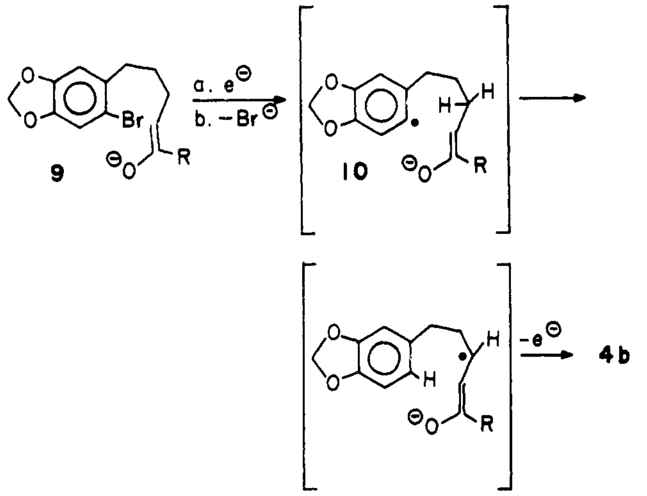
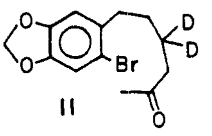
α,β-unsaturated ketone (**4b**) and the reduction product (**5c**). From **8**, the yield of monomeric material was 31%, trace amounts of reduction product (**5d**, 3%) and the six-membered ring (entry 8, 3%), and larger amounts of the α,β-unsaturated ketone (**4c**, 7%) and the eight-membered ring (entry 8, 19%).

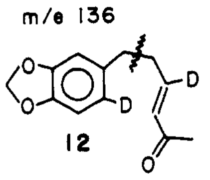
In related experiments, the enolate anions were generated quantitatively using potassium amide. Irradiation produced a larger proportion of product resulting from cyclization through the unsubstituted (presumably, kinetic) enolate. From **6** (entry 7) under these conditions, only reduction product **5c** (23% yield) and the seven-membered ring (21% yield) were obtained. From 8 (entry 8), the reduction product **5d** (3%) and the eight-membered ring (11%) were obtained. There was only a trace of the six-membered ring.

The formation of unsaturated ketones with concomitant replacement of halogen by hydrogen suggested the possibility of intramolecular hydrogen atom transfer from the β position of the enolate (e.g., **9** in Scheme I) to the transient phenyl radical (i.e., in **10**);[6] then hydrogen-atom abstraction through a six-atom transition state would produce the enone–radical anion (Scheme I), the usual species formed in electron transfer to α,β-unsaturated ketones. This reaction would serve as a propagation step in the radical-chain mechanism,[7] and intermolecular reactions of the intermediates might explain the low yields of monomeric products sometimes observed. Consistent with this hypothesis, the dideuterated analogue **11** under the usual reaction conditions produced the unsaturated ketone (i.e., **12**) with 2.0 ± 0.1 deuterium atoms/molecule and 1.0 ± 0.1 deuteriums/unit in the mass spectral fragment at *m/e* 136, the piperonyl ring unit.

Scheme I




11



12

There has been no direct evidence reported which implicates hydrogen-atom transfer from the enolate anion as a significant side reaction in intermolecular examples of the photo-S$_{\text{RN}}$1 reaction.[8] However, alkyl-substituted enolate anions, where the β hydrogen is available, are known[9] to undergo the photo-S$_{\text{RN}}$1 reaction much less efficiently than unsubstituted analogues. For example, the lithium enolate of *tert*-butyl 2-methylpropionate reacted with *p*-bromoanisole upon irradiation to give *tert*-butyl 2-(*p*-methoxyphenyl)-2-methylpropionate in 5% yield; the major product was anisole (35–50%). Lithio *tert*-butyl acetate reacted under the same conditions, affording *tert*-butyl (*p*-methoxyphenyl)acetate (67%) and *tert*-butyl di(*p*-methoxyphenyl)acetate (29%). Irradiation of the enolate from *tert*-butyl 2-(trideuteriomethyl)-3,3,3-trideuteriopropionate with *p*-bromoanisole under the usual conditions produced anisole in 54% yield, with 35% of it labeled with one deuterium, confirming the major role of H-atom abstraction from the enolate.

These studies suggest that the photo-S$_{\text{RN}}$1 reaction of enolate anions with aryl halides can be efficient for intramolecular cases as well as in the well-established intermolecular examples, but, when a hydrogen atom is present at the β carbon in the enolate anion, hydrogen-atom transfer to the transient phenyl radical is generally the dominant process.[10]

References and Notes

(1) J. F. Bunnett and J. E. Sundberg, *J. Org. Chem.*, **41**, 1702 (1976), and references therein.

