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Chemistry of Boranes. XXIV.[1] Carbonylation of Derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ with Oxalyl Chloride[2]

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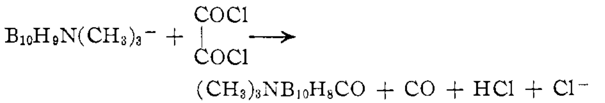
Reaction of oxalyl chloride with $1\text{-}B_{10}H_9S(CH_3)_2^-$, $B_{12}H_{11}N(CH_3)_3^-$, and $2\text{-}B_{10}H_9N(CH_3)_3^-$ gave, respectively, $1,6\text{-}(CH_3)_2SB_{10}H_8CO$, $(CH_3)_3NB_{12}H_{10}CO$, and 2,4- and $2,7(8)\text{-}(CH_3)_3NB_{10}H_8CO$. Resolution of the 2,7(8)- isomer of $(CH_3)_3NB_{10}H_8CO$ was achieved, and the (+) isomer converted to $(+)2,7\text{-}B_{10}H_8[N(CH_3)_3]_2$, which confirms the assigned stereochemistry. Reaction of $1,6\text{-}(CH_3)_2SB_{10}H_8CO$ with nitrous acid gave the trisubstituted derivative $1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2$, which was converted to $1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}NH_2\text{-}10\text{-}N_2$, $(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}NC_5H_5$, and related derivatives. The significance of the high stereospecificity exhibited by oxalyl chloride is discussed.

A recent report[3] has described the preparation of $B_{12}H_{10}(CO)_2$ and $1,10\text{-}B_{10}H_8(CO)_2$ by reaction of carbon monoxide with $H_2B_{12}H_{12}\cdot xH_2O$ and $1,10\text{-}B_{10}H_8(N_2)_2$, respectively. The broad chemistry found for these carbonyls emphasized the need to investigate the preparation and chemistry of monocarbonyl derivatives of polyhedral boranes.

Results

$(CH_3)_3NB_{10}H_8CO$.—Oxalyl chloride reacted with $2\text{-}B_{10}H_9N(CH_3)_3^{-}$ [4] in acetonitrile solution at room temperature to give $(CH_3)_3NB_{10}H_8CO$ (**1**) in high yield (up to 87%) as a colorless sublimable solid (eq. 1). Under these conditions, the reaction was complete within 10 min. as evidenced by cessation of carbon monoxide evolution. Chemically, the carbonyl group of **1** appears to be similar to those of $1,10\text{-}B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$.[3] Treatment of **1** with hydroxylamine-O-sulfonic acid[3,5] gave $(CH_3)_3NB_{10}H_8NH_3$ which was methylated[4] to give $B_{10}H_8[N(CH_3)_3]_2$ (**2**) (eq. 2). Comparison of the X-ray powder pattern of **2** with those of 2,4- and $2,7(8)\text{-}B_{10}H_8[N(CH_3)_3]_2$[4] showed that **2** was indeed a mixture of these isomers. A quantitative estimate of the isomeric composition of the carbonyl derivative **1** was obtained by gas chromatography which showed 34% 2,4- and 66% $2,7(8)\text{-}(CH_3)_3NB_{10}H_8CO$ in a sample representing an 87% yield preparation. The composition of the product did not change significantly in runs where lower yields were obtained.



$$B_{10}H_9N(CH_3)_3^- + \begin{matrix}COCl\\ |\\ COCl\end{matrix} \longrightarrow \underset{\mathbf{1}}{(CH_3)_3NB_{10}H_8CO} + CO + HCl + Cl^- \quad (1)$$

$$\underset{\mathbf{1}}{(CH_3)_3NB_{10}H_8CO} \xrightarrow[H_2O]{NH_2OSO_3H} (CH_3)_3NB_{10}H_8NH_3 \xrightarrow[NaOH]{(CH_3)_2SO_4} \underset{\mathbf{2}}{B_{10}H_8[N(CH_3)_3]_2} \quad (2)$$

Resolution of $2,7(8)\text{-}(CH_3)_3NB_{10}H_8CO$.—Treatment of an aqueous solution of $H_3O(CH_3)_3NB_{10}H_8COOH$ with a solution of brucine in dilute hydrochloric acid gave a precipitate of the brucine salt of $(CH_3)_3NB_{10}H_8CO\text{-}OH^-$. Extraction of the crude salt with warm ethanol removed the relatively soluble brucine salt of $2,4\text{-}(CH_3)_3NB_{10}H_8COOH^-$, leaving a reasonably pure diastereomeric mixture of brucine salts of 2,7- and $2,8\text{-}(CH_3)_3NB_{10}H_8COOH^-$. Fractional crystallization of the diastereomeric mixture from ethanol–acetonitrile gave crystals which could be decomposed to (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$ which after sublimation had $[\alpha]_D$ +22°. Decomposition of the brucine salt obtained from the mother liquors gave (−)2,8- (or 2,7-) $(CH_3)_3NB_{10}H_8CO$ with $[\alpha]_D$ −14°. Gas chromatography of (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$ showed it to be free of 2,4- isomer and confirmed the assignment of peaks in the gas chromatogram of crude **1**. (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$ ($[\alpha]_D$ 22°) was converted as shown in eq. 2 to (+)2,7- (or 2,8-) $B_{10}H_8[N(CH_3)_3]_2$ with $[\alpha]_D$ +13°. The configurational relationship of (+)**1** and (+)**2** is supported by the optical rotatory dispersion data which were described earlier.[2]

$(CH_3)_3NB_{12}H_{10}CO$.—Reaction of $B_{12}H_{11}N(CH_3)_3$[6] with oxalyl chloride in refluxing acetonitrile proceeded slowly to give $(CH_3)_3NB_{12}H_{10}CO$ (**3**) in low yield. In order to determine the stereochemistry of the product a sample of **3** was converted to $B_{12}H_{10}[N(CH_3)_3]_2$ (**4**) as shown in eq. 3. Thin-layer chromatography of **4** on silica gel showed the presence of 1,12- and 1,7-, but no $1,2\text{-}B_{12}H_{10}[N(CH_3)_3]_2$.[4] Thus, **3** must be a mixture of 1,7- and 1,12- isomers.

$$\underset{\mathbf{3}}{(CH_3)_3NB_{12}H_{10}CO} \xrightarrow[H_2O]{NH_2OSO_3H} (CH_3)_3NB_{12}H_{10}NH_3 \xrightarrow[NaOH]{(CH_3)_2SO_4} \underset{\mathbf{4}}{B_{12}H_{10}[N(CH_3)_3]_2} \quad (3)$$

$(CH_3)_2SB_{10}H_8CO$.—Oxalyl chloride reacted with $Cs[1\text{-}B_{10}H_9S(CH_3)_2]$[1,7] in refluxing acetonitrile to give $1,6\text{-}(CH_3)_2SB_{10}H_8CO$ (**5**) in good yield. The stereochemi-

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[1] Part XXIII: W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, **4**, 280 (1965).

