TABLE II

MAJOR ABSORPTION BANDS BETWEEN 1350–800 CM.$^{-1}$

No.	Out-of-plane C–H deformation			Other major bands			
			Monosubstituted *p*-benzoquinones				
2	901	825		1312	1280	1095	1002
8	904	821		1309	1277	1095	975
14	910	836		1298	1278	1095	977
18	916	865	858[a]	1295	1275	1092	979
22	913	850		1302	1285	1086	977
			2,3-Disubstituted *p*-benzoquinones				
3	841			1290	1256	1104	1050
9	836			1270	1235	1092	1012
15	844			1303	1269	1099	1019
19	853[a]	844		1306	1268	1098	1016
23	846			1301	1274	1095	1017
			2,5-Disubstituted *p*-benzoquinones				
4	897			1310	1225–1205[b]		1025
10	900			1310	1222–1200[b]	1187	995
16	910			1321	1225–1208[b]	1182	1019
20	913	856[a]		1320	1225–1202[b]	1182	1015
24	912			1320	1227–1203[b]	1183	1017
			2,6-Disubstituted *p*-benzoquinones				
5	907			1281	1041		
11	911			1272	1007		
17	919			1297	1013		
21	919	853[a]		1288	1010		
25	918			1295	1012		

[a] These bands are attributable to C–N stretching vibrations of aromatic nitro- group (*cf.* R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952)) [b] The broadness of these bands seems to be associated with the absorption of solvent ($CHCl_3$) in this region. The spectra in CS_2 showed a sharp, well defined peak in this region.

tensity bands (1310–1270 and 1275–1235 cm.$^{-1}$. In 2,5-disubstituted isomers a similar pair occurs at 1227–1200 and 1187–1183 cm.$^{-1}$ accompanied by a weak band between 1320–1310 cm.$^{-1}$. On the other hand, the 2,6-isomers exhibit only a single medium or strong intensity band between 1297–1272 cm.$^{-1}$. It is impossible at the present time to assign these bands to any particular mode of molecular vibrations. However, their usefulness in arriving at the structure of isomeric, disubstituted *p*-benzoquinones cannot be overlooked.

Experimental

The spectra were all recorded in solution (0.1 *M*), on a Beckman IR-4 spectrophotometer equipped with a NaCl prism. The chloroform[20] and carbon disulfide used were ANALAR grade (B.D.H.) and reagent grade (Merck), respectively. The spectra were calibrated by the use of a polystyrene film. The sources of the *p*-benzoquinones studied are listed in the footnotes to Table I.

Bromo-*p*-benzoquinone.—This was obtained by duplicating the procedure described,[21] m.p. 56–57°: ν $CHCl_3$ 904,821 (C–H deformation), 1682 ($\rangle C{=}O$ stretching) cm.$^{-1}$.

2,6-Dibromo-*p*-benzoquinone.—This material was synthesized as described,[22] m.p. 132–133°, reported 130–131°. ν $CHCl_3$ 911 (C–H deformation), 1663, 1703 ($\rangle C{=}O$ stretching) cm.$^{-1}$. λmax 290 mμ (log ϵ 4.18), 352 mμ (log ϵ 2.92); reported[23] λmax 291 mμ (log ϵ 4.11), 352 mμ (log ϵ 2.90).

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(20) Although chloroform is used as a solvent of choice, in order to eliminate the hydrogen bonding as a possible source of frequency shift; wherever possible, (solubility permitting) the spectra of compounds exhibiting a doublet in the $\rangle C{=}O$ region are also recorded in carbon disulfide. Thus the carbonyl region of compounds No. 2, 5, 11, 17 and 25 in carbon disulfide also exhibit a doublet. The $\Delta\nu$ value between these two bands are found to be essentially identical with those observed when chloroform was used.

(21) von E. Sarauw, *Ann.*, **209**, 93 (1881).

(22) van Erp, *Rec. trav. chim.*, **30**, 284 (1911).

(23) E. A. Braude, *J. Chem. Soc.*, 490 (1945).

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The Reaction of Decaborane with Amines and Related Compounds[1]

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Strongly basic aliphatic amines form salt-type adducts with decaborane without the evolution of hydrogen. The treatment of decaborane with *sym*-diethylthiourea, a poor electron donor, results in the formation of $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$ with the stoichiometric evolution of hydrogen. A two-step mechanism is proposed for this second order reaction. Nitrogen heterocycles do not participate in completely defined reactions with decaborane.

The reactivity of decaborane ($B_{10}H_{14}$) with nitrogen compounds appears to be quite dependent on the electron donor ability of the nitrogen substrate and experimental conditions. Fetter and Burkardt[2] report that decaborane and pyridine react at 0° in the absence of solvents to form $B_{10}H_{14}(C_5H_5N)_2$ without the evolution of hydrogen. In benzene and at higher temperatures, however, the reaction evolves hydrogen in amounts which are inversely proportional to the pyridine: decaborane ratio.

