Competitive C-O Cleavage, S-O Cleavage, and Electron Transfer in the $LiAlH_4$ Reduction of Hindered Disulfonates

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The reaction of heterogeneous slurries of $LiAlH_4$ with several alkanesulfonate substrates is reported. The reducible functional group(s) in each of the substrates is attached to the 1 and/or 4 position of a bicyclo[2.2.2]octyl skeleton. The ratio of S-O to C-O bond cleavage reflects a strong transannular electronic effect and is shown to vary with changes in solvent. A new reaction leading to carbon-carbon bond cleavage is also demonstrated, and the competition among these three pathways is shown to be related to both solvent composition and to the heterogeneity of the reaction. The powerful effect of even small amounts of HMPA in THF is delineated and a possible electron-transfer mechanism is presented to account for the carbon-carbon bond cleavage product.

In the course of other work on the elaboration of symmetrically substituted bicyclo[2.2.2]octyl derivatives[2] we observed a mixture of S-O and C-O bond cleavage in the $LiAlH_4$ reduction of ditosylate I (eq 1). While the expected result of such reactions is simple hydride displacement of tosylate, we were not surprised by this result since displacements at neopentyl centers are notoriously difficult.[3] We were, however, surprised that monotosylate II yielded virtually the same product distribution as was obtained from ditosylate I (eq 2). Our interest was further peaked by the total absence of any product of double C-O bond cleavage, VI, from the reduction of I and by the presence, albeit in small amounts, of a seemingly anomalous reduction product, V, in both reactions. These features, coupled with a literature report that the rate of reduction of simple tosylates by $LiAlH_4$ is strongly solvent dependent,[4a] prompted us to look at the solvent dependence of this S-O vs. C-O balance. We herein report the results of this study. It has led us to an understanding of the total absence of dimethyl compound (VI) as a reaction product and has suggested an intriguing third pathway in this reaction scheme in addition to the simple balance of S-O and C-O bond cleavage. It is this third pathway, a single electron transfer reaction from $LiAlH_4$, that may be responsible for the formation of the anomalous C-C bond cleavage product (V). Moreover, we have found that although this single electron transfer pathway is only a minor process, its importance varies in a reasonable way with solvent composition and also depends on the heterogeneity of the reducing medium.

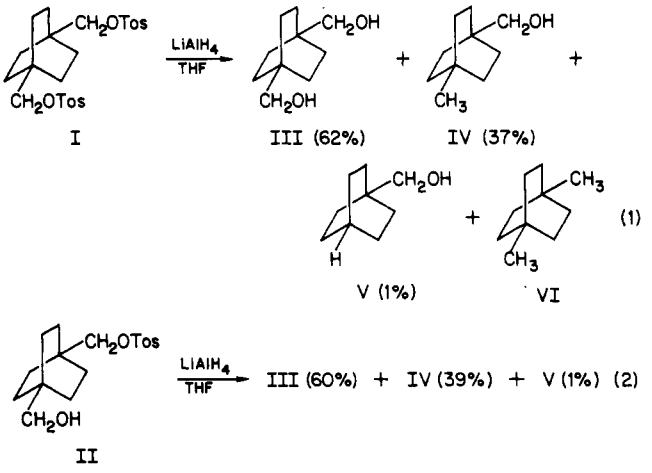


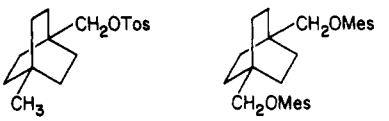
Table I. Product Ratios of $LiAlH_4$ Reductions of I, II, VII, and VIII

entry	substrate[a]	solvent	III, %	IV, %	V, %
1	I	Et_2O[b]	92	8	
2	I[e]	THF[b]	62	37	1
3	I[f]	THF[b]		81-95	5-19
4	I[e]	HMPA[c]		95	5
5	II	THF[b]	60	39	1
6	VII	Et_2O[b]		100	
7	VII	HMPA[c]		100	
8	VIII	THF[b]	100		
9	VIII[d]	HMPA[c]	17	82	1

[a] Concentration of substrate = 0.1-0.4 × 10^{-2} M. Concentration of $LiAlH_4$ = 21-43 × 10^{-2} M. [b] Reaction done at reflux. [c] Reaction temperature = 69 ± 3 °C. [d] Average of two experiments. [e] Average of three experiments. [f] Represents 22 separate experiments with HMPA added to the THF at a level of 0.15 mol % to 13.3 mol %.

