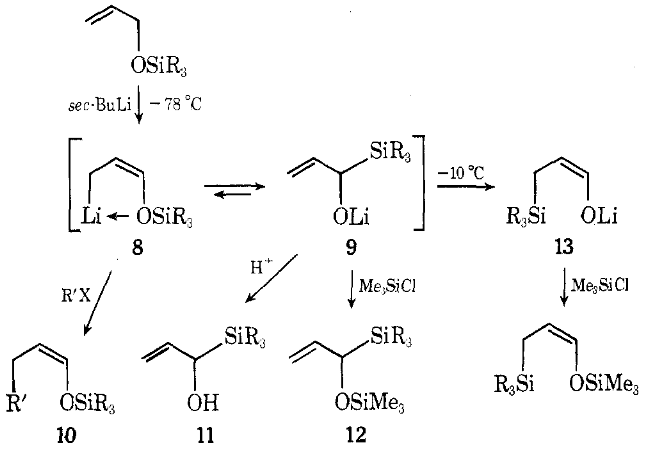
for equatorial attack on **5** and **7** are very similar, a severe 1,3-diaxial methyl–trimethylsilyl interaction would be expected to destabilize the transition state for axial addition to isophorone.

Unlike most other conjugate additions, the 1,4 addition of trimethylsilyllithium to enones appears to be a kinetic process since 1,2 adducts like **9** are stable to the reaction conditions reported above (−78 °C). As we reported previously, allyloxy carbanions (**8**) derived from allyl silyl ethers are in rapid equilibrium with the corresponding silyl alkoxide **9**.[4] Such species may be alkylated on carbon to give **10** or they may be protonated or silylated on oxygen to give **11** or **12**. If, however, the allyloxy carbanion reagent is allowed to warm to approximately −10 °C, it undergoes irreversible rearrangement to the silyl enolate **13**.



R = Me, Et

The marked preference for a kinetic 1,4 addition with axial attack is most compatible with an electron-transfer mechanism. Other reagents (R_2CuLi and Li/NH_3) believed to react with enones by electron-transfer processes show similar regiochemistry and stereochemistry.[16,17] Further support for this mechanism is given by a number of reports which indicate that silyl anions are potent one-electron reducing agents.[18] For example, trimethylsilylsodium has been reported to reduce benzophenone and naphthalene to the corresponding radical anions and to effect reductive coupling of alkyl halides.

The following procedure for synthesis of **4** illustrates the preparation and use of the trimethylsilyllithium reagent. A solution of 0.50 ml (2.5 mmol) hexamethyldisilane[9] in 2 ml of anhydrous HMPA was cooled to 0 °C under nitrogen. Ethereal methyllithium (2 mmol) was added via syringe and the resulting deep red solution was stirred for 15 min to complete the preparation of trimethylsilyllithium. Anhydrous THF (10 ml) was added and the solution was immediately chilled to −78 °C. A solution of 144 mg (1.5 mmol) of 2-cyclohexenone in 1 ml of THF was then added dropwise. After stirring an additional 5 min, 0.5 ml of methyl iodide was injected and the mixture was allowed to warm slowly to 0 °C. The reaction mixture was poured into 50 ml of pentane and thoroughly washed with water (2 × 25 ml) to remove HMPA. Drying ($MgSO_4$) and solvent removal gave a colorless oil (308 mg). Kugelrohr distillation (1 mm, oven 80 °C) gave 268 mg (97%) of *trans*-3-trimethylsilyl-2-methylcyclohexanone (**4**): ir (neat) 1710, 1250, 853, 838 cm^{-1}; NMR δ^{CDCl_3} 1.10–2.44 (8 H, m), 1.03 (3 H, d, J = 6.5 Hz), 0.6 (9 H, s); MS (70 eV) 184 (15) (parent), 179 (53), 156 (9), 155 (12), 141 (19), 75 (75), 74 (22), 73 (100), 67 (20), 59 (45), 58 (32), 53 (25), 45 (90), 44 (20), 43 (78), 42 (22), 42 (62).

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Facile Reduction of Alkyl Tosylates with Lithium Triethylborohydride. An Advantageous Procedure for Deoxygenation of Cyclic and Acyclic Alcohols

Summary: Lithium triethylborohydride rapidly reduces *p*-toluenesulfonate esters of both cyclic and acyclic alcohols to the corresponding alkanes in excellent yields and is applicable even to tosylates derived from hindered alcohols.

