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RAPID REDUCTION OF ALKYL TOSYLATES WITH LITHIUM TRIETHYLBOROHYDRIDE. A CONVENIENT AND ADVANTAGEOUS PROCEDURE FOR THE DEOXYGENATION OF SIMPLE AND HINDERED ALCOHOLS. COMPARISON OF VARIOUS HYDRIDE REAGENTS *

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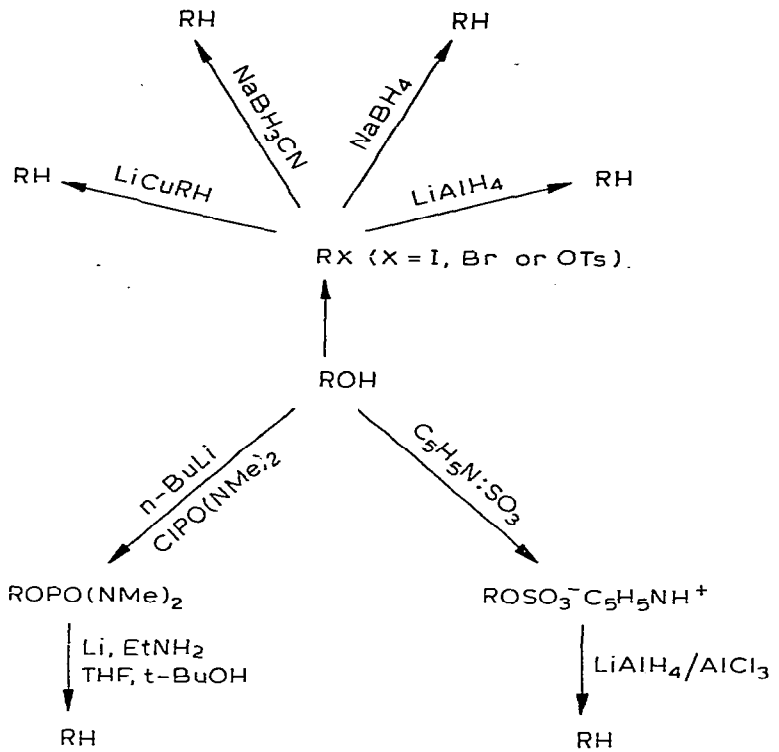
Summary

Lithium triethylborohydride (super-hydride) in tetrahydrofuran reduces the *p*-toluenesulfonates of primary and secondary alcohols to the corresponding alkanes in excellent yields. The reaction is general and applicable even to tosylates derived from cycloalkanols, hindered alcohols, and polyhydroxy derivatives. Examination of the scope of the reaction and comparison with the results realized with other hydridic reducing agents reveals the advantages of this new procedure.

