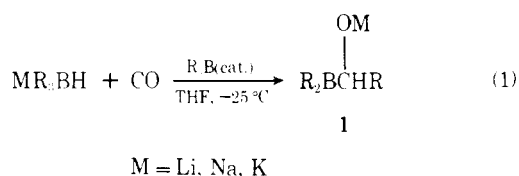## Trialkylborane-Induced Reaction of Carbon Monoxide with Alkali Metal Trialkylborohydrides: A Remarkable Correlation of Boron-11 Nuclear Magnetic Resonance Spectra with Reactivity

*Summary:* Whereas undissociated alkali metal trialkylborohydrides fail to react at 0–25 °C with carbon monoxide, rapid reaction is induced by the presence of a small quantity of free trialkylboranes. This discovery provides a new understanding of the reaction mechanism for the carbonylation of organoboranes in the presence of hydrides.

*Sir:* Whereas lithium trialkylborohydrides react readily with carbon monoxide at 25 °C, the corresponding potassium compounds[1] do not. Comparison of the ^{11}B NMR spectra reveals that the lithium compounds exhibit a single peak, with the potassium compounds exhibiting well-resolved doublets.[2] The addition of small amounts of trialkylboranes results in collapse of the doublet into a singlet.[2] Furthermore, the presence of a small amount of free trialkylborane in the potassium trialkylborohydride achieves rapid and complete absorption of carbon monoxide. Thus a small amount of free trialkylborane converts the doublet into a singlet and the inert trialkylborohydride into a reactive system. The reaction provides a new, simple entry to the presumed dialkylborylalkylmethylates (1), highly valuable synthetic intermediates (eq 1).[3]

$$\text{MR}_3\text{BH} + \text{CO} \xrightarrow[\text{THF, } -25\,°C]{\text{R}_3\text{B(cat.)}} \overset{\overset{\displaystyle\text{OM}}{|}}{\text{R}_2\text{B}}\text{CHR} \qquad (1)$$

$$1$$

$$\text{M} = \text{Li, Na, K}$$

Attempts to extend the carbonylation of trialkylboranes in the presence of lithium trimethoxyaluminohydride[4,5] to

**Table I. Rates of Carbonylation of the Alkali Metal Triethylborohydrides**

| borohydride[a] | temp., °C | time, h | % CO absorption |
|---|---|---|---|
| LiEt₃BH | −25 | <1 | 100 |
| NaEt₃BH | 25 | 12 | 92 |
| KEt₃BH | 25 | 25 | 0 |
| KEt₃BH[b] | −25 | <1 | 100 |

[a] The experiments were carried out using 10 mmol of the borohydride. [b] Approximately 10 mol % of excess Et₃B added.

triphenylborane encountered difficulties.[6] The reaction proved to be very sluggish, in contrast to the trialkylborane derivatives. In exploring possible routes around this difficulty, we examined the reaction of carbon monoxide with lithium, sodium, and potassium triethylborohydrides. The lithium compound reacted readily with carbon monoxide at −25 °C and atmospheric pressure. The potassium compound failed to react, even over 25 h at 25 °C. The sodium compound was intermediate in reactivity.

A possible explanation was suggested by the ^{11}B NMR spectra. Potassium triethylborohydride exhibits a well-defined doublet at $\delta$ −12.9, $J_{B-H}$ = 70 Hz, relative to BF₃·OEt₂. The spectrum for the sodium derivative is similar. The lithium compound as normally prepared exhibits a singlet at $\delta$ −11.1. Addition of small amounts of triethylborane to potassium triethylborohydride causes collapse of the doublet to a singlet, presumably the result of hydride exchange that is rapid relative to the NMR time scale (eq 2).

$$\text{KEt}_3\text{BH} + \text{BEt}_3 \rightleftharpoons \text{Et}_3\text{B} + \text{KEt}_3\text{BH} \qquad (2)$$
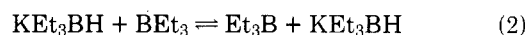
Thus, the singlet observed for the freshly prepared lithium salt presumably results from the presence of a small quantity of free triethylborane.

These ^{11}B NMR results suggested the possibility that the inertness of the potassium triethylborohydride toward carbon monoxide is due to the absence of free triethylborane. Indeed, the addition of ∼10 mol % of triethylborane to the reaction mixture caused both the collapse of the doublet and a rapid absorption of carbon monoxide complete in <1 h at −25 °C. These results are summarized in Table I.

