Azomethine Derivatives. Part VI.[1] The Action of Diphenylketimine on Diborane, Trisdimethylaminoborane, Trimethylborate, Boron Trifluoride and Boron Trichloride

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Diphenylketimine and diborane form an adduct $Ph_2C{:}NH,BH_3$ which at 120° loses hydrogen and rearranges to the borazine $(Ph_2CHNBH)_3$, for which the i.r., ^1H n.m.r. and mass spectroscopic results are given. Diphenylketimine reacts with trisdimethylamino-borane to replace dimethylamino- by diphenylketimino-groups, but even with an excess of the imine, incompleteness of reaction and difficulties of separating the products make the reaction unsuitable for the preparation of trisdiphenylketiminoborane. Boron trichloride and an excess of diphenylketimine likewise give impure trisdiphenylketiminoborane. Boron trifluoride and diphenylketimine give the adduct $Ph_2C{:}NH,BF_3$ which is sufficiently stable to withstand vacuum sublimation at 100—120°. Trimethylborate does not react with diphenylketimine at 70°.

In Part I[2] we described the effect of diphenylketimine on some organoboranes R_3B, and showed that when $R = Me$ it was possible to isolate the adduct, $Ph_2C{:}NH,BMe_3$, which eliminated methane at 160—200° to form the azomethine derivative $Ph_2C{:}NBMe_2$. We now describe a study of other systems $Ph_2C{:}NH{-}BX_3$ (where $X = H$, NMe_2, OMe, F, or Cl), in which we have explored the possibility of isolating adducts $Ph_2C{:}NH,BX_3$ and have investigated whether the elimination of HX from such systems would allow the preparation of derivatives $(Ph_2C{:}N)_nBX_{3-n}$, particularly $(Ph_2C{:}N)_3B$, trisdiphenylketiminoborane which we have previously prepared from boron tribromide and diphenylketiminolithium.[1]

Diborane and diphenylketimine reacted in hexane to precipitate the adduct $Ph_2C{:}NH,BH_3$ which even at 20° eliminated hydrogen slowly. Its identity was deduced from analytical data and its i.r. spectrum, in which a medium-intensity band at 3257 cm.$^{-1}$ could be assigned to ν(N–H), a set of medium-intensity absorptions at 2410, 2288, and 2252 cm.$^{-1}$ could be assigned to B–H stretching vibrations, and a strong band at 1620 cm.$^{-1}$ could be assigned to the azomethine stretching vibration ν(C=N). The frequency of this last band is *higher* than ν(C=N) for diphenylketimine itself (1603 cm.$^{-1}$). Increase in ν(C=N) on co-ordination indeed appears to be a general feature of diarylketimine adducts, *e.g.*, $Ph_2C{:}NH,BF_3$ (see below) has ν(C=N) 1628 cm.$^{-1}$, $Ph_2C{:}NH_2^+Cl^-$ (the adduct of diphenylketimine and a proton) has ν(C=N) 1653 cm.$^{-1}$ while methiodides $[Ar_2C{:}NMeAr]^+I^-$ have higher values of ν(C=N) than the parent imines.[3] This increase may be contrasted with the marked *decrease* in the carbonyl stretching frequency on co-ordination observed with the isoelectronic ketones (whether alkyl or aryl)[4] and also with acid chlorides and esters which likewise co-ordinate through the carbonyl group.[5] This decrease has generally been attributed to a weakening of the C=O link consequent upon drainage of electronic charge from oxygen. A similar effect should also apply to ketimine adducts. The argument put forward by Goulden,[3] that co-ordination of diarylketimines *increases* the azomethine bond order by offsetting the electron-withdrawing effect of the aryl groups should (but evidently does not) apply equally to diarylketone adducts. Whatever the reason for the increase in ν(C=N) of diphenylketimine on co-ordination, the magnitude of the increase appears to reflect the Lewis acidity of the acceptor moiety (cf. $BF_3 > BH_3 > BMe_3$[2]).