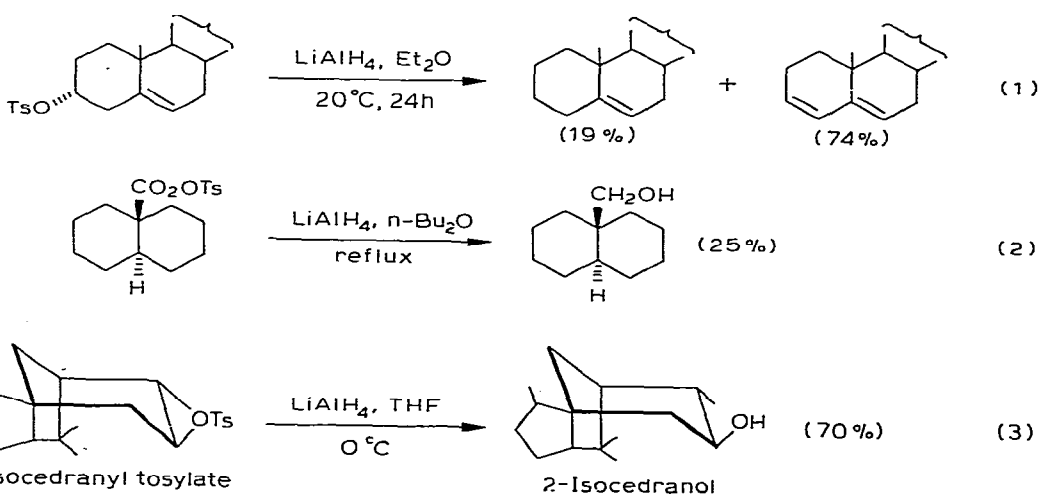
Introduction

Conversion of alcohols to the corresponding alkanes is a key functional group transformation, often encountered in synthetic organic chemistry. A number of both direct as well as indirect deoxygenation procedures have been developed. The majority of these procedures require the conversion of the alcohol component to an activated derivative (such as tosylate, bromide, etc.) and subsequent reduction of the derivative with a metal hydride reducing agent [1] (Scheme 1). The most common procedure frequently employed by organic chemists is the reduction of *p*-toluenesulfonate ester of the alcohol with lithium aluminum hydride [2]. This method proceeds satisfactorily with relatively unhindered primary tosylates. Unfortunately, with the more hindered alcohols as well as with certain cycloalkanols, the yield of the desired alkane is drastically reduced as a result of two significant side reactions [3]: (1) elimination to form olefins (especially predominant in cyclic systems), and, (2) attack at the sulfur-oxygen bond to form the parent alcohol (eq. 1—3).

* Dedicated to Professor Herbert C. Brown for his contributions to chemistry.



SCHEME 1. Representative procedures for the deoxygenation of alcohols.



Developing a good synthetic procedure for the deoxygenation of cycloalkanols and other hindered alcohols is desirable since these structures are not uncommon in natural products.

In recent years, a number of new organometallic reducing agents have evolved

by the modification of the parent reagents: lithium aluminum hydride, lithium borohydride, alane, borane, etc. [4]. Of these, alkali metal trialkylborohydrides have emerged as exceptionally powerful reducing agents, capable of reducing hindered alkyl halides, epoxides, quaternary ammonium salts, ketones, etc., rapidly and cleanly [5]. Indeed, preliminary exploratory studies clearly indicated the advantages of these new reagents for this synthetic transformation [6]. Recent developments in the hydroboration area have made available a variety of trialkylboranes with fascinating structural features; now these can be readily converted to their corresponding alkali metal trialkylborohydrides [7]. Consequently, it appeared desirable to explore the applicability of these new reagents for the reduction of alkyl tosylates to the corresponding alkanes. The effect of various hydride reagents, solvent, temperature, and the metal ion were also compared. The results of these investigations are reported in the present paper.

Results and discussion

Reaction conditions and general procedure

For understanding the general characteristics of the reaction, separate reactions on 3—5 mmol scale were carried out. The general procedure adopted was to add a standard solution of the tosylate ester in the given solvent to a vigorously stirring solution of the hydride reducing agent. Reactions were monitored by GLC utilizing a suitable internal standard. Reaction mixtures were stirred at 0, 25, or 65°C. In reactions involving trialkylborohydrides, two equivalents of the reagent were utilized for every equivalent of the tosylate [5i].

In the case of preparative scale reactions (~25 mmol), a standard solution of lithium triethylborohydride in tetrahydrofuran (THF) was added to the solution of tosylate in THF. The reaction was allowed to proceed for the desired reaction time. Then the excess hydride was destroyed and the organoborane oxidized. The organic extract was washed with water to remove ethanol produced in the oxidation. Stripping off the volatile solvents and distillation of the residue yielded the alkane in excellent yield.

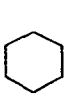
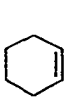
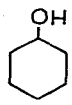
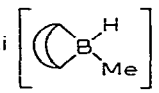
Comparative study. Effect of the reducing agent, temperature, solvent and metal ion

It was of interest to examine the effectiveness of various hydride reducing agents for the reduction of alkyl tosylates to alkanes. The cyclohexyl moiety is prevalent in a number of naturally occurring molecules of biological interest such as steroids, terpenes, etc. Accordingly, the reaction of cyclohexyl tosylate with various hydride reducing agents was examined; other factors such as the effect of the steric bulk of the reagent, metal ion, solvent, and temperature were also briefly examined. The results are summarized in Table 1.