Results

We have used four reduction substrates. In addition to compounds I and II, we have synthesized tosylate VII[3,5] and dimesylate VIII. Reaction products III and IV were



well known to us from previous work,[2] and an authentic sample of V[6] was prepared from bromobicyclo[2.2.2]octane by lithium-halogen exchange, carboxylation, and reduction.

The reductions of the sulfonates were done with excess $LiAlH_4$ in freshly distilled, dry solvents. After workup, products were analyzed by both gas chromatography and by NMR. The stability of products III, IV, and V to reduction by $LiAlH_4$ under all of our conditions was demonstrated. The hydrolytic stability of I, II, VII, and VIII to the conditions of our workup with aqueous base was also verified. The results of these reductions are summarized in Table I.

The changes in product distribution on going from ethereal solvents to HMPA prompted a study of reaction media using varying amounts of HMPA in THF. We used

(1) NIH-Career Development Awardee, 1983-1988.
(2) Kumar K.; Wang, S. S.; Sukenik, C. N. *J. Org. Chem.* **1984**, *49*, 665.
(3) For references to S_N2 reactions on substrates like I, II, and VII, see: Holtz, H. D.; Stock, L. M. *J. Am. Chem. Soc.* **1965**, *87*, 2404 and references therein.
(4) (a) Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550. (b) Kraus, W.; Chassin, C.; Chassin, R. *Tetrahedron* **1969**, *25*, 3681.
(5) Gervits, E. S.; Sokolova, I. M.; Petrov, A. A. *Neftekhimiya* **1977**, *17*, 179; *Chem. Abstr.* **1977**, *87*, 38976g.
(6) Grob, C. A.; Ohta, M.; Renk, E.; Weiss, A. *Helv. Chim. Acta* **1958**, *41*, 1191.

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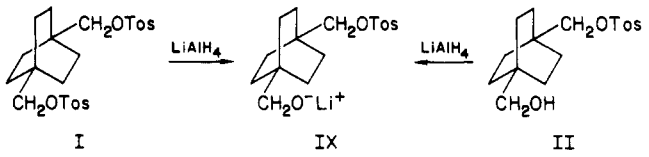
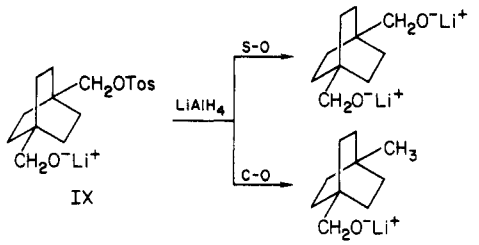
Scheme I



Scheme II



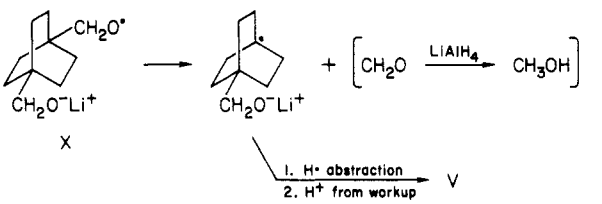
(Table I, entry 3) mixtures of HMPA in THF which were as low as 0.02 M HMPA (0.15 mol %). The amount of HMPA was varied (0.45, 0.76, 1.0, 1.1, 1.2, 1.5, 2.9, 6.0, and 13.3 mol %) up to pure HMPA (Table I, entry 4). These reactions yielded no diol III and variable amounts of alcohol V (5–20%). While the dominant production of IV was very reproducible, the percentage contribution of V was less predictable. What can be said with certainty is that no V is produced in Et_2O; a trace amount is seen in pure THF; and even a small amount of HMPA added to the THF leads to a significant increase in the formation of V.

