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AMINE BORANES—X

ALKYLIDENEAMINO t-BUTYLBORANES. THE HYDROBORATION OF NITRILES WITH TRIMETHYLAMINE t-BUTYLBORANE

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Abstract—The hydroboration of aliphatic and aryl nitriles with trimethylamine t-butyl borane results in the formation of 1:1 adducts, RCH=NBHt-Bu. The principal products have been shown to be nitrogen-bridged cyclic dimers. Thermal soaking of the dimeric products results in the quantitative formation of less soluble and higher-melting materials which are either stereoisomers or stoichiomers. The reactions of dimeric benzylideneamino t-butylborane include acid hydrolysis to yield benzaldehyde.

THE reaction of acetonitrile with diborane has been reported to yield an adduct, $CH_3CN{\cdot}BH_3$ which is in part converted to N,N′,N″-triethylborazine upon pyrolysis.[1] More recent studies of the reactions of acetonitrile, n-propionitrile, benzonitrile and acrylonitrile with diborane have reaffirmed the existence of such 1:1 borane-nitrile adducts which were not well characterized.[2] Brown and Subba Rao[3] have shown that diborane may function as a reagent for the reduction of nitriles to the corresponding primary amine. In view of the facile hydroboration of 1-alkenes and 1-alkynes with trimethylamine t-butylborane,[4] it was of compelling interest to examine the reactions of this sterically encumbered borane derivative with representative nitriles.

RESULTS AND DISCUSSION

Aliphatic nitriles. Acetonitrile, propionitrile, n-butyronitrile and i-butyronitrile were each treated with an equimolar quantity of trimethylamine t-butylborane in diglyme solution at 100°. Trimethylamine was smoothly evolved. Fractional distillation of the reaction mixtures at reduced pressure afforded low yields of high-boiling products. In every case except that of n-butyronitrile, these products crystallized on standing at room temperature. Further purification was obtained by recrystallization from ethanol. Analyses indicated these materials to be 1:1 adducts of t-butylborane and the starting nitrile. The melting point ranges observed with these materials suggested that they were not homogenous although a good crystalline habit was always observed after the first recrystallization. The i-butyronitrile product melted at 58-60°, resolidified and melted again at 110°. The molecular weight of each product was determined by the cryoscopic method in benzene solution and corresponded to that of dimer. The infrared spectrum of each product contained a B-H stretching band at 2390 cm^{-1} and a C=N stretching band at 1660 cm^{-1}. The B^{11} NMR spectra of the liquid n-butyronitrile and the crystalline acetonitrile products displayed doublets

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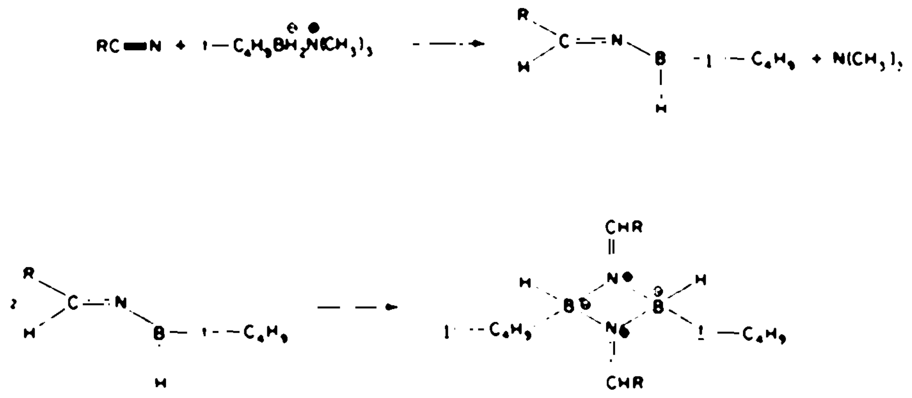
[1] A. B. Burg, *Rec. Chem. Progr. (Kresge-Hooker Sci. Libr.)* 15, 159 (1954).

[2] H. J. Emeleus and K. Wade, *J. Chem. Soc.* 2614 (1960).

[3] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.* 82, 681 (1960).

