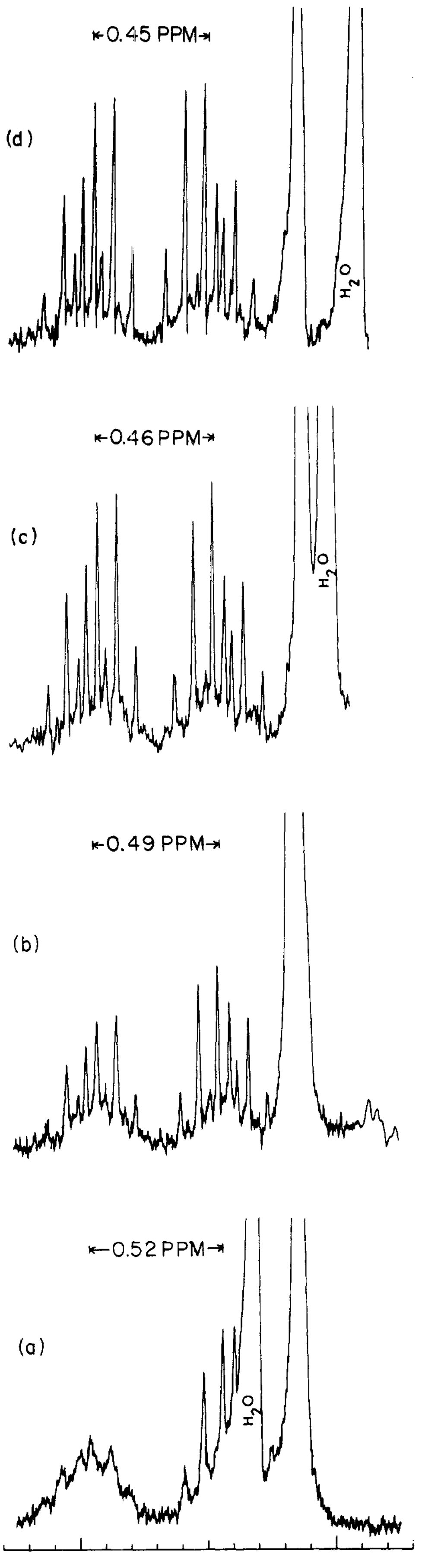

Figure 2. ^1H NMR spectra (100 MHz) of ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (**3**) in Me_2SO-d_6 at various temperatures: (a) 32 °C, (b) 60 °C, (c) 80 °C, (d) 100 °C.

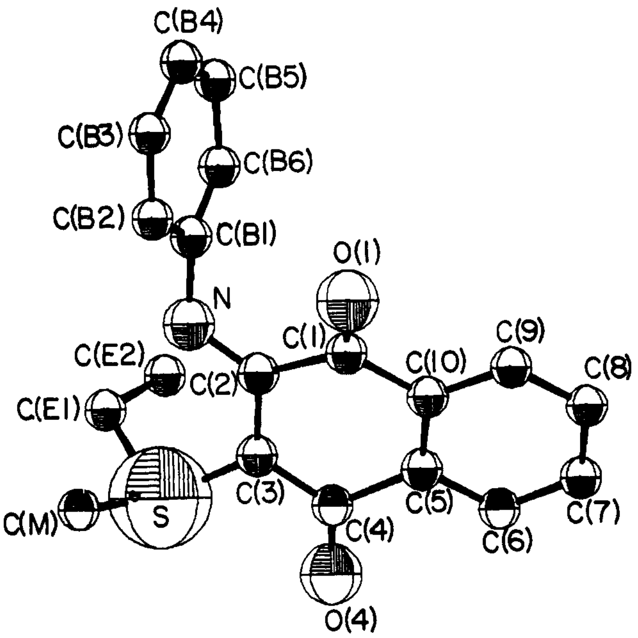

Figure 3. A perspective representation of the structure of ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (**3**).

31914-13-3; **6**, 31914-17-7; **7**, 57893-97-7; triethyloxonium tetrafluoroborate, 368-39-8.

