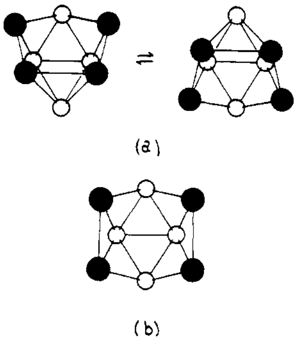

Figure 1. Possible structures for $(CH_3)_4C_4B_4H_4$. The closed circles represent C–CH_3 groups while the open circles represent B–H groups.

a CO and H_2 mixture.[6] Fractionation of the reaction resulted in the isolation of two new compounds. Compound I has an empirical formula $C_8B_4H_{16}$ ($^{12}C_8{}^{11}B_4{}^1H_{16}{}^+$, calcd 156.1625 amu, obsd 156.1608 amu), while compound II has an empirical formula $C_{12}B_4H_{22}$ ($^{12}C_{12}{}^{11}B_4{}^1H_{22}{}^+$, calcd 210.2095 amu, obsd 210.2094 amu). The former was produced with a net yield of ~10%, while the latter was isolated in trace quantities only. As the fraction containing I was contaminated with hydrocarbons of similar volatility, final purification was achieved by gas liquid chromatography. The pure material is a clear, colorless, air-stable liquid.

The mass spectrum of I exhibits little cage or hydrogen fragmentation which is consistent with a single carborane cage with no bridge hydrogens. The parent ion envelope requires no more than four borons while the p + 1 relative intensity is consistent with eight carbons. The gas phase infrared spectrum exhibits a very strong B–H stretch at 2550 cm^{-1}. The 25.2-MHz ^{11}B FTNMR spectrum in CD_2Cl_2 contains two heavily overlapped B–H doublets of equal area, with chemical shifts of -11.7 ppm ($J = 155$ Hz) and -12.5 ppm ($J = 195$ Hz) *upfield* relative to $BF_3 \cdot O(C_2H_5)_2$. The 100-MHz ^1H FTNMR spectrum contains a single sharp methyl resonance at δ 2.07 from -40 to 25 °C.

Compound I is formulated as $(CH_3)_4C_4B_4H_4$, the *C*-tetramethyl derivative of $C_4B_4H_8$, which is isoelectronic with the known compounds B_8H_{12} and $C_2B_6H_{10}$. The most probable structures of I are shown in Figure 1. Electron counting rules[7] suggest the nido structure (a) for I. This agrees with the ^1H NMR only if the molecule is fluxional above -40 °C as indicated. A static, arachno structure (b) is also consistent with the NMR results.[8] Note that B_8H_{12} is known to have the arachno structure in the solid state[9] and the arachno structure is preferred for $C_2B_6H_{10}$.[10]

On the basis of the mass spectrometric results alone, II is formulated as $(CH_3)_6C_6B_4H_4$, the *C*-methyl derivative of $C_6B_4H_{10}$, which is isoelectronic with the known compound, $C_2B_8H_{14}$.[11] Further characterization of II must await improvement in reaction yield; however, the existing evidence suggests that the reaction has produced the first example of a six-carbon carborane.

The mechanism whereby the carboranes are formed is unknown;[12] however, it is reasonable to assume that a reaction analogous to that occurring in the $C_4H_4Fe(CO)_3$ system takes place.[4] The fact that 2 and 3 mol of the alkyne are added to the borane fragment suggests a similarity to the pathway proposed for the cyclic polymerization of acetylenes by metal complexes.[13] The type of reaction observed here constitutes a new, rational route for the insertion of carbon atoms into the borane age. As it may be possible to use this method for the insertion of other atoms into cages, ferraboranes are potentially very useful synthetic intermediates.

Acknowledgment. The support of the National Science Foundation through Grant CHE75-10938 is gratefully acknowledged.

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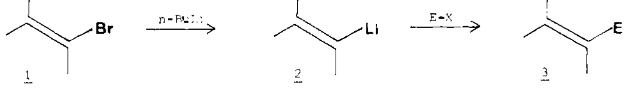
β-Lithioenamines. New Reagents for Synthesis

Sir:

We wish to report a general method for the synthesis of a new group of reagents, β-lithioenamines **2**; these are highly versatile synthetic intermediates, since their nonambident anions present an extremely nucleophilic carbon for electrophilic attack.

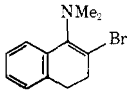
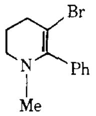
The β-lithioenamines **2** can be prepared quickly, in quantitative yield, by the halogen-metal exchange reaction of an organolithium compound (*n*-BuLi, *t*-BuLi) with a β-bromoenamine **1**.

The β-lithioenamines **2** react vigorously at low temperature with various electrophiles (H_2O, D_2O, I_2, RI, RCHO; see Table I), generating β-substituted enamines **3**.



A typical experiment consisted of adding *n*-butyllithium (4.5 mL of 1.3 M ether or hexane solution) dropwise to the β-bromoenamine **1d** (1.24 g, 5.0 mmol) in 10 mL of THF, at -70 °C, under nitrogen. After 10 min of stirring at -70 °C, a solution of methyl iodide (0.78 g, 5.5 mmol) in 1 mL of THF was added rapidly, while the internal temperature was maintained at about -65 to -70 °C. After addition was complete, the reaction mixture was allowed to warm to room temperature (~30 min), while stirring. The reaction mixture was then treated with 3 mL of 5 mM aqueous Na_2CO_3. The crude liquid was distilled (62 °C (0.75 mm)) to yield 0.67 g (75%) of 2,2-dimethyl-3-morpholino-3-pentene.

