sharp cutoff at *m/e* 104 which corresponds to the $^{12}C_3{}^{11}B_5{}^1H_{13}{}^+$ ion.

$2,3\text{-}(CH_3)_2CB_5H_7$.—The 32.1-Mc/sec ^{11}B nmr spectrum of $2,3\text{-}(CH_3)_2CB_5H_7$ (Figure 1H) consisted of a low-field singlet and three doublets of relative areas 1:1:2:1, respectively. The 60-Mc/sec ^1H nmr spectrum consisted of two broad peaks of equal area at τ 8.10 and 9.40 relative to internal TMS which were assigned to the resonances of the methyl groups at the 2 and 3 positions. The mass spectrum exhibited a sharp cutoff at *m/e* 104 which corresponds to the $^{12}C_3{}^{11}B_5{}^1H_{13}{}^+$ ion.

$1,2,3\text{-}(CH_3)_3CB_5H_6$.—The 32.1-Mc/sec ^{11}B nmr spectrum of $1,2,3\text{-}(CH_3)_3CB_5H_6$ (Figure 1I) consisted of a low-field singlet, two doublets, and a high -field singlet of relative areas 1:1:2:1, respectively. The 60-Mc/sec ^1H nmr consisted of three peaks of equal areas at τ 8.05, 9.32, and 10.57 relative to internal TMS which were assigned to the resonances of the methyl groups at the 2, 3, and 1 positions, respectively. The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

$1\text{-}C_2H_5\text{-}2\text{-}CH_3CB_5H_7$.—The 32.1-Mc/sec ^{11}B nmr spectrum of $1\text{-}C_2H_5\text{-}2\text{-}CH_3CB_5H_7$ (Figure 1J) consisted of two doublets and a singlet of relative areas 2:2:1, respectively. The 60-Mc/sec ^1H nmr spectrum consisted of a broad singlet of area 3 at τ 7.95 assigned to the C–CH_3 resonance and a partially resolved triplet of area 3.0 at τ 9.57 and a broad peak of area 2.1 at τ 10.23 relative to internal TMS, both assigned to the ethyl protons which are consistent with values previously observed.[10] The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

$2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$.—The 32.1-Mc/sec ^{11}B nmr spectrum of $2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$ (Figure 1K) consisted of a low-field singlet and three doublets of relative areas 1:1:2:1, respectively. The 60-Mc/sec ^1H nmr spectrum consisted of a singlet of area 3 at τ 8.08 assigned to the C–CH_3 resonance and a singlet of area 4.6 at τ 8.89 assigned to the B–C_2H_5 resonance[10] relative to internal TMS. The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

The most significant feature of the infrared spectra of these compounds is the strong absorption between 1850 and 1950 cm^{-1} due to bridge hydrogen vibrations.

Acknowledgment.—We wish to thank Pomona College, Claremont, Calif., for the use of their mass spectrometer and Messrs. Timm Paxson and Ken Parsons for taking the mass spectra. This research was supported in part by the Office of Naval Research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

A New Synthesis of Amine– and Phosphine–Boranes

BY K. C. NAINAN AND G. E. RYSCHKEWITSCH

Received July 7, 1969

A new, rapid, and high-yield synthesis of borane adducts with amines and phosphines has been developed. It is based on the reaction of sodium borohydride and iodine in the presence of the donor. The procedure is applicable to adducts of ammonia, primary, secondary, and tertiary amines, di- and triamines, pyridines, triphenylphosphine, and diphosphines. The following new compounds have been prepared: 2-methoxypyridine–borane, 2,2′-dipyridyl–bis(borane), bis(diphenylphosphino)methane–bis(borane), and 1,2-bis(diphenylphosphino)ethane–bis(borane).

Amine–boranes constitute an important class of boron–nitrogen compounds since they or their derivatives provide a direct entry to the synthesis of aminoboranes or borazines[1,2] or to boron cations.[3–5] It is therefore of considerable importance to develop more simple and convenient methods of synthesis of amine–boranes from readily available starting materials. Present methods involve either direct combination of amine and diborane, reaction of ethereal lithium borohydride with ammonium salts,[6] transamination of an already formed amine–borane,[7,8] or less direct methods like reduction of an appropriate boron compound using hydrogen or borohydride.[9–11]

We wish to report here a convenient one-step synthesis of borane adducts using sodium borohydride, appropriate donors, and iodine. The method is simple and it gives boranes with good yield and high purity. The new method was successfully worked out for the synthesis of ammonia–borane, boranes of different aliphatic amines which include primary and secondary monoamines and tertiary di- and triamines, and boranes of substituted pyridines and for the synthesis of phenyl-substituted phosphine–boranes.