The decomposition of diphenylketimine–borane at 120° did not afford a diphenylketiminoborane. Although hydrogen was eliminated as expected, simultaneous migration of a hydrogen atom from boron to the azomethine carbon reduced the C=N double bond to a single bond, and the product isolated was the borazine $(Ph_2CHNBH)_3$:

$$Ph_2C{:}NH,BH_3 \longrightarrow \tfrac{1}{3}(Ph_2CHNBH)_3 + H_2$$

The identity of the product was established by analytical,

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[1] Part V, I. Pattison, K. Wade, and B. K. Wyatt, preceding paper.

[2] I. Pattison and K. Wade, *J. Chem. Soc.* (*A*), 1967, 1098.

[3] J. D. S. Goulden, *J. Chem. Soc.*, 1953, 997.

[4] B. P. Susz and I. Cooke, *Helv. Chim. Acta*, 1954, **37**, 1273; B. P. Susz and P. Chalandon, *ibid.*, 1958, **41**, 1332; B. P. Susz, *Compt. rend.*, 1959, **248**, 2569; D. E. H. Jones and J. L. Wood, *J. Chem. Soc.* (*A*), 1967, 1140.

[5] D. Cook, 'Friedel-Crafts and Related Reactions," ed. G. Olah, Interscience, New York, 1963, vol. I, p. 767.

i.r., ^{1}H n.m.r., and mass spectroscopic methods. Elemental analyses confirmed the empirical formula, and the i.r. spectrum, which had no absorptions in the N–H or C=N stretching regions, had three bands in the B–H stretching region (2525m, 2433m, and 2404m cm.$^{-1}$) and a very strong absorption at 1355 cm.$^{-1}$ in the region typical of borazines.[6]

The ^{1}H n.m.r. spectrum of the borazine as a dilute solution in hexadeuteriobenzene was recorded with cyclohexane as internal reference. Two multiplets at τ 2·8$_9$ (relative intensity 6) and at 3·0$_0$ (intensity 4) [τ(Me$_4$Si) 10·0] clearly originated from the aromatic protons and a singlet at τ 3·9$_6$ (intensity 1) could be assigned to the aliphatic proton. Absorptions attributable to boron-attached protons were not detected, presumably because spin–spin coupling to ^{11}B would give rise to a widely-spaced quartet the components of which would be expected to be broad and of low intensity.

As borazynes $(RNBX)_n$ may be tetrameric[7] in cases where the substituents R and X are too bulky to be accommodated about the planar six-membered ring of the (trimeric) borazine, the molecular complexity of the present compound was investigated by mass spectroscopy, which confirmed the trimer (borazine) structure. Masses, relative intensities, and assignments of the main peaks having $m/e > 255$ are given in the Table. Peaks generally occurred in sets. The masses quoted relate to fragments in which all the boron atoms are ^{11}B—in all cases attendant ^{10}B satellites were observed at 1, 2, and 3 mass units below these, and fragments having one or two fewer hydrogen atoms than the fragments quoted caused the set of peaks to extend in most cases over six mass units. No peak corresponding to a tetramer $(Ph_2CHNBH)_4$ was observed, and the measured mass of the parent ion, 579·3201, was within 2·3 p.p.m. of that calculated for $(Ph_2CHN^{11}BH)_3$. The only peaks at higher mass than this could be attributed to a trace of impurity in which one boron of the borazine had Ph$_2$CN, not hydrogen, as substituent. The main feature of the breakdown pattern, apart from loss of individual hydrogen atoms (probably from boron), was the successive loss of phenyl or diphenylmethyl groups leaving the ring intact. The peaks at m/e = 166, 167, and 168, corresponding to Ph$_2$C$^+$, Ph$_2$CH$^+$, and Ph$_2$CH$_2$$^+$ were understandably very intense, as diphenylmethane was found to be a major product of the thermal decomposition of $(Ph_2CHNBH)_3$. Significantly, although a peak at m/e = 180 (Ph$_2$CN$^+$) had previously been found to be a major feature of the mass spectra of azomethine derivatives $(Ph_2C{:}NMR_2)_{1\,\mathrm{or}\,2}$ (where M = B,[2] Al,[8] or Ga[9]) such a peak was absent from the spectrum of $(Ph_2CHNBH)_3$. A further interesting feature of the spectrum at $m/e < 255$ was the appearance of sets of peaks at half-integer intervals ranging from masses 251, 212½, and 174 and of relative intensities 1, 8, and 2 respectively which evidently corresponded to the doubly-charged ions $(Ph_{6-n}C_3H_3N_3B_3)^{2+}$ resulting from loss of one, two, or three phenyl groups from the parent.