Discussion

Given the complete absence of any dimethyl product VI, even from reductions where extensive C–O bond cleavage must be occurring in the formation of IV (Table I, entries 2, 3, 4, 5, and 8), and given the virtual identity of the products formed from I and II comparing entries 2 and 5 and comparing a number of mixed THF/HMPA experiments included in entry 3, we suggest that the preferred first step in the $LiAlH_4$ reduction of these hindered sulfonates is always S–O bond cleavage. Thus the initial reactions of I and II both lead to the formation of the same intermediate, IX (Scheme I). It is then the reduction of IX which is partitioned into various reaction pathways. Consistent with this, reduction of monotosylate VII yields only the product of S–O bond cleavage, alcohol IV (Table I, entries 6 and 7), regardless of solvent. Also consistent with this preference for S–O bond cleavage is the shift, in both THF and HMPA, toward more S–O cleavage in going from ditosylate I to the "less-hindered-at-sulfur" dimesylate, VIII (Table I, entries 2, 4, 8, and 9).

The further reduction of IX is now subject to a solvent-dependent partitioning which reflects the solvation (or lack thereof) of the Li^+ in various reaction media (Scheme II). In diethyl ether the solvation of the Li^+ is poor and therefore it is tightly ion paired to the alkoxide. This effectively dissipates any charge buildup in that end of the molecule and allows the formation of a second alkoxide at the other end of the molecule by the normally preferred S–O bond cleavage route. That is, in solvents like diethyl ether the behavior of IX is quite similar to that of I and VII. However, in going to solvents which better solvate the Li^+, like THF and ultimately HMPA, the extent of negative charge buildup at the alkoxide of IX is accentuated and the balance of reaction pathways for the remaining reducible functional group of IX is now shifted away from S–O bond cleavage toward C–O bond cleavage, thus avoiding dianion formation (Scheme II). Hence, the

Scheme III



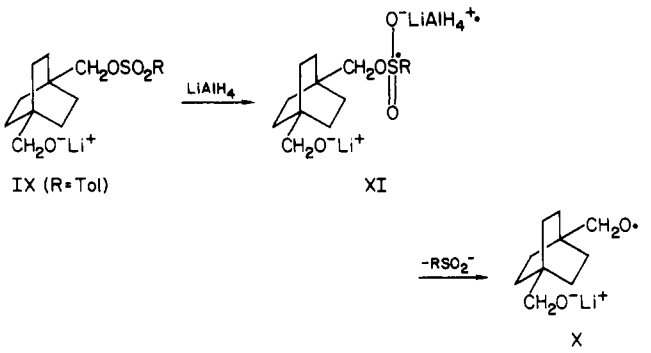
greatest amount of C–O bond cleavage is seen in HMPA, the solvent that best separates the ion pair of IX. The power of even small amounts of HMPA to "shut off" the second S–O bond cleavage is best seen by noting the effectiveness of even 0.15 mol % HMPA in THF (Table I, entry 3). Alternative explanations which focus on the complexation of Li^+ to the sulfonate leaving group[4] have been used to explain the shift from C–O to S–O cleavage in going from protic to aprotic media,[2,3] but they do not account for the dramatic product shift observed in the presence of HMPA in comparing the reduction of IX (by C–O cleavage) to the reduction of VII (by S–O cleavage). Nor do they account for the selective formation of the "cross-product" IV from I or VIII in HMPA.

Beyond these large solvent effects, we have found a parallel perturbation of the S–O/C–O bond cleavage ratio as a function of reaction heterogeneity. All substrates, intermediates, and products are completely soluble in any of our reaction media. While $LiAlH_4$ is quite soluble in all of our solvents,[7] solutions of $LiAlH_4$ from which all solids have been removed, either by centrifuging and decanting or by medium (10–15 μm) or coarse (20–25 μm) filters, evidence a significant reduction in the ratio of III/IV produced. Specifically, while heterogeneous reaction in Et_2O or THF (Table I, entries 1 and 2) gave approximately 90% and 60% III, respectively, the results from 10 separate filtration experiments show that the corresponding homogeneous solutions yield only 20–40% of this product. We note that the reproducibility among these filtration experiments is worse than that for the heterogeneous slurry experiments despite the fact that all resulting solutions were optically clear. We suspect that variable product ratios (±10%) resulted from poor control over the removal of particles in the 5–100-μm range. Nevertheless, these results still clearly suggest that, while ion-pairing in Et_2O and/or THF is important to the charge neutralization needed to allow S–O bond cleavage in IX, complexation of IX to the heterogeneous particles (metal) is also important for charge dissipation. Removal of this material does not completely eliminate the formation of III, as is the case with the addition of even small amounts of HMPA, but it still does have a dramatic effect on the formation of III.

