept-2-ene (26.0 g, 93 mmol) in EtOAc (200 mL) was shaken at room temperature for 6 h in the presence of W-4 Raney Nickel[25] (prepared from 50% Ni-Al alloy). The reaction mixture was filtered and concentrated to give the title compound in quantitative yield, mp 75 °C after recrystallization from aqueous EtOH. $^1$H NMR ($CDCl_3$): $\delta$ 0.59 (s, 4 H), 1.5-2.1 (m, 4 H), 2.10 (d, $J$ = 7.9 Hz, 2 H), 4.78 (s, 2 H). Anal. Calcd for $C_9H_{12}Br_2$: C, 38.60; H, 4.31. Found: C, 38.51; H, 4.41.

**7,7-Dimethylenebicyclo[2.2.1]hept-2-ene.** Zn-Cu couple[26] (45 g) was added to a warm solution of 1,2-dibromo-7,7-dimethylenebicyclo[2.2.1]heptane (18.0 g, 65 mmol) in 95% EtOH (400 mL), and the mixture was refluxed for 5 h. The solid was filtered, and the filtrate was poured into $H_2O$ (1.0 L). The mixture was extracted with pentane (2 × 50 mL), the combined extracts were washed twice with $H_2O$ and dried over $MgSO_4$, and the pentane was removed with an efficient fractionating column. The residue was distilled to give 5.1 g (66%) of the title compound, bp 52-53 °C (30 Torr) ((lit.[24] bp 63 °C (60 Torr)).

**7,7-Dimethylene-*exo*-2-acetoxy-*exo*-3-(chloromercurio)bicyclo[2.2.1]heptane.** A solution of 7,7-dimethylenebicyclo[2.2.1]hept-2-ene (13.0 g, 108 mmol) and $Hg(OAc)_2$ (34.0 g, 105 mmol) in glacial AcOH (500 mL) was stirred at room temperature for 12 h, and then 900 mL of 2% aqueous NaCl was added. The solid that formed was filtered, washed with $H_2O$, air-dried, and recrystallized from EtOAc to give 26.0 g (75%) of the title compound, mp 97 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.33-0.83 (m, 4 H), 1.00-1.90 (m, 4 H), 1.97 (s, 3 H), 2.45-2.65 (m, 2 H), 2.74 (d, $J$ = 7.3 Hz, 1 H). Anal. Calcd for $C_{11}H_{15}CHgO_2$: C, 31.81; H, 3.64. Found: C, 31.82; H, 3.65.

**7,7-Dimethylene-*exo*-3-deuterio-*exo*-bicyclo[2.2.1]heptan-2-ol and Tosylate 4.** Reduction of 7,7-dimethylene-*exo*-2-acetoxy-*exo*-3-(chloromercurio)bicyclo[2.2.1]heptane (20.8 g, 50 mmol) with sodium amalgam and NaOD in $D_2O$ according to the procedure of Jensen, Miller, Cristol, and Beckley[11] gave the crude alcohol, which was tosylated[12a] to give 6.6 g (45% for two steps) of 4, mp 59-60 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.17-0.75 (m, 4 H), 1.00-2.00 (m, 7 H), 2.46 (s, 3 H), 4.61 (d, $J$ = 7 Hz, 1 H), 7.67 (q, 4 H).

***exo*-2-Acetoxy-*exo*-3-(bromomercurio)bicyclo[2.2.1]hept-5-ene.** A solution of bicyclo[2.2.1]hepta-2,5-diene (20.2 g, 0.22 mol) and $Hg(OAc)_2$ (49.8 g, 0.16 mol) in AcOH (120 mL) was stirred at room temperature for 10 min and poured into 200 mL of 10% aqueous KBr. From the oil that soon separated, the aqueous AcOH was decanted and the oil was crystallized at -20 °C. The solid was filtered and washed with $H_2O$ several times to give 65 g of crude product. Recrystallization from EtOAc (200 mL) gave 53.0 g (80%) of the title compound, mp 127 °C (lit.[24] mp 127-128 °C). $^1$H NMR ($CDCl_3$): $\delta$ 1.78 (s, 2 H), 2.10 (s, 3 H), 2.75 (dd, $J$ = 7.2 and 2.5 Hz, 1 H), 3.14 (s, 1 H), 3.33 (s, 1 H), 5.10 (d, $J$ = 7.1 Hz, 1 H), 6.22 (d of q, $J$ = 17.0 and 3.0 Hz, 2 H).

