Azomethine Derivatives. Part IX.[1] Preparation of Dialkylideneammonium Salts *via* Diarylketiminodiphenylmethyl Chlorides

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The diarylketiminodiphenylmethyl chlorides $Ph_2C{:}NCClPh_2$ and *p*-tolyl$_2C{:}NCClPh_2$ have been prepared from Ph_2CCl_2 and $R_2C{:}NLi$ in benzene. Reactions, normally in toluene, between these chlorides and the Lewis acids BCl_3, $AlCl_3$, and $SbCl_5$ have been used to prepare the dialkylideneammonium salts $Ph_2C{:}N{:}CPh_2^+ MX_n^-$ ($MX_n^- = BCl_4^-, AlCl_4^-$, or $SbCl_6^-$) and *p*-tolyl$_2C{:}N{:}CPh_2^+ SbCl_6^-$, the ionic structures of which are supported by their electrical conductivities in nitrobenzene, and also by a band in their i.r. spectra centred at 1845 cm.$^{-1}$, assigned to $\nu(C{:}N{:}C)$. The ion $Ph_2C{:}N{:}CPh_2^+$ also features prominently in the mass spectrum of $Ph_2C{:}NCClPh_2$.

Unsuccessful attempts to prepare the tetraphenylborate $Ph_2C{:}N{:}CPh_2^+ BPh_4^-$ from $Ph_2C{:}NCClPh_2 + NaBPh_4$, and from $Ph_2C{:}NH_2^+Cl^- + NaBPh_4 + Ph_2C{:}Y$ (Y = O or NH) are described. $Ph_2C{:}NH_2^+ Cl^-$ and $NaBPh_4$ in boiling toluene gave $Ph_2C{:}NBPh_2$. Ph_2CCl_2 and $2Ph_2C{:}NLi$ in boiling toluene gave $(Ph_2C{:}N)_2CPh_2$.

WE here describe some salts containing a new class of cation, the dialkylideneammonium cation $[R_2C{:}N{:}CR_2]^+$, which is isoelectronic with and apparently isostructural with allenes[2] $R_2C{:}C{:}CR_2$.

Salts of the cations $[Ph_2C{:}N{:}CPh_2]^+$ and [*p*-tolyl$_2$-$C{:}N{:}CPh_2]^+$ were prepared in order to study further the interesting relationship that exists between unsaturated organic compounds and cations formally derived from them by replacing a multiply bonded carbon atom by a positively charged nitrogen, *e.g.*, compare alkynes $RC{:}CR$ with nitrilium cations[3] $[RC{:}NR]^+$, or alkenes $R_2C{:}CR_2$ with imonium cations[4] $[R_2C{:}NR_2]^+$. Such cations apparently have the same shape and essentially the same bond multiplicity as the isoelectronic carbon compound, even though in principle the skeletal bond order could be lowered, and the shape at nitrogen changed, by contributions from carbonium ionic forms such as $RC^+{=}NR$ or $R_2C^+{-}NR_2$.[5]

The route used for the preparation of the dialkylideneammonium salts was chosen by analogy with a convenient route to nitrilium salts, which result from the action of Lewis acids on imidoyl chlorides [equation (1)].[3] We accordingly investigated the action of Lewis

$$RCCl{:}NR + MCl_n \longrightarrow [RC{:}NR]^+[MCl_{n+1}]^- \quad (1)$$

acids on ketiminomethyl chlorides $R_2C{:}NCClPh_2$, a class

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of compound we found to be accessible from the ketiminolithium[6] $R_2C{:}NLi$ and dichlorodiphenylmethane Ph_2CCl_2 [equations (2) and (3)].

$$R_2C{:}NLi + Ph_2CCl_2 \longrightarrow LiCl + R_2C{:}NCClPh_2 \qquad (2)$$

$$R_2C{:}NCClPh_2 + MCl_n \longrightarrow [R_2C{:}N{:}CPh_2]^+[MCl_{n+1}]^- \qquad (3)$$

Chan and Rochow[7] recently described the preparation of the N-substituted imine $Ph_2C{:}NCPh_3$ by the ready reaction between $Ph_2C{:}NLi$ and Ph_3CCl. Diphenylketiminolithium also reacts, though less readily, with Ph_2CCl_2 in boiling benzene (see Experimental section) to form diphenylketiminodiphenylmethyl chloride $Ph_2C{:}NCClPh_2$. This compound, which slowly decomposed to diphenylketimine and benzophenone on prolonged exposure to moist air, reacted further with $Ph_2C{:}NLi$ in boiling toluene to form the bisketimino-derivative $(Ph_2C{:}N)_2CPh_2$. A covalent constitution $Ph_2C{:}NCClPh_2$, rather than an ionic structure $Ph_2C{:}N{:}CPh_2{}^+Cl^-$ was indicated by its i.r. spectrum, in which a strong absorption at 1620 cm.$^{-1}$ could be identified as ν(C:N), and a doublet at 730 and 724 cm.$^{-1}$ as ν(C–Cl); [*cf.* $Ph_2C{:}NCPh_3$,[7] which has ν(C:N) at 1621 cm.$^{-1}$, and Ph_3CCl,[8] which has ν(C–Cl) at 746 and 735 cm.$^{-1}$]. There was no absorption in the range 1650—2000 cm.$^{-1}$ where absorptions believed to be characteristic of the cation $Ph_2C{:}N{:}CPh_2{}^+$ occur (see Table 1, and discussion below). Also consistent with a covalent structure for $Ph_2C{:}NCClPh_2$ was the low electrical conductivity of its solutions in nitrobenzene (Table 1): 1 : 1 electrolytes normally have conductivities in the range 20—30 ohm^{-1} cm.^{2} mole^{-1} in $PhNO_2$.[9] The related compound *p*-tolyl$_2$C:NCClPh$_2$, from *p*-tolyl$_2$C:NLi and Ph_2CCl_2 in boiling benzene, had similar i.r. absorptions and low electrical conductivity in nitrobenzene.