---

(1) K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press, New York, N. Y., 1965.

(2) R. A. Geanangel and S. G. Shore, *Preparative Inorg. Reactions*, **3**, 123 (1966).

(3) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(4) J. E. Douglass, *ibid.*, **86**, 5431 (1964).

(5) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967).

(6) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

(7) H. C. Brown, H. I. Schlesinger, and S. Z. Cardon, *ibid.*, **64**, 325 (1942).

(8) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

(9) R. Koster, *Angew. Chem.*, **69**, 64 (1957).

(10) E. C. Ashby and W. E. Foster, *J. Am. Chem. Soc.*, **84**, 3407 (1962).

(11) K. Lang and F. Schubert, U. S. Patent 3,037,985 (1962).

Table I

Yields and Melting Points of Amine– and Phosphine–Boranes

Compounds	Yield of borane, %[h]	Mp of crude product, °C	Mp of recrystallized product, °C	Lit. mp, °C
Ammonia–borane	73			
2-Picoline–borane	94	44–45.5	45–46.5	46–48;[a] 40[b]
4-Picoline–borane	80	64–67	72–73	72–73[b]
2,4,6-Collidine–borane	91	96–97	98–100	99.2–100.3[a]
2-Methoxypyridine–borane	81	63–66	69–70	...
Di-*n*-propylamine–borane	88	28–29	28.5–29.5	30[c]
Dimethylamine–borane	62	33–34.5	35	36[d]
Isopropylamine–borane	84	60–61.5	61.5–62.5	65[c]
TMED·$2BH_3$[j]	81	177–182.5	181–183	182.5–184[e]
PMDET·$3BH_3$[j]	91	170–175 dec	182–188.5	185–186[f]
2,2′-Dipyridyl–bis(borane)	67	*i*	*i*	...
Triphenylphosphine–borane	96	183–186	189	189[g]
Bis(diphenylphosphino)methane–bis(borane)	87	185–186.5 dec.	186.5–188 dec	...
1,2-Bis(diphenylphosphino)ethane–bis(borane)	97	159.5–167.5 dec.	162–167.5 dec	...

[a] E. R. Birnbaum, Ph.D. Dissertation, University of Florida, 1961. [b] J. A. Bigot, Th. J. DeBoar, and F. L. J. Sixma, *Rec. Trav. Chim.*, **76,** 996 (1957). [c] H. Noth and H. Beyer, *Chem. Ber.*, **93,** 928 (1960). [d] E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *J. Am. Chem. Soc.*, **81,** 3550 (1959). [e] N. E. Miller and E. L. Muetterties, *ibid.*, **86,** 1033 (1964). [f] F. E. Walker and R. K. Pearson, *J. Inorg. Nucl. Chem.*, **27,** 1981 (1965). [g] M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, *J. Chem. Soc.*, 899 (1965). [h] Based on iodine. [i] White crystalline compound turns light brown at 129–131°, becomes dark brown on continuous heating, and does not melt even at 300°. [j] TMED = tetramethylethylenediamine; PMDET = pentamethyldiethylenetriamine.

Table II

Analysis of New Borane Adducts

Compounds[a]	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
2-$CH_3Opy \cdot BH_3$	58.63	58.61	8.14	8.05	11.40	11.38
$C_{10}H_8N_2 \cdot 2BH_3$	65.26	65.11	7.67	7.54	15.23	15.02
$(C_6H_5)_2PCH_2CH_2P(C_6H_5) \cdot 2BH_3$	73.23	72.97	7.09	7.20	...	...
$(C_6H_5)_2PCH_2P(C_6H_5)_2 \cdot 2BH_3$	72.88	72.70	6.80	6.68	...	...

[a] py = pyridine; $C_{10}H_8N_2$ = 2,2′-dipyridyl.

Experimental Section

Sodium borohydride was supplied in good purity (98+%) by Metal Hydrides, Inc. Various amines and phosphines were obtained from commercial sources. All other chemicals and solvents were reagent grade and were used without any further purification. Amines and solvents were dried by calcium hydride and 3A molecular sieves.

