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# Azomethine Derivatives. Part I. Reactions between Diphenylketimine and Trimethylborane, Triethylborane, and Triphenylborane

By I. Pattison and K. Wade, Chemistry Department, University of Durham

Diphenylketimine reacts reversibly with trimethylborane below 20° to give the solid adduct Ph<sub>2</sub>C:NH,BMe<sub>3</sub> which at 160-200° slowly forms methane and the azomethine derivative Ph<sub>2</sub>C:N·BMe<sub>2</sub>. Dissociation vapour-pressure measurements and infrared and proton magnetic resonance spectroscopy of the adduct show diphenylketimine to be intermediate in donor power between nitriles and amines. Mass spectroscopy of Ph<sub>2</sub>C:N·BMe<sub>2</sub> reveals this compound to exist unassociated in the vapour phase at 200°, providing the first example of a boron-nitrogen analogue of an allene, although the B-N bond order appears to be appreciably lower than the C=N bond order.

No evidence of adducts was obtained in studies of the systems  $Ph_2C:NH-BR_3$  (R = Et or Ph). Diphenylketimine and triethylborane at 155° gave ethylene and Ph<sub>2</sub>C:NCHPh<sub>2</sub>. Features of the mass, infrared, and proton magnetic resonance spectra of the products of these reactions are discussed.

CERTAIN azomethine derivatives  $(RR'C:N\cdot MR_2'')_2$  of Group III elements M can be prepared by addition reactions of nitriles. For example, the hydroboration of nitriles RCN by organoboron hydrides (R"<sub>2</sub>BH)<sub>2</sub> leads to aldimine derivatives (RCH:N·BR''<sub>2</sub>)<sub>2</sub>.<sup>1,2</sup> Both

<sup>2</sup> J. E. Lloyd and K. Wade, J. Chem. Soc., 1964, 1649.

<sup>1</sup> M. F. Hawthorne, Tetrahedron, 1962, 17, 117.

aldimine (RCH:N·AlR''<sub>2</sub>)<sub>2</sub> and ketimine (RR''C:N·AlR''<sub>2</sub>)<sub>2</sub> derivatives of aluminium can be prepared from the nitrile RCN and an appropriate organoaluminium compound  $(R''_{2}AlH \text{ or } R''_{3}Al)^{3,4}$  while aldimine derivatives

<sup>3</sup> J. E. Lloyd and K. Wade, *J. Chem. Soc.*, 1965, 2662. <sup>4</sup> J. R. Jennings, J. E. Lloyd, and K. Wade, *J. Chem. Soc.*, 1965, 5083.

of gallium are accessible by such reactions as  $(1).^5$  However, the lower reactivity of organo-boron and -gallium

$$2PhCN + 2GaEt_3 \longrightarrow (PhCH:N\cdot GaEt_2)_2 + 2C_2H_4 \qquad (I)$$

compounds than of organoaluminium compounds towards insertion of an unsaturated functional group like nitrile causes ketimine derivatives (RR'C:NMR"2), of boron and gallium to be inaccessible by this general route. We have accordingly explored the possibility of preparing ketimine derivatives of boron by reaction (2) of a ketimine with organoboron compounds. This

$$R_2 C: NH + R_3'B \longrightarrow R_2 C: N \cdot BR_2' + R'H$$
(2)

reaction would be analogous to the well-established method (3) of attaching amino-groups to boron by use of secondary amines.6 The ketimine chosen was di-

$$R_2 NH + BX_3 \longrightarrow R_2 NBX_2 + HX$$
(3)