[2] (a) A portion of this work was reported in preliminary form: W. R. Hertler, *J. Am. Chem. Soc.*, **86**, 2949 (1964). (b) Systematic names for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are decahydrodecaborate(2−) and dodecahydrododecaborate(2−), respectively.

[3] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *ibid.*, **86**, 115 (1964).

[4] W. R. Hertler and M. S. Raasch, *ibid.*, **86**, 3661 (1964).

[5] This reaction has recently been applied to organic carboxylic acids by G. B. Bachman and J. E. Goldmacher *J. Org. Chem.*, **29**, 2576 (1964).

[6] H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

[7] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L Muetterties, *ibid.*, **84**, 1056 (1962).

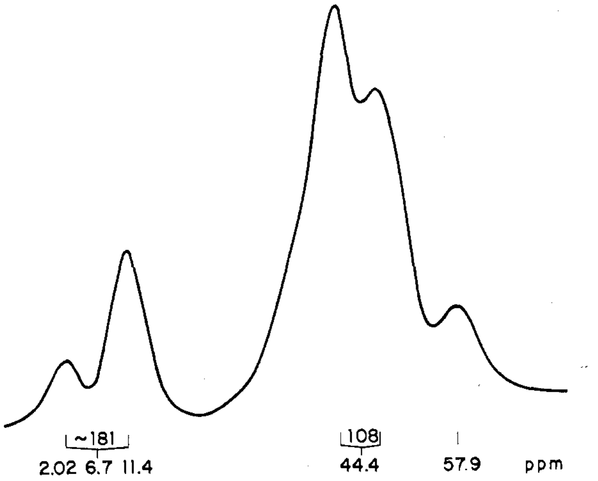


Figure 1.—B^{11} n.m.r. spectrum of 1,6-$(CH_3)_2SB_{10}H_8CO$ in acetone (*J* in c.p.s.).

cal assignment is based on the conversion of **5** to 1,6-$(CH_3)_2SB_{10}H_8NH_3$ (**6**) with hydroxylamine-O-sulfonic acid (eq. 4). The **6** obtained from this reaction is identical with 1,6-$(CH_3)_2SB_{10}H_8NH_3$ prepared earlier by two other methods.[4] Recent correlations have confirmed the 1,6- assignment for **6**.[1] The assignment of the carbonyl group to an equatorial boron atom is corroborated by the B^{11} n.m.r. spectrum (Figure 1) which is discussed in the Experimental section.

$$\underset{\mathbf{5}}{1,6\text{-}(CH_3)_2SB_{10}H_8CO} \xrightarrow[H_2O]{NH_2OSO_3H} \underset{\mathbf{6}}{1,6\text{-}(CH_3)_2SB_{10}H_8NH_3} \qquad (4)$$

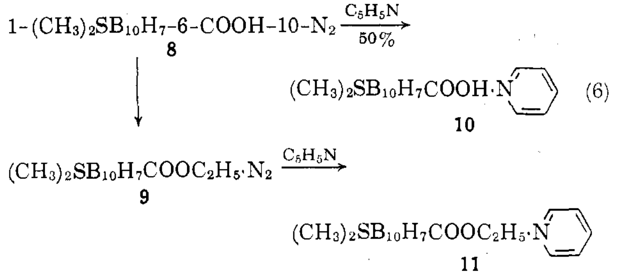
Treatment of aqueous **5** with tetramethylammonium chloride gave $(CH_3)_4N[1,6\text{-}(CH_3)_2SB_{10}H_8COOH]$ which, in agreement with the assigned structure, is soluble in dilute aqueous sodium hydroxide, but insoluble in dilute acid.

Addition of **5** to alkaline hydrogen peroxide led to a vigorous reaction and formation of 1,6-$(CH_3)_2SB_{10}H_8OH^-$ which was isolated as the tetramethylammonium salt (**7**). The stereochemical assignment for **7** is based on the assumption that no stereochemical change occurs in the conversion of the carbonyl group to a hydroxyl group. Recent studies have shown that while thermal rearrangements of substituted derivatives of $B_{10}H_{10}^{2-}$ do occur, they are high-energy processes not likely to be encountered under the usual reaction conditions.[8] Of particular significance is the fact that **7** is identical with the $(CH_3)_4N[(CH_3)_2SB_{10}H_8OH]$ prepared by other methods.[1] This confirms the equatorial assignment for the hydroxyl group in the latter material[1] and, hence, in 2-$B_{10}H_9OH^{2-}$,[7,9] which has been correlated with **7**.[1]

$(CH_3)_2SB_{10}H_7COOH\cdot N_2$.—Treatment of aqueous $(CH_3)_2SB_{10}H_8CO$ with nitrous acid (eq. 5) gave a yellow precipitate which on reduction with zinc and hydrochloric acid gave $(CH_3)_2SB_{10}H_7COOH\cdot N_2$ (**8**). Since nitrous acid has already been shown to attack $B_{10}H_{10}^{2-}$ [3] and its derivatives[1,8] preferentially at the apical positions, it is *presumed* that the diazonium group in **8** is located on the apex adjacent to the carboxyl group (*i.e.*, 1,6,10- stereochemistry). The powerful electron-donating ability of the polyhedron in spite of the presence of two cationic substituents is attested by the pK_a of **8**, which is 8.0 in 50% aqueous ethanol (for benzoic acid pK_a = 5.65). Esterification of **8** was readily accomplished with ethanolic hydrogen chloride, which gave 1-$(CH_3)_2SB_{10}H_7$-6-$COOC_2H_5$-10-N_2 (**9**) in quantitative yield.

