Notes

Contribution from the Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey

Reaction Products from Decaborane and Amides

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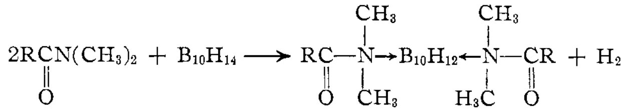
Nitriles,[1] amines,[2] or phosphines[3] possess one site for electrophilic attack by decaborane, whereas the amides possess two potential sites, the amido oxygen and nitrogen. These two nucleophilic centers in the amides can presumably bond to boron; but as will be shown in this note preferential nucleophilic attack on the decaborane takes place with nitrogen to give a 6,9-disubstituted compound. These findings are consistent with the thermodynamic calculations of Skinner[4] which show that nitrogen is more effective than oxygen in back coordination with boron.

Other workers have reported the formation of bis(amide)decaborane products[5,6] from tertiary amides and decaborane. In one case the product is broadly characterized as an $L_2B_{10}H_{12}$ product,[5] and, in the other case,[6] preferential attack at the oxygen is indicated.

In this study the interaction of tertiary, secondary, and primary amides with decaborane was studied and in each case infrared evidence indicates preferential nitrogen–boron interaction. The tertiary and secondary amides interacted with decaborane at temperatures below 50° to form an amidodecaborane and evolved 1 mole of hydrogen per mole of decaborane consumed. The resultant products were white to off-white crystalline materials which show C=O stretch absorptions ("amide I band") in the infrared. At higher temperatures (>70°) a supervening reaction occurs and additional hydrogen is evolved; the products change from white, crystalline powders to orange-red resins, and the infrared absorption pattern shows a diminution of absorption at the C=O stretching mode frequency. The appearance of a new band we attribute to C—O—B is indicative of intial attack at the –N: site. With primary amides little or no reaction occurs at ambient temperatures and higher temperatures are necessary for compounds to form. The reactions at higher temperatures occur with the evolution of 2 moles of hydrogen, presumably 1 mole from decaborane and 0.5 mole from each mole of amide entering into reaction. The primary amide–decaborane infrared spectra reveal an –NH absorption and no $-NH_2$ absorption; it is most likely that a covalent N–B bond is formed as opposed to the coordinate covalent N–B bond formed with the tertiary and secondary amides.

Results

Treatment of decaborane with the tertiary amides N,N-dimethylacetamide and N,N-dimethylformamide in benzene at room temperature for 24–48 hr. resulted in the formation of a benzene-insoluble bis(amide)-decaborane and the evolution of approximately 1 mole of hydrogen per mole of $B_{10}H_{14}$ consumed.



$$2\underset{\underset{\textstyle O}{\|}}{RC}N(CH_3)_2 + B_{10}H_{14} \longrightarrow \underset{\underset{\textstyle O}{\|}}{RC}\text{—}\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{N}}\!\rightarrow\! B_{10}H_{12}\!\leftarrow\!\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle H_3C}{|}}{N}}\text{—}\underset{\underset{\textstyle O}{\|}}{CR} + H_2$$

Variation of the amide–decaborane mole ratio over the range 6:1 to 1:2 resulted in the same over-all stoichiometry. The rate of reaction of dimethylacetamide was greater than that of dimethylformamide, an effect consistent with the relative base strengths of these two amides.

In a typical experiment 8.7 g. (0.1 mole) of dimethylacetamide dissolved in 120 ml. of dry benzene was added dropwise at room temperature to 6.1 g. (0.05 mole) of decaborane dissolved in 600 ml. of dry benzene. The reaction mixture was heated to 50–52° and maintained at this temperature for 5 hr. The resultant white solid was filtered and washed with dry benzene to yield 8.1 g. of dry bis(N,N-dimethylacetamide)decaborane (I), m.p. 137–138° dec. It is slightly soluble at room temperature in ethyl acetate, acetone, diglyme, and ethyl alcohol and is insoluble in benzene and alkanes. *Anal.* Calcd. for $C_8H_{30}O_2N_2B_{10}$ (2:1 mole ratio of dimethylacetamide to decaborane): B, 36.73; N, 9.52. Found: B, 35.43; N, 9.91. The infrared spectrum[7] of I contains a strong B–H stretching absorption at 2500 cm.$^{-1}$, a BH deformation at 990 cm.$^{-1}$, and an amide I band at 1629 cm.$^{-1}$. The B–H–B bridge could not be detected.

Bis(dimethylformamide)decaborane (II) was a white crystalline solid which decomposed at 156–157° without liquefaction. It is slightly soluble in formamide and soluble in nitrobenzene. The infrared spectrum of II contains a strong B—H stretch absorption at 2494 cm.$^{-1}$ and a C=O stretch (the "amide I band") at 1675 cm.$^{-1}$. The B—H—B bridge absorption at 1812 cm.$^{-1}$ is noticeably absent, as it also was found to be in 6,9-bis(acetonitrile)decaborane. Hence, we believe that the amidodecaboranes are 6,9-disubstituted, as is the acetonitrile analog.[8]

The interaction of three secondary amides (N-methylformamide, N-methylacetamide, and 2-pyrollidone) with decaborane was studied. The reactions were con-

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[6] R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

[7] All infrared spectra obtained on KBr pellets in a Perkin-Elmer Model 21 infrared recording spectrophotometer.