phenylketimine, which is readily prepared from benzonitrile by the Grignard route, and is relatively resistant to hydrolysis and to polymerisations or rearrangements. Dialkylketimines with small alkyl groups appear to be highly susceptible to polymerisations or rearrangements, so much so that the dimethyl compound Me<sub>2</sub>C:NH, which would have afforded a means of preparing isopropylideneaminoboranes Me<sub>2</sub>C:N·BR<sub>2</sub>, has apparently never been isolated during attempts at its preparation by use of methyl cyanide and Grignard or lithium reagents.7 Unsuccessful attempts have been made in these laboratories<sup>8</sup> to prepare diethylketimine, by methanolysis of the products of reactions between EtCN and EtLi or EtMgX,9 or by acetylacetone cleavage at  $-78^{\circ}$  of products of reactions of EtCN with Et<sub>3</sub>Al.<sup>4,10</sup> It is likely that the instability of dialkylketimines is in part associated with the presence of hydrogen attached to the carbons  $\alpha$  to the azomethine group [as in  $(>CH)_2C=NH$ , a disadvantage avoided by the use of diphenylketimine. Hydrogen atoms attached to the  $\alpha$ carbon atom of a nitrile cause serious complications in the preparation of azomethine derivatives by use of addition reactions of nitriles, as the predominant reaction involves cleavage of alkane, e.g., (4).<sup>4</sup>

$$MeCN + Me_{3}AI \longrightarrow \frac{1}{n}(Me_{2}AI \cdot CH_{2}CN)_{n} + MeH$$
(4)

We have studied the systems  $Ph_2C:NH-R_3B$  (R = Me, Et, or Ph). Azomethine derivatives of boron were obtained only in the system Ph<sub>2</sub>C:NH-Me<sub>3</sub>B. Trimethylborane and diphenylketimine form an unstable solid adduct Ph<sub>2</sub>C:NH,BMe<sub>3</sub> over which the dissociation pressure of trimethylborane is 28 mm. at 23.5°. The change of dissociation pressure of this adduct with temperature over the range 0-44° corresponds to a heat of dissociation for the solid adduct into liquid diphenylketimine and gaseous trimethylborane of the order of 4 kcal. mole<sup>-1</sup>. Our own vapour-pressure measurements on diphenylketimine over the temperature range 110-185° correspond to a heat of vaporisation of 16.6 kcal. mole<sup>-1</sup>. Accordingly, an upper limit of 4 + 16.6 =20.6 kcal. mole<sup>-1</sup> can be set on the value of the heat of dissociation of gaseous Ph<sub>2</sub>C:NH,BMe<sub>3</sub> into gaseous Ph<sub>2</sub>C:NH and gaseous Me<sub>3</sub>B. The actual value will differ from this by an amount equal to the heat of sublimation of crystalline Ph<sub>2</sub>C:NH,BMe<sub>3</sub>, which cannot be measured directly but is likely to be about 16 kcal. mole<sup>-1</sup>, by analogy with structurally similar organic compounds.11

The approximate value of 5 kcal. mole<sup>-1</sup> for the heat of dissociation of Ph<sub>2</sub>C:NH,BMe<sub>3</sub> in the gas phase can be compared with the gas-phase heats of dissociation of the secondary amine adducts Me<sub>2</sub>NH,BMe<sub>3</sub> (19.3 kcal.  $mole^{-1}$ ),<sup>12</sup> Et<sub>2</sub>NH,BMe<sub>3</sub> (16·3 kcal. mole<sup>-1</sup>),<sup>13</sup> and  $(CH_2)_3NH,BMe_3$  (22.5 kcal. mole<sup>-1</sup>).<sup>14</sup> We previously found no evidence of adduct formation in systems RCN-Me<sub>2</sub>B,<sup>2</sup> and conclude that towards trimethylborane as the reference acid diphenylketimine is intermediate in donor power between amines and nitriles. In view of the weak donor power of diphenylketimine towards trimethylborane, it is not surprising that we were unable to detect complex formation in the systems of diphenylketimine with the weaker Lewis acids Et<sub>3</sub>B and Ph<sub>3</sub>B.

The infrared spectrum of a Nujol mull of the adduct Ph<sub>2</sub>C:NH,BMe<sub>3</sub> contains a band at 1604 cm.<sup>-1</sup> attributable to v(C=N). The frequency of this band is essentially the same as that of the corresponding band in the spectrum of the free ketimine, whether in the liquid phase or in chloroform solution. Co-ordination at the imine nitrogen atom might be expected to result in drift of electrons from the azomethine group and accordingly reduction of  $\nu$ (C=N), analogous to the decrease in  $\nu(C=O)$  observed on adduct formation by carbonyl compounds.15 The absence of any appreciable change in  $\nu$ (C=N) on formation of Ph<sub>2</sub>C:NH,BMe<sub>3</sub> is consistent with the very weak co-ordinate link in this compound.