$$\underset{\mathbf{5}}{1,6\text{-}(CH_3)_2SB_{10}H_8CO} + \xrightarrow[2.\ Zn\text{-}HCl]{1.\ HONO,\ H_2O} \underset{\mathbf{8}}{(CH_3)_2SB_{10}H_7COOH\cdot N_2} \qquad (5)$$

Replacement of the diazonium group of **8** occurred in refluxing pyridine to give the pyridinium zwitterion **10** (see eq. 6). The corresponding ethyl ester **11** was prepared from **9** and refluxing pyridine. It is assumed that the stereochemistry of **8** is retained in **9**, **10**, and **11**.



$$\begin{tikzcd}
\underset{\mathbf{8}}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2} \arrow[r, "C_5H_5N", "50\%"'] \arrow[d] & \underset{\mathbf{10}}{(CH_3)_2SB_{10}H_7COOH\cdot NC_5H_5} \\
\underset{\mathbf{9}}{(CH_3)_2SB_{10}H_7COOC_2H_5\cdot N_2} \arrow[r, "C_5H_5N"] & \underset{\mathbf{11}}{(CH_3)_2SB_{10}H_7COOC_2H_5\cdot NC_5H_5}
\end{tikzcd} \qquad (6)$$

1-$(CH_3)_2SB_{10}H_7$-6-NH_2-10-N_2.—Replacement of the carboxyl group of **8** with an amino group was accomplished as shown in eq. 7 by conversion to an acyl chloride and thence to an isocyanate which was hydrolyzed to $(CH_3)_2SB_{10}H_7NH_2\cdot N_2$ (**12**). A salt (**13**) of the amine **12** was prepared with $H_2B_{12}Cl_{12}$.[10] The amine salt **13** was also obtained by treatment of **8** with hydroxylamine-O-sulfonic acid[3] followed by $B_{12}Cl_{12}^{2-}$ (eq. 8) or by treatment of **8** with hydrazoic acid and $B_{12}Cl_{12}^{2-}$ (eq. 9).

$$\begin{tikzcd}
\underset{\mathbf{8}}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2} \arrow[r, "(COCl)_2"] & (CH_3)_2SB_{10}H_7COCl\cdot N_2 \arrow[d, "NaN_3"] \\
\underset{\mathbf{12}}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}NH_2\text{-}10\text{-}N_2} \arrow[r, "1.\ HCl", "2.\ NaOH"'] \arrow[d, "H_2B_{12}Cl_{12}"] & (CH_3)_2SB_{10}H_7NCO\cdot N_2 \\
\underset{\mathbf{13}}{[(CH_3)_2SB_{10}H_7NH_3\cdot N_2]_2B_{12}Cl_{12}} &
\end{tikzcd} \qquad (7)$$

$$\underset{\mathbf{8}}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2} \xrightarrow[B_{12}Cl_{12}^{2-}]{NH_2OSO_3H} \underset{\mathbf{13}}{[(CH_3)_2SB_{10}H_7NH_3\cdot N_2]_2B_{12}Cl_{12}} \qquad (8)$$

$$\underset{\mathbf{8}}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2} \xrightarrow[H_2B_{12}Cl_{12}]{NaN_3} \underset{\mathbf{13}}{[(CH_3)_2SB_{10}H_7NH_3\cdot N_2]_2B_{12}Cl_{12}} \qquad (9)$$

Discussion

The reaction of oxalyl chloride with substituted derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is best understood as an electrophilic substitution on the polyhedral borane

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[8] W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 5434 (1964).

[9] W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, **86**, 3973 (1964).

[10] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

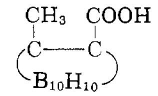
anion since a boron–carbon bond rather than a boron–oxygen bond is formed. It is difficult to conceive of a carbon atom of oxalyl chloride being involved in a nucleophilic attack on a boron atom. The greater reactivity of 2-$B_{10}H_9N(CH_3)_3^-$ than $B_{12}H_{11}N(CH_3)_3^-$ toward oxalyl chloride is consistent with the assumption of an electrophilic substitution process since, in general, derivatives of $B_{10}H_{10}^{2-}$ have been observed to be more reactive toward electrophilic reagents than are the corresponding derivatives of $B_{12}H_{12}^{2-}$. It seems reasonable to assume that the initial product of the reaction between oxalyl chloride and 2-$B_{10}H_9N(CH_3)_3^-$ is an α-ketoacyl chloride which then decomposes rapidly to the observed borane carbonyl, carbon monoxide, and chloride ion (eq. 1).

The stereochemical results of this reaction are of special significance. In its reactions with 1-$B_{10}H_9S(CH_3)_2^-$ and 2-$B_{10}H_9N(CH_3)_3^-$, oxalyl chloride exhibits a high selectivity for equatorial positions. No apical carbonylation was detected in either $(CH_3)_2SB_{10}H_8CO$ (**5**) or $(CH_3)_3NB_{10}H_8CO$ (**1**), and because of the high yield in the latter case we can assign a *minimum* value of 6.7 to the ratio of equatorial/apical substitution. LCAO–MO calculations for $B_{10}H_{10}^{2-}$ [11,12] have placed greater electron density at the apical positions than at the equatorial positions in the ground state, and this result led to the prediction[13] that electrophilic substitution of $B_{10}H_{10}^{2-}$ and 1-$B_{10}H_9X^{2-}$ should occur preferentially at the apex. Although several examples of apical electrophilic substitution on $B_{10}H_{10}^{2-}$ have been reported,[1,3,7,8] there have also been instances where electrophilic substitution reactions have led to predominantly equatorial products.[3,9,14] In the reaction of oxalyl chloride with 2-$B_{10}H_9N(CH_3)_3^-$, our results show a greater than statistical preference for equatorial substitution. If ground-state electron density is really a factor in producing apical substitution in, for instance, the reaction of nitrous acid with $B_{10}H_{10}^{2-}$,[3] 1-$B_{10}H_9S(CH_3)_2^-$,[1] and 2-$B_{10}H_9N(CH_3)_3^-$,[8] the question immediately arises as to why the reaction of oxalyl chloride with 1-$B_{10}H_9S(CH_3)_2^-$ and 2-$B_{10}H_9N(CH_3)_3^-$ produces exclusively equatorial substitution. This question cannot be answered at present since position of substitution must be intimately related to mechanism of substitution (or more precisely to structures of transition states in substitution reactions), and no detailed mechanistic studies for any electrophilic substitution reaction of $B_{10}H_{10}^{2-}$ or its derivatives have been reported. The differences in stereochemical behavior of nitrous acid and oxalyl chloride may reflect the operation of two grossly different mechanisms of substitution, or, alternatively, the mechanisms may be similar and the stereochemical results may arise from factors such as solvent, temperature, and steric effects. Further studies are clearly necessary to provide a basis for rationalization of stereochemical consequences of electrophilic substitution reactions on $B_{10}H_{10}^{2-}$ and its derivatives. The information which is now available, however, does not seem to support a general correlation of position of substitution with ground-state electron density.