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Lithium Triethylborohydride Reduction of Alkyl Methanesulfonate Esters[1,2]

Richard W. Holder* and Michael G. Matturro[3]

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

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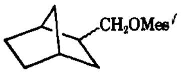
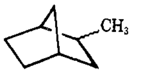
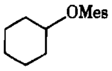
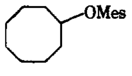
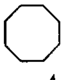
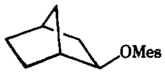
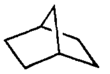
In the course of preparing some hydrocarbons for another study we required an efficient procedure for the transformation $>C{=}O \rightarrow >CH_2$ for cases in which the carbonyl group is in a sterically hindered neopentyl environment. A number of techniques are available for this reduction,[4] but after trying several of these with uncertain or unsatisfactory results, we decided to test lithium triethylborohydride ($LiEt_3BH$, or Super Hydride) on alkyl methanesulfonate esters (mesylates). This reagent is a powerful hydride donor toward alkyl halides,[9] and we reasoned that it might behave in an analogous fashion toward alkyl mesylates. Further, these esters are usually stable, easily handled compounds, and are ordinarily acces-

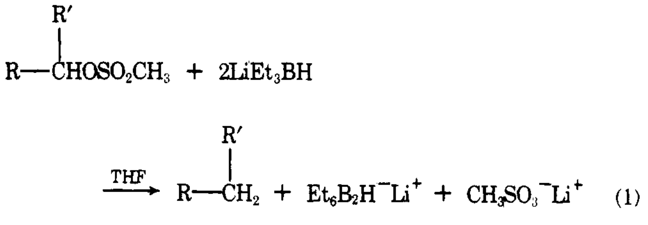
Table I. Reduction of Alkyl Methanesulfonates (ROMes) with Lithium Triethylborohydride[a]

Registry no.	Compd	Time, h[b]	Temp, °C	Product[c]	Yield, %[d]
16156-51-7	n-$C_7H_{15}OMes$	0.5	25	n-Heptane	90
16427-42-2	$(CH_3)_3C{-}CH_2OMes$	3.0	60	Neopentane	69[e]
62078-83-5	$CH_3(CH_2)_4\underset{CH_3}{\underset{\mid}{C}}HOMes$	0.5	25	n-Heptane	92
62078-84-6		4.0	60		96[f]
16156-56-2		4.0	60		68
					12
62078-85-7		24.0	25		93[g]
28627-77-2		4.0	75[h]		65
62107-93-1	$(PhCH_2CH_2)_2CHOMes$	6.0	25	$(PhCH_2CH_2)_2CH_2$	99

[a] The reactions, except where noted, were conducted in THF at either room temperature (25 °C) or reflux (60 °C) using a 2.1-fold excess of $LiEt_3BH$. [b] Not necessarily minimum times. [c] Except where noted no alkenes or alcohols were detected. All products are known compounds and in each case isolated samples had spectral properties corresponding to literature descriptions. [d] Except where noted these are VPC yields, utilizing an internal standard and corrected for detector response. [e] Yield calculated by measuring gas volume. [f] Mixture of endo and exo isomers. [g] Trace of cyclooctene noted. [h] Reaction run in benzene solution.

sible by two high-yield steps (>C=O → >CHOH → >CHO-SO_2CH_3). Finally, the desired reductive displacement does occur with the less powerful lithium aluminum hydride,[4,10] albeit in poor yields for sterically hindered cases.[11]

Treatment of the mesylates of the alcohols recorded in Table I with 2.1 equiv of $LiEt_3BH$ as a 1 M solution in tetrahydrofuran (THF) rapidly produced the corresponding alkanes in high yields (eq 1). An extra 1 equiv of the hydride

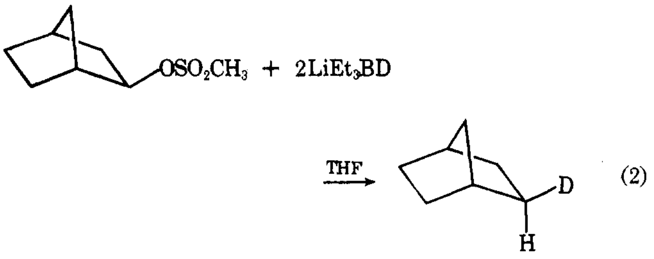


$$R{-}\overset{R'}{\overset{\mid}{C}}HOSO_2CH_3 + 2LiEt_3BH \xrightarrow{THF} R{-}\overset{R'}{\overset{\mid}{C}}H_2 + Et_6B_2H^-Li^+ + CH_3SO_3^-Li^+ \quad (1)$$

reagent proved necessary, evidently because initially formed triethylboron itself reacts readily to form a relatively unreactive complex of stoichiometry $Et_6B_2H^-$.[12]

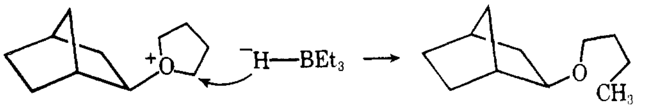
Rough kinetic studies in several cases established the enhanced reactivity of $LiEt_3BH$ relative to $LiAlH_4$. For example, for n-heptyl mesylate after 0.5 h at 25 °C the reaction was 90% complete with $LiEt_3BH$ but only 59% complete with $LiAlH_4$.