Mass spectrum of $(Ph_2CHNBH)_3$

m/e	Relative intensity	Assignment
758	0·2	$(Ph_2CH)_3N_3B_3H_2NCPh_2$
579	50	$(Ph_2CH)_3N_3B_3H_3$
502	100	$(Ph_2CH)_3N_3B_3H_3$ – Ph
425	10	$(Ph_2CH)_3N_3B_3H_3$ – 2Ph
412	1	$(Ph_2CH)_2N_3B_3H_3$
348	4	$(Ph_2CH)_3N_3B_3H_3$ – 3Ph
335	3	$(Ph_2CH)_2N_3B_3H_3$ – Ph
258	2	$(Ph_2CH)_2N_3B_3H_3$ – 2Ph

Trisdimethylaminoborane and diphenylketimine, when held at 150° under nitrogen (1 atmos.) under a reflux condenser, reacted with evolution of dimethylamine:

$$(Me_2N)_3B + nPh_2C{:}NH \longrightarrow (Ph_2C{:}N)_nB(NMe_2)_{3-n} + nMe_2NH$$

This reaction is analogous to the transamination reaction of aminoboranes in which a relatively involatile secondary amine displaces a more volatile amine (such as dimethylamine) from an aminoborane,[10] *e.g.*,

$$(Me_2N)_3B + 3R_2NH \longrightarrow (R_2N)_3B + 3Me_2NH$$

Even when an excess of diphenylketimine was used, however, the i.r. spectrum of the viscous liquid produced still contained bands at 2933 and 2865 cm.$^{-1}$ indicative of aliphatic C–H, showing that not all the dimethylamino-groups had been replaced by diphenylketimino-groups. This was confirmed by the detection (by i.r. spectroscopy) of small quantities of dimethylamine in the ammonia evolved when samples of the materials were heated with concentrated aqueous sodium hydroxide. Moreover, the analytical results were consistent with contamination of the trisdiphenylketiminoborane $(Ph_2C{:}N)_3B$ by some amino(bisketimino)borane $(Ph_2C{:}N)_2BNMe_2$. Removal of unchanged diphenylketimine was difficult; it is a relatively oily liquid, soluble in the same solvents as the boron derivative, and capable of vacuum distillation from the mixture only very slowly at temperatures low enough to prevent decomposition of the ketiminoborane.

Trimethoxyborane and diphenylketimine were recovered essentially unchanged after being held at 70° for 4 hr. under dry nitrogen under a reflux condenser. The lack of reaction in this system is consistent with the general tendency for boron–nitrogen links to be cleaved by water or alcohols.

Boron trifluoride and diphenylketimine gave an adduct $Ph_2C{:}NH,BF_3$ in which the co-ordinate link was strong enough to allow vacuum sublimation at 100—120° as a means of purification. Although this compound decomposed above about 180° to a yellow, involatile, insoluble solid, the identity of the product

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[6] R. E. Hester and C. W. J. Scaife, *Spectrochim. Acta*, 1966, **22**, 755.

[7] H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 1965, 6421.

[8] K. Wade and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1967, 1339.

[9] J. R. Jennings, I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1967, 1608.