The proton magnetic resonance spectrum of Ph<sub>2</sub>C:NH,BMe<sub>3</sub> was recorded using perdeuteriobenzene as solvent with tetramethylsilane as internal standard The spectrum consisted of a singlet of low intensity at  $\tau 0.0$  attributable to the nitrogen-attached proton, a strong multiplet centred on  $\tau 2.63$ , arising from the aromatic protons, and a singlet at  $\tau 9.80$  due to the methyl groups. The chemical shift of this last peak can be compared with the value  $\tau 9.25$  for trimethylborane itself in the same solvent. The change in chemical

<sup>&</sup>lt;sup>5</sup> J. R. Jennings and K. Wade, unpublished observations,
<sup>6</sup> W. Gerrard, "The Organic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, "Academic Chemistry of Boron," Academic Chemistry of Boron, "Academic Chemistry of Boron, " Press, 1961.

 <sup>&</sup>lt;sup>7</sup> R. W. Layer, *Chem. Rev.*, 1963, 63, 489.
 <sup>8</sup> K. Wade and B. K. Wyatt, unpublished observations.
 <sup>9</sup> P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, 1961, 26, 4886.

 <sup>&</sup>lt;sup>10</sup> B. Bogdanovic, Angew. Chem. Internat. Edn., 1965, 4, 954.
 <sup>11</sup> T. E. Jordan, "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.

<sup>12</sup> H. C. Brown, H. Bartholomay, and M. D. Taylor, J. Amer. Chem. Soc., 1944, 66, 435.

<sup>&</sup>lt;sup>13</sup> H. C. Brown and M. D. Taylor, J. Amer. Chem. Soc., 1947,

<sup>69, 1332.</sup> <sup>14</sup> H. C. Brown and M. Gerstein, J. Amer. Chem. Soc., 1950, 72, 2926.

<sup>&</sup>lt;sup>15</sup> D. Cook, "Friedel-Crafts and Related Reactions," ed. G. Olah, Interscience, New York, 1963, vol. I, p. 767.

shift,  $\Delta \tau$ , on co-ordination is in the direction expected on electronic grounds, as the co-ordinate link supplies electronic charge to the boron with consequent electron drift to the boron-attached methyl groups. Moreover, the magnitude of  $\Delta \tau$  is significantly lower than  $\Delta \tau$  for the change Me<sub>3</sub>B  $\longrightarrow$  Me<sub>3</sub>N,BMe<sub>3</sub> (1.08),<sup>16</sup> affording further evidence of the relative donor properties of diphenylketimine and trimethylamine.

The diphenylketimine-trimethylborane adduct underwent the expected reaction with elimination of methane when heated in a tube at  $160-200^{\circ}$  for 24 hr., but the azomethine derivative Ph2C:N·BMe2 was isolated in only very poor yield (ca. 15%) from the mixture, a high proportion of the reactants remaining unchanged. Subsequent experiments, involving heating at  $180^{\circ}$  for 2 weeks, gave yields in excess of 50%. Clearly, the elimination of methane occurs only slowly even under such forcing conditions, and in this respect the system is similar to the dimethylamine-trimethylborane system in which the adduct Me<sub>2</sub>NH,BMe<sub>3</sub>, itself readily prepared below room temperature, but tending to dissociate at room temperature, eliminates methane to form Me<sub>2</sub>N·BMe<sub>2</sub> only when heated at 300°. The somewhat readier elimination of methane from the diphenylketimine adduct than from the dimethylamine adduct may well reflect the greater acid character of the nitrogenattached hydrogen atom of diphenylketimine.