[8] J. V. M. Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

ducted in benzene and at ambient temperature for 24–72 hr.; benzene-insoluble crystalline products were obtained. Gas evolution was between 0.9 and 1.0 mole per mole of decaborane utilized.

Bis(N-methylformamide)decaborane (III) was an off-white solid which neither melted nor decomposed up to 250°. The infrared spectrum of III displayed an NH stretch at 3300 cm.$^{-1}$, a B—H stretching frequency at 2488 cm.$^{-1}$, and a C=O stretch at 1669 cm.$^{-1}$. Once again the B—H—B absorption was not present. (*Caution!*—The product stored in a vial, presumably under nitrogen, detonated spontaneously while awaiting elemental analysis.)

Bis(N-methylacetamide)decaborane (IV) was a white solid which decomposed at about 200° with no liquefaction to 305°. *Anal.* Calcd. for $B_{10}H_{12} \cdot 2CH_3C(=O)NH(CH_3)$: B, 40.60. Found: B, 40.90. The infrared spectrum of IV displayed stretching frequencies at 3333 cm.$^{-1}$ (-NH), 2488 cm.$^{-1}$ (B—H), 1005 cm.$^{-1}$ (B—H deformation), and 1634 cm.$^{-1}$ (C=O); no B—H—B bridge absorption was evident. The rate of reaction of N-methylacetamide with decaborane was slower than the interaction of decaborane with N,N-dimethylformamide.

The proposed reaction for the above two materials is essentially the same as that shown previously.

In contrast to the previous products the interaction of 2-pyrollidone with decaborane produced a 3:1 product with the evolution of 1 mole of gas per mole of decaborane utilized. The third mole of 2-pyrollidone may be present as a mole of solvation, *i.e.*, $(Pyr)_2B_{14}H_{12}Pyr$, or of the form $PyrH^+[B_{10}H_{11}Pyr,Pyr]$. The product, bis(2-pyrollidone)decaborane pyrollidonate (V) starts to decompose at 200°; no liquefaction occurs to 305°. *Anal.* Calcd. for $B_{10}H_{12} \cdot 3C_4H_7NO$: B, 28.8. Found: B, 28.7. The infrared spectrum of V displays the NH stretch at 3356 cm.$^{-1}$, the B—H absorption at 2500 cm.$^{-1}$, and the C=O stretching frequency at 1656 and 1653 cm.$^{-1}$; no B—H—B bridge absorption was displayed.

In marked contrast to the tertiary and secondary amides, the primary amides (formamide, acetamide, adipamide, and acrylamide) underwent little or no reaction at ambient temperatures. At 40° acetamide interacted with decaborane to produce 2 moles of hydrogen per mole of decaborane consumed. A white solid product was isolated (VI) which did not melt to 250° but which did change color from white to orange as it was heated. The product was soluble in alcohol (with decomposition), ethyl acetate, dimethylformamide, pyridine (with formation of a yellow color), and diglyme (formation of a transitory blue color). The infrared spectrum of VI contains an -NH stretch at 3367 cm.$^{-1}$ a B—H stretch at 2513 cm.$^{-1}$, a B—H deformation at 1010 cm.$^{-1}$, and a C=O doublet at 1672 and 1650 cm.$^{-1}$. These data are consistent with the formation of a covalent compound; the $B_{10}H_{10}^{2-}$ compound would be expected to show absorption peaks[6] at about 2450 and 1034 cm.$^{-1}$. When the reaction was conducted at benzene reflux an orange product was isolated with respective absorptions at 3356, 2525, and 1656 cm.$^{-1}$. The latter spectrum lacked definition about 1429 cm.$^{-1}$ and the C=O absorption was diminished.

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Copper(II) Complexes of Secondary and Tertiary N-Substituted Ethylenediamines

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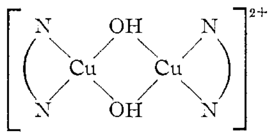
Several investigators[2-4] have reported that secondary and tertiary ethylenediamines such as N-methyl-N,N′-diethyl-, N,N,N′-triethyl-, and N,N′-diisopropylethylenediamine form hydroxy-bridged dinuclear complexes of the type



in aqueous solutions instead of the normal bis and tris amine complexes. Measurements[5-7] of the formation constants between Cu(II) and N-alkyl-substituted ethylenediamines demonstrate that the first and, especially, the second formation constant is lower than for ethylenediamine. Steric requirements of the ligands have been invoked to explain both the lower formation constants and formation of the dinuclear complexes, but since the majority of the work was done in aqueous solutions, the equilibria and complex formation are affected by solvation terms, ion-pair association, and entropy effects.[8-10]

In order to resolve the apparent paradox between the instability of secondary and tertiary amine–metal complexes and amine basicity toward the proton, we[11,12] have studied transition metal coordination complexes of N-substituted ethylenediamines. This paper re-

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[1] Abstracted from the M.S. Thesis of S. A. E. at The Ohio State University, June 1963. National Science Foundation Fellow, Summer 1962.

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