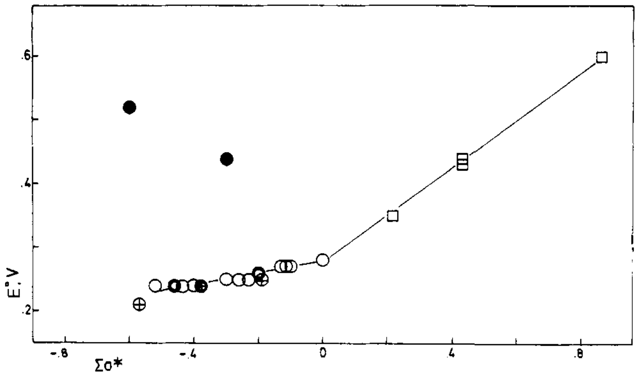


Figure 1. $E°$ vs. $\Sigma\sigma^*$ plot for some tetraalkylhydrazines: ○, *n*-alkyl compounds (ref 1, compounds **1–14**); ⊕, isopropyl, methyl substituted (ref 1, compounds **15–18**); ●, *tert*-butyltrimethyl and 1,2-di-*tert*-butyl-1,2-dimethyl (ref 1, compounds **19** and **20**); □, benzyl, methyl (Table I).

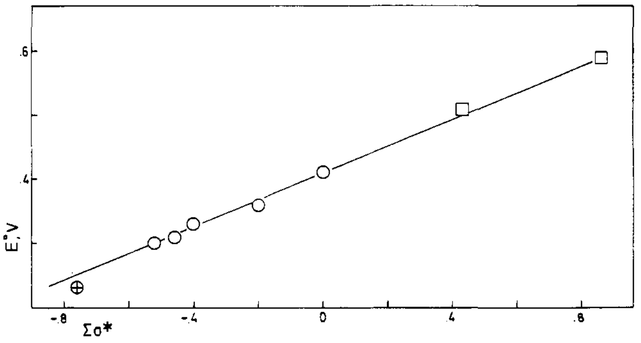
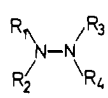
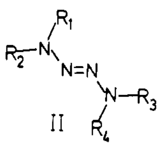


Figure 2. $E°$ vs. $\Sigma\sigma^*$ plot for the 2-tetrazenes of Table I.

seemed to us to be a crucial group to include, because it has the opposite sign for σ^* as saturated alkyl groups, eliminating the parallelism of Taft steric and electronic effects which has been emphasized by Charton.[10] A positive slope for an $E°$ vs. $\Sigma\sigma^*$ plot is expected, because a less electron-releasing alkyl group (more positive σ^*) should cause an electron to be removed less easily (more positive $E°$). Including data for benzylated hydrazines (see Table I) causes a sharp break in the Taft plot (Figure 1), which is roughly linear if either *n*-alkyl or benzyl, methyl substituted compounds are considered separately. Because benzyl is large, in addition to being electron withdrawing relative to methyl, perhaps the reason for the break in the correlation of Figure 1 is not a breakdown in Taft's σ^* values, but simply steric, benzyl raising $E°$ for the same reason that *tert*-butyl does. To test this hypothesis, $E°$ values for some



I



II

tetraalkyl-2-tetrazenes (II) were determined. There is a clear structural analogy between I and II, and the formal charge at the dialkyl nitrogen is nearly as high in $II^{+\cdot}$ as in $I^{+\cdot}$ (the dialkyl nitrogen ESR splitting constants for the tetramethyl cations are 13.1[4] and 10.9[12] G, an admittedly imperfect but highly indicative experimental measure of charge density for these systems). The key difference between I and II oxidation is the fact that little steric strain will be introduced upon flattening at the dialkylamino groups of II, in contrast to the case for I. As shown in Figure 2, the effect of alkyl group homologation upon $E°$ is significantly greater for II than for I, and the Taft plot is linear, including both *n*-alkyl[13] and benzyl substituted tetrazenes. These results indicate that $E°$ values for even tetra-*n*-alkylhydrazines are quite detectably influenced by steric differences, but that the electronic effect of changing alkyl group size is somewhat larger in magnitude.[14] Work intended to quantitatively separate the steric and electronic effects of alkyl group substitution upon I oxidation, using II as a model, is currently in progress.[15]

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(13) The downward deviation for tetraisopropyl-2-tetrazene apparent in Figure 2 might also be caused by a steric effect, release of R_1NR_2 interaction upon flattening at nitrogen. Experiments to elucidate this point are underway.

(14) Solvation effects are clearly of great importance in ionic reactions, as work like that of ref 8 shows. It is clear from IP_v data in the vapor phase that a far greater sensitivity to alkyl group homologation and α branching is observed in the absence of solvent.[1] Although σ^* values do a good job of quantitatively correlating the size of the effect for hydrazines, a better correlation is obtained by comparing one set of photoelectron spectroscopy data with another; see B. J. Cocksey, D. H. Eland, and W. Danby, *J. Chem. Soc. B*, 790 (1971). The solvation effect seems quite nonspecific for tetraalkylhydrazine oxidation, because the same $E°$ patterns are observed for solvents as different as acetonitrile and methylenene chloride.[1]

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Synthesis of $(CH_3)_4C_4B_4H_4$. An Example of Photochemical Addition of an Alkyne to a Borane via a Ferraborane Intermediate

Sir:

The production of carboranes from alkyne-boron hydride mixtures under various reaction conditions is well known.[1] However, carboranes containing other than two carbons are relatively rare.[2] In an examination of the electronic structure of some ferraboranes, similarities (and differences) were noted between the structures of $B_4H_8Fe(CO)_3$ and $C_4H_4Fe(CO)_3$.[3] Pettit has shown[4] that reactions between cyclobutadiene and unsaturated molecules coordinated to iron take place readily. Coordination of the unsaturated molecule to iron apparently occurs after the photolytic ejection of a carbon monoxide molecule from cyclobutadiene iron tricarbonyl. In the case of alkynes, this is followed by cycloaddition. An analogous reaction with the ferraborane would produce a carborane. Herein is reported evidence for the formation of two new carboranes by the photolysis of $B_4H_8Fe(CO)_3$ in the presence of 2-butyne. As the ferraborane itself is prepared by the direct reaction of $Fe(CO)_5$ and B_5H_9,[5] two readily available compounds, this constitutes a convenient route to these carboranes.

Irradiation at 254 nM of a bright orange solution of 0.6 mmol of $B_4H_8Fe(CO)_3$ and 20 mmol of 2-butyne in 2.8 mL of diethyl ether for 17 h in a Rayonet photochemical reactor resulted in a dark solution and the production of 1.8 mmol of

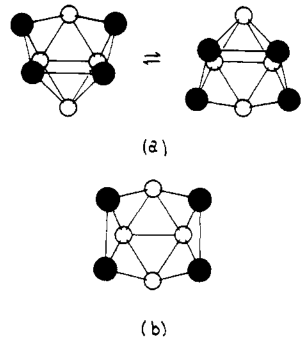

Figure 1. Possible structures for $(CH_3)_4C_4B_4H_4$. The closed circles represent C–CH_3 groups while the open circles represent B–H groups.

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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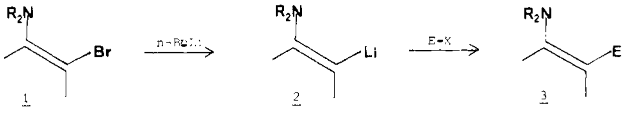
β-Lithioenamines. New Reagents for Synthesis

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.