A further point of similarity between  $Ph_2C:N\cdot BMe_2$ and  $Me_2N\cdot BMe_2$  is their state of association. The aminoborane is monomeric in the gas phase at room temperature, although apparently associated in the liquid phase.<sup>17</sup> We have been unable to obtain reliable molecular weight data on solutions of the azomethine derivative  $Ph_2C:N\cdot BMe_2$  in benzene, in which its solubility is low, but have recorded the mass spectrum of the compound. Mass and intensity values for the main peaks are listed in Table 1, together with suggested assignments. Significantly, there is no peak at higher m/e

#### TABLE 1

mass spectroscopic results for 1 mgcart blue	Mass s	pectroscopic	results	for	Ph <sub>2</sub> C:N·BMe <sub>2</sub>
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m e	Relative intensity	Assignment
221, 220	17, 4	Ph,CN·BMe,
206, 205	100, 25	Ph <sub>2</sub> CN·BMe
191, 190	2, 0.5	Ph <sub>2</sub> CNB
180	51	$Ph_2CN$
166	2	Ph <sub>2</sub> C
144, 143	5, 1	PhCN·BMe <sub>2</sub>
103	97	PhCN
77	42	Ph
41, 40	35, 9	$Me_2B$
15	4	Me

values than 221, the molecular weight of monomeric  $Ph_2CNBMe_2$ , and no set of peaks was observed with the characteristic relative intensities associated with the presence of two boron atoms in a fragment. Peaks attributable to fragments containing boron occurred in pairs differing by one mass unit and with the higher mass peak some four times as intense as the lower, as expected

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from the natural abundances of  ${}^{11}B(80\%)$  and  ${}^{10}B(20\%)$ . We have elsewhere studied the mass spectra of azomethine derivatives of boron (MeCH:N·BR<sub>2</sub>)<sub>2</sub> which were known by vapour-density measurements to be dimeric in the gas phase, and found that these spectra contain several intense peaks corresponding to fragments with the (BN)<sub>2</sub> ring intact.<sup>5</sup> We therefore conclude that the mass spectrum of  $Ph_2C:N\cdot BMe_2$  provides evidence either that this compound exists in the gas phase solely in the form of monomeric molecules or that. if associated species are present, these dissociate unexpectedly readily. The remaining major peaks in the mass spectrum (Table 1) show that the main features of the breakdown pattern involve the loss of the terminal methyl groups from boron or (less readily) phenyl groups from carbon, or fission of the molecular skeleton at the B-N bond. Fission at the C=N bond is of relatively minor importance. These observations suggest that, although the formula of the monomer  $Ph_2C=N \Rightarrow BMe_2$ can be written with a multiple  $N \Rightarrow B$  link to give a molecule isoelectronic with an allene Ph<sub>2</sub>C=C=CMe<sub>2</sub>, the present evidence does not indicate a high bond order for the B-N link. Further evidence is being sought from the infrared spectrum of this compound in the gas phase. As the compound, even if monomeric in the gas phase, may nevertheless be associated in the condensed phase, the Nujol mull spectrum should not be interpreted automatically in terms of a monomeric model. However, the position of the azomethine stretching absorption  $[v(C=N) \ 1662 \ cm.^{-1}]$  is at a higher frequency than previously observed for associated azomethine derivatives  $(Ph_{2}C:N\cdot M_{n}X)_{m}$  or  $(PhCH:N\cdot MX_{n})_{m}$  where M = B, Al, Ga, or Zn,<sup>3-5,18</sup> and it is tempting to interpret this high frequency as evidence for the presence of uncoordinated C=N in the boron compound, as co-ordination normally reduces v(C=N). The present compound is, we believe, the first boron-nitrogen compound formally analogous to an allene to be described.

The proton magnetic resonance spectrum of  $Ph_2C:N\cdot BMe_2$  as a dilute solution in perdeuteriobenzene was recorded, with cyclohexane as internal reference, and found to consist of two multiplets in the region  $\tau 2.7-2.9$ , clearly originating from the aromatic protons, and a singlet at  $\tau 9.7_0$  originating from the methyl protons. The absorptions due to aromatic protons, a multiplet at  $\tau 2.7_7$  (relative intensity 2) and a multiplet at  $\tau 2.84$  (relative intensity 3), probably arose from the ortho and meta-para protons, respectively, which would become differentiated on substitution of an electron-withdrawing group in the benzene nucleus.