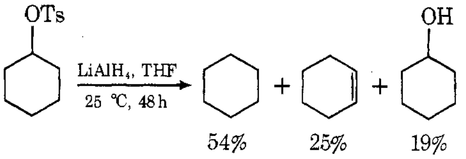
Sir: Deoxygenation of alcohols to the corresponding alkanes, a frequently encountered transformation in synthetic organic chemistry, is usually achieved by the reduction of *p*-toluenesulfonate ester of the alcohol with lithium aluminum hydride.[1] Although this procedure works satisfactorily with relatively unhindered primary alcohols, the results are less favorable for the more hindered alcohols as well as for certain cycloalkanols. In such cases, the yield of the desired alkane

Table I. Reduction of Representative Alkyl Tosylates with Lithium Triethylborohydride in Tetrahydrofuran (THF)[a]

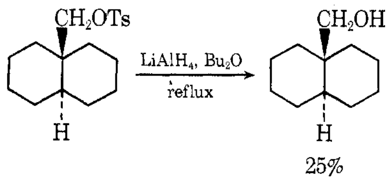
Compound	Time, hr	Products[b, c]	%
n-Octyl tosylate	0.25	*n*-Octane	96
2-Methyl-1-pentyl tosylate	0.25	2-Methylpentane	98
2-Octyl tosylate	0.25	*n*-Octane	99
Cyclopentyl tosylate	0.25	Cyclopentane	100
Cyclohexyl tosylate	12.0	Cyclohexane	80
		Cyclohexene	20
Cycloheptyl tosylate	0.5	Cycloheptane	100
Cyclooctyl tosylate[d]	0.5	Cyclooctane	97.5
		Cyclooctene	2.5
2,2-Dimethyl-1-hexyl tosylate[e]	3.0	2,2-Dimethylhexane	81
		2,2-Dimethyl-1-hexanol	9

[a] In all cases solutions were 0.25 M in tosylate and 0.5 M in $LiEt_3BH$ at 25 °C. [b] The yields reported were determined by GLC using a suitable internal standard and authentic synthetic mixtures. [c] Except where indicated, no olefins or alcohols were detected. [d] Isolated in 81% yield. [e] At 65 °C.

is often reduced as a result of two significant side reactions: (a) elimination to form olefins, and (b) attack at the sulfur-oxygen bond to form the parent alcohol (eq 1 and 2).[2]



(1)



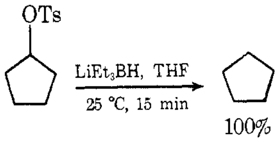
(2)

Recently, lithium triethylborohydride (Super Hydride) has emerged as an exceptionally powerful nucleophilic reducing agent capable of reducing hindered alkyl halides, epoxides, and quaternary ammonium salts rapidly and cleanly to the desired products.[3-6] It appeared possible that lithium triethylborohydride might overcome these difficulties. Accordingly, we tested the effectiveness of this reagent for the reduction of representative alkyl tosylates to the corresponding alkanes[7] (Table I).

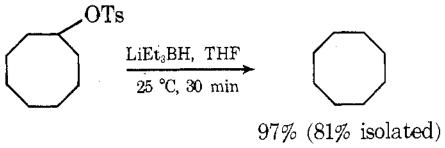
Tosylates of primary alcohols such as *n*-octyl tosylate and 2-methyl-1-pentyl tosylate are rapidly converted into *n*-octane and 2-methylpentane in yields of 96 and 98%, respectively (eq 3).

$$CH_3(CH_2)_6CH_2OTs \xrightarrow[25\ ^\circ C,\ 15\ min]{LiEt_3BH,\ THF} \underset{96\%}{CH_3(CH_2)_6CH_3} \quad (3)$$

The secondary tosylate, 2-octyl tosylate, is also quantitatively reduced to *n*-octane in 15 min. Even more important is the reduction of cycloalkyl tosylates. Thus, cyclopentyl, cycloheptyl, and cyclooctyl tosylates are rapidly reduced to their corresponding alkanes in excellent yields (eq 4 and 5).



(4)



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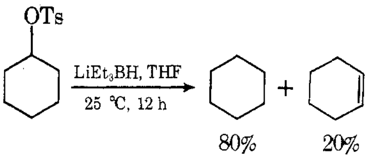
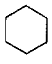
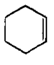
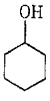
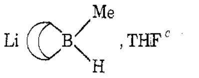


(6)

The reduction of cyclohexyl tosylate is comparatively sluggish requiring 12 h for completion, producing 80% cyclohexane, 20% cyclohexene, and only traces of cyclohexanol (eq 6). This represents a major improvement over the results realizable with lithium aluminum hydride.[2a] Further, the cyclohexyl moiety is prevalent in many naturally occurring molecules of biological interest, such as steroids, terpenes, etc. Consequently, we undertook to examine the reaction of cyclohexyl tosylate, the model compound, with various hydridic reducing agents; other parameters, such as the influence of solvent, metal ion, steric bulk of the reagent, etc. were also briefly examined (Table II). The conventional reagent, lithium aluminum hydride, yields a mixture of cyclohexane, cyclohexene, and cyclohexanol. The alkoxy derivatives of lithium aluminum hydride and aluminum hydride are essentially ineffective for this reduction. Further, the tosylate is essentially inert to borane–THF, disiamylborane, thexylborane, 9-BBN, and lithium borohydride. It is quite evident that the less hindered trialkylborohydrides, such as lithium *B*-methyl-9-borabicyclo[3.3.1]nonyl hydride and lithium triethylborohydride, are preferred over the more hindered reagents. The metal ion does not seem to alter the course of the reaction significantly. However, solvent does exert a major role; THF is preferred over ether and benzene. Lowering the temperature increases the substitution/elimination ratio only slightly. Sulfur-oxygen bond cleavage is unimportant in all of the reductions examined utilizing trialkylborohydride. In short, the results of the comparative study clearly indicates the advantages of lithium *B*-methyl-9-borabicyclo[3.3.1]nonyl hydride and lithium triethylborohydride over the conventional re-