Another interesting feature of the reaction of oxalyl chloride with substituted derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is the fact that no substitution occurred at positions adjacent to the substituted boron atoms. Specifically, no 1,2-$(CH_3)_3NB_{12}H_{10}CO$, 1,2-$(CH_3)_2SB_{10}H_8CO$, or 2,3-, 2,1-, or 2,6(9)-$(CH_3)_3NB_{10}H_8CO$ was formed. This contrasts with the reaction of hydroxylamine-O-sulfonic acid with substituted derivatives of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ in which minor amounts of vicinally substituted products were obtained,[4] and the reaction of dimethyl sulfoxide with 2-$B_{10}H_9N(CH_3)_3^-$ in which a small amount of 1,2-$(CH_3)_2SB_{10}H_8N(CH_3)_3$ was formed.[1] Apparently oxalyl chloride shows a higher degree of sensitivity to steric and/or electronic effects of the substituents than does hydroxylamine-O-sulfonic acid or dimethyl sulfoxide.

The stereochemical assignments for 2,7(8)-$B_{10}H_8[N(CH_3)_2CH_2Cl]_2$[14] and 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$[4] (based on B^{11} n.m.r. spectral data) have been confirmed by the resolution of 2,7(8)-$(CH_3)_3NB_{10}H_8CO$ followed by conversion to optically active 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$. The only stereochemistry possible for an optically active $B_{10}H_8[N(CH_3)_3]_2$ is 2,7(8)- or 2,6(9)-. 2,7(8)- stereochemistry seems more reasonable than 2,6(9)- stereochemistry on both steric and electronic grounds, especially in the case of $B_{10}H_8[N(CH_3)_2CH_2Cl]_2$.[14]

A limited comparison of the electronic effects of the formally neutral acid $(CH_3)_2SB_{10}H_8COOH \cdot N_2$ (**8**) with those of other neutral polyhedral systems, 1-methyl-2-carboranylcarboxylic acid (**14**) and neo-1-methyl-carboranylcarboxylic acid (**15**)[15] can be made by comparing acid strengths. The pK_a of **8** is 8.00, while the pK_a values of **14** and **15** are 2.74 and 3.14, respectively.[15]



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Thus, at least with respect to substituents on the cage carbon atoms, the carborane and neocarborane polyhedra are electron withdrawing relative to a benzene ring while the B_{10} cage of **8** is electron donating in spite of the presence of two formally positive substituents. We presume that the electron donation is by an inductive mechanism.

It is also interesting to compare the electronic spectra of 1-$(CH_3)_2SB_{10}H_7$-6-NH_2-10-N_2 (ϵ_{255} 25,000) and 1,10-$(CH_3)_2SB_{10}H_8N_2$[1] (ϵ_{252} 20,600). The very small spectral differences in the two compounds argue against important conjugative effects between adjacent apical and equatorial positions of the polyhedron in the electronically excited state.

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[11] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

[12] R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

[13] R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 520 (1962).

[14] W. R. Hertler, *Inorg. Chem.*, **3**, 1195 (1964).

[15] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

Experimental[16]

$(CH_3)_3NB_{10}H_8CO$.—A mixture of 14.4 g. (0.0575 mole) of $(CH_3)_4N[2\text{-}B_{10}H_9N(CH_3)_3]$, 1 l. of anhydrous acetonitrile, and 20 ml. of oxalyl chloride was stirred at room temperature for 30 min. Gas evolution occurred during the first 10 min., and the initially dark amber color became somewhat lighter. The solution was evaporated under reduced pressure and the residue was dissolved in water and passed through an acid ion-exchange resin. The effluent was evaporated to dryness under reduced pressure, and the residue was sublimed at 140° (0.5 mm.) to give 8.3 g. (71%) of colorless $(CH_3)_3NB_{10}H_8CO$, m.p. 175–178°. Recrystallization from benzene–cyclohexane raised the m.p. to 184–185°. *Anal.* Calcd. for $(CH_3)_3NB_{10}H_8CO$: C, 23.6; H, 8.45; B, 53.3; N, 6.90; mol. wt., 203. Found: C, 23.9; H, 8.44; B, 53.4; N, 6.9; mol. wt., 201.

The infrared spectrum of the product (Nujol) shows absorption at 2500 (B–H str.), 2130 ($-C\equiv O$), and 1470 cm.$^{-1}$ ($(CH_3)_3N-$). The ultraviolet spectrum of the product in methylene chloride shows end absorption with a shoulder at $\sim$320 mμ (ϵ 540). Gas chromatography on Apiezon (programmed temperature) of a sample of sublimed (but not recrystallized) $(CH_3)_3NB_{10}H_8CO$ from a run in which the yield of product was 87% showed only two peaks, corresponding to 66% 2,7(8)-$(CH_3)_3NB_{10}H_8CO$ (retention time 24.5 min.) and 34% 2,4-$(CH_3)_3NB_{10}H_8CO$ (retention time 26.6 min.). Runs in which the overall yield of $(CH_3)_3NB_{10}H_8CO$ varied to as low as 71% showed no significant deviation from the 2:1 ratio of 2,7(8)-:2,4- isomer as determined by gas chromatography.