A possible mechanism for the carbonylation is given in eq 3. Reversible coordination of the triethylborane with carbon monoxide is followed by reduction of the carbonyl adduct by the triethylborohydride.[7] Subsequent migration of an ethyl

$$\text{Et}_3\text{B} + \text{CO} \rightleftharpoons \overset{-}{\text{Et}_3}\overset{+}{\text{B}}{:}\text{C}{\equiv}\overset{+}{\text{O}}{:} \longleftrightarrow \overset{-}{\text{Et}_3}\overset{+}{\text{B}}{:}\text{C}{=}\overset{..}{\text{O}}{:}$$

$$\overset{-}{\text{Et}_3}\overset{+}{\text{B}}{:}\text{C}{=}\overset{..}{\text{O}}{:} + \text{MEt}_3\text{BH} \longrightarrow \overset{-+}{\text{Et}_2}\text{BCHOM} + \text{Et}_3\text{B} \qquad (3)$$
$$\qquad\qquad\qquad\qquad\qquad\quad |\!\!\nearrow$$
$$\qquad\qquad\qquad\qquad\qquad\text{Et}$$
$$\qquad\qquad\qquad\qquad\qquad\downarrow$$
$$\qquad\qquad\qquad\qquad\quad 1\,(\text{R} = \text{Et})$$

group from boron to carbon forms 1 (R = Et) and triethylborane. The latter is recycled until all the triethylborohydride
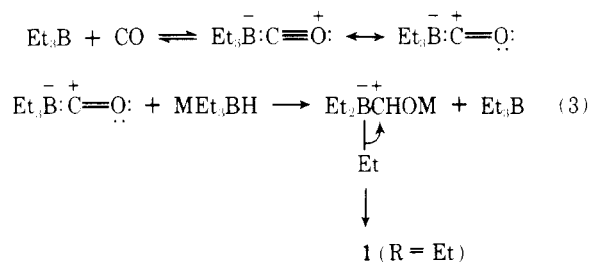
**Table II. Carbonylation of Alkali Metal Trialkylborohydrides at Atmospheric Pressure Followed by Hydrolysis or Oxidation[a,b]**

| MR₃BH | | workup procedure | product (% yield, GLC) |
|---|---|---|---|
| M | R₃B | | |
| lithium | triethylborane | hydrolysis[c] | 1-propanol (92)[f] |
| sodium | triethylborane | hydrolysis[c] | 1-propanol (71) |
| potassium | triethylborane | hydrolysis[c] | 1-propanol (80) |
| lithium | tri-*sec*-butylborane | hydrolysis[c] | 2-methyl-1-butanol (94)[f] |
| potassium | tri-*sec*-butylborane | hydrolysis[c] | 2-methyl-1-butanol (87) |
| lithium | tricyclopentylborane | hydrolysis[c] | cyclopentylmethanol (90) |
| sodium | tricyclohexylborane | hydrolysis[c] | cyclohexylmethanol (88) |
| lithium | B-*n*-butyl-9-BBN | hydrolysis[d] | 1-pentanol (98)[g] |
| lithium | B-cyclopentyl-9-BBN | oxidation | cyclopentylmethanal (85) |
| sodium | B-cyclopentyl-9-BBN | hydrolysis[d] | cyclopentylmethanol (86)[f] |
| lithium | B-cyclohexyl-9-BBN | hydrolysis[e] | cyclohexylmethanol (79) |

[a] Carbonylation at 25 °C unless stated otherwise. [b] Trialkylborohydrides prepared from trialkylboranes and the alkali metal hydrides except for the *sec*-butyl derivatives, which were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisc. [c] Heated to reflux with aqueous NaOH. [d] Heated to reflux with ethanol and aqueous NaOH. [e] Heated to reflux with ethanolic KOH. [f] Carbonylation at −25 °C. [g] Carbonylation at 0 °C.

is consumed. Thus the triethylborane serves as a catalyst in this reaction.

The product of this reaction must be an intermediate corresponding to 1 (R = ethyl), or an association product. Simple evaporation of the THF permits isolation of this intermediate. The $^{11}$B NMR spectrum exhibits a broad singlet at $\delta$ −2.74 in the lithium case, suggesting its possible existence as an "ate" complex in the form of the dimer 2. However, instead of ex-

$$\left[ \begin{array}{c} RHC \overset{O}{\diagdown} BR_2 \\ R_2B \underset{O}{\diagup} CHR \end{array} \right]^{2-} \quad 2Li^+$$

2
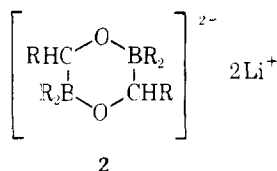
ploring the structure of these intermediates at this time, we preferred to establish that hydrolysis with base provided the homologated alcohols ($RCH_2OH$), and oxidation with hydrogen peroxide provided the corresponding aldehydes (RCHO), both in excellent yields. The procedure also provides a valuable new route to the intermediate, free of the aluminum alkoxides which accompanied earlier carbonylation procedures.