At this point in our discussion, the combination of Schemes I and II effectively accounts for (1) the observed trend in the reductions of both I and VIII in going from diethyl ether to THF to HMPA; (2) the total lack of dimethyl reduction product even in HMPA; (3) the identical distribution of products observed from I and II; and (4) the shift in products from the near complete C–O bond cleavage of IX in HMPA to the complete S–O bond cleavage of VII under the same conditions. The observed electronic effect of one end of the molecule on the other is most striking. It is, however, consistent with a variety of studies on the effect that various substituents directly bonded to the 1-position have on the chemistry and

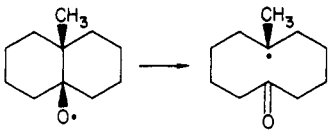
(7) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975; Chapter 9, pp 257–259.

Scheme IV



spectroscopy of functional groups at the 4-position of such ring systems.[8]

The remaining question to be addressed concerns the mechanism of formation of alcohol V. We suggest that a reasonable possibility involves the β-cleavage process shown in Scheme III. The work of Macdonald and O'Dell[9] shown in eq 3 provides direct precedent for this kind of



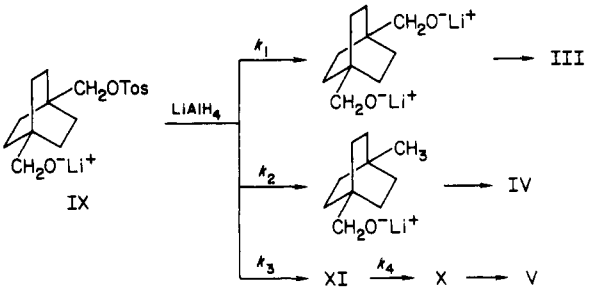
(3)

fragmentation. Their study demonstrated the facility with which this β-cleavage occurs when the incipient radical is at a tertiary center. Significantly, the stability of the bridgehead radical in the bicyclo[2.2.2]octyl skeleton has been clearly demonstrated by a number of workers.[10]

Having suggested that X is the direct precursor of V, we must consider the origin of X. The combination of recent demonstrations by Ashby and co-workers[11] of the ability of $LiAlH_4$ to transfer an electron to both alkyl iodides and bromides and the fact that tosylates have reduction potentials only slightly higher than those of the halides[12,13] suggests that the process shown in Scheme IV may be responsible for the formation of X. The S–O bond cleavage required in going from XI to X is well precedented for the decomposition of authentic, electrochemically generated tosylate radical anions.[13]

The remaining point that must be addressed in understanding the formation of V is why the alkoxy radical in X undergoes β-cleavage instead of further reduction to the alkoxide anion, the observed fate for the authentic alkoxy radical in a simple neopentyl system.[13] We see no diol product from I in THF:HMPA or in pure HMPA. However, we must note that the transfer of a second electron to X would result in the same dianion that S–O bond cleavage of IV would have generated. The problems with this dianion in a medium with extensive cation solvation have already been discussed. Alternatively stated, in simple reductions of monotosylates, the reduction of an alkyl tosylate to its radical anion is usually more difficult

Scheme V



than the transfer of the second electron to the alkoxy radical to make an alkoxide anion. However, in our case, the reduction of IX to XI is *easier* than the reduction of X to a dianion. Therefore, among the options available to X, the most favorable is cleavage to the relatively stable bridgehead radical.