[4] M. F. Hawthorne, *J. Amer. Chem. Soc.* In press.

with δ = +9·9 × 10^{-6} and +19·2 × 10^{-6} relative to trimethyl borate. This evidence and that cited above leaves no doubt that these products are dimers of alkylideneamino t-butylboranes formed by bridging boron atoms through the alkylideneamino groups.[6] Thus the overall reactions may be written



The stereochemical consequences of this formulation will be discussed below. Characterization data for these materials are presented in Table 1.

Aryl nitriles. In accord with the results described above, benzonitrile and its *p*-methoxy-, *p*-chloro-, *p*-fluoro, *p*-methyl and *m*-methyl derivatives yielded crystalline, high melting products when treated with trimethylamine t-butylborane in diglyme solution at 100°. In each of these cases, except that of the *m*-methyl derivative, the crude crystalline products were separated into two pure crystalline fractions. The fraction formed in highest yield in each system was always found to be the lower melting and to display usefully high solubility in common organic solvents. Analyses of each pair of reaction products proved their compositions to be that of 1 : 1 adducts of the starting nitrile and t-butylborane. In general, the more soluble member of each pair of products melted near 140° while the less soluble member melted near 190°. It was observed that the lower-melting materials resolidified when heated above their melting points and again melted near the melting point of the higher-melting fraction. The conversion of the lower-melting member to the higher-melting member of the benzonitrile product pair was quantitatively accomplished by fusion. The infrared spectrum of the fused product was identical to that of the higher-melting member.

Examination of the infrared spectrum of each of the compounds described above in a Nujol mull revealed the following facts. In every case a C═N stretching band was observed at 1640 cm^{-1}. Significant differences were observed in the fingerprint region from compound to compound but these differences could not be correlated with the melting point and solubility properties. Every member of the lower-melting series of hydroboration derivatives except those derived from *p*-methoxy- and *m*-methylbenzonitriles, displayed a B—H stretching doublet at 2350 and 2400 cm^{-1}. The two exceptions gave sharp B—H stretching at 2350 cm^{-1} as did every member of the higher-melting series. The apparent B—N stretching doublet of the lower-melting series was observed as a sharp singlet at 2350 cm^{-1} in methylene chloride solution. Thus, this anomaly is undoubtedly a result of interactions in the crystalline state.

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[6] Methylamino t-butylborane dimer displays a doublet in its B^{11} NMR spectrum with δ = +9·7 and +18·0

Molecular weight determinations were made with each member of the more soluble series of derivatives. The cryoscopic method was employed in benzene solvent. In each case the lower-melting and most soluble products proved to be dimers. That these dimers are nitrogen-bridged was indicated from the position of the B^{11} NMR resonances obtained with the benzonitrile product. A doublet was observed with δ = + 10 and + 20 in acetonitrile solution relative to trimethyl borate.

Table 1 reports the characterization data obtained for the derivatives of any nitriles

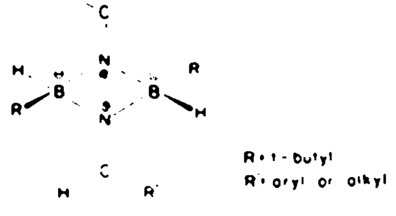
If, as the facts presented above indicate, the new materials described in this study are nitrogen-bridged stoichiomers of aldylideneamino t-butylboranes, one would expect the substituted benzylidene derivatives to absorb strongly in the ultraviolet. This was observed. The higher-melting benzylidene derivative had λ_{max} 274 mμ, ϵ 9000 and the lower melting member λ_{max} 273 mμ, ϵ 11,400. The corresponding p-methoxy compounds had λ_{max} 302 mμ, ϵ 18,500 and λ_{max} 302 mμ, ϵ 18,000, respectively. Extinction coefficients were calculated on the basis of monomer molecules. Short wave-length absorption was not well defined. In contrast, the products derived from aliphatic nitriles exhibited end absorption only.