***exo*-3-Deuteriobicyclo[2.2.1]hept-5-en-2-ol and Tosylate 5.** Reduction of *exo*-2-acetoxy-*exo*-3-(bromomercurio)bicyclo[2.2.1]hept-5-ene (21.6 g 50 mmol) with sodium amalgam and NaOD in $D_2O$ according to the procedure of Jensen, Miller, Cristol, and Beckley[11] gave the crude alcohol, which was tosylated[12a] to give 4.9 g (37% for two steps) of 5, mp 43 °C (lit.[27] mp 49-51 °C). $^1$H NMR ($CDCl_3$) $\delta$ 1.47-1.70 (m, 2 H), 2.45 (s, 3 H), 2.81 (s, 1 H), 2.94 (s, 1 H), 4.49 (d, $J$ = 6.8 Hz, 1 H), 6.04 (d of q, $J$ = 36.5 and 3.2 Hz, 2 H), 7.51 (q, 4 H).

**Elimination Reaction Procedure and Hydrocarbon Analyses.** Solutions of potassium alkoxides in triglyme were prepared by reacting KH with the corresponding alcohol in triglyme under nitrogen.[7] For reactions of 0.125 M tosylate with 0.25 M potassium alkoxide and 0.25 M 18-crown-6 in triglyme at 60 °C, hydrocarbon products were removed from the reaction vessel with a slow nitrogen sweep[15] and were trapped and analyzed by GC and GC-MS as reported previously.[7] For reaction of 0.125 M 4 with 0.25 M potassium *tert*-butoxide in triglyme in the absence of 18-crown-6, the reaction was conducted at 80 °C.

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**Supplementary Material Available:** Proton NMR spectra of tosylates 4 and 5 (2 pages). Ordering information is given on any current masthead page.

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## Solvolytic Stereoselective Dehalogenation of *vic*-Dihalides[1]

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The debromination of *vic*-dibromides has been a subject of investigation with diverse reducing agents[2] in different solvents under a variety of reaction conditions. Both stereospecific and stereoselective dehalogenations have been reported with various reagents, but little is known about the role of solvents in these reactions except that methanol[3] is reported to bring about methanolysis of *meso*-stilbene dibromide (eq 1). *meso*- and *dl*-stilbene dibromides (1) have invariably been chosen as model substrates, and varying amounts of (*Z*)-stilbene (2) have been reported from *dl*-1, unlike *meso*-1 which gives (*E*)-2 stereospecifically and stereoselectively.

$$\underset{\text{Meso- or dl-}}{\text{RCHBr CHBr R}} \xrightarrow{\text{Reagent, Solvent}} \underset{\text{E- or Z-}}{\text{RCH=CHR}} \qquad (1)$$

This is the first report on the quantitative debromination of *meso*- and *dl*-stilbene dibromides (1) and *meso*- and *dl*-dimethyl-2,3-dibromosuccinates (3) by dry *N*,*N*-dimethylformamide (DMF) at 155-160 °C under $N_2$ atmosphere to give the (*E*)-alkene in the *absence* of any reagent whatsoever. The debrominations were complete in 90 min, and even at 100 °C we observed 19% debromination of *meso*-1 in 60 min with DMF. Thus, we believe that some of the previous reports on debromination with different reagents in DMF,[2f,4b,c,5] especially at elevated temperature,

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