(2) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

(3) (a) M. F. Semmelhack, B. P. Chong, R. D. Stauffer, T. D. Rogerson, A. Chong, and L. D. Jones, *J. Am. Chem. Soc.*, **97**, 2507 (1975); (b) M. F. Semmelhack, R. D. Stauffer, and T. D. Rogerson, *Tetrahedron Lett.*, 4519 (1973).

(4) All new compounds showed satisfactory spectral data (^{1}H NMR, IR, low resolution mass spectra). The starting compounds in entries 1, 2, 3, 5, 6, 7, and 8 and the products in entries 1, 2, and 3 of Table I have given satisfactory combustion analysis.

(5) The α,β ketone **4b** was prepared by aldol condensation between pinacolone and 3-(3,4-methylenedioxophenyl)propionaldehyde and fully characterized. Upon treatment with potassium *tert*-butoxide in liquid ammonia (approximately the conditions for the photo-S$_{\text{RN}}$1 reaction except in darkness), the α,β isomer was converted essentially quantitatively to the β,γ isomer **3**. Therefore we believe the α,β-unsaturated ketone **4b** to be the first-formed product from the photo-S$_{\text{RN}}$1 reaction of **1**.

(6) The intermediacy of phenyl radicals in the photo-S$_{\text{RN}}$1 reaction has been suggested and supported by Bunnett and his coworker.[2]

(7) The radical-chain mechanism has been proposed by R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 683 (1972).

(8) Bunnett and Sundberg have obtained hexamethyloctanedione as a rate-depressing side product in the reaction of diisopropyl ketone enolate with iodobenzene.[1]

(9) (a) T. Bargar, unpublished work at Cornell; (b) ref 1.

(10) We wish to acknowledge generous financial support from the Public Health Service through NIH Grant AI-08687. In addition we are grateful to Mr. Jeffery Hayes who carried out the experimental tests for one of the entries in the table (entry 4).

(11) Recipient of a Camille and Henry Dreyfuss Teacher-Scholar Grant, 1973–1978.

(12) National Institutes of Health predoctoral trainee, 1973–1976.

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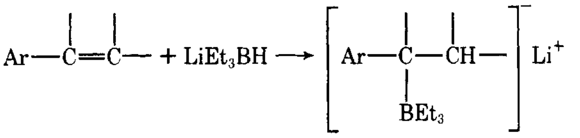
Nucleophilic Hydroboration of Substituted Styrenes with Lithium Triethylborohydride. A Simple Convenient Procedure for the Markownikoff Hydroboration of Aromatically Conjugated Olefins and the Synthesis of Mixed Organoboranes with the Benzylic (α-Arylalkyl) Moiety

Summary: Lithium triethylborohydride (LiEt$_3$BH) adds to substituted styrenes under relatively mild conditions to give the corresponding tetraalkylborates, readily hydrolyzed to the corresponding saturated hydrocarbons or protonolyzed with strong acids to the mixed trialkylboranes containing a benzylic group.

Sir: We wish to report a simple regiospecific addition of lithium triethylborohydride to aromatically conjugated olefins under remarkably mild conditions to give the addition product 1 (eq 1). Furthermore, by the treatment of 1 with water, the



$$\mathrm{Ar{-}\overset{|}{C}{=}\overset{|}{C}{-}} + \mathrm{LiEt_3BH} \longrightarrow \left[\mathrm{Ar{-}\underset{BEt_3}{\overset{|}{C}}{-}\overset{|}{C}H{-}}\right]^{-}\mathrm{Li^+} \quad (1)$$

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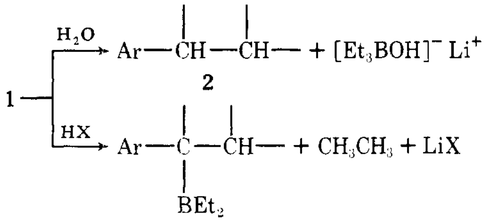
corresponding saturated hydrocarbon **2** is obtained in excellent yield (eq 2). On the other hand, treatment of **1** with strong



$$\mathbf{1}\begin{cases}\xrightarrow{\mathrm{H_2O}} \underset{\mathbf{2}}{\mathrm{Ar{-}\overset{|}{C}H{-}\overset{|}{C}H{-}}} + [\mathrm{Et_3BOH}]^-\mathrm{Li^+} \\ \xrightarrow{\mathrm{HX}} \mathrm{Ar{-}\underset{BEt_2}{\overset{|}{C}}{-}\overset{|}{C}H{-}} + \mathrm{CH_3CH_3} + \mathrm{LiX}\end{cases} \quad (2)$$

3

acids, such as methanesulfonic acid or hydrochloric acid, yields the Markownikoff mixed trialkylborane **3** in excellent yield (eq 2). Consequently, this procedure provides a new synthetic route to mixed organoboranes containing the reactive benzylic (α-arylalkyl) moiety.