Although the attack of $LiEt_3BH$ on alkyl bromides was demonstrated to occur with configurational inversion, implicating an S_N2 mechanism for the displacement,[9] treatment of the mesylate of *exo*-2-norborneol with $LiEt_3BD$ (eq 2),



followed by NMR analysis of the VPC-purified norbornane,[16] showed essentially complete retention of configuration (95 ± 5% exo-2-D). Presumably the enhanced leaving group ability of the methanesulfonate anion relative to bromide[17] results in a transformation of the mechanism to S_N1 for this easily ionizable substrate.[18] A further indication of a possible S_N1 component in secondary systems is that the mesylates of both 1-heptanol and 2-heptanol react at comparable rates (Table I).

The intervention of the 2-norbornyl carbonium ion in eq 2 is also supported by the formation of 35% *exo*-2-n-butoxynorbornane when the reaction is run in THF. This unusual product could come from attack on a THF molecule involved in solvation, as shown below:



Lithium triethylborohydride cleaves epoxides easily,[19] and lithium tri-*tert*-butoxyaluminohydride in the presence of triethylboron rapidly opens the THF ring at 25 °C.[20] No analogous ethers were formed in any of our other experiments, however, and no formation of 1-butanol could be detected.

In any case, when the reaction was run in about 95:5 benzene–THF[21] to minimize ether formation the yield of norbornane was raised from 21% to 65%. Carrying out the experiment of eq 2 in benzene resulted in isolation of norbornane that contained 60 ± 5% exo-2-D. Thus the S_N1 component is less important in the less ionizing medium.

After submission of our preliminary results we became aware of the independently conceived and executed work of Krishnamurthy and Brown who have developed the reduction of alkyl p-toluenesulfonate esters (tosylates) with $LiEt_3BH$.[23,24] Our work presented in this note therefore corroborates and extends their recently published results. Although our preoccupation with the development of the reaction has kept us from applying it to the original synthetic targets, the combination of our results with those of Krishnamurthy and Brown make it clear that $LiEt_3BH$ reduction of both the mesylates and tosylates of a wide variety of aliphatic alcohols is a procedure of sufficient utility and generality to be added to those previously available for the reduction of carbonyl groups to methylene groups.

Experimental Section

Materials. $LiEt_3BH$ and $LiEt_3BD$ were purchased as 1 M solutions in THF from Aldrich Chemical Co. Reactant alcohols were either commercially available or prepared by unexceptional procedures. The mesylates were made by a standard literature method;[25] in all cases IR and NMR established the absence of reactant alcohol after the esterification.

General Procedure for Reductions. To a dry, N_2-flushed, round-bottom flask equipped with reflux condenser, magnetic stir bar, and rubber stopple was introduced by syringe x mmol of mesylate and x mL of dry THF. With stirring, $2.1x$ mL of a 1 M $LiEt_3BH$ solution in THF was added in one portion by syringe. The resulting reaction was stirred under N_2 for the time period and at the temperature recorded in Table I for each mesylate. A useful signal of reaction progress was found to be formation of lithium methanesulfonate, which precipitated.

After the reduction period, the vessel was cooled in an ice bath and excess hydride quenched by dropwise addition of water. The organoboranes were oxidized by adding $0.7x$ mL of 3 N NaOH, followed by the slow, dropwise addition of $0.7x$ mL of 30% H_2O_2. The ice bath was removed and the reaction mixture refluxed for 1 h. VPC analyses were measured from the THF layer of the cooled product mixture.[26]

Isolation of products was accomplished by pouring the reaction mixture into $10x$ mL of water, extraction with pentane, washing to remove dissolved THF, drying ($MgSO_4$), and concentration to the crude product by flash distillation. Final purification for structural studies was accomplished using standard preparative VPC techniques.

Acknowledgment. We are grateful to Dr. R. E. Williams and Professors H. C. Brown, R. O. Hutchins, and R. T. Paine for helpful suggestions.

Registry No.—Heptane, 142-82-5; neopentane, 463-82-1; *exo*-2-methylnorbornane, 872-78-6; *endo*-2-methylnorbornane, 765-90-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; cyclooctane, 292-64-8; norbornane, 279-23-2; 1,5-diphenylpentane, 1718-50-9.

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(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of New Mexico Research Allocations Committee for the support of this research.