The conventional reagent, lithium aluminum hydride, yields a mixture of cyclohexane, cyclohexene, and cyclohexanol. The alkoxy derivatives of lithium aluminum hydride, lithium trimethoxyaluminohydride [8a], and lithium tri-t-butoxyaluminohydride [8b], are essentially inert. Aluminum hydride is also inert [8c]. Borane [8d], 2,3-dimethyl-2-butylborane ($ThBH_2$) [8e], bis(3-methyl-2-butyl)borane (Sia_2BH) [8f], 9-borabicyclo[3.3.1]nonane (9-BBN) [8g], and lithium borohydride, all are essentially inert to cyclohexyl tosylate.

TABLE 1

REDUCTION OF CYCLOHEXYL TOSYLATE WITH VARIOUS HYDRIDE REDUCING AGENTS

Reagent	Reagent/ROTs	Temperature (°C)	Product composition [a] (%)		
					
$LiAlH_4$, THF [b]	2.0	25	54	25	20
$LiAlH_4$, Et_2O [c]	1.0	25	37	54	9
$LiAl(OMe)_3H$, THF [d]	4.0	25	0	0	0
$LiAl(O\text{-}t\text{-}Bu)_3H$, THF [e]	4.0	25	0	0	0
AlH_3, THF [f]	1.3	0	0	0	0
BH_3, THF [g]	1.3	0	0	0	0
$ThBH_2$, THF [h]	2.0	0	0	0	0
Sia_2BH, THF [i]	4.0	0	0	0	0
9-BBN, THF [j]	4.0	25	0	0	0
$LiBH_4$, THF [c]	2.0	25	<2	0	2
 , THF [c]	2.0	25	84	16	0
	2.0	0	88	12	0
$LiEt_3BH$, THF [c]	2.0	25	80	20	0
	2.0	0	84	16	0
$LiEt_3BH$, DG [c]	2.0	25	79	21	0
$NaEt_3BH$, THF [c]	2.0	25	83	17	0
$NaEt_3BH$, C_6H_6 [c]	2.0	25	18	82	0
Li-*n*-Bu_3BH, THF [c]	2.0	25	82	12	0
Li-*i*-Bu_3BH, THF [c]	2.0	25	79	21	0
Li-*s*-Bu_3BH, THF [c]	2.0	25	52	48	0
$LiSia_3BH$, THF [c]	2.0	25	20	80	0

[a] Analysis by GLC. Normalized yields. [b] Ref. 3a. [c] Present work. [d] Ref. 8a. [e] Ref. 8b. [f] Ref. 8c. [g] Ref. 8d. [h] Ref. 8e. [i] Ref. 8f. [j] Ref. 8g.

Sodium borohydride in DMSO [1b, c] and sodium cyanoborohydride in HMPA [1d] have been reported to react with alkyl tosylates sluggishly and incompletely. Recently, cyclohexyl tosylate has been reduced to cyclohexane in 80% yield utilizing excess (4 equivalents) of $LiCuH(n\text{-}C_4H_9)$ complex in ether at 25°C [1h].

A number of alkali metal trialkylborohydrides with alkyl groups of increasing steric requirements were also investigated. All of the trialkylborohydrides examined react with cyclohexyl tosylate rapidly and smoothly. It is 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. It is clearly evident that increasing the steric bulk of the alkyl substituent on boron in trialkylborohydrides drastically decrease the substitution/elimination ratio.

The influence of the alkali metal ion in the course of the reaction appears to be insignificant.

Solvent does exert a major role in the product ratio. Clearly, tetrahydrofuran (THF) possesses major advantages over other solvents such as ether, diglyme (DG), benzene, etc.

Lowering the temperature favors substitution over elimination.

It should be pointed out that the regeneration of the parent alcohol resulting from sulfur—oxygen bond cleavage is unimportant for all of the reductions examined utilizing trialkylborohydrides.