The B^{11} n.m.r. spectrum of $(CH_3)_3NB_{10}H_8CO$ in acetone shows a multiplet at 11, 18, and 21.3 p.p.m. which probably represents two unsubstituted apical boron atoms and one $N(CH_3)_3$-substituted equatorial boron atom. A larger multiplet at 39.5, 46.2, and 52.4 p.p.m. would then represent seven equatorial boron atoms, one of which is $C\equiv O$-substituted and is probably located beneath the high-field tail.

$B_{10}H_8[N(CH_3)_3]_2$ from $(CH_3)_3NB_{10}H_8CO$.—To a solution of 500 mg. (2.46 mmoles) of $(CH_3)_3NB_{10}H_8CO$ in water was added 600 mg. of hydroxylamine-O-sulfonic acid with concomitant evolution of carbon dioxide. The gum which separated was methylated by refluxing in a mixture of 8 ml. of water and 1 ml. of 10% sodium hydroxide solution while making ten additions of 0.8 ml. of 10% aqueous sodium hydroxide and 0.1 ml. of dimethyl sulfate at 8-min. intervals. Finally 2 ml. of 10% sodium hydroxide was added, and refluxing was continued for 15 min. On cooling, 580 mg. of $B_{10}H_8[N(CH_3)_3]_2$ was obtained. Thin-layer chromatography of the crude product on silica gel showed that it consisted of 2,4- and 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$.[4] Recrystallization from acetone–ethanol gave crystals, the X-ray powder pattern of which showed the presence of 2,4- and 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$.

Resolution of 2,7(8)-$(CH_3)_3NB_{10}H_8CO$.—A solution of 9 g. of $(CH_3)_3NB_{10}H_8CO$ (mixture of 2,4- and 2,7(8)- isomers) in water was treated with a solution of 24 g. of brucine in dilute aqueous hydrochloric acid, and the precipitate was collected by filtration. The gummy solid was recrystallized from a small volume of ethanol, and the resulting solid was extracted with hot ethanol (to remove the last of the 2,4- isomeric salt). The remaining solid was recrystallized twice from ethanol containing a little acetonitrile to give 6.2 g. of crystals. This product was dissolved in aqueous acetonitrile and passed through an acid-exchange column, and the effluent was evaporated to dryness *in vacuo*. The residue was sublimed at 0.5 mm. to give 1.59 g. of crystalline (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$, $[\alpha]^{28}D$ +22° (1.8 g./100 ml. in acetone), m.p. 207–208.5° (cor.). The extent of resolution has not been determined.

The mother liquor from the recrystallization of the salt of the (+) isomer was evaporated, and the residue converted as above to 1.59 g. of crystals of (−)2,8- (or 2,7-) $(CH_3)_3NB_{10}H_8CO$, $[\alpha]^{23}D$ −14° (2.4 g./100 ml. in acetone), m.p. 195–196.5° (cor.).

The ethanol extract of the crude brucine salt was evaporated, and the residue was converted as described above to 730 mg. of 2,4-$(CH_3)_3NB_{10}H_8CO$ (contaminated with a little 2,7(8)- isomer). A 210-mg. sample of this 2,4-$(CH_3)_3NB_{10}H_8CO$ was converted as described above to 2,4-$B_{10}H_8[N(CH_3)_3]_2$, $[\alpha]^{25}D$ 0°, (2 g./100 ml. in DMF). A second crop of product contained some 2,7(8)- isomer.

Heating a sample of (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$ at 200° for 5 min. caused no decrease in optical rotatory power.

(+)2,7- (or 2,8-) $B_{10}H_8[N(CH_3)_3]_2$.—To an aqueous solution of 200 mg. of (+)2,7- (or 2,8-) $(CH_3)_3NB_{10}H_8CO$ ($[\alpha]D$ +22°) was added 400 mg. of hydroxylamine-O-sulfonic acid. The resulting precipitate was collected by filtration. The filter cake was transferred to 30 ml. of refluxing water and treated three times with 5 ml. of 10% aqueous sodium hydroxide and 0.6 ml. of dimethyl sulfate. The resulting precipitate was collected by filtration to give 215 mg. of solid. Recrystallization from acetone–ethanol gave 150 mg. of (+)2,7- (or 2,8-) $B_{10}H_8[N(CH_3)_3]_2$, $[\alpha]^{25}D$ +13° (1.9 g./100 ml. in acetonitrile). The infrared spectrum and X-ray powder pattern of the product are identical with those of authentic 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$.[5]

$(CH_3)_3NB_{12}H_{10}CO$.—A mixture of 10 g. of $(CH_3)_4N[B_{12}H_{11}N(CH_3)_3]$,[6] 700 ml. of acetonitrile, and 7 ml. of oxalyl chloride was refluxed for 2 hr. and then evaporated under reduced pressure. The residue was extracted with hot water, leaving 4.1 g. of unchanged $(CH_3)_4N[B_{12}H_{11}N(CH_3)_3]$. The aqueous extract was passed through an acid-exchange column, and the effluent was treated with "Darco" and evaporated to a yellow solid which was sublimed at 220° (0.5 mm.) giving 715 mg. of white crystals of $(CH_3)_3NB_{12}H_{10}CO$. Recrystallization from benzene containing a small amount of acetonitrile gave crystals of m.p. 249–250.5°. *Anal.* Calcd. for $B_{12}H_{19}C_4NO$: C, 21.1; H, 8.44; B, 57.2; N, 6.17. Found: C, 21.5; H, 8.88; B, 55.4, 56.4; N, 6.34, 6.35.

The infrared spectrum of the product showed absorption at 2500 (B—H) and 2180 cm.$^{-1}$ ($C\equiv O$).