Recently, trialkylborohydrides have received considerable attention owing to their remarkable nucleophilic characteristics in the reduction of organic functional groups.[1] However, only one example of the addition of these reagents to olefins has been reported, namely, addition of sodium triethylborohydride to ethylene, which requires drastic conditions of high temperature (~150 °C) and pressure (1000 psi).[2] A related reaction which proceeds much more readily is the conjugate addition of trialkylborohydrides to α,β-unsaturated carbonyl derivatives.[3]

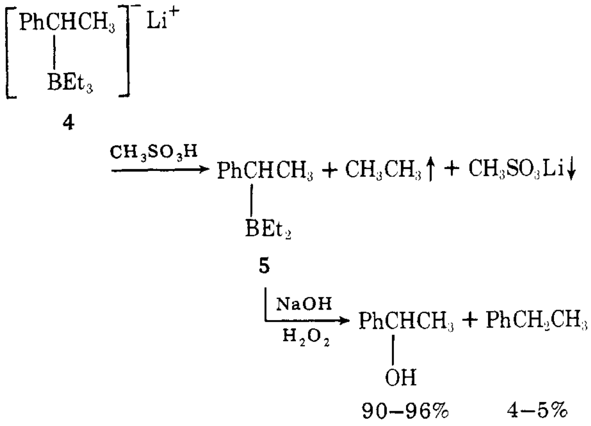
In the course of an investigation of the reducing properties of lithium triethylborohydride toward representative functional groups in tetrahydrofuran (THF), we observed that at 0 °C the reagent slowly adds in a 1:1 molar ratio to styrene.[4] At 65 °C, the reaction is over in 6 h. These observations prompted us to examine the reaction in detail.

The product is reasonably stable thermally, resisting dissociation.[5] Hydrolysis of the product (**4**) of the above reaction is readily achieved by water in 1–2 h at 65 °C. GC analysis of this mixture, after oxidation with alkaline hydrogen peroxide, showed that ethylbenzene had been formed in nearly quantitative yield (based on the styrene used). Also, the amount of ethanol formed indicated that a quantitative yield of triethylborane was present (eq 3).

$$\mathbf{4} \xrightarrow[\text{THF, 65 °C, 1–2 h}]{\mathrm{H_2O}} \underset{92\text{–}99\%}{\mathrm{C_6H_5CH_2CH_3}} + \underset{\sim 100\%}{\mathrm{Et_3B}} \quad (3)$$

Deuterolysis with D_2O using similar conditions yielded pure α-deuterioethylbenzene, indicating that boron must be attached in the position α to the phenyl group.

4 behaves quite differently toward strong acids. Treatment of **4** with an equimolar quantity of methanesulfonic acid[6] at room temperature brings about an immediate evolution of gas with formation of white precipitate. GC analysis of the resulting mixture, after oxidation, revealed a 90–96% yield of 1-phenylethanol (free of the 2 isomer) with a 4–5% yield of ethylbenzene.[7] The analysis also revealed the loss of approximately one-third of the ethyl groups. This establishes that the acid selectively protonates one of the ethyl groups in **4** to form **5** (eq 4). The absence of 2-phenylethanol confirms the conclusion that boron must be attached exclusively to the carbon atom α to the phenyl group. Thus the procedure provides a convenient new route to mixed organoboranes containing the reactive benzylic (α-arylalkyl) moiety.