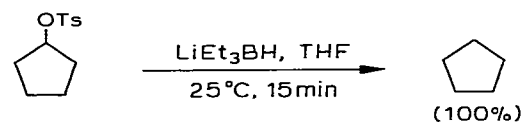
The results of this comparative study clearly indicate that lithium *B*-methyl-9-borabicyclo[3.3.1]nonyl hydride and lithium triethylborohydride are the reagents of choice for the reduction of alkyl tosylates. Of these two, lithium triethylborohydride was selected for the detailed study because of its simpler preparation and greater availability.

Synthetic applicability and scope of the reaction

p-Toluenesulfonates 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. 4).

$$CH_3(CH_2)_6CH_2OTs \xrightarrow[25°C,\ 15\ min]{LiEt_3BH,\ THF} \underset{(96\%)}{CH_3(CH_2)_6CH_3} \qquad (4)$$

The secondary tosylate, 2-octyl tosylate, is converted into n-octane in quantitative yield in 15 min. Even cycloalkyl tosylates which are susceptible to elimination reactions undergo clean reduction. Thus, cyclopentyl, cycloheptyl, and cyclooctyl tosylate, all are reduced to their corresponding cycloalkanes in excellent yields in 15—30 min (eq. 5 and 6).



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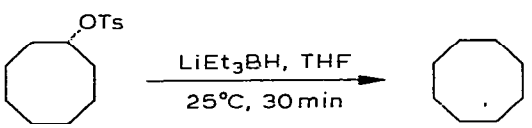
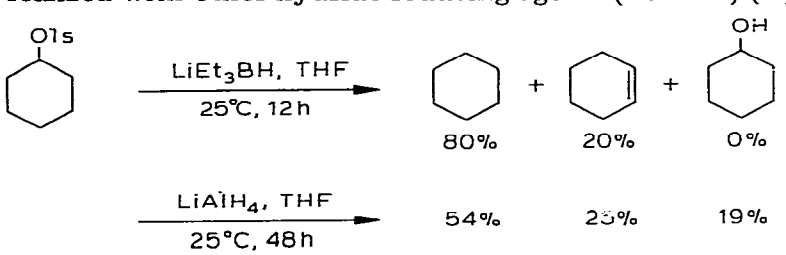


(6)

(97%, 81% isolated)

The reduction of cyclohexyl tosylate is comparatively sluggish, requiring 12 h for completion at 25°C, producing 80% of cyclohexane, 20% of cyclohexene, and only traces of cyclohexanol. This is a major improvement over the results realized with other hydride reducing agents (Table 1) (eq. 7).

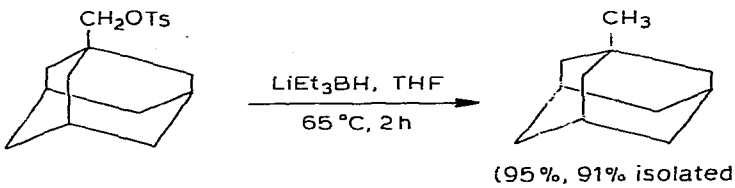


(7)

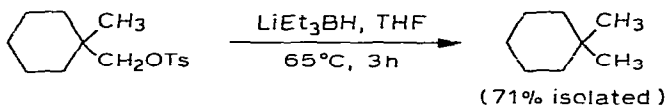
The reactions involving lithium triethylborohydride are far faster than those involving lithium aluminum hydride.

Even more important is the reduction of hindered tosylates. These are reduced

at a rate even slower than that of cyclohexyl tosylate. However, the reaction is reasonably rapid at 65°C (refluxing THF) providing a satisfactory yield of the products. Thus, tosylates of 2,2-dimethyl-1-hexanol, 1-adamantanemethanol, and 1-methylcyclohexanemethanol, all were converted into their corresponding alkanes in excellent isolated yields, free of isomeric alkanes, confirming the value of this procedure for such transformations (eq. 8 and 9).