We have also found that, just as reaction heterogeneity greatly enhanced the formation of III in Et_2O and THF, so too, this heterogeneity is essential for the formation of V in HMPA or in HMPA containing media. That is, filtered versions of all HMPA containing reactions (Table I, entries 3, 4, and 9) showed only traces ($\leq$1%) of V. Additional experiments have also shown that the $LiAlH_4$ residue itself is not effective in producing V in the absence of solubilized $LiAlH_4$. We therefore suggest that the electron transfer is in fact from the $LiAlH_4$ but is somehow mediated by the particles in the reaction. The role of this metallic residue is unclear but it may be comparable to that of an electrode: a catalyst for the electron transfer process.

In conclusion, we suggest the following balance to be in effect (Scheme V). In solvents like Et_2O and THF where ion-pairing is prevalent, $k_1 \gg k_2$, and k_3 is small since electron transfer in solvents with low dielectric constants is disfavored. In the presence of HMPA, there is little or no ion-pairing; k_1 is thus badly disfavored due to the resulting dialkoxide formation. Since k_3 also results in dianion (XI) formation, it too is not optimal. Despite the higher dielectric constant of HMPA, the potential needed to reduce IX to dianion XI is still relatively high. Therefore, the products in both pure HMPA and in THF with small amounts of added HMPA are products which reflect the competition between k_2, as a path that does not require any dianion formation, and the HMPA enhanced electron transfer[14] pathway, k_3, which can ultimately relieve its (less severe) dianion problem by dissociation to radical X (k_4). Once X is formed, it rapidly gives V via the irreversible steps shown in Scheme III.[15,16]

Experimental Section

Proton nuclear magnetic resonance spectra were obtained on a Varian A-60A or a Varian XL-200 spectrometer. They are reported as ^1H NMR (solvent), chemical shift in δ units, multiplicity, number of hydrogens. Carbon NMR were obtained on

(8) See, for example: Adcock, W.; Khor, T. C. *J. Org. Chem.* **1978**, *43*, 1272. Ritchie, C. D.; Megerle, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 1452. Wilcox, C. F.; Leung, C. *J. Am. Chem. Soc.* **1968**, *90*, 336. Sotheeswaran, S.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2042. Wilcox, C. F.; McIntyre, J. S. *J. Org. Chem.* **1965**, *30*, 777.

(9) Macdonald, T. L.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1501.

(10) (a) Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194. (b) Fort, R. C.; Hiti, J. *J. Org. Chem.* **1977**, *42*, 3968 and references therein.

(11) (a) Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1763. (b) **Note Added in Proof**: Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545.

(12) Weinberg, N. L. "Technique of Electroorganic Synthesis, Part II"; Wiley: 1975; Chapter VIII and Appendix.

(13) Yousefzadeh, P.; Mann, C. K. *J. Org. Chem.* **1968**, *33*, 2716.

(14) Precedent for significant enhancement of a single electron transfer process by the addition of 10% HMPA or Me_2SO to THF in seen in: Ashby, E. C.; Argyropoulos, J. N.; Meyer, G. R.; Goel, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 6788.

(15) Another possibility for electron transfer from $LiAlH_4$ in our system is in the initial S–O cleavage of I or in the clean S–O cleavage of VII. One could suggest that the reduction potentials of I and VII are lower than that of IX and that electron transfer is even more favorable. However, we have no evidence to differentiate this possibility from the alternative of hydride attack on sulfur.

(16) Other examples of recent interest in single electron transfer in nucleophillic processes can be found in: (a) Guthrie, R. D.; Nutter, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7478. (b) Russell, G. A.; Ros, F. *J. Am. Chem. Soc.* **1982**, *104*, 7349.

the XL-200 and are fully proton decoupled. They are reported as chemical shift values in δ units. Analytical gas chromatography was performed on both a Varian Model 2700 and a Perkin Elmer Model 3920B gas chromatograph and preparative work was done on a Varian Model 920 chromatograph. Mass spectra were recorded on an AE-1-Kratos Model MS-30 mass spectrometer. All melting points and boiling points are uncorrected.