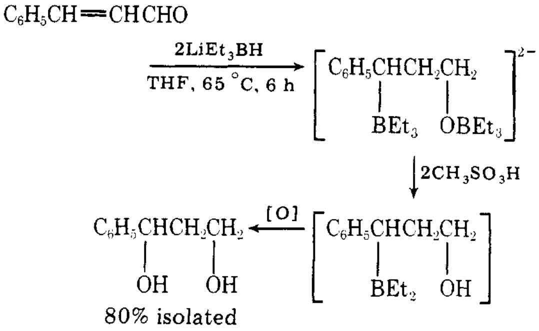


$$\underset{\mathbf{4}}{\left[\mathrm{\underset{BEt_3}{\underset{|}{PhCHCH_3}}}\right]^-\mathrm{Li^+}} \xrightarrow{\mathrm{CH_3SO_3H}} \underset{\mathbf{5}}{\mathrm{\underset{BEt_2}{\underset{|}{PhCHCH_3}}}} + \mathrm{CH_3CH_3}\uparrow + \mathrm{CH_3SO_3Li}\downarrow \quad (4)$$

$$\mathbf{5} \xrightarrow[\mathrm{H_2O_2}]{\mathrm{NaOH}} \underset{90\text{–}96\%}{\mathrm{\underset{OH}{\underset{|}{PhCHCH_3}}}} + \underset{4\text{–}5\%}{\mathrm{PhCH_2CH_3}}$$

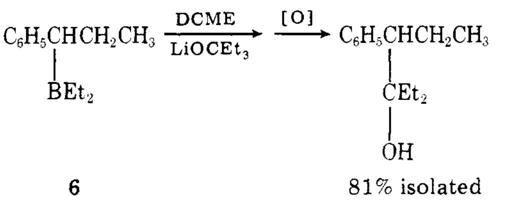
Substituted styrenes (p-methoxy, p-chloro) give similar results. As anticipated for a nucleophilic hydroboration reaction, the rate of the addition is faster for p-chloro and slower for p-methoxy, a trend which is opposite to that observed in the electrophilic hydroboration by 9-BBN.[8] Methyl substitution on the double bond, as in *trans*-propenylbenzene and isopropenylbenzene, reduces the rate of reaction, compared with the parent compound, styrene, itself. Some of these slow reactions can be greatly facilitated by running them at 100 °C in diglyme (DG).[9]

The double bond in cinnamaldehyde also adds the reagent readily, following the initial reduction of the aldehyde group. Oxidation of the intermediate provides 1-phenyl-1,3-propanediol (isomerically pure) in good yield (eq 5).



$$\mathrm{C_6H_5CH{=}CHCHO} \xrightarrow[\text{THF, 65 °C, 6 h}]{\mathrm{2LiEt_3BH}} \left[\mathrm{\underset{BEt_3}{\underset{|}{C_6H_5CH}}\underset{OBEt_3}{\underset{|}{CH_2CH_2}}}\right]^{2-}\mathrm{2Li^+} \xrightarrow{\mathrm{2CH_3SO_3H}} \left[\mathrm{\underset{BEt_2}{\underset{|}{C_6H_5CH}}\underset{OH}{\underset{|}{CH_2CH_2}}}\right] \xrightarrow{[\mathrm{O}]} \underset{80\%\ \text{isolated}}{\mathrm{\underset{OH}{\underset{|}{C_6H_5CH}}\underset{OH}{\underset{|}{CH_2CH_2}}}} \quad (5)$$

The intermediate trialkylborane **5** and **6** were also isolated (64% each) and characterized.[10] The DCME reaction[11] of **6** gave an excellent yield of the corresponding tertiary alcohol (eq 6).



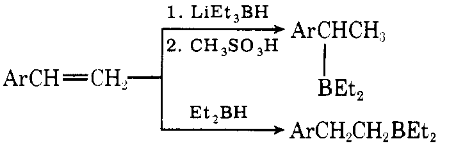
$$\underset{\mathbf{6}}{\mathrm{\underset{BEt_2}{\underset{|}{C_6H_5CHCH_2CH_3}}}} \xrightarrow[\mathrm{LiOCEt_3}]{\mathrm{DCME}} \xrightarrow{[\mathrm{O}]} \underset{81\%\ \text{isolated}}{\mathrm{\underset{\underset{OH}{|}}{\underset{CEt_2}{\underset{|}{C_6H_5CHCH_2CH_3}}}}} \quad (6)$$

1,1-Diphenylethylene rapidly adds the reagent (9 h, 0 °C). However, the ate complex is evidently unstable and dissociates into the organolithium derivative and triethylborane. Thus, the reaction mixture immediately develops a deep reddish color, not present in the other reactions, indicating the probable presence of 1-lithio-1,1-diphenylethane, rather than its triethylborane complex.[12] The color immediately disappears upon addition of either water or strong acid, yielding only a single product, 1,1-diphenylethane, 96%.

The following procedure for the reaction of styrene is representative. A dry 50-mL flask equipped with a septum-covered inlet, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was flushed with nitrogen.

