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A NEW CLASS OF COMPOUNDS. ISOCYANIDE - BORANE ADDUCTS.

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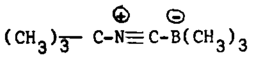
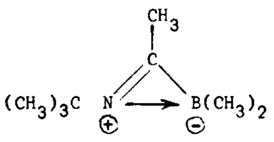
We wish to disclose evidence for the preparation of one member of a hitherto unreported class of compounds, and to note some of its interesting properties. When an equimolar mixture of t-butyl isocyanide[1] and trimethyl boron,[2] either without solvent or in diethyl ether, is warmed from -190° to -60°, a facile reaction ensues, evidenced by a rapid decrease in pressure. Upon removal of volatile materials at -20° in high vacuum, a white crystalline solid, m.p. 68-70°, is obtained in quantitative yield. The solid is air-sensitive and thermally unstable. We formulate this compound as the isocyanide-borane adduct (1) on the basis of the following evidence. Reaction occurs in a 1:1 stoichiometry, regardless of which reagent has been employed in a small excess. The proton resonance spectrum ($CDCl_3$, - 20°) consists of a symmetrical triplet at $\delta = 1.45$ ppm. ($J_{NH} = 2.0$ cps.) and a singlet at $\delta = -0.12$ ppm., relative to tetramethylsilane, in the area ratio of 1:1. These signals are attributed to C-methyl and B-methyl resonances, respectively. The appearance of a sharp triplet due to N-H spin-spin splitting indicates a high degree of electrical symmetry surrounding the nitrogen atom[3] and suggests a linear geometry for the adduct. Thus (1) is isosteric with di-t-butylacetylene. Whereas the chemical shift and coupling constant for the C-methyls are nearly the same as those reported for t-butyl isocyanide,[4] the B-methyl proton chemical shift occurs at 0.90 ppm. higher applied field

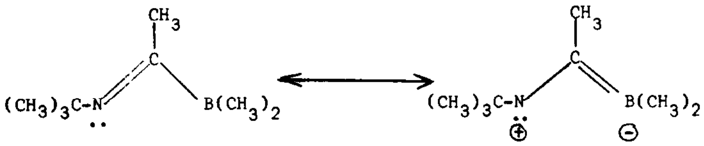


$(CH_3)_3-C-\overset{\oplus}{N}\equiv\overset{\ominus}{C}-B(CH_3)_3$

1



2a



2b

than that reported for trimethylboron.[5a,b] We take this as evidence that the adduct is largely associated in solution.[5b] Further, the chemical shifts of (1) are nearly unchanged in benzene or dioxane solutions. The infrared spectrum ($CDCl_3$) exhibits a strong absorption at 2247 cm.$^{-1}$ $(-\overset{\oplus}{N}\equiv\overset{\ominus}{C}:)$. The reported maximum for t-butyl isocyanide[6] is at 2134 cm.$^{-1}$. The magnitude of this frequency difference is nearly identical to that reported for tetrakis - (methyl isocyanide) cobalt (II),[7] and is of the same sign. The mass spectrum of compound (1) supports the 1:1 salt structure. Although a parent peak is absent, prominent peaks at mass M-15 $[(CH_3)_3CNC\overset{|}{B}(CH_3)_2]$, M-56 $[(CH_3)_3CNC-]$, M-71 $[-\overset{|}{\underset{|}{C}}-B(CH_3)_3]$, M-82 $[(CH_3)_3C-]$, and M-98$[-B(CH_3)_2]$ are in accord with the proposed structure for (1).

A correlation between B-methyl chemical shift and stability of the complex in trialkylboron adducts which was proposed by Coyle and Stone[5b] suggests that (1) should possess a stronger central C-B bond in solution than either thioether-boranes (δ = 0.78 ppm. for B-methyl), ether-boranes (δ = 0.78 ppm. for B-methyl), or amine-boranes (δ = 0.66 ppm. for B-methyl). This thesis is supported by our observation that a solution of (1) in diglyme does not evolve a substantial amount of *t*-butyl isocyanide upon treatment with hexadecylamine, even at 50°. That this phenomenon is due to equilibrium and not to kinetic control is ascertained from the fact that *t*-butyl isocyanide readily displaces trimethylamine from $(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{B}(CH_3)_3$ under less vigorous conditions. Adduct (1) does, however, exert a vapor pressure of approximately 1 mm. at 0°, and sublimes readily in high vacuum.

Whereas (1) reacts rapidly and in a complex manner with chloroform at room temperature, pure solid (1) isomerizes nearly quantitatively to yield (2) on long standing at room temperature in an evacuated tube. In contrast to (1), compound (2) is stable at room temperature, insensitive to air and moisture, and sublimes only slowly at 80-90°/0.1μ pressure. Compound (2) is soluble in ether, chloroform and benzene, but insoluble in water. It crystallizes as large, colorless plates from benzene, m.p. 119 - 120.5° (dec.). The proton resonance spectrum in benzene consists of three lines, with δ = 2.57 ppm. (very broad), δ = 1.18 ppm. (sharp), and δ = 0.20 ppm. (broad), in the area ratio of 1:3:2. We attribute these signals to $=\overset{|}{C}-CH_3$, $\underset{\oplus\;\ominus}{-\overset{|}{\underset{|}{C}}-CH_3}$, and $-\overset{|}{B}-CH_3$, respectively. The infrared spectrum no longer shows $-N\equiv C:$, but suggests $>C=N-$ ($\nu_{max.}$ 1548 cm.$^{-1}$). The mass spectrum of (2) is completely consistent with a monomeric structure, the most prominent peaks appearing at M-15 $[(CH_3)_3CNC(CH_3)\overset{|}{B}CH_3]$, M-41 $[(CH_3)_3CN\overset{|}{C}CH_3]$, and M-98 ($-B(CH_3)_2$ *or* $CH_3\overset{|}{C}=N-$). The absence of large peaks corresponding to (B-N) - containing fragments suggests that back-bonding, as represented in structure (2a) is weak of absent, and that (2) may be best represented as resonance hybrids (2b). Comparison of the observed B-methyl chemical shift to that of model compounds, vinyl dimethylborane[5a] (δ = 0.82 ppm.) and trimethylamine-borane (δ = 0.66 ppm.) indicates substantial charge character on the boron atom in (2). Quantitative elemental analysis affords C,69.1%; H,13.30%. Required for $C_8H_{18}NB$:C,69.09%; H,13.05%. While our data strongly support a monomeric structure for (2), examination of scale molecular models suggests that in less hindered systems dimerization to form a 2,5-dibora-2,5-dihydropyrazine ring is reasonable. Such a structure has been recently proposed for the product of a similar reaction.[8]

Thus a sequence of two simple, high yield reactions provide access to novel hetero-systems. Efforts to extend these reactions to isocyanide-boron hydride systems have thus far proven unfruitful, due to the extreme vigor with which the first and subsequent reactions occur.

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