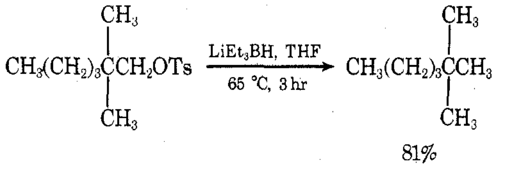
Table II. Reduction of Cyclohexyl Tosylate with Various Hydride Reducing Agents

Reagent	Temp, °C	Product composition,[a] %		
				
$LiAlH_4$, THF[b]	25	54	25	19.5
$LiAlH_4$, Et_2O[c]	25	38	55	7
$LiAlH(O\text{-}tert\text{-}Bu)_3$, THF[d]	0	0	0	0
$LiAlH(OCH_3)_3$, THF[e]	25	0	0	0
AlH_3, THF[f]	0	0	0	0
BH_3–THF[g]	0	0	0	0
9-BBN, THF[c]	25	0	0	0
$LiBH_4$, THF[c]	25	Trace	0	Trace
 , THF[c]	25	84	16	0
	0	88	12	0
$LiEt_3BH$, THF[c]	25	80	20	0
	0	84	16	0
$LiEt_3BH$, DG[c]	25	79	21	0
$NaEt_3BH$, THF[c]	25	83	17	0
$NaEt_3BH$, C_6H_6[c]	25	18	82	0
Li-*sec*-Bu_3BH, THF[c]	25	52	48	0

[a] Analysis by GLC. Normalized yields. [b] Reference 2a. [c] Present study. [d] H. C. Brown and P. M. Weissman, *Israel J. Chem.*, 1, 430 (1963). [e] H. C. Brown and P. M. Weissman, *J. Am. Chem. Soc.*, 87, 5614 (1965). [f] H. C. Brown and N. M. Yoon, *ibid.*, 88, 1464 (1966). [g] H. C. Brown, P. Heim, and N. M. Yoon, *ibid.*, 92, 1637 (1970).

agents for the reduction of the tosylates of related structures.

Finally, the hindered tosylate, 2,2-dimethyl-1-hexyl tosylate, is reduced at a rate even slower than that exhibited by cyclohexyl tosylate. However, the reaction is reasonably rapid at 65 °C (refluxing THF), providing a satisfactory yield of the desired product, 2,2-dimethylhexane, free of isomeric alkanes (eq 7).



$$\mathrm{CH_3(CH_2)_3\overset{CH_3}{\underset{CH_3}{C}}CH_2OTs} \xrightarrow[65\ ^\circ\mathrm{C},\ 3\ \mathrm{hr}]{\mathrm{LiEt_3BH,\ THF}} \underset{81\%}{\mathrm{CH_3(CH_2)_3\overset{CH_3}{\underset{CH_3}{C}}CH_3}} \qquad (7)$$

The following procedure for the reduction of cyclooctyl tosylate is representative. An oven-dried, 300-ml flask equipped with a side arm fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled to room temperature under a dry stream of nitrogen. THF (20 ml) was introduced, followed by 7.1 g (25 mmol) of cyclooctyl tosylate. The mixture was cooled to 0 °C (ice bath). To this stirred solution, lithium triethylborohydride,[8] 33.3 ml (50 mmol), of a 1.5 *M* solution in THF was added and the ice bath removed. The mixture was stirred for 2 h (~25 °C). Excess hydride was decomposed with water. The organoborane was oxidized with 20 ml of 3 N NaOH and 20 ml of 30% H_2O_2. Then the THF layer was separated. The aqueous layer was extracted with 2 × 20-ml portions of *n*-pentane. The combined organic extracts were washed with 4 × 15-ml portions of water to remove ethanol produced in the oxidation. Organic extract was dried ($MgSO_4$) and the volatile solvents were removed by distillation. Distillation of the residue yields 2.27 g (81%) of cyclooctane as colorless liquid, bp 142–146 °C, $n^{20}\mathrm{D}$ 1.4630. GLC analysis indicated 97% cyclooctane and 3% cyclooctene.

In conclusion, it is evident that lithium triethylborohydride possesses certain major advantages over the conventional reagents for the deoxygenation of certain cycloalkyl and hindered alcohols, with attack at the sulfur–oxygen bond and the elimination curtailed considerably.

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