Stereochemistry of Reaction of Oxalyl Chloride with $B_{12}H_{11}N(CH_3)_3^-$.—A mixture of 10 g. of $(CH_3)_4N[B_{12}H_{11}N(CH_3)_3]$, 700 ml. of acetonitrile, and 10 ml. of oxalyl chloride was refluxed for 2 hr. and evaporated *in vacuo*. The residue was extracted with hot water, and the extract was passed through an acid ion-exchange column. The effluent was treated with "Darco" and concentrated *in vacuo* to about 75 ml. The resulting solution was treated with 15 g. of hydroxylamine-O-sulfonic acid (with warming), and the resulting precipitate collected by filtration to give 2.76 g. of $(CH_3)_3NB_{12}H_{10}NH_3$; 840 mg. of the product was converted by the procedure described in the preceding experiment to 880 mg. (88%) of $B_{12}H_{10}[N(CH_3)_3]_2$. Thin-layer chromatography on silica gel showed the presence of 1,7- and 1,12-$B_{12}H_{10}[N(CH_3)_3]$. No 1,2- isomer was observed.

1,6-$(CH_3)_2SB_{10}H_8COOH^-$.—A mixture of 5 g. of $Cs[1\text{-}B_{10}H_9S(CH_3)_2]$,[1] 10 ml. of oxalyl chloride, and 500 ml. of acetonitrile was refluxed for 45 min. and evaporated under reduced pressure. The residue was treated with hot water and filtered. Addition of tetramethylammonium chloride to the filtrate gave 1.65 g. of tan $(CH_3)_4N[1,6\text{-}(CH_3)_2SB_{10}H_8COOH]$. Recrystallization from water gave 1.37 g., m.p. 251–253°. A portion of this material was dissolved in water and passed through an acid-exchange column. The effluent was boiled with "Darco, filtered," and treated with tetramethylammonium chloride. The resulting precipitate was recrystallized from water, giving white plates of $(CH_3)_4N[1,6\text{-}(CH_3)_2SB_{10}H_8COOH]$, m.p. 264–265°. *Anal.* Calcd. for $B_{10}H_{27}C_7SNO_2$: C, 28.3; H, 9.15; B, 36.4; S, 10.8. Found: C, 28.7; H, 9.35; B, 36.9; S, 10.8.

The infrared spectrum of the product showed absorption at 1615 cm.$^{-1}$ consistent with a COOH function.

1,6-$(CH_3)_2SB_{10}H_8CO$.—A mixture of 5 g. of $Cs[1\text{-}B_{10}H_9S(CH_3)_2]$, 500 ml. of acetonitrile, and 10 ml. of oxalyl chloride was refluxed under nitrogen for 45 min. and then evaporated under reduced pressure. The residue was dissolved in hot water and

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[16] Melting points are corrected unless otherwise indicated. B^{11} n.m.r. spectra were determined at 19.25 Mc. with methyl borate as external standard. Decoupling experiments were performed with an NMR Specialties Model SD60 spin decoupler.

passed through an acid-exchange column. The effluent was evaporated to dryness and sublimed at 140° (0.5 mm.), giving 2.5 g. of 1,6-$(CH_3)_2SB_{10}H_8CO$ as a white solid. Two recrystallizations from cyclohexane–benzene gave plates with m.p. 108–109°. *Anal.* Calcd. for $B_{10}H_{14}C_3SO$: C, 17.5; H, 6.84; B, 52.4; S, 15.4; mol. wt., 227. Found: C, 17.7; H, 6.57; B, 52.6; S, 15.3, 15.5; mol. wt., 208, 216. The infrared spectrum of the product showed absorption at 2500 (split, B—H) and 2140 cm.$^{-1}$ (C≡O).

The B^{11} n.m.r. spectrum of 1,6-$(CH_3)_2SB_{10}H_8CO$ (Figure 1) shows a doublet at 6.7 p.p.m. (J = 181 c.p.s.) which can be assigned to an unsubstituted apical boron atom. This doublet collapses on irradiating at 60 Mc. A single peak at 11.4 p.p.m. can be assigned to an apical boron atom with a $(CH_3)_2S$ substituent. This peak is coincident with the high-field half of the 6.7 p.p.m. doublet. A large unsymmetrical doublet at 44.4 p.p.m. (J = 108 c.p.s.) represents seven unsubstituted equatorial boron atoms. This doublet can be decoupled to give a single peak. A small peak at 57.9 p.p.m. represents the equatorial boron atom substituted with a C≡O group. This peak is unaffected by irradiation at 60 Mc. The occurrence of the apical doublet at 6.7 p.p.m. rather than the more common 14–18 p.p.m. range for $B_{10}H_{10}^{2-}$ derivatives can be attributed to the fact that this apical boron atom is adjacent to the C≡O-substituted equatorial boron atom (*i.e.*, 1,6- rather than 1,2- stereochemistry). Analogous effects were reported earlier.[4]

1,6-$(CH_3)_2SB_{10}H_8NH_3$ from $(CH_3)_2SB_{10}H_8CO$.—A solution of 150 mg. of 1,6-$(CH_3)_2SB_{10}H_8CO$ in water was treated with excess hydroxylamine-O-sulfonic acid with warming until carbon dioxide evolution ceased. The resulting precipitate was collected by filtration to give 125 mg. of 1,6-$(CH_3)_2SB_{10}H_8NH_3$. Recrystallization from water gave 105 mg. of long needles, m.p. 282–283°. Both the infrared spectrum and the X-ray powder pattern of the product were identical with those of the 1,6-$(CH_3)_2SB_{10}H_8NH_3$ prepared earlier.[4]

1,6-$(CH_3)_2SB_{10}H_8OH^-$ from 1,6-$(CH_3)_2SB_{10}H_8CO$.—$(CH_3)_2SB_{10}H_8CO$ (100 mg.) was added to a cold solution of 30% hydrogen peroxide and sodium hydroxide causing vigorous evolution of gas. Addition of tetramethylammonium chloride gave 100 mg. of white solid. Recrystallization from water gave plates of $(CH_3)_4N[1,6\text{-}(CH_3)_2SB_{10}H_8OH]$ which was found to be identical with respect to infrared spectrum and X-ray powder pattern with $(CH_3)_4N[(CH_3)_2SB_{10}H_8OH]$ prepared by other methods.[1]