[10] H. Nöth, *Z. Naturforsch.*, 1961, **16*b***, 470; W. D. English, A. L. McCloskey, and H. Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122.

was not established. The related amine adduct Me_2NH,BF_3 eliminates hydrogen fluoride at 250°:[11]

$$2Me_2NH,BF_3 \xrightarrow{250°} \tfrac{1}{2}(Me_2NBF_2)_2 + Me_2NH_2^+BF_4^-$$

Boron trichloride and diphenylketimine, by contrast, eliminated hydrogen chloride so readily that even at −78° diphenylketimine hydrochloride was deposited from a hexane solution of the mixture, and no adduct $Ph_2C{:}NH,BCl_3$ could be isolated. The reaction between boron trichloride (1 mol.) and an excess of diphenylketimine (6 mol.) was therefore studied as a possible route to trisdiphenylketiminoborane:

$$BCl_3 + 6Ph_2C{:}NH \longrightarrow (Ph_2C{:}N)_3B + 3Ph_2C{:}NH_2^+Cl^-$$

Essentially the theoretically expected quantity of diphenylketimine hydrochloride was formed which could be filtered off; removal of solvent from the filtrate under reduced pressure left a syrup which had an i.r. spectrum similar to that of authentic $(Ph_2C{:}N)_3B$.[1] Analysis revealed traces of chlorine, however, and some diphenylketimine distilled out when a sample was held at 100° *in vacuo*. Towards boron trichloride, therefore, diphenylketimine is intermediate in reactivity between dimethylamine[12] and diphenylamine.[13] Dimethylamine in excess replaces all three chlorine atoms of boron trichloride to give trisdimethylaminoborane,[12] whereas diphenylamine replaces one chlorine under mild conditions and only one further at higher temperatures in the presence of triethylamine:[13]

$$BCl_3 \xrightarrow{Ph_2NH} Ph_2NBCl_2 \xrightarrow{Ph_2NH-Et_3N} (Ph_2N)_2BCl$$

In conclusion, although an excess of diphenylketimine reacts with either trisdimethylaminoborane or boron trichloride to give some trisdiphenylketiminoborane, the physical and chemical properties of the product (a viscous, thermally rather unstable, involatile liquid) are such as to make difficult its separation from unchanged diphenylketimine and other reaction products.

EXPERIMENTAL

Materials.—Methanolysis of the product of the reaction between benzonitrile and phenylmagnesium bromide in diethyl ether gave diphenylketimine which was purified by vacuum distillation (b. p. 90—95°/10^{-3} mm.). Boron trifluoride–diethyl ether complex was purified by fractional distillation under dry nitrogen (b. p. 125—126°). Diborane, from lithium aluminium hydride and boron trifluoride–diethyl ether complex in diethyl ether solvent, was purified by trap-to-trap distillation in the vacuum line. Boron trichloride, boron tribromide, trimethyl borate, and trisdimethylaminoborane (from boron trichloride and dimethylamine in hexane at −78°)[12] were all distilled before use.

Manipulations were carried out using a conventional vacuum line, nitrogen-filled glove box, or nitrogen-filled apparatus as appropriate. Solvents (diethyl ether, pentane, hexane, benzene, and toluene) were dried over sodium.

Spectra.—I.r. spectra in the range 2—25 μ were recorded on a Grubb–Parsons prism grating GS2A spectrometer or Spectromaster. N.m.r. spectra were recorded at 60 Mc./sec.$^{-1}$ on a Perkin-Elmer R10 spectrometer. Mass spectra were recorded on an A.E.I. M.S.9 instrument at 70 ev and an accelerating potential of 8 kv, using a source temperature of 150—250° and electromagnetic scanning. Compounds were introduced by direct insertion into the ion source.