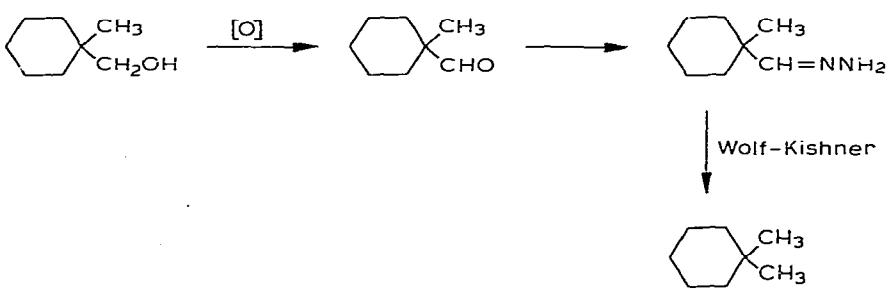
(8)



(9)

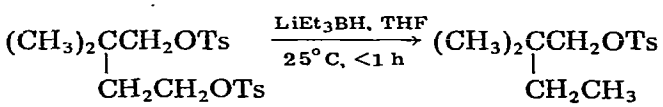
Reduction of the tosylate ester of 1-adamantanemethanol with lithium aluminum hydride has been reported to yield 1-methyladamantane in only 25% yield [3c].

In fact the usual procedure for the deoxygenation of such hindered alcohols involves the oxidation of the alcohol to the aldehyde followed by Wolf—Kishner reduction of the hydrazone derivative of the aldehyde (eq. 10).



(10)

Finally, it is possible to selectively deoxygenate a less hindered hydroxyl group in the presence of a more hindered hydroxyl group in a polyhydroxy compound. Thus, the ditosylate of 2,3-dimethyl-1,4-butanediol is selectively and cleanly reduced to 2,2-dimethyl-1-butyl tosylate in an isolated yield of 86% (eq. 11). Such transformations should be highly useful in carbohydrate chemistry in the synthesis of deoxy sugars.



(11)

(86% isolated)

TABLE 2

REDUCTION OF REPRESENTATIVE ALKYL TOSYLATES WITH LITHIUM TRIETHYLBOROHYDRIDE IN TETRAHYDROFURAN [a]

Compound	Temperature (°C)	Time (h)	Product [b,c,d]	%
n-Octyl tosylate	25	0.25	n-Octane	96
2-Methyl-1-pentyl tosylate	25	0.25	2-Methylpentane	98
2-Octyl tosylate	25	0.25	n-Octane	99
Cyclopentyl tosylate	25	0.25	Cyclopentane	100
Cyclohexyl tosylate	25	12.00	Cyclohexane	80
			Cyclohexene	20
Cycloheptyl tosylate	25	0.5	Cycloheptane	100
Cyclooctyl tosylate	25	0.5	Cyclooctane	98(82)
2,2-Dimethyl-1-hexyl tosylate	65	3.0	2,2-Dimethylhexane	81
			2,2-Dimethyl-1-hexanol	9
1-Adamantanemethyl tosylate	65	2.0	1-Methyladamantane	95(91)
1-Methylcyclohexanemethyl tosylate	65	3.0	1,1-Dimethylcyclohexane	(71)
2,2-Dimethyl-1,4-*bis*(*p*-toluenesulfonyloxy)butane	25	0.5	2,2-Dimethyl-1-butyl tosylate	(86)

[a] Reactions for GLC analysis were carried out at 0.25 *M* in tosylate and 0.5 *M* in $LiEt_3BH$. [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] Numbers in parentheses indicate the isolated yield.

The results of reduction of representative alkyl tosylates, with lithium triethylborohydride in tetrahydrofuran are summarized in Table 2.

Conclusions

The reduction of *p*-toluenesulfonate esters of alcohols to the corresponding alkanes was explored with a number of hydride reducing agents. Of these, lithium triethylborohydride in tetrahydrofuran exhibits major advantages over the conventional reagents in overcoming the difficulties previously encountered in carrying out this transformation. The reaction is rapid, essentially clean, and quantitative. Even highly hindered tosylates and cycloalkyl tosylates are smoothly reduced. Both undesirable side reactions, the elimination and the attack of the hydride at the sulfur—oxygen bond, are either absent or greatly diminished. The present reaction provides yet another valuable application of the new reagent, lithium triethylborohydride, which should find major application in organic synthesis.