Of the other organoboranes treated with diphenylketimine, triphenylborane did not react with diphenylketimine at temperatures up to 200° during periods of up to one week. In all cases both reactants were recovered essentially unchanged, although traces of

<sup>&</sup>lt;sup>16</sup> T. D. Coyle and F. G. A. Stone, J. Amer. Chem. Soc., 1961, 83, 4138.

<sup>&</sup>lt;sup>17</sup> E. Wiberg and P. Buchheit, unpublished work quoted by J. Goubeau in the "F.I.A.T. Review of German Science, 1939— 46, Inorg. Chem.," 1949, **1**, 228.

<sup>&</sup>lt;sup>18</sup> I. Pattison and K. Wade, unpublished observations.

benzene were detected in experiments carried out under the more extreme conditions.

Triethylborane reacted with diphenylketimine on heating at 160° for a week, but in a manner different from trimethylborane. Ethylene, not ethane, was the volatile reaction product, being formed in roughly twice the molar quantities that triethylborane was consumed, as if the consumption of triethylborane involved essentially the reaction  $Et_3B \longrightarrow [EtBH_2] + 2C_2H_4$ . The only involatile product identified was the N-substituted ketimine Ph<sub>2</sub>C:NCHPh<sub>2</sub> which was formed in some 30% yield from the diphenylketimine taken.

This unexpected product was identified as follows. Full elemental analysis revealed the appropriate proportions of carbon, hydrogen, and nitrogen, and the absence of boron. The proton magnetic resonance spectrum (C<sub>6</sub>D<sub>6</sub> solution) contained absorptions which could be assigned to aromatic protons ( $\tau 2.66$  intensity 20) and to an aliphatic proton ( $\tau 4.39$ , intensity 1). No absorption was observed which could be assigned to an ethyl group, nor to a nitrogen-attached proton. The infrared spectrum contained no absorption attributable to v(N-H), but a peak at 1628 cm.<sup>-1</sup> could readily be assigned to v(C=N).

Table	2
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Mass spectroscopic results for Ph<sub>2</sub>C:NCHPh<sub>2</sub>

m e	Relative intensity	Assignment
347	100	Ph <sub>2</sub> CN·CHPh <sub>2</sub>
270	10	Ph <sub>2</sub> CN•CHPh or PhCN•CHPh <sub>2</sub>
193	2	Ph <sub>2</sub> , 1, or g CN·CHPh <sub>0</sub> , 1, or z
192	<b>2</b>	193 minus H
180	17	Ph <sub>2</sub> CN
167	53	Ph <sub>2</sub> CH
166	43	PhaC
116	2	CN•CHPh
115	10	CN·CPh
103	6	PhCN
89	7	PhC
77	59	Ph

The strongest peak in the mass spectrum of the material occurred at m/e 347, and the accurate mass of this fragment was found to be within 1 p.p.m. of that calculated for C<sub>26</sub>H<sub>21</sub>N. Mass and intensity data for the main peaks in the mass spectrum are in Table 2, together with suggested assignments. All the major peaks can be assigned to fragments arising from a molecule Ph<sub>2</sub>C:NCHPh<sub>2</sub>. The only peak at a mass higher than 347 was a feeble peak (relative intensity 1) at m/e 375, which could be attributed to traces of a contaminant, probably Ph<sub>2</sub>C:NCEtPh<sub>2</sub>.

The manner in which Ph<sub>2</sub>C:NCHPh<sub>2</sub> comes to be formed in this reaction deserves comment. It is well known 7 that amines R'NH2 displace ammonia from imines R<sub>2</sub>C:NH to form N-substituted imines R<sub>2</sub>C:NR', and it seems likely that in the present reaction some diphenylketimine is reduced to the amine stage Ph<sub>2</sub>CHN by interaction with Et-B groups, which in the process lose ethylene. A subsequent condensation between the amine and an unreduced diphenylketimine molecule would afford Ph<sub>2</sub>C:NCHPh<sub>2</sub>, the nitrogen eliminated probably ending bound to boron in the final reaction

mixture in oligomers or polymers, such as  $(EtBNH)_n$ which would have been undetected because of the method used to work up the mixture.