Analyses.—Boron was determined by ignition of a weighed sample of compound in oxygen, solution of the resulting oxide in water, and subsequent titration of the boric acid with sodium hydroxide in the presence of mannitol, with Bromothymol Blue as indicator. Carbon and hydrogen were determined by conventional combustion techniques. Nitrogen was determined by the Kjeldahl method. Fluorine was determined by the sodium-fusion method described by Belcher and Tatlow[14] with the modification that the aqueous sodium fluoride formed was passed through an anion-exchange column and the resulting hydroxide was determined by acidimetry.

Reaction of Diphenylketimine with Diborane.—Diborane (0·050 g., 1·8 mmole) was condensed on a frozen solution of diphenylketimine (0·60 g., 3·3 mmole) in hexane (15 c.c.) at −196° in a tube; this was sealed and warmed to room temperature with shaking. Some hydrogen (9 c.c., 0·4 mmole) was evolved, and a white precipitate separated which was collected, washed with toluene, and identified as the *adduct* $Ph_2C{:}NH,BH_3$ decomp. 90—95° (Found: C, 81·6; H, 7·5; B, 5·5. $C_{13}H_{14}BN$ requires C, 80·0; H, 7·2; B, 5·6%), $\nu_{max.}$ (Nujol mull) 3257m, 2410m, 2288m, 2252m, 1620s, 1603sh, 1582m, 1499s, 1314m, 1289sh, 1280s, 1193s, 1188s, 1176s, 1148vs, 1085m, 1066w, 1047w, 1038m, 1007m, 972s, 933m, 894m, 858m, 850m, 824w, 788s, 752s, 736s, 721m, 700vs, 696sh, 667w, 630m, 617w, 602w, 561w, 546m, and 448m cm.$^{-1}$. It was insoluble in hexane, benzene, and toluene, and reacted with acetone and water with evolution of hydrogen.

Thermal Decomposition of $Ph_2C{:}NH,BH_3$.—A sample of the adduct (3·9 g., 20 mmole) when held at 120° for 2 hr. in a tube gave hydrogen (330 c.c., 15 mmole) and *NN′N″*-tris(diphenylmethyl)borazine, $(Ph_2CHNBH)_3$, m. p. 104° (from toluene–hexane) [Found: C, 81·6; H, 6·8; N, 7·0%; *M* (mass spectrum), 579·3201. $C_{39}H_{36}B_3N_3$ requires C, 80·8; H, 6·2; N, 7·2%; *M*, 579·3188], $\nu_{max.}$ (Nujol mull) 2525m, 2433m, 2404m, 1495s, 1355vs, 1335s, 1312m, 1263m, 1176s, 1170s, 1149s, 1142sh, 1081m, 1063s, 1032s, 1003w, 975w, 962w, 952w, 923w, 909m, 900s, 826w, 760m, 735s, 698vs, 667w, 663w, 638vw, 617vw, 611m, and 585s cm.$^{-1}$. When held at 130° for 48 hr. the borazine decomposed with formation of diphenylmethane, b. p. 80° and 10^{-3} mm., identified by comparison of its i.r. and ^1H n.m.r. spectra with those of an authentic sample.

Reaction of Diphenylketimine with Trisdimethylaminoborane.—A mixture of trisdimethylaminoborane (1·4 g., 10 mmole) and diphenylketimine (5·4 g., 30 mmole) was held at 150° for 36 hr. under dry nitrogen at 1 atmos. with a reflux condenser fitted with a gas outlet. Dimethylamine was evolved and identified by its i.r. spectrum. The reaction mixture turned dark brown. An attempt to distil the residue under reduced pressure gave distillates of trisdimethylaminoborane (0·085 g., 0·57 mmole) and diphenylketimine. The involatile dark brown viscous liquid residue was dissolved in toluene–hexane, the solution was filtered, and solvent was removed under reduced pressure. The

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[11] J. F. Brown, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

[12] E. Wiberg and K. Schuster, *Z. anorg. Chem.*, 1933, **77**, 213.

[13] D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *J. Chem. Soc.*, 1962, 4088.