General Procedure.—The apparatus consists of a nitrogen-flushed 250-ml two-necked flask fitted with a pressure-compensated dropping funnel and an outlet tube leading to a bubbler containing a benzene-amine mixture. In a typical experiment a stoichiometric quantity of iodine in 1,2-dimethoxyethane (monoglyme) was added dropwise to a stirred mixture of sodium borohydride (15–20% excess) and the amine (7–10% excess) with monoglyme. Quantities were calculated on the basis of the equation

$$2NaBH_4 + 2R_3N + I_2 \longrightarrow 2NaI + 2R_3NBH_3 + H_2 \qquad (1)$$

where R_3N = amine. The general work-up of this preparative method is exemplified by the synthesis of 2-picoline–borane.

2-Picoline–Borane.—To sodium borohydride, 1.390 g (36.77 mmol), and to 3.000 g (32.26 mmol) of 2-picoline in 40 ml of dry monoglyme, iodine, 3.855 g (15.18 mmol), in 35 ml of monoglyme was added dropwise over a period of about 3 hr. The reaction mixture was kept stirred throughout the experiment, while the hydrogen gas was escaping through the bubbler. About 5 ml of glycol ether was used to wash down the sides of the funnel at the end of the reaction. The solvent was then removed by pumping and the resulting solids were extracted with 130 ml of dry benzene to separate the soluble amine–borane from sodium iodide and unreacted sodium borohydride. The insoluble solid (NaI and $NaBH_4$) was dried and weighed 4.700 g (calculated from eq 1: 4.800 g). An acidified aqueous solution of the solid did not give a precipitate with excess ammonium hexafluorophosphate. The infrared spectrum of the solid did not show any characteristic absorptions for amine derivatives and the proton nmr spectrum was blank. Thus no bis(amine)boron cation was present.

The filtrate, evaporated to dryness, weighed 3.056 g (94% yield), mp 44–45.5° (lit. 46–48°). The ^1H and ^{11}B nmr and infrared spectra were identical with those of an authentic sample prepared from diborane. Shortening the period of iodine addition to 20 min under otherwise identical conditions did not change the yield.

A portion of the product (1.121 g), dissolved in 50 ml of benzene, was precipitated with 20 ml of hexane. The recovered material (0.759 g, 68%) melted at 45–46.5°.

Ammonia–Borane.—The apparatus and general work-up of the preparation of NH_3BH_3 were similar to that of 2-picoline–borane. Ammonia, 0.350 g, was passed into 50 ml of monoglyme, and 1.143 g (30.24 mmol) of sodium borohydride was added to it. Iodine, 2.538 g (9.99 mmol), dissolved in 40 ml of monoglyme was added dropwise over a period of about 45 min. After reaction, the solvent was pumped off and 150 ml of anhydrous diethyl ether (dried over calcium hydride for several days) was added to extract the ammonia–borane. The filtrate, evaporated to dryness, weighed 0.450 g (73% yield). The properties and infrared spectrum of the white crystalline residue were identical with those reported in literature.[12–14] The amount of calculated hydridic hydrogen was 9.79%; the amount found was 9.62%.[15]

The infrared spectrum of the ether-insoluble residue indicates absorptions of unreacted borohydride overlapped by absorptions of the diamminedihydridoboron(1+) cation. The cation might

---

[12] S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 6084 (1955).

[13] S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

[14] R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 59.

[15] Hydridic hydrogen as determined by the iodate method: E. Jensen, D. Lyttle, and W. Struck, *Anal. Chem.*, **24**, 1843 (1952).

TABLE III

PROTON AND ^{11}B NMR DATA OF AMINE– AND PHOSPHINE–BORANES[a]