The reaction appears to be quite general. It was applied to representative trialkylboranes without difficulty. It also works quite satisfactorily with B-alkyl-9-BBN derivatives. The results are summarized in Table II.

The reaction was also successfully applied to lithium triphenylborohydride. Addition of a small amount of excess triphenylborane resulted in rapid carbonylation. (However, subsequent hydrolysis gave diphenylmethane, indicating a second migration.)

The reaction of alkali metal hydrides with trialkylboranes provides a convenient route, with only a few exceptions, to the alkali metal trialkylborohydrides.[8,9] This circumvents the need in most cases for utilizing either lithium trimethoxy-aluminohydride[4,5] or lithium tri-*tert*-butoxyaluminohydride,[10] thereby avoiding the presence of the corresponding aluminum alkoxide in the reaction mixture.

The following procedure for the carbonylation of lithium tri-*sec*-butylborohydride is representative. A dry 200-mL flask fitted with magnetic stirring bar and septum inlet was attached to the automatic gasimeter,[11,12] adapted for carbonylation as previously described.[13] The system was flushed with nitrogen while the flask cooled. It was then immersed in a dry ice/o-xylene bath at −25 °C. Lithium tri-*sec*-butylborohydride (9.6 mL, 1.04 M) in THF (10 mmol) was introduced. The system was flushed with carbon monoxide and vigorous stirring was begun. Carbon monoxide (10 mmol) was absorbed in approximately 18 min. The system was flushed with nitrogen and the reaction flask was transferred to a reflux condenser. Aqueous sodium hydroxide (10 mL, 3 N) was added and the mixture was heated to reflux for 2 h. After cooling, the flask was immersed in an ice bath and 4 mL of 30% hydrogen peroxide was added. The ice bath was removed and stirring was continued for 1 h at room temperature. *n*-Hexadecane (5 mmol; 1.46 mL) was added as an internal standard. Anhydrous potassium carbonate (14 g) was added and dissolved. The THF layer was separated and dried over anhydrous magnesium sulfate, and then powdered 3 Å molecular sieves. GLC analysis revealed 9.4 mmol of 2-methyl-1-butanol.

The present development emphasizes the value of $^{11}$B NMR in understanding the unusual phenomena often encountered in borane chemistry. We are continuing to explore the synthetic potential of this novel reaction.

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## 1-(Trimethylsilyl)benzene Oxides: Synthesis, Aromatization, and Reactions of Carbanions from Desilylation

*Summary:* The synthesis, acid-catalyzed aromatization, and reaction of carbanions from desilylation of 1-(trimethylsilyl)-benzene oxides are described.

*Sir:* Cleavage of the Si–O or, in certain cases, the Si–C bond by F$^-$ has become a useful transformation for organic synthesis.[1] Application of the reaction to simple α-(trimethylsilyl)oxiranes affords the corresponding oxiranyl anion that abstracts H$^+$ (or D$^+$) from the reaction medium to afford the desilylated epoxide.[2]

We wish to report the preparation and quantitative desilylation of 1-(trimethylsilyl)benzene oxide–oxepins 1a–c with F$^-$ under various conditions. Synthesis of 1a–c was effected by conversion of the known dienes 2a–c[3] to 3a–c[4] and subsequent elimination of HBr with DBN in THF to afford the arene oxides.[5,6] Whereas 1a and 1c reacted with 4-methyl-1,2,4-triazoline-3,5-dione to afford the expected Diels–Alder adducts 4a and 4c[7,8] from the benzene oxide valence isomer, 1b afforded adduct 5b[5,8] (100%) from reaction of the oxepin valence isomer. It is interesting to note that 2,7-dimethyloxepin reacts with azodicarboxylate esters to afford similar adducts from the oxepin valence isomer that are not stable but undergo Claisen rearrangement to a cyclopropyl ketone.[9] Adduct 5b is stable at room temperature.

Reaction of 1a–c with F$^-$ affords an anionic intermediate (6 or 7) that quantitatively abstracts H$^+$ (or D$^+$) from the reaction medium to afford exclusively 8a–c, i.e., no tautomerism of the anionic intermediate to phenoxide anion occurs under the reaction conditions (Table I). In acetonitrile the rate of desilylation of 1a with the different F$^-$ sources follows the order $(n\text{-Bu})_4NF \gg Et_4NF > KF/crown$ ether. The reaction in acetonitrile is immeasurably slow if an excess (20 equiv) of $H_2O$ is added, but the reaction in both acetonitrile and dimethyl sulfoxide occurs with 1 equiv of $H_2O$ ($D_2O$) present.