[14] R. Belcher and J. C. Tatlow, *Analyst*, 1951, **76**, 593.

viscous liquid residue was apparently impure trisdiphenylketiminoborane $(Ph_2C{:}N)_3B$ (Found: C, 78·5; H, 4·9; B, 2·3. Calc. for $C_{39}H_{30}BN_3$: C, 84·9; H, 5·4; B, 2·0%), $\nu_{max.}$ (liquid film) 3424w, 3250w, 3058s, 3020s, 2968w,sh, 2933m,sh, 2865s, 2793m, 1961w, 1892w, 1815w, 1767w, 1647m, 1624m,sh, 1600s, 1570s, 1515vs, 1493vs, 1449vs, 1416s, 1360vs, 1318s, 1290s, 1274sh, 1250sh, 1196s, 1181s, 1153s, 1134w, 1103s, 1075m, 1031s, 1003m, 977wm, 931m, 909sh, 892vs, 847w, 789vs, 761vs, 743m, 728w, 721w, 704—690vs,br, 673sh, 645m, 623vs, 607w, 593m, and 570w cm.$^{-1}$. This spectrum was very similar to, but contained more bands than, the spectrum of authentic trisdiphenylketiminoborane prepared from $3Ph_2C{:}NLi + BBr_3$. Alkaline hydrolysis, however, gave some dimethylamine as well as ammonia.

Reaction of Diphenylketimine with Trimethoxyborane.—Diphenylketimine (5·4 g., 30 mmole) and trimethoxyborane (1·0 g., 10 mmole) were held at 70° for 4 hr. under dry nitrogen at 1 atmos. under a reflux condenser. It was found that most of the trimethoxyborane (0·95 g.) could be recovered from the mixture by distillation. Subsequent distillation of the residual brown liquid at 100—110° under reduced pressure gave unchanged diphenylketimine (5 g.), leaving a trace of involatile brown solid which gave a green flame when burnt.

Reaction of Diphenylketimine with Boron Trifluoride.—Diphenylketimine (1·8 g., 10 mmole) in diethyl ether (20 ml.) was added to boron trifluoride–diethyl ether complex (1·4 g., 10 mmole) in diethyl ether (20 ml.) with stirring. A white solid separated immediately, which was collected on a sintered glass disc, washed, and identified as the *boron trifluoride–diphenyl ketimine adduct*, $Ph_2C{:}NH,BF_3$; this could be sublimed *in vacuo* at 100—120° but which decomposed above about 180° melting eventually at 207° to a yellow liquid (Found: C, 62·8; H, 4·1; F, 24·3; N, 5·6. $C_{13}H_{11}BF_3N$ requires C, 62·6; H, 4·4; F, 22·9; N, 5·6%), $\nu_{max.}$ (Nujol mull) 3279s, 1628vs, 1592s, 1572m, 1504m, 1330m, 1319m, 1282s, 1190m, 1182m, 1170s, 1143s, 1121s, 1087s, 1070vs, 1031m, 1001m, 978sh, 963s, 935s, 915s, 899m, 851m, 794s, 769vw, 750m, 724m, 704s, 694m, 667vw, 655w, 611vw, 592s, 565vw, and 551m cm.$^{-1}$.

Reaction of Diphenylketimine with Boron Trichloride.—Boron trichloride (1·4 g., 13 mmole) was condensed at −78° on a stirred solution of diphenylketimine (14 g., 77 mmole) in hexane (100 ml.). Diphenylketimine hydrochloride (7·6 g., 35 mmole) identified by its i.r. spectrum, was deposited. Solvent was removed under reduced pressure and the residual viscous suspension was stirred with benzene (30 ml.). The benzene solution was filtered, benzene was removed under reduced pressure, and when the residual viscous liquid was held at 100° and 10^{-3} mm. pressure, some diphenylketimine distilled. The involatile residual syrup was identified by its i.r. spectrum as trisdiphenylketiminoborane $(Ph_2C{:}N)_3B$, contaminated by some chloride (detected as traces of silver chloride in a sample of nitric acid hydrolysate).

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