Similar dependence on reaction conditions was reported for the treatment of decaborane with a strong electron donor such as dimethylamine, resulting in the formation of adducts which may contain 1–3 moles of amine per mole of boron hydride.[3] No hydrogen evolution was reported for this particular reaction. Diethylcyanamide,

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[1] Taken in part from the dissertation submitted by Donald E Hoffman to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1960.

[2] N. R. Fetter and L. A. Burkardt, Abstracts of Papers, 135th National Meeting, Am. Chem. Soc., Boston, Mass., 1959, p. 45 M.

[3] S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).

a weak electron donor, and decaborane are reported to react stoichiometrically at room temperature in diethyl ether to evolve one mole of hydrogen for each mole of product formed.[4]

Reactions of decaborane with nitrogen compounds of different basicities have been extended at room temperature to include alkylated pyridine and quinoline derivatives, aliphatic amines and alkylated thioureas.

Results and Discussion

Decaborane dissolves in alkylated pyridine, quinoline and isoquinoline derivatives at room temperature to form highly colored solutions from which solids slowly precipitate without the evolution of hydrogen. In *n*-pentane solutions the decaborane-heterocycle reactions result in hydrogen evolution in amounts which are not necessarily consistent with the formation of a single decaborane-heterocycle species.

For the treatment of decaborane with pyridine in benzene, hydrogen evolution is inversely proportional to pyridine:decaborane ratios in the range of 1.5:1 to 5.5:1.[2] In our work pyridine: decaborane ratios varying from 4:1 to 8:1 resulted, respectively, in 0.4 and 0.5 mole of hydrogen being evolved for each mole of decaborane participating in the reaction. Although elemental analyses of the non-melting solids generally agreed with the formula decaborane-(heterocycle)$_2$ regardless of whether the nitrogen compound was a pyridine, quinoline or isoquinoline derivative, it is not possible to discern if the product from these reactions might be solely $B_{10}H_{13}$(heterocycle)$_2$ or a mixture of $B_{10}H_{14}$(heterocycle)$_2$ and $B_{10}H_{12}$(heterocycle)$_2$. In the case of pyridine the possible existence of a $B_{10}H_{13}(C_5H_5N)_2$ species is suggested in the general equation proposed by Fetter and Burkardt.[2]

The addition of strong electron donors such as aliphatic amines to *n*-pentane solutions of decaborane at room temperature results in the immediate precipitation of white-pale yellow solids. Unlike reactions with heterocycles in solvents, these reactions do not evolve hydrogen, even when amine:decaborane ratios vary from 1:1 to 10:1, respectively. Although elemental analyses of the solids were inconclusive, spectroscopic evidence was obtained at 268 and 330 mμ for the $B_{10}H_{13}$ anion in acetonitrile solutions containing the product from the decaborane–diethylamine reaction. Several authors[5,6] have interpreted bands in the vicinity of 265 and 330 mμ as being characteristic of the $B_{10}H_{13}$ anion. The evidence suggests the formation of a decaborane–amine salt in an acid–base type reaction since decaborane is acidic ($pK_a = 3.5$)[7] and the aliphatic amines have comparable pK values ($pK_b = 3$–4).

Nitrogen compounds of very poor electron donor ability such as the thioureas react with decaborane to evolve hydrogen. The treatment of decaborane with monoalkylated thioureas in benzene yields insoluble, hygroscopic, white solids in addition to hydrogen. With *sym*-diethylthiourea, a benzene solution of decaborane forms a stable, nonhygroscopic crystalline solid with the formula $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$.

Kinetic studies of the reaction of decaborane with *sym*-diethylthiourea were carried out by measuring the rate of hydrogen evolution. Since one mole of hydrogen was evolved for each mole of decaborane used as a reactant, it was assumed that each mole of gas evolved represented the reaction of one mole of boron hydride. Results indicate that the second order reaction is first order with respect to both a decaborane–thiourea ion pair complex $[B_{10}H_{13}^-][H^+(C_2H_5NH)_2CS]$ and thiourea. The rate determining step is probably that represented in reaction 2.

$$B_{10}H_{14} + (C_2H_5NH)_2CS \overset{\text{fast}}{\rightleftarrows} [B_{10}H_{13}^-][H^+\cdot (C_2H_5NH)_2CS] \quad (1)$$

$$[B_{10}H_{13}^-][H^+\cdot(C_2H_5NH)_2CS] + (C_2H_5NH)_2CS \xrightarrow[\text{rate determining}]{\text{slow}} B_{10}H_{12}\cdot[(C_2H_5NH)_2CS]_2 + H_2 \quad (2)$$

A similar two-step mechanism was proposed for the reaction of decaborane with aromatic amines.[8]

Experimental

Purification of Reagents.—Decaborane (m.p. 99.7–100°) was recrystallized from dry olefin-free *n*-pentane.

Pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine were dried over lithium aluminum hydride prior to distillation. Anhydrous sodium sulfate was used to dry quinoline, 2-methylquinoline, 8-methylquinoline and isoquinoline which were subsequently vacuum distilled.

n-Butylamine, *t*-butylamine, cyclohexylamine, diethylamine, di-*n*-butylamine and triethylamine were dried with lithium aluminum hydride before being distilled from barium oxide.

sym-Diethylthiourea (m.p. 76–77°) was recrystallized from benzene.

Decaborane–Nitrogen Heterocycle Reactions.—Decaborane reacted at room temperature with the following heterocycles: pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, quinoline, 2-methylquinoline, 8-methylquinoline and isoquinoline. In a large excess of heterocycle no hydrogen was evolved and the orange-red reaction products were completely soluble. However, when decaborane (5.0×10^{-4} mole) and pyridine (20×10^{-4} mole) were mixed in 5.0 ml. of *n*-pentane, 2.1×10^{-4} mole of hydrogen was evolved, corresponding to 0.42 mole of gas for each mole of decaborane participating in the reaction. In a similar experiment, 0.50 mole of hydrogen was evolved per mole of decaborane when 40×10^{-4} mole of pyridine was mixed with 5.0×10^{-4} mole of boron hydride.

The highly colored products were only slightly soluble in water, benzene, ethanol, cyclohexane, diethyl ether, chloroform, carbon disulfide, *n*-pentane, carbon tetrachloride, N,N-dimethylformamide and diethylene glycol dimethyl ether. Elemental analyses indicated molar ratios of decaborane:heterocycle of 1:2, respectively. As a typical example, a B:N ratio of 4.7:1.0 was obtained for the decaborane-2-methylquinoline derivative, the theoretical value being 5.0:1.0. The thermally stable solids did not melt or decompose below 300° and were not attacked by hydrochloric acid.

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[4] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).

[5] G. W. Schaeffer, J. J. Burns, T. J. Klingen, L. A. Martincheck and R. W. Rozett, Abstracts of Papers, 135th National Meeting, Am. Chem. Soc., Boston, Mass., 1959, p. 44-M.

[6] M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 1825 (1960).

[7] R. W. Atteberry, *J. Phys. Chem.*, **62**, 1458 (1958).

[8] H. C. Beachell and B. F. Dietrich, *J. Am. Chem. Soc.*, **83**, 1347 (1961).

Decaborane–Aliphatic Amine Reactions.—Decaborane reacted rapidly at room temperature with *n*-butylamine, cyclohexylamine, *t*-butylamine, diethylamine, di-*n*-butylamine and triethylamine in benzene, chloroform and *n*-pentane. The white or pale yellow, hygroscopic products were insoluble in benzene, *n*-pentane, chloroform, carbon tetrachloride, ethanol, 1,4-dioxane, diethyl ether and ethylene glycol dimethyl ether. A slight solubility was evident in water. The *t*-butylamine and cyclohexylamine derivatives sintered at 160°; the other products decomposed at 95–105°. When decaborane and triethylamine were mixed in chloroform in molar ratios of 1:1, 1:3, 1:5, 1:7 and 1:10, respectively, no hydrogen was evolved even when the mixtures of reactants were shaken for 4 hr.

Acetonitrile solutions of the product derived from diethylamine showed a moderately strong absorption band at 330 mμ and a band of weaker intensity at 268 mμ (Perkin-Elmer Spectracord Model 4000).

Decaborane–Alkylated Thiourea Reactions.—Benzene solutions of decaborane reacted with methylthiourea, ethylthiourea and *sym*-diethylthiourea to liberate hydrogen at room temperature. The monoalkylated thioureas formed white, hygroscopic solids. Sym-diethylthiourea yielded a white, crystalline solid (m.p. 177°) which was very slightly soluble in water, benzene, diethyl ether and carbon tetrachloride. The treatment of decaborane (2.54×10^{-4} mole) with *sym*-diethylthiourea (5.30×10^{-4} mole) in 5.0 ml. of benzene liberated 2.50×10^{-4} mole of hydrogen. This corresponds to 0.98 mole of gas per mole of decaborane. The amount of hydrogen produced at 25.0° was used to calculate a reproducible second order rate constant $k = 1.33 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

Anal. Calcd. for $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$: C, 31.21; H, 9.43; N, 14.56; S, 16.67; B, 28.12. Found: C, 30.39; H, 8.59; N, 13.90; S, 16.25; B, 26.59.