This formation of Ph<sub>2</sub>C:NCHPh<sub>2</sub> from diphenylketimine and triethylborane is clearly analogous to the formation of ButCH:NCH2But (in 30% yield) from Bu<sup>t</sup>CN and Bu<sup>t</sup>MgCl at 150°, <sup>19</sup> and to the formation of PhCH:NCH<sub>2</sub>Ph in the reduction of PhCN by R<sub>2</sub>AlH at 45°.20 Other examples involving boron-nitrogen systems are also known, e.g., the formation of  $Et_2N \cdot B_2H_5$ in the reaction between diborane and methyl cyanide,<sup>5</sup> while the formation of a compound C<sub>8</sub>H<sub>17</sub>N (either Me<sub>2</sub>CH·CH:NBu<sup>i</sup> or Me<sub>2</sub>C:CH·NHBu<sup>i</sup>) in the pyrolysis of (Bu<sup>i</sup>NH)<sub>2</sub>BPh may well occur by a similar mechanism.<sup>21</sup>

#### EXPERIMENTAL

Materials.-Diphenylketimine was obtained by methanolysis of the product of the reaction between benzonitrile and phenylmagnesium bromide in diethyl ether, and was purified by vacuum distillation (b. p.  $90-95^{\circ}/\sim 10^{-3}$  mm.).<sup>9</sup> Trimethylborane was prepared from methylmagnesium bromide and boron trifluoride-dibutyl ether complex in dibutyl ether. The reaction was carried out at 70°, whereupon the solvent-free product could be swept from the reaction vessel in a stream of nitrogen and purified by distillation in the vacuum line. Triethylborane was prepared from ethylmagnesium bromide and boron trifluoride-diethyl ether complex in boiling diethyl ether, and distilled (b. p. 95°). Crude triphenylborane was recrystallised (m. p. 142°) from diethyl ether.

Manipulations were carried out in a conventional vacuum line, nitrogen-filled glove boxes, or nitrogen-filled apparatus as appropriate. Molecular weights were determined cryoscopically in benzene.

Spectra.--Infrared spectra were recorded on the Grubb-Parsons prism-grating spectrometers GS2A or Spectromaster in the range 2-25µ. Nuclear magnetic resonance spectra were recorded at 60 Mc. sec.<sup>-1</sup> 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, with a source temperature of 150-250° and electromagnetic scanning. Compounds were introduced through a heated inlet system at up to  $200^{\circ}$ .

Analyses .-- Boron was determined by ignition of a weighed sample of compound in oxygen, dissolution of the resulting oxide in water, and subsequent titration of the boric acid with sodium hydroxide in the presence of mannitol (bromothymol blue). Carbon and hydrogen were estimated conventionally and nitrogen by the Kjeldahl method.

Reaction of Diphenylketimine and Trimethylborane.-Trimethylborane (0.62 g., 11 mmoles) was condensed on diphenylketimine (2.06 g., 11 mmoles) in 20 ml. of pentane at  $-196^{\circ}$ . The mixture was allowed to warm to room temperature, whereupon the adduct Ph<sub>2</sub>C:NH,BMe<sub>3</sub> precipitated as a white solid which was characterised by its infrared spectrum: v<sub>max.</sub> (Nujol mull) 1604vs, 1564s, 1543ms, 1319m, 1297s, 1276s, 1284s, 1203m, 1193m, 1157m, 1111w, 1081s,

E. J. Blanz and H. S. Mosher, J. Org. Chem., 1958, 23, 492.
 A. E. G. Miller, J. W. Biss, and L. H. Schwartzman, J. Org. Chem., 1959, 24, 627.
 J. A. Semlyen and P. J. Flory, J. Chem. Soc. (A), 1966, 191.