$(CH_3)_2SB_{10}H_7COOH \cdot N_2$.—$Cs[1\text{-}B_{10}H_9S(CH_3)_2]$[1] (20 g., 0.064 mole) was stirred in 500 ml. of acetonitrile, and oxalyl chloride (7 ml., 0.082 mole) was added. The mixture was stirred at ambient temperature for 15 min. and then at reflux temperature for 45 min. It was cooled to room temperature, 15 ml. of water was added cautiously, and the solution was evaporated to dryness in a stream of air. The residue was dissolved in 5% aqueous sodium hydroxide, and the solution was passed through an ion-exchange column containing excess IR 120(H) resin. Another preparation identical with this was made, and the acidic solutions were combined, treated with decolorizing carbon at the boiling point, and then adjusted in volume to 2 l. The solution was chilled in an ice–water bath and sodium nitrite (80 g., 1.16 moles) was added followed by the slow addition, with stirring, of 40 ml. (0.5 mole) of 12 M hydrochloric acid. A brown solid separated. (*Caution:* This solid is explosive and exceedingly sensitive when dry. It should not be handled in a dry state.) This solid was filtered, washed with water, and left damp. It was extracted with three 100-ml. portions of glyme resulting in complete dissolution. Zinc dust (40 g., 0.6 g.-atom) and 30 ml. (0.36 mole) of 12 M hydrochloric acid were added to the combined extracts, and the dark brown mixture was stirred until the liquid phase was almost colorless. The mixture was filtered, and the filtrate was slowly diluted with 1.5 l. of water to precipitate 18 g. of crude $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ containing a small amount of $(CH_3)_2SB_{10}H_8N_2$. This mixture was separated by extraction with 140 ml. of 4% sodium hydroxide. Acidification of the filtered extracts precipitated 17 g. (53% yield) of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$. This was further purified by dissolution in a mixture of 200 ml. of glyme and 25 ml. of water, followed by filtration and slow dilution of the filtrate with 500 ml. of water to reprecipitate 12 g. of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$. Five grams of this was recrystallized from a solution of 60 ml. of ethanol and 40 ml. of water to obtain 2.7 g. of analytically pure crystalline material (dec. pt. 191–192°). It is necessary that all traces of hydrogen chloride be removed from the product before recrystallization from alcoholic media or substantial esterification occurs. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7COOH \cdot N_2$: C, 14.4; H, 5.6; B, 43.2; N, 11.2; S, 12.8; neut. equiv., 250; mol. wt., 250. Found: C, 14.4; H, 6.0; B, 43.7; N, 11.4; S, 12.9; neut. equiv., 249; mol. wt., 245 (cryoscopic in dimethyl sulfoxide). Ultraviolet $\lambda_{max}^{CH_3CN}$ 251 mμ (ϵ 23,200); pK_a = 8.00 (50% aqueous alcohol). The infrared spectrum of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ in a Nujol mull has absorption bands at 2520, 2475 (s, doublet B—H), 2260 (s, N≡N), and 1660 (s, C═O) cm.$^{-1}$, as well as absorptions at 1282 (s), 1170 (w), 1130 (w), 1100 (w), 1040 (m), 995 (m), 970 (w), 995 (s), 705 (s), and 685 (w) cm.$^{-1}$.

$(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot N_2$.—A solution of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ (7.5 g., 30 mmoles) in 75 ml. of alcohol and 5 ml. of 12 M hydrochloric acid was boiled for 5 min. and allowed to cool. $(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot N_2$ (3.8 g., 45%) separated as a crystalline solid (m.p. 125°). Partial concentration of the mother liquors gave a second crop of crystals (1.6 g., 18%) identical by infrared analysis with the first crop. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot N_2$: C, 21.6; H, 6.5; B, 38.9; N, 10.1. Found: C, 21.5; H, 7.0; B, 39.1; N, 10.2. Ultraviolet $\lambda_{max}^{CH_3CN}$ 250 mμ (ϵ 23,200), 392 mμ (ϵ 25.6). The infrared spectrum in a potassium bromide wafer includes bands at 2530 (s, B—H), 2280 (s, N≡N), 1680 (s, C═O), 1210 (s), 1105 (m), 1040 (s), 1010 (m), and 960 (m) cm.$^{-1}$.

In smaller scale runs, the esterification was accomplished in quantitative yield by dissolving $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ in alcoholic hydrochloric acid as above and then evaporating the solution to dryness in an open dish on a steam bath. The residue was a quantitative yield of the desired ester in crystalline form, identified by infrared analysis. No esterification occurs in the absence of hydrochloric acid.

$(CH_3)_2SB_{10}H_7COOH \cdot NC_5H_5$.—A solution of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ (2 g., 8 mmoles) in 50 ml. of pyridine was refluxed for 5 hr. The solution was mixed with 200 ml. of water to obtain a clear solution. The addition of 75 ml. of 12 M hydrochloric acid precipitated 1.2 g. (50%) of $(CH_3)_2SB_{10}H_7COOH \cdot NC_5H_5$ as a golden brown solid. The analytical sample (m.p. 269–270°) was obtained as a cream-colored crystalline solid by recrystallization from aqueous glyme. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7COOH \cdot NC_5H_5$: C, 31.9; H, 6.3; B, 35.9; N, 4.6. Found: C, 32.0; H, 6.6; B, 35.6; N, 4.6. Ultraviolet $\lambda_{max}^{CH_3CN}$ 309 mμ (ϵ 8100), 235 mμ (ϵ 9000), $\lambda_{max}^{0.1\,N\ NaOH}$ 298 mμ (ϵ 7300).

$(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot NC_5H_5$.—A solution of $(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot N_2$ (5 g., 18 mmoles) in 100 ml. of pyridine was refluxed for 22 hr. during which time 430 ml. of gas (97%) was evolved. The resulting solution was poured into 1200 ml. of water to precipitate 2 g. (34%) of $(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot NC_5H_5$. This was recrystallized from 75 ml. of 50% aqueous alcohol (1.2 g. recovery), m.p. 207–209°. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7COOC_2H_5 \cdot NC_5H_5$: C, 36.5; H, 6.9; B, 32.8; N, 4.2. Found: C, 36.2; H, 7.6; B, 32.9; N, 4.2. Ultraviolet $\lambda_{max}^{CH_3CN}$ 310 mμ (ϵ 8150), 235 mμ (ϵ 7300).