The syntheses and spectral data for I, II, III, and IV have been reported.[2] All solvents were freshly distilled from an appropriate drying agent under a nitrogen atmosphere. $LiAlH_4$ was used as received from four different lots from two different vendors (Aldrich, Alfa) with no change in results. All other reagents were used as received unless otherwise indicated. While only dimesylate VIII is a heretofore unreported compound, our modified preparations of V and VII are also reported below.

Synthesis of Bicyclo[2.2.2]octane-1-methanol (V). Following a procedure modeled after that reported by Zimmerman et al.[17] for related materials, 1-bromobicyclo[2.2.2]octane[18] (200 mg, 1.06 mmol) was dissolved in Et_2O (25 mL) in a 50-mL flame-dried round-bottomed flask under N_2. While stirring at −78 °C, *tert*-butyl lithium (4 mL, 1.2 M in pentane) was added by syringe and the reaction was allowed to stir for 30 min. A slow stream of bone dry CO_2 (gas, Matheson) was bubbled through the reaction for 15 min at −78 °C, and the reaction was allowed to slowly come to room temperature and continue to stir for 5 h. The Et_2O was removed from this reaction product and it was redissolved in freshly distilled THF. This THF solution was added to a slurry of $LiAlH_4$ (large excess) in THF and was heated at reflux for 16 h. Workup with H_2O and aqueous NaOH yielded a sample of alcohol V which was shown by NMR and IR to be identical with that reported in the literature.[6,19] This sample of V was compared to V generated in the $LiAlH_4$ reductions of I and II by NMR and by coinjection on three different GC columns (15% SE-30 on Chrom W AW-DMCS, 100/120 mesh, 6 ft × $^1/_8$ in.; 15% OV-17 on Chrom W AW-DMCS, 100/120 mesh, 9 ft × $^1/_8$ in.; 15% Carbowax 20M on Chrom W AW-DMCS, 100/120 mesh, 9 ft × $^1/_8$ in.). GC–MS also confirmed the identity of V.

Synthesis of 4-Methylbicyclo[2.2.2]octane-1-methanol Toluenesulfonate (VII). A pure sample of alcohol IV (40 mg) was obtained by preparative gas chromotography (15% SE-30 on Chrom W AW-DMCS, 60/80 mesh, 6 ft × $^1/_4$ in.). It was treated with tosyl chloride (152 mg, 0.89 mmol) in 1.5 mL of dry pyridine. This mixture was stored under a $CaCl_2$ drying tube in a refrigerator for three days. It was poured into a mixture of concentrated HCl and ice and extracted into Et_2O. The combined organic layers were washed with H_2O and saturated aqueous NaCl, dried over Na_2SO_4, and concentrated under vacuum. The crude product (58 mg) was recrystalized from hexane: mp 121–122 °C (lit.[3] mp 127.5–129 °C); ^{13}C NMR ($CDCl_3$) 144.5, 132.9, 129.7, 127.9, 78.2, 32.5, 31.9, 28.2, 28.0 (two unresolved signals), 21.6.

Synthesis of Bicyclo[2.2.2]octane-1,4-dimethanol Bis(methanesulfonate) (VIII). Diol III (100 mg, 0.59 mmol) was treated with methanesulfonyl chloride (0.2 mL, 296 mg, 2.59 mmol) in dry pyridine (1.4 mL). After two days in the refrigerator under a $CaCl_2$ drying tube, the product, VIII, (185.9 mg, 97%) was isolated as described for VII: mp 141–142 °C; ^1H NMR ($CDCl_3$) 3.89 (s, 4 H), 3.0 (s, 6 H), 1.54 (s, 12 H); ^{13}C NMR ($CDCl_3$) 76.8, 37.2, 32.4, 27.4; MS (70 eV), calcd 326.0858 no parent detected; ($M - CH_3SO_3$) calcd 231.1056, obsd 231.1093. Anal. Calcd for $C_{12}H_{22}O_6S_2$: C, 44.16; H, 6.80. Found: C, 43.77; H, 6.86.