1055s, 1031m, 1026m, 1000m, 998m, 986m, 960w, 951m, 922w, 897s, 855vw, 849vw, 791w, 782s, 769m, 757m, 733w, 727w, 694vs, 662vw, 623m, 607vw, 570vw, and 535w cm.<sup>-1</sup>. Trimethylborane could be pumped readily from the adduct at room temperature; the dissociation pressure at 23.5° was 28 mm. Vapour pressures in the temperature range  $0-44^{\circ}$  can be represented to within 1 mm. by the equation  $\log_{10} p$  (mm.) =  $4 \cdot 220 - (802 \cdot 1/T)$ .

Thermal Decomposition of Ph<sub>2</sub>C:NH,BMe<sub>3</sub>.—Trimethylborane (0.56 g., 10 mmoles) was condensed on diphenylketimine (1.81 g., 10 mmoles) at  $-196^{\circ}$  in an evacuated tube, and the mixture was then kept at 160° for 24 hr. Methane (0.019 g., 1.16 mmoles) was recovered from the tube and identified by its infrared spectrum, together with some unchanged trimethylborane (0.32 g., 5.7 mmoles). The residue, a brown solid, was dissolved in toluenepentane from which colourless crystals of dimethyl-( $\alpha$ -phenylbenzylideneamino)borane, Ph<sub>2</sub>C:NBMe<sub>2</sub>, m. p. 173°, separated on cooling (Found: B, 4.8; N, 6.3. C<sub>15</sub>H<sub>16</sub>BN requires B, 4.9; N, 6.3%);  $\nu_{max}$  (Nujol mull) 1662s, 1597w, 1580w, 1488m, 1439m, 1337m, 1295m, 1280s, 1166m, 1152w, 1124w, 1110w, 1087m, 1074m, 1054s, 1024s, 1014s, 952m, 932w, 910w, 897vw, 848w, 839w, 800m, 756m, 741m, 734m, 717sh, 706s, 696m, 592m, and 537m cm.<sup>-1</sup>.

Reaction of Diphenylketimine with Triethylborane.—Triethylborane (0.98 g., 10.0 mmoles) was condensed on diphenylketimine (1.81 g., 10.0 mmoles) at  $-196^{\circ}$  in an evacuated tube, which was sealed and kept at  $155^{\circ}$  for one week. The volatile contents of the tube were then trans-

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ferred to the vacuum line and identified by their infrared spectra as ethylene (0·16 g., 5·8 mmoles) and triethylborane (0·62 g., 6·3 mmoles). The residual involatile yellow solid was dissolved in hexane from which crystals, m. p. 152—153·5°, separated on cooling which were identified as the *ketimine* Ph<sub>2</sub>C:NCHPh<sub>2</sub> (Found: C, 89·4; H, 5·3; N, 4·5. C<sub>26</sub>H<sub>21</sub>N requires C, 89·8; H, 6·0; N, 4·0%);  $\nu_{max}$ . (Nujol mull) 1628vs, 1592s, 1570m, 1488s, 1116m, 1290sh, 1280s, 1250m, 1178m, 1152m, 1073m, 1036m, 1028s, 1021sh, 1000m, 947w, 913m, 864w, 839w, 777s, 760w, 743s, 726m, 702vs, 694vs, 667w, 658m, 640m, 619m, 606m, and 594s cm.<sup>-1</sup>.

Reaction of Diphenylketimine with Triphenylborane.—Triphenylborane and diphenylketimine were recovered after being heated together to  $160^{\circ}$  for several hours. No evidence of adduct formation was found, but after several days' heating at  $160^{\circ}$  a trace of benzene was detected in the mixture, which still, however, consisted essentially of the starting materials.

Vapour Pressure of Diphenylketimine.—Vapour pressures in the range 110—185° could be represented to within 1 mm. by the equation  $\log_{10} p$  (mm.) = 8.553 - (3192/T), corresponding to 1 mm. at 100° and 10 mm. at 148.3°.

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