(3) American Chemical Society Petroleum Research Fund Undergraduate Scholar, 1975–1976.

(4) Conventional procedures are compiled in (a) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, New York, N.Y., 1972; (b) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971. More recently developed methods include use of sodium cyanoborohydride or tetrabutylammonium cyanoborohydride,[5] reduction of the tetramethylphosphorodiamidate derivative of the corresponding alcohol,[6] treatment of mesylates or halides with copper hydride reagents,[7] and formation of the tosylhydrazone followed by reduction with catecholborane or other active hydrides.[8]

(5) (a) R. D. Hutchins, B. E. Maryanoff, and C. A. Milewski, *Chem. Commun.*, 1097 (1971); *Org. Synth.*, **53**, 107 (1973); (b) R. O. Hutchins and D. Kandasamy, *J. Am. Chem. Soc.*, **95**, 6131 (1973).

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(12) This phenomenon has been observed before,[13–15] but apparently has not been discussed explicitly in the open literature.

(13) A. Khuri, Ph.D. Dissertation, Purdue University, 1960.

(14) R. E. Williams, K. M. Harmon, and J. R. Spielman, Office of Naval Research Report AD-603782, 1964.

(15) C. A. Brown, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug. 30–Sept. 3, 1976, No. ORGN-153.

(16) A. P. Marchand and N. W. Marchand, *Tetrahedron Lett.*, 1365 (1971).

(17) Expected to be closely analogous to the *p*-toluenesulfonate leaving group, which departs about 5×10^3 more easily than bromide: R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189 (1971).

(18) In this case $LiEt_3BH$ evidently acts as a carbonium ion trap in much the same way as does BH_4^-: H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).

(19) S. Krishnamurthy, R. M. Shubert, and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 8486 (1973).

(20) H. C. Brown, S. Krishnamurthy, and R. A. Coleman, *J. Am. Chem. Soc.*, **94**, 1750 (1972).

(21) The $LiEt_3BH$ was transferred to benzene by pumping off the THF in the standard manner,[22] but it proved impossible to remove the last traces of THF.

(22) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975, p 229 ff.

(23) S. Krishnamurthy and H. C. Brown, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 30–Sept 3, 1976, No. ORGN-172.

(24) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **41**, 3064 (1976).

(25) Analogous to a procedure suggested by P. v. R. Schleyer for tosylate preparation: L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 1180.

(26) Control experiments established the absence of product alkane and internal standard in the lower layer. Internal standards were either introduced at this point or before reduction; no difference in calculated yields was noted.

The Basicity of Enones. Substituent Effects and the Correlation of Protonation with H_A

J. L. Jensen* and Anita T. Thibeault

Department of Chemistry, California State University, Long Beach, California 90840

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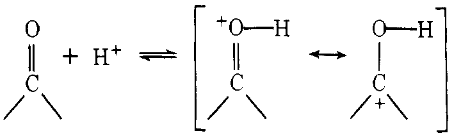
The basicity of carbonyl compounds is of considerable interest since most acid-catalyzed reactions proceed via a preequilibrium protonation of the carbonyl group, followed by some sort of nucleophilic attack.

Scheme I



Arnett has recently reported thermodynamic pK_as for 52 protonated carbonyl compounds, based on heats of ionization in fluorosulfonic acid.[1] Of particular interest to a kinetic study we carried out[2] are the basicities of α,β-unsaturated ketones. These compounds as a class are much more basic than other ketones by 3–5 pK_a units.[1] There have been several recent reports of basicity studies on a series of alicyclic α,β-unsaturated ketones.[3,4] However, the only reported pK_a value for a protonated noncyclic α,β-unsaturated ketone is 2.4 for 4-methyl-3-penten-2-one.[1,5] We wish to report pK_as for several α,β-unsaturated ketones demonstrating a sizable substituent effect on pK_a.

Acidity Dependence. Table I presents pK_a values measured in aqueous $HClO_4$ and H_2SO_4 solutions. Plots of log $[BH^+]/[B]$ vs. $-H_A$ gave straight lines of slope 1.0 for 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one; thus protonation of acyclic α,β-unsaturated ketones follows the acidity function based on amide protonation (H_A)[9] at least through 75% (12 M) H_2SO_4 and 65% (10.5 M) $HClO_4$. This result is consistent with previous studies on cyclopentenones and cyclohexenones.[4]

It is striking that protonation of 3-alkenones follows H_A so closely throughout such a broad range of acidity. This requires that the f_B/f_{BH^+} ratio for the protonation of amides and