Table I. β-Lithioenamines. Synthesis and Reactions

	Conditions of Br–Li exchange using n-BuLi			Enamines 3	
β-Bromoenamines 1	Temp, °C	h	E (reagent)	% yield[a]	Bp, °C (mmHg)
$EtCBr{=}CHNC_4H_8O$ (**1a**)[b]	−70	1.5	Me (MeI)	45[c]	78 (20)
t-$BuCBr{=}CHNC_4H_8O$ (1b)[d]	−70	1.5	H (H_2O)	70[e]	87 (15)
			D (D_2O)	70[e]	87 (15)
			Me (MeI)	64[e]	96 (15)
			Et (EtI)	45[e]	68 (15)
t-$BuCBr{=}CHNEt_2$ (1c)[d]	−20	2.5	Me (MeI)	45[e]	65 (23)
t-$BuC(NC_4H_8O){=}CHBr$ (1d)[b]	−70	10 min[f]	Me (MeI)	75[g]	62 (0.75)
			n-Bu (n-BuI)	50[g]	92 (0.7)
			I (I_2)	50[g,h]	[h]
			MeCHOH– (MeCHO)	50[g]	95 (0.7)
$PhC(NMe_2){=}CHBr$ (1e)[i]	−70	0.5	Me (MeI)	60[c,j]	92 (15)[j]
			Et (EtI)	40[c]	80 (0.65)
			n-Bu (n-BuI)	45[c]	88 (0.8)
 (1f)[b]	−70	1	Me (MeI)	55[c]	96 (0.7)
 (1g)[b]	−70	1.5	Me (MeI)	65[c]	90 (0.6)
			n-Bu (n-BuI)	55[c]	105 (0.7)

[a] Yields of distilled products are given except where noted. The IR, NMR, and mass spectral data are fully compatible with the structures shown; purity was established by gas chromatography. [b] Prepared from the parent enamine according to the procedure of ref 2; the crude bromoenamine was used after filtration and removal of the solvents. Bromoenamine 1g and its parent enamine have already been reported: L. Duhamel and J. M. Poirier, *Tetrahedron Lett.*, 2437 (1976). [c] Based on parent nonhalogenated enamine. [d] Prepared from the bromoaldehyde according to the procedure cited in ref 1. [e] Based on distilled bromoenamine. [f] The quantitative bromine–lithium exchange was also observed with t-BuLi after 30 mn at −70 °C. [g] Based on crude bromoenamine. [h] The β-iodoenamine was decomposed by distillation. [i] Bromine (1.6 g, 10 mmol) in 10 mL of THF was added at −60 °C under nitrogen to dimethylamino 1-phenyl-1-ethylene (1.47 g, 10 mmol) in 25 mL of THF. The reaction mixture was allowed to warm up to 0 °C, and then 18 mL (23 mmol) of n-BuLi (1.3 M in ether solution) was added at −70 °C, [j] Based on 1-phenyl-1-propanone obtained by hydrolysis.

β-Bromoenamines are readily available either by reaction of secondary amines with α-halocarbonyl compounds,[1] or by bromination of the parent enamines and subsequent addition of 1 equiv of base to the intermediate α-bromoiminium salt.[2] If the base was a tertiary amine, such as triethylamine, the crude bromoenamine was used without distillation after filtering the triethylamine hydrobromide and removing the solvent under reduced pressure. When the base used was n-butyllithium, the β-lithioenamine was prepared in a one-pot reaction directly from the parent enamine, as indicated by the following equation.

$$PhC(NMe_2){=}CH_2 \xrightarrow[\text{2.2 equiv of } n\text{-BuLi, } -70°]{\text{1.1 equiv of } Br_2\text{, THF, } -60\ °C} PhC(NMe_2){=}CHLi$$

Bromine-lithium exchange reactions have been observed with various β-bromoenamines: open-chain aldo- and ketoenamines, **1a–d**, and cyclic and heterocyclic enamines, **1f** and **1g**. The ease of exchange decreases with crowding;[3] thus, at −70 °C, the halogen-metal exchange was complete with bromoenamine **1d** after a reaction period of only 10 min, whereas, with the more crowded isomeric β-bromoenamine **1b**, it was only 60% complete after 10 min. With the very crowded enamine **1c**, reaction was only 30% complete after 4.5 h at −70 °C; in this last case, the reaction rate was greatly accelerated by adding small amounts of HMPA (9:1 THF:HMPA, 70% after 4.5 h at −70 °C), or when the temperature was raised (100% after 2.5 h at − 20 °C).

Thus we have in hand β-lithioenamines which can serve in synthesis as equivalents of delocalized anions $^-CC{=}Z \leftrightarrow C{=}CZ^-$ (Z = O,[4] NR,[5-7] N-NMe_2[8]).

Several characteristic advantages of these reagents should be mentioned: (1) their formation is quantitative and rapid even from quite hindered bromoenamines; (2) their reactions with electrophiles are rapid even at very low temperature; (3) alkylation takes place without competitive N-alkylation or polysubstitution; (4) the resulting products are enamines which can be isolated or easily transformed into the corresponding carbonyl compounds.

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Reactions of Coordinated Molecules.
15. Preparation and Coordination of the Metallo Analogue of the Triacetylmethanide Anion, *fac*-$(OC)_3Re(CH_3CO)_3^{2-}$

Sir:

We recently reported the preparation of the metallo acetylacetonate anion, **1**, and its coordination to aluminum(III) ion affording the neutral, tris-chelate complex analogous to