Additional evidence for the assumed structure of the nitrile-t-butylborane adducts was obtained from the acid hydrolysis of the benzonitrile product in aqueous ethanol. Benzaldehyde was isolated in 48 per cent yield from the hydrolysis of the lower-melting member of the product pair. Hydrogen and t-butylboronic acid were also observed as reaction products. The hydrolysis reaction is described by the equation

$$(t\text{-}C_4H_9BHN{=}CH\phi)_2 + 2H_3O^+ + 4H_2O \rightarrow$$
$$2\phi CHO + 2H_2 + 2NH_4^+ + 2t\text{-}C_4H_9B(OH)_2$$

Stereochemistry and stoichiomers. As shown above, the hydroboration products derived from aliphatic nitriles and the lower-melting, more soluble products derived from aryl nitriles are dimers. The position of the B^{11} NMR resonances of these compounds prove that they are nitrogen-bridged. Such cyclic structures present a number of possible stereoisomers. Thus, the bulky t-butyl groups could be *cis*- or *trans*- with respect to each other and the alkylidene or benzylidene amino groups could assume a *syn* or an *anti*- arrangement. Thus, *cis-syn*, *cis-anti*, *trans-syn* and *trans-anti* configurations are possible. Of these possibilities the *trans-anti* isomer (I) would be predicted to be the more stable.

The question arises as to the nature of the higher-melting products obtained directly



I

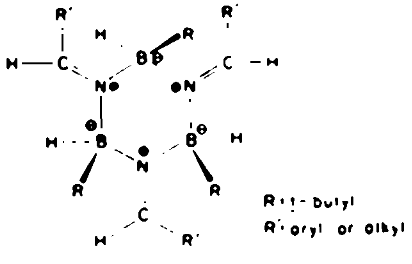
Table 1. Alkylideneamino and substituted benzylideneamino-t-butylboranes

R in RCH=NBHt-Bu	Yield (%)	m.p. (b.p./mm) °C	Found (%)				Calc. (%)			
			C	H	N	B	C	H	N	B
Methyl	22	75–78 (72–78/0.8)	64.88	12.72	12.37	9.83	64.92	12.71	12.62	9.75
Ethyl	20	79–83 (84–93/0.8)	67.28	12.67	11.07	8.77	67.24	12.90	11.20	8.65
n-Propyl	40	(86–88/0.1)	68.84	12.82	10.18	7.69	69.10	13.05	10.07	7.78
i-Propyl	41	57–60* (84–94/0.4)	69.15	13.16	9.95	7.79	69.10	13.05	10.07	7.78
Phenyl	63	141–143	76.16	9.32	8.21	6.52	76.33	9.31	8.10	6.26
	6.5	191–193	76.56	9.37	7.99	6.29	76.33	9.31	8.10	6.26
p-Methoxyphenyl	89	145–146	70.81	8.87	6.90	5.52	70.96	8.93	6.90	5.33
	9.5	185–187	70.89	9.02	7.21	5.58	70.96	8.93	6.90	5.33
p-Chlorophenyl	74	138–140	63.53	7.47	6.65	5.40	63.66	7.28	6.75	5.21
	8.2	190–191	63.67	7.21	6.87	5.40	63.66	7.28	6.75	5.21
p-Fluorophenyl	93	137–139	69.18	8.20	7.44	5.72	69.15	7.91	7.33	5.66
	0.5	180–182	69.32	8.18	7.55	5.83	69.15	7.91	7.33	5.66
p-Methylphenyl	89	146–148	77.28	9.60	7.28	5.56	77.03	9.70	7.49	5.78
	6	187–188	76.95	9.75	7.46	5.75	77.03	9.70	7.49	5.78
m-Methylphenyl	90	124–126	76.88	9.91	7.49	5.48	77.03	9.70	7.49	5.78

* Second melting point observed at 110° on continued heating.

during the hydroboration reaction or formed by thermal treatment of the lower-melting products.