Compounds[a]	^1H resonances		^{11}B resonances		
	Proton	δ, ppm	δ, ppm	Multiplicity	J_{B-H}, cps
$2\text{-}CH_3py\cdot BH_3$	$2\text{-}CH_3$	2.72	31.9	4	101
	$H_{3.5}$	7.33			
	H_4	7.88			
	H_6	8.72			
$4\text{-}CH_3py\cdot BH_3$	$4\text{-}CH_3$	2.48	30.6	4	100
	$H_{3,5}$	7.33			
	$H_{2,6}$	8.40			
$2\text{-}OCH_3py\cdot BH_3$	$2\text{-}OCH_3$	4.07	32.9	4	100
	$H_{3,5}$	7.05			
	H_4	8.00			
	H_6	8.45			
$2,4,6\text{-}(CH_3)_3py\cdot BH_3$	$4\text{-}CH_3$	2.33	36.2	4	98
	$2,6\text{-}CH_3$	2.70			
	$H_{3,5}$	7.07			
$(CH_3\overset{\beta}{CH_2}\overset{\alpha}{CH_2})_2NH\cdot BH_3$	$\alpha\text{-}CH_2$	1.72	34.2	4	95
	$\beta\text{-}CH_2$	2.68			
	$-CH_3$	0.98			
$(CH_3)_2NH\cdot BH_3$	$-CH_3$	2.48	32.4	4	94
$(CH_3)_2\underset{\underset{H}{\vert}}{C}NH_2\cdot BH_3$	$-CH_3$	1.25	38.5	4	95
	$-CH$	3.02			
$(CH_3)_2N(CH_2)_2N(CH_3)_2\cdot 2BH_3$	$-CH_3$	2.62	28.7	4	100
	$-CH_2$	3.15			
$C_{10}H_8N_2\cdot 2BH_3$	$H_{3,3',\ 5,5'}$	7.66	30.7[c]	4	99
	$H_{4,4'}$	8.11			
	$H_{6,6'}$	8.83			
$(CH_3)_2N(CH_2)_2\underset{\underset{CH_3}{\vert}}{N}(CH_2)_2N(CH_3)_2\cdot 3BH_3$	$-CH_3$	2.65	29.5[b,c]	4	96 ± 4
	$-CH_2$	3.21			
$(C_6H_5)_3P\cdot BH_3$	$-C_6H_5$	7.47	55.8	8	$J_{B-H} = 98$ $J_{B-P} = 57$
$(C_6H_5)_2PCH_2P(C_6H_5)_2\cdot 2BH_3$	$-C_6H_5$	7.46	55.4		
	$-CH_2$ (triplet, $J = 11.5$ cps)	3.27			
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\cdot 2BH_3$	$-C_6H_5$	7.49	58.4		
	$-CH_2$ (doublet, $J = 3.0$ cps)	2.38			

[a] All the δ values represent the centers of the resolvable or complex multiplets. ^1H and ^{11}B spectra were run in methylene chloride. The ^1H chemical shifts are measured relative to tetramethylsilane, internal, and ^{11}B shifts are measured with respect to trimethyl borate, external. py = pyridine; $C_{10}H_8N_2$ = 2,2′-dipyridyl. [b] In nitromethane. [c] The ^{11}B nmr obtained at 32.1 Mc.

have been formed by decomposition of ammonia–borane at room temperature.[13]

Synthesis of the other amine–boranes was accomplished as with 2-picoline–borane. Pentamethyldiethylenetriamine–tris(borane) was obtained as the insoluble residue when the solids remaining after evaporation of the monoglyme were extracted with water. The borane adduct of 2,2′-dipyridyl was only slightly soluble in benzene. A preparation from 3.095 g (19.3 mmol) of amine and a slight excess of I_2 gave 0.568 g of benzene-soluble extract, mostly unreacted amine, and, after water extraction, 2.441 g (13.2 mmol, 68%) of the 1:2 adduct.

The yields of boranes and the melting points of the crude and recrystallized products are given in Table I. Analytical data for new compounds are listed in Table II. Analyses were performed by Peninsular ChemResearch, Inc., Gainesville, Fla.

Triphenylphosphine–Borane.—To triphenylphosphine, 9.157 g (34.95 mmol), and to sodium borohydride, 1.569 g (41.50 mmol), in 40 ml of monoglyme, iodine, 4.296 g (16.91 mmol), in 40 ml of glyme was added dropwise over about 3 hr. After the solvent was evaporated, triphenylphosphine–borane was extracted with 200 ml of benzene; on evaporation 7.750 g of borane was obtained (83%, mp 182–186°). A second extraction with 200 ml of methylene chloride yielded an additional 1.231 g of borane (mp 183–186°). The total yield of triphenylphosphine–borane was about 96%.

A portion of the crude product (1.812 g) was treated with 35 ml of dry hexane and filtered. The hexane-insoluble portion, dissolved in 70 ml of benzene, was precipitated with 80 ml of hexane (recovery 66%; mp 189°). Analyses for new phosphorus-containing boranes are given in Table II.