Experimental

General comments

All glassware was dried at least 4 h at 140°C, assembled hot, and cooled under a stream of prepurified nitrogen (Airco). All reactions were carried out under a dry nitrogen atmosphere. Hypodermic syringes with stainless steel needles, dried in the oven, and purged with nitrogen were utilized for transferring the

solutions of organometallics and hydride reagents. Reactions were stirred magnetically using ovendried Teflon-coated stirring bars.

Materials

Solvents, organometallics, and metal hydrides were stored under nitrogen. Most liquids were kept in Teflon stopcock protected ampoules. Tetrahydrofuran was distilled from excess lithium aluminum hydride. Diethyl ether, benzene, and pyridine (Mallinckrodt, AR) were stored over molecular sieves. Commercial *p*-toluenesulfonyl chloride (reagent grade) was used as received. Most olefins and alkanes employed in this study were from Phillips Petroleum Company (≥99% pure).

Most of the alcohols utilized in this study were the commercial products of the highest purity. They were further purified by recrystallization or distillation when necessary. 1-Adamentanemethanol, 1-methylcyclohexanemethanol, and 2,2-dimethyl-1,4-butanediol were prepared in excellent yields (80—90%) by borane-methylsulfide reduction of the corresponding carboxylic acids [9].

Alkyl tosylates were prepared from the parent alcohols by pyridine *p*-toluenesulfonyl chloride procedure. They were further purified by recrystallization from suitable solvents (solids) or cooling to —78°C (Dry-Ice) and repeatedly washing with n-pentane (liquids). Physical constants agreed satisfactorily with constants in the literature. Their purity was further checked by ^{1}H NMR by measuring the ratio of integrated area of aromatic protons (AB quartet) of the tosylate group to the methylene or methine protons (—CH_2OTs or ⩵CHOTs) of the alcohol component.

Lithium triethylborohydride, lithium tri-n-butylbotohydride, lithium triisobutylborohydride, and sodium triethylborohydride were synthesized from alkali metal hydride (Ventron Corporation) and the appropriate trialkylboranes (Callery Chemical Co.) [7a]. Lithium tri-s-butylborohydride, lithium *B*-methyl-9-borabicyclo[3.3.1]nonyl hydride, and lithium trisiamylborohydride were synthesized from the corresponding trialkylboranes and t-butyllithium [7c]. The purity of these hydride reagents was checked by ^{11}B NMR. The majority of these reagents are now commercially available from Aldrich Chemical Co., Milwaukee, Wisconsin.

Spectra

^{1}H NMR spectra were recorded in a Varian T-60 spectrometer (60 MHz, CCl_4 or $CDCl_3$, TMS) and ^{11}B NMR ($BF_3 \cdot OEt_2$) were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) with a Nicolet 1080 data acquisition system.

GLC analysis

GLC analyses were carried out with a Varian 1200 FID Chromatograph fitted with stainless steel columns.

Representative procedure for product analysis by GLC

Reduction of cyclopentyl tosylate to cyclopentane with lithium triethylborohydride is representative. An oven-dried, 25-ml flask equipped with a sidearm fitted with a Silicon rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled to room temperature under

dry nitrogen. The flask was immersed in a water bath (ca. 25°C). Then 4.5 ml of THF was injected into the reaction flask followed by 4.0 ml (6 mmol) of a 1.5 *M* solution in THF of $LiEt_3BH$. n-Octane, 0.49 ml (3 mmol), was injected into the reaction flask to serve as the internal standard. Finally, 3 ml of a 1.0 *M* solution in THF of cyclopentyl tosylate (3 mmol) was introduced and the resulting mixture was stirred well. Analysis of the reaction by GLC (5% SE-30 column, 12 ft × 0.125 in, coated on AW-DMCS Chromosorb W) at the end of 15 min indicated the presence of 99% cyclopentane. After 1 h, excess hydride was destroyed and the organoborane was oxidized. GLC analysis indicated the complete absence of cyclopentene (30% adiponitrile column, 6 ft × 0.125 in), and cyclopentanol (5% Carbowax 20M column, 6 ft × 0.125 in).