General Procedure for Heterogeneous $LiAlH_4$ Reductions and Their Analyses. A three-necked, 100 mL, 14/20-jointed flask was flame-dried under N_2 and fitted with a magnetic stir bar and a condensor and charged with 20 mL of the indicated solvent and 400–500 mg of $LiAlH_4$ (10.5 to 12.5 mmol). A sample, typically 30–50 mg (0.07–0.2 mmol), of the substrate to be reduced was dissolved in 10 mL of the indicated solvent and added to the $LiAlH_4$ slurry at room temperature. The reactions were heated (Et_2O and THF to their respective boiling points and HMPA at 69 ± 3 °C) for 17–48 h. There was no variation in product ratio as a function of reaction time. Workup involved the addition of 15 mL of H_2O, 15 mL of 15% NaOH, and 45 mL of H_2O, followed by partitioning between H_2O and Et_2O. The Et_2O extracts were dried and concentrated under vacuum before analysis. In those reactions containing HMPA, the product was redissolved in CH_2Cl_2 and washed extensively with H_2O to remove residual HMPA. This water wash along with the initial aqueous workup obviated any possibility of identifying the CH_3OH product suggested in Scheme III. Analysis by GC (15% SE-30 on Chrom W AW-DMCS, 100/120 mesh, 6 ft × $^1/_8$ in., 140–180 °C) gave an elution order of V (2.8 min), IV (3.1 min), and III (10.2 min). GC traces were integrated by "cut and weigh" of at least two copies. Product mixtures were also analyzed by integration of the ^1H NMR spectrum on the XL-200. The agreement between GC and NMR analysis was always better than ±5%, thus no internal standards were used. Material recovery was always better than 80%. Almost all reactions were done at least twice and subjected to at least two analyses for each reaction. Results in Table I are average product ratios. The stability of products III, IV, and V to the reduction conditions was demonstrated.

General Procedure for Homogeneous $LiAlH_4$ Reductions, Their Analyses, and Their Control Experiments. A flame-dried 100-mL, 14/20-jointed Schlenk flask with either a 10–15 or 20–25 μm fritted filter was kept under N_2 and was charged with 40 mL of the indicated solvent and 1 g of $LiAlH_4$ (26.4 mmol). The mixture was stirred for 4 h. The crude suspension of $LiAlH_4$ was transferred into the filter and a small positive pressure of N_2 was applied to facilitate the filtration. The filtrate is a homogeneous solution of $LiAlH_4$. The substrate to be reduced (30–50 mg) was dissolved in 10 mL of the indicated solvent and added to the homogeneous $LiAlH_4$ solution at room temperature. The reactions were heated (Et_2O and THF to their respective reflux and HMPA at 69 ± 3 °C) for 17–48 h. There was no variation in product ratio with reaction time. Workup and analysis were the same as above for the unfiltered reactions.

Resuspension of the $LiAlH_4$ residue alone in fresh solvent gave no detectable reduction products. Reconstitution of the original $LiAlH_4$ slurry by adding the residue from the funnel to solubilized $LiAlH_4$ (all under N_2) gave results identical (±2%) with the heterogeneous $LiAlH_4$ slurry experiments.

Acknowledgment. Stimulating discussions with Prof. R. Fort, Prof. E. Yeager, and Prof. E. Ashby are gratefully acknowledged, as is a sample of bromobicyclo[2.2.2]octane provided by Prof. Fort. Financial support for this work was provided by the NIH (GM-27355).

Registry No. I, 88412-20-8; II, 898-81-7; III, 826-45-9; IV, 28305-83-1; V, 2574-42-7; VI, 56579-29-4; VII, 2509-44-6; VIII, 94499-51-1; IX, 94499-52-2; $LiAlH_4$, 16853-85-3; CO_2, 124-38-9; 1-bromobicyclo[2.2.2]octane, 7697-09-8; 1-lithiobicyclo[2,2,2]octane, 931-99-7; lithium bicyclo[2.2.2]octane-1-carboxylate, 94499-55-5.

(17) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933.

(18) A sample of this compound was graciously provided by Prof. R. C. Fort.

(19) Barfield, M.; Brown, S. E.; Canada, E. D.; Ledford, N. D.; Marshall, J. L.; Walter, S. R.; Yakali, E. *J. Am. Chem. Soc.* **1980**, *102*, 3355.