The flask was charged with 17.2 mL of a 1.54 M solution of $LiEt_3BH$ (26.4 mmol) in THF,[13] 8 mL of a 3 M solution of isopropylbenzene in THF (internal standard), and 2.8 mL of THF. To this well-stirred solution, 8 mL of a 3 M solution of styrene (24 mmol) in THF was injected and the mixture was refluxed overnight.[14] The mixture was cooled to room temperature and a 7.5-mL aliquot (equivalent to 5.0 mmol of styrene) was transferred to another flask. Then 0.35 mL (5.5 mmol) of methanesulfonic acid was added dropwise while vigorously stirring. Gas evolution was observed with concurrent formation of a white precipitate. The mixture was stirred for 15 min at room temperature and oxidized in the usual manner. After the aqueous layer was saturated with potassium carbonate, GC analysis (Carbowax 20M) indicated a 91% yield of 1-phenylethanol and a 4% yield of ethylbenzene. The remaining reaction mixture was treated with 5 mL of water and refluxed for 2 h. After oxidation, GC analysis showed a 96% yield of ethylbenzene. There was no 1-phenylethanol detectable.

The present procedure provides a new type of hydroboration leading to synthesis of Markownikoff organoboranes. Consequently, it is now possible to control the direction of the hydroboration of aromatically conjugated olefins by choosing an appropriate reagent (eq 7). This development also provides a valuable new route to mixed organoboranes containing the highly reactive benzylic (α-arylalkyl) moiety.



$$\mathrm{ArCH{=}CH_2}\ \begin{cases} \xrightarrow[\text{2. } CH_3SO_3H]{\text{1. } LiEt_3BH} \underset{\displaystyle \mathrm{BEt_2}}{\mathrm{ArCHCH_3}} \\ \xrightarrow{Et_2BH} \mathrm{ArCH_2CH_2BEt_2} \end{cases} \qquad (7)$$

References and Notes

(1) For review, see S. Krishnamurthy, *Aldrichimica Acta*, **7**, 55 (1974).

(2) (a) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **83**, 369 (1961); (b) P. Binger and R. Köster, *Inorg. Synth.*, **15**, 138 (1974).

(3) B. Ganem et al., *J. Org. Chem.*, **40**, 146, 2846 (1975); **41**, 2194 (1976).

(4) By using 4 equiv of the reagent (1.0 M), styrene utilizes 0.44 equiv of hydride in 24 h at 0 °C. At 25 °C, 1.0 equiv is utilized in ~12 h.

(5) GC analysis using low injector-port temperature (30 °C) showed that the product exists as a strong triethylborane complex.

(6) Hydrogen chloride or concentrated hydrochloric acid works equally well.

(7) Formation of the hydrolyzed product during the oxidation stage is a well-known phenomenon for benzylic-type organoboranes. See H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1966); A. J. Weinheimer and W. E. Marsico, *J. Org. Chem.*, **27**, 1926 (1962). Such ready hydrolysis has rendered difficult the synthesis of benzylic organoboranes through application of benzylic Grignards or the corresponding lithium derivatives.

(8) H. C. Brown , R. Liotta, and C. G. Scouten, *J. Am. Chem. Soc.*, **98**, 5297 (1976).

(9) $LiEt_3BH$ in diglyme is prepared from LiH and Et_3B using a procedure similar to that for preparation of the reagent in THF: H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **94**, 7159 (1972).

(10) The ^1H and ^{11}B NMR spectra of the organoborane intermediates **5** and **6** corresponded to the structures. Oxidation with alkaline hydrogen peroxide gave the corresponding alcohol (GC).

(11) (a) H. C. Brown and B. A. Carlson, *J. Org. Chem.*, **38**, 2422 (1973); (b) H. C. Brown, J.-J. Katz, and B. A. Carlson, *ibid.*, **38**, 3968 (1973).

(12) Lithium aluminum hydride reacts with 1,1-diphenylethylene to give the corresponding benzylic carbanions: I. Granoth and Y. Segall, *J. Chem Soc., Chem. Commun.*, 887 (1974).

(13) The reagent is available from Aldrich Chemical Co., as 1 M solution in THF.

(14) Although 1 mol of the reagent is consumed per mole of styrene in 6 h, it is sometimes necessary to reflux the solution for longer time (overnight is sufficient) to realize a quantitative yield of the products.

(15) Graduate research assistant on Grant No. DA-ARO-D-31-124-73-G148, supported by the U.S. Army Research Office (Durham).

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