General preparative procedures for the reduction of alkyl tosylates with lithium triethylborohydride

A. Reduction of cyclooctyl tosylate to cyclooctane. An oven-dried, 300-ml flask equipped with a sidearm fitted with a Silicon 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. Tetrahydrofuran (20 ml) was introduced, bollowed by 7.1 g (25 mmol) of cyclooctyl tosylate. The mixture was cooled to 0°C (ice-bath). To this stirred solution, lithium triethylborohydride, 33.3 ml (50 mmol) of a 1.5 *M* solution in THF was added and the ice-bath was removed. The mixture was stirred for 2 h (ca. 20°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. 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, b.p. 142—146°C, n_D^{20} 1.4630. GLC analysis indicated the product to be 97% cyclooctane and 3% cyclooctene.

B. Reduction of 1-adamantanemethyl tosylate to 1-methyladamantane. The experimental setup was the same as in the previous experiment. 1-Adamantanemethyl tosylate, 8 g (25 mmol), was placed in the reaction flask followed by 10 ml of dry THF. To this solution of the tosylate in THF, lithium triethylborohydride, 33.3 ml (50 mmol), of a 1.5 *M* solution in THF was added. The mixture was stirred well and brought to a gentle reflux (~65°C) and maintained at that temperature for a period of 2 h. Then the contents of the flask were cooled to room temperature, excess hydride was destroyed with water, and triethylborane was oxidized ($NaOH/H_2O_2$). The reaction mixture was worked up as in the previous experiment. Removal of the volatile solvents yielded 3.4 g (97%) of 1-methyladamantane as a white solid which was purified by sublimation, m.p. 98—101°C.

C. Reduction of 1-methylcyclohexanemethyl tosylate. A typical reaction setup was assembled and 1-methylcyclohexanemethyl tosylate, 7.05 g (25 mmol), was placed in the reaction flask and dissolved in 10 ml of tetrahydrofuran. The hindered tosylate was reduced with lithium triethylborohydride, 33.3 ml (50 mmol) at the refluxing temperature (65°C) for 3 h. After the usual workup, followed by distillation, gave 2.0 g (71%) of 1,1-dimethylcyclohexane as a

colorless liquid, b.p. 120°C, n_D^{20} 1.4310.

D. Selective reduction of the ditosylate of 2,2-dimethyl-1,4-butanediol to 2,2-dimethyl-1-butyl tosylate. A typical reaction setup was assembled. Ditosylate of 2,2-dimethyl-1,4-butanediol (m.p. 84—85°C), 5.33 g (12.5 mmol) was placed in the reaction flask and dissolved in 15 ml of tetrahydrofuran. The flask was immersed in a water bath (ca. 25°C). Lithium triethylborohydride, 17 ml (25 mmol), of a 1.5 *M* solution in tetrahydrofuran was introduced. The resulting mixture was stirred well for 30 min at 25°C. Then the excess hydride was destroyed and the organoborane was oxidized ($NaOH/H_2O_2$). The organic layer was separated and the aqueous layer extracted with 2 × 15-ml portions of ether. The combined organic extracts were washed with 3 × 15 ml portions of water and dried (Na_2SO_4). Removal of the volatile solvents gave 2.75 g (86%) of 2,2-dimethyl-1-butyl tosylate as a colorless, viscous liquid, n_D^{20} 1.4965; ^1H NMR (CCl_4, TMS): δ 0.8 to 1.5 (11, $(CH_3)_2C$—, $-CH_2CH_3$), 2.45 (s, 3, $-C_6H_4-CH_3$), 3.7 (s, 2, $-CH_2OTs$), 7.5 (q, 4, aromatic) ppm.

Acknowledgments

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References

1 (a) R.O. Hutchins, D. Hoke, J. Keogh and D. Koharshi, Tetrahedron Lett., (1969) 3495; (b) H.M. Bell, C.W. Vanderslice and A. Spehar, J. Org. Chem., 34 (1969) 3923; (c) R.O. Hutchins, B.E. Maryanoff and C.A. Milewski, Chem. Commun., (1971) 1097; (d) R.O. Hutchins, D. Kandasamy, C.A. Maryanoff, D. Masilamani, and B.F. Maryanoff, J. Org. Chem., 42 (1977) 82; (e) R.E. Ireland, D.C. Muchmore and U. Hengartner, J. Amer. Chem. Soc., 94 (1972) 5048; (f) E.J. Corey and K. Achiwa, J. Org. Chem., 34 (1969) 3667; (g) S. Masamune, P.A. Rossy and G.S. Bates, J. Amer. Chem. Soc., 95 (1973) 6452; (h) S. Masamune, G.S. Bates and P.E. Geroghiow, ibid., 96 (1974) 3686.