Since thermal rupture of a B-N bond in the 4-membered cyclic dimers provides a possible mechanism for both *cis-trans* and *syn-anti* interconversions it is reasonable to assume that every isolated dimer species has the preferred stereochemistry shown in I. The markedly great change in properties which occurs upon heating these dimers suggests that the higher-melting products are not mere stereoisomers of the lower-melting dimers but are actually higher stoichiomers of optimum stereochemistry such as 6-membered, nitrogen-bridged cyclic trimers (II). If the trimer ring is in the chair configuration, then a *cis*-equatorial arrangement of t-butyl groups would most likely prevail.



II

EXPERIMENTAL

Materials. Nitriles were commercially available materials of high purity. Trimethylamine t-butylborane was prepared as previously described[4] and used without further purification. The diglyme employed was purified by distillation from lithium aluminium hydride at reduced pressure.

Preparation of alkylideneamino t-butylboranes. To a solution of 0.10 mole of the aliphatic nitrile dissolved in 25 ml of diglyme at 100° was added 13.0 g (0.10 mole) of crude trimethylamine t-butylborane. The addition was carried out in a dropwise fashion in a nitrogen atmosphere and with magnetic stirring. The addition required 1 hr. The reaction mixture was then heated for one additional hour and cooled to room temperature. The reaction product mixture was added to 200 ml of water and the oily product separated by extraction with diethyl ether. The ether extract was washed three times with 50 ml portions of water, separated, dried over magnesium sulfate and evaporated at reduced pressure. The residual oil was transferred to a small still pot and fractionated with a spinning band distillation column at reduced pressure. Table 1 reports yields, boiling points and melting points of crystallized distillates. Analytical samples were prepared by recrystallization from ethanol-water.

Preparation of substituted benzylideneamino t-butylboranes. One tenth mole of the proper substituted benzonitrile was dissolved in 25 ml of diglyme and treated with 13.0 g (0.10 mole) of trimethylamine t-butylborane as described above. Following the heating period the product mixture was treated with 200 ml of diethyl ether and filtered. The filtrate was washed well with water, dried over magnesium sulfate and the solvent removed at reduced pressure. The ether insoluble product was recrystallized from acetonitrile or benzene. The ether soluble product was recrystallized from acetonitrile or ethanol-water. Table 1 provides the yields, melting points and analytical data obtained for these products.

Conversion of the lower-melting benzylideneamino t-butylborane product to the higher-melting product. One gram of the ether soluble product derived from benzonitrile (m.p. 141-143°) was placed in a small flask equipped with a nitrogen inlet and outlet. The flask was heated by an oil bath and the temperature slowly raised from 140° to 162°. During this interval the product melted and crystallized. The flask was then heated to 169°, cooled and the crystalline product washed with diethyl ether. The product melted at 185-189° and was identical to the authentic higher-melting product in the infrared.

Preparation of benzaldehyde from benzylideneamino t-butylborane. To a cooled solution of 20 g of concentrated sulfuric acid in 60 ml of 25% aqueous ethanol was added 17.3 g (0.10 mole) of the lower-melting benzylideneamino t-butylborane. The mixture was gently refluxed under nitrogen for 12 hr, cooled and added to 400 ml of water. The products were separated by three extractions with diethyl ether. The combined ethereal extracts were evaporated to dryness under reduced pressure. An infra-red spectrum of the crude product indicated it to be a mixture of t-butylboronic acid and benzaldehyde.

The crude product was dissolved in 75 ml of ether and the ethereal solution extracted three times with 100 ml portions of 10% sodium bisulfite. The aqueous extract was then treated with 100 g of potassium bicarbonate and the liberated benzaldehyde extracted with three 50 ml portions of diethyl ether. The combined ether extracts were dried over magnesium sulfate and the ether removed by evaporation at reduced pressure at 10. The product was shown to be pure benzaldehyde by infra-red identification and weighed 5.1 g or 48% of theory.

Molecular weight determinations. Molecular weight determinations were carried out in duplicate using a conventional cryoscopic apparatus and dry benzene as solvent. Results were reproducible and agreed with theory to within ±2%.

Nuclear magnetic resonance measurements. A Varian high resolution nuclear magnetic resonance spectrometer was employed with a 12.8 mc B^{11} probe. Benzene was routinely employed as solvent and a capillary tube which contained trimethylborate provided the reference resonance.

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