Nmr Spectra.—Proton nmr spectra of the boranes were taken in CH_2Cl_2 with a Varian A-60 instrument with tetramethylsilane as internal reference, and ^{11}B nmr spectra were obtained at 19.3 Mc with trimethyl borate as the external reference using CH_2Cl_2 as the solvent. The chemical shifts, δ, in parts per million, and observed B–H coupling constants, J, in cycles per second, are reported in Table III. In general, the ^{11}B resonances were quartets for all of the amine–boranes, as expected. The ^{11}B spectrum of triphenylphosphine–borane is more complex than that of the amine–boranes due to additional B–P coupling. It is an octet composed of overlapping quartets with $J_{B-H} = 98$ Hz and $J_{B-P} = 57$ Hz. The integrated intensities of the proton spectra agreed well with the expected values. In the proton spectra, there is a definite downfield shift in all of the resonances relative to corresponding peaks for the free amines or phosphines. Resonances belonging to the pyridine ring protons were assigned on the basis of their relative intensities, their multiplicity, and their relative chemical shifts.[16-18]

Infrared Spectra.—All infrared spectra of the boranes were run in potassium bromide disks using a Beckman IR-10 spectrophotometer. The assignments of the various bands were made by a straightforward comparison between the spectra of the borane adducts and the spectra of the amines and phosphines. The infrared spectrum of triphenylphosphine–borane is identical with that published in the literature[19] (608 cm^{-1} for B–P stretching; very near 2400 and 2240 cm^{-1} for asymmetric and symmetric B–H stretching, respectively; 1135 cm^{-1} for BH_3 bending; 1060 cm^{-1} for BH_3 wagging). In general, the vibrational frequencies of the BH_3 group of the amine–boranes are similar to the infrared data reported in the literature.[14,20]

Results and Discussion

The present results demonstrate the convenience, rapidity, and apparently quite general applicability of this synthesis of borane adducts. The reactions proceed essentially quantitatively according to eq 1. The most likely reaction path is initial hydride abstraction by I_2, followed by trapping of the liberated BH_3 group by the amine[5]

$$BH_4^- + I_2 \longrightarrow BH_3 + HI$$

$$BH_3 + H_{3-n}NR_n \longrightarrow H_{3-n}NR_nBH_3$$

Whether HI reacts directly with an additional mole of BH_4^- or whether it is temporarily trapped by amine does not affect the eventual result since ammonium salts are known to react with borohydrides to yield amine–boranes.[6] In spite of serious efforts to detect boron cations in the product, none, except in the reaction of ammonia, was found. The lack of formation of boron cations, which are formed rapidly in the reaction of iodine with amine–boranes in the presence of amines,[21] carries the strong implication that borohydride reacts much more rapidly with iodine than do borane adducts, in agreement with the expected higher hydridic activity of BH_4^-.

The new borane adducts were characterized by means of elemental analyses, nmr, and their infrared spectra which showed, in addition to the bands corresponding to the amine or phosphine structure, the expected B–H stretches and deformations and new bands for the B–N or B–P stretches. A new, strong absorption at 1110 cm^{-1} was found in the infrared spectra of all the three phosphine–boranes and it may be assigned as the characteristic band for phenyl-substituted tetracoordinate phosphorus.[22,23] Proton nmr spectra for the new phosphine derivatives are noteworthy. The bis(phosphino)methane–borane shows the triplet for the CH_2 group expected from coupling of both phosphorus atoms to the protons as does the parent donor. The bis(phosphino)ethane derivative shows only a doublet for the CH_2 groups, whereas the uncoordinated phosphine shows a triplet. The latter pattern corresponds to virtual coupling of both phosphorus atoms to the protons.[24,25] On coordination to BH_3, this coupling was not observed, a phenomenon which also has been observed on coordination of bisphosphino derivatives to alkyl groups or to sulfur or oxygen.[24,25]

In summary, the present synthesis offers several distinct advantages over previous methods, without sacrifice of generality: the use of diborane is avoided, starting materials and apparatus are readily available, and high yields of product which often does not require further purification are obtained.

Acknowledgment.—Supported of this work by the National Institutes of Health under Grant GM-13650 is gratefully acknowledged.

---

(16) E. B. Backer, *J. Chem. Phys.*, **23**, 1981 (1955).

(17) H. J. Bernstein and W. G. Schneider, *ibid.*, **24**, 469 (1956).

(18) W. S. Brey, Jr., M. E. Fuller, G. E. Ryschkewitsch, and A. S. Marshall, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 100.

(19) M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, *J. Chem. Soc.*, 899 (1965).

(20) A. R. Katritzky, *ibid.*, 2049 (1959).

(21) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).

(22) R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

(23) S. R. Jain and H. H. Sisler, *ibid.*, **8**, 1243 (1969).

(24) A. J. Cartey and R. K. Harris, *Chem. Commun.*, 234 (1967).

(25) J. J. Brophy and M. J. Gallagher, *Australian J. Chem.*, **20**, 503 (1967).