2 (a) N.G. Gaylord, Reduction with Complex Metal Hydrides, Interscience Publishers, Inc., New York, N.Y., 1956, p. 855—875; (b) H.O. House, Modern Synthetic Reactions, W.A. Benjamin, Inc., Menlo Park, California, 1972, p. 45—130.

3 (a) H.C. Brown, P.M. Weismann and N.M. Yoon, J. Amer. Chem. Soc., 88 (1966) 1458; (b) D.H.R. Barton and C.J.W. Brooks, J. Chem. Soc., (1951) 257; (c) H. Stetter, M. Schwartz and A. Hirschhorn, Chem. Ber., 92 (1959) 1629; (d) D.H. Ball and F.W. Parrish, Advan. Carbohydrate Chem., 23 (1968) 233; (e) L.J. Dolby and D.R. Rosencrantz, J. Org. Chem., 2[illegible] (1963) 1888; (f) J.A. Marshall and R.A. Ruden, ibid., 36 (1971) 594; (g) S.P. Acharya and H.C. Brown, ibid., 35 (1970) 196.

4 H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, New York, 1972.

5 (a) S. Krishnamurthy, Aldrichimica Acta, 7 (1974) 55; (b) H.C. Brown, S. Krishnamurthy and R.A. Coleman, J. Amer. Chem. Soc., 94 (1972) 1750; (c) H.C. Brown and S. Krishnamurthy, ibid., 94 (1972) 7159; (d) 95 (1973) 1669; (e) S. Krishnamurthy, R.M. Schubert and H.C. Brown, ibid., 95 (1973) 8486; (f) S. Krishnamurthy and H.C. Brown, ibid , 98 (1976) 3383; (g) S. Krishnamurthy, F. Vogel and H.C. Brown, J. Org. Chem., 42 (1977) 2534; (h) M.P. Cooke, Jr. and R.M. Parlman, ibid., 40 (1975) 531; (i) H.C. Brown, A. Khuri and S. Krishnamurthy, J. Amer. Chem. Soc., 99 (1977) 6237.

6 (a) S. Krishnamurthy and H.C. Brown, J. Org. Chem., 41 (1976) 3064; (b) R.W. Holder and M.G. Matturo, ibid., 42 (1977) 2166.

7 (a) H.C. Brown, S. Krishnamurthy and J.L. Hubbard, J. Amer. Chem. Soc., in press; (b) C.A. Brown and S. Krishnamurthy, J. Organometal. Chem., 156 (1978) 111; (c) E.J. Corey, S.M. Albonico, U. Koelliker, T.K. Schaff and R.K. Varma, J. Amer. Chem. Soc., 93 (1971) 1491.

8 (a) H.C. Brown and P.M. Weissman, J. Amer. Chem. Soc., 87 (1965) 5614; (b) Israel J. Chem., 1 (1963) 430; (c) H.C. Brown and N.M. Yoon, J. Amer. Chem. Soc., 88 (1966) 1464; (d) H.C. Brown, P. Heim and N.M. Yoon, ibid., 92 (1970) 1637; (e) J. Org. Chem., 37 (1972) 2942; (f) H.C. Brown, D.B.

Bigley, S.K. Arora and N.M. Yoon, J. Amer. Chem. Soc., 92 (1970) 7161; (g) H.C. Brown, S. Krishnamurthy and N.M. Yoon, J. Org. Chem., 41 (1976) 1778.

9 (a) N.M. Yoon, C.S. Pak, H.C. Brown, S. Krishnamurthy and T.P. Stocky, J. Org. Chem., 38 (1973) 2786; (b) C.F. Lane, Aldrichimica Acta, 8 (1975) 20; (c) S. Krishnamurthy and K.L. Thompson, J. Chem. Educ., 54 (1977) 778.