$(CH_3)_2SB_{10}H_7NH_2 \cdot N_2$. (A).—A mixture of hydroxylamine-O-sulfonic acid (10 g., 89 mmoles), $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ (3.0 g., 12 mmoles) and 200 ml. of 50% aqueous ethanol was refluxed for 3 hr. It was then concentrated to about 75 ml. in a stream of air and excess hydrated $H_2B_{12}Cl_{12}$ was added. $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}^{2-}$ precipitated and was recrystallized from aqueous acetonitrile (1.6 g., 13% yield). The product was initially an oil but crystallized slowly. It was dried at 80° under vacuum. This salt darkened at 239° but did not melt to 400°. *Anal.* Calcd. for $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}^{2-}$: C, 4.8; H, 3.2; B, 34.5; N, 8.4; Cl, 42.6. Found: C, 4.5;

H, 3.4; B, 33.9; N, 7.7; Cl, 42.7. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$ 247 mμ (ε 53,500).

(**B**).—Oxalyl chloride (4 ml., 41 mmoles) was added to a mixture of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ (5 g., 20 mmoles) and 60 ml. of acetonitrile. The mixture was refluxed 7 hr., cooled, and sodium azide (2 g., 62 mmoles) was added. The mixture was stirred overnight, during which time 800 ml. of gas (32.8 mmoles) was evolved. The solution was stirred into 700 ml. of water to precipitate 5.2 g. of a dark brown solid. Infrared analysis suggested this was $(CH_3)_2SB_{10}H_7NCO \cdot N_2$, but it was not obtained in analytically pure form. Glyme (50 ml.) and 4.2 g. of the crude isocyanate were mixed with 10 ml. of 12 *M* hydrochloric acid. Virtually all the solid dissolved and remained in solution during the addition of two more 10-ml. portions of 12 *M* hydrochloric acid. During the additions the dark solution became hot and gas was evolved. It was concentrated to 30 ml. on a steam bath, 45 ml. of water was added, and the solution was filtered through "Celite" filter aid. Mixing an aliquot with hydrated $H_2B_{12}Cl_{12}$ precipitated $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}$, identical by infrared analysis with that prepared above. The major part of the solution was made alkaline with sodium hydroxide. $(CH_3)_2SB_{10}H_7NH_2 \cdot N_2$ precipitated and was recrystallized from water, dec. pt. 105–107°. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7NH_2 \cdot N_2$: C, 10.8; H, 6.8; B, 48.9; N, 19.0. Found: C, 11.5; H, 7.0; B, 48.9; N, 18.2. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$ 255 mμ (ε 25,000).

(**C**).—Sodium azide was added to a solution of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ in concentrated aqueous $H_2B_{12}Cl_{12}$. Gassing ensued and $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}^{2-}$, identified by infrared analysis, separated.

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The Manganese-Catalyzed Carbonylation of Amines

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Decacarbonyldimanganese and pentacarbonylmethylmanganese have been found to catalyze the carbonylation of primary aliphatic amines almost exclusively to 1,3-dialkylureas. Ammonia and di-*n*-butylamine virtually do not react. Aniline reacts very slowly giving 1,3-diphenylurea in low yield. The formation of 1,3-dialkylureas is accompanied by the evolution of hydrogen, so that little or no gas absorption was observed during the reaction. A mechanism of reaction is proposed involving the attack of the amine on an alkylformamide group bonded to the manganese. A simplified procedure for the preparation of decacarbonyldimanganese is also described.

Introduction

Kinetic data concerning the reaction of pentacarbonylalkylmanganese compounds with nucleophilic reagents have been previously reported[1,2] in the case of L = carbon monoxide.

$$\mathrm{RMn(CO)_5 + L \longrightarrow RCOMn(CO)_4L} \tag{1}$$

Kinetic studies of the reaction of $CH_3COMn(CO)_5$ with phosphorus- and nitrogen-containing ligands

$$\mathrm{CH_3COMn(CO)_5 + L \longrightarrow CO + CH_3COMn(CO)_4L} \tag{2}$$

are now being completed and the results will be reported later.

The present paper reports some catalytic reactions in which primary aliphatic amines can be converted into disubstituted ureas by the use of decacarbonyldimanganese and pentacarbonylmethylmanganese as catalytic precursors. This study was originated by the observation of some anomalies found during the kinetic investigation of reaction 2 with L = amines. Catalytic carbonylations of primary, secondary, and tertiary amines are known to occur in the presence of group VIII metal carbonyls or of metal halides capable of being transformed to metal carbonyls in the reaction conditions.[3–9] Alkylformamides are usually obtained in the course of these reactions, although dialkylureas are also reported[5] to be formed when large amounts of nickel iodide are employed. Aniline appears to be unique in giving almost exclusively diphenylurea.[5,6] Finally, diphenylurea was the main by-product during the reaction of aniline, carbon monoxide, and olefins to give anilides using $Co_2(CO)_8$ as catalyst.[10]

The catalytic properties of decacarbonyldimanganese and related compounds in the carbonylation reactions of amines do not appear to have been investigated. It has now been found that $Mn_2(CO)_{10}$ and $CH_3Mn(CO)_5$ catalyze the reaction. Moreover, manganese seems to differ from the above-mentioned metals since primary aliphatic amines react giving almost exclusively dialkylureas and secondary aliphatic amines are virtually unreacted. Other interesting features of the manganese system will be discussed later in the text.

Experimental

(1) **Materials.**—Tetrahydrofuran and diisopropyl ether were dried over sodium, distilled over $LiAlH_4$, and stored under nitrogen. *n*-Butylamine and cyclohexylamine were dried over KOH pellets and fractionated. Aniline was distilled and stored under nitrogen. Di- and tri-*n*-butylamine were fractionated under reduced pressure. Anhydrous manganese(II) acetate was prepared by drying the commercially available hydrate product over P_2O_5 at room temperature for several days under high vacuum.

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