TABLE 1

I.r. spectroscopic band frequencies and electrical conductivities of $R_2C{:}NCClPh_2$ and $R_2C{:}N{:}CPh_2{}^+ MX_n{}^-$

Compound	ν(C=N) (cm.$^{-1}$)	ν(C=N=C) (cm.$^{-1}$)	Molar conductivity[a] (ohm^{-1} cm.^{2} mole^{-1})
$Ph_2C{:}NCClPh_2$	1620	—	<1
p-tolyl$_2$C:NCClPh$_2$	1626	—	<1
$Ph_2C{:}N{:}CPh_2{}^+ BCl_4{}^-$	—	*ca.* 1845	26
$Ph_2C{:}N{:}CPh_2{}^+ AlCl_4{}^-$	—	*ca.* 1845	24
$Ph_2C{:}N{:}CPh_2{}^+ SbCl_6{}^-$	—	*ca.* 1845	27
p-tolyl$_2$C:N:CPh$_2{}^+$ SbCl$_6{}^-$	—	*ca.* 1845	22

[a] 0·001M-Solutions in nitrobenzene.

Despite the covalent structures of both these ketiminomethyl chlorides, the ions $Ph_2C{:}N{:}CPh_2{}^+$ and *p*-tolyl$_2$C:N:CPh$_2{}^+$ featured prominently in their respective mass spectra. The intensities and suggested assignments for the major high-mass peaks in the spectrum of $Ph_2C{:}NCClPh_2$ are in Table 2. The breakdown pattern for *p*-tolyl$_2$C:NCClPh$_2$ was similar. The spectra of both compounds also contained a peak at *m*/*e* = 332 ($Ph_2C{:}CPh_2{}^+$?), the intensity of which varied markedly from sample to sample as if it arose from varying amounts of impurity rather than from breakdown of $R_2C{:}NCClPh_2$.

TABLE 2

Mass spectroscopic results for $Ph_2C{:}NCClPh_2$

m/*e*	Relative intensity	Assignment
346	98	Ph_2CNCPh_2
269	8	Ph_2CNCPh
203	3	$Ph_2C^{37}Cl$
201	10	$Ph_2C^{35}Cl$
181	22	Ph_2CNH
180	100	Ph_2CN

The ions $Ph_2C{:}N{:}CPh_2{}^+$ and *p*-tolyl$_2$C:N:CPh$_2{}^+$ were formed chemically by reaction of the ketiminomethyl chlorides with Lewis acids. The reddish brown solid compounds $Ph_2C{:}N{:}CPh_2{}^+ BCl_4{}^-$, $Ph_2C{:}N{:}CPh_2{}^+ SbCl_6{}^-$, and *p*-tolyl$_2$C:N:CPh$_2{}^+$ SbCl$_6{}^-$ separated immediately from reactions at 16° between BCl_3 or $SbCl_5$ (1 mol.) and $R_2C{:}NCClPh_2$ (1 mol.) in toluene. The tetrachloroaluminate $Ph_2C{:}N{:}CPh_2{}^+ AlCl_4{}^-$ was prepared similarly from $Ph_2C{:}NCClPh_2$ and $AlCl_3$ in toluene at 60—70°, and also in the absence of solvent at 150—160°, although at this temperature slight decomposition occurred.

The empirical formulae of the dialkylideneammonium salts were confirmed by C, H, and Cl analyses, and their ionic constitutions by the molar conductivities of their M/1000 solutions in $PhNO_2$ (Table 1). The i.r. spectrum of each compound contained a moderately strong broad absorption over the range 1820—1870 cm.$^{-1}$ apparently consisting of three components centred at 1825, 1845, and 1865 cm.$^{-1}$ which however could not be resolved into separate bands. We attribute the principal absorption in this region to a skeletal stretching vibration ν_{asym}(C:N:C). A structure $Ph_2C{:}N{\cdot}C^+Ph_2$ with a non-linear C=N–C skeleton and only one double C:N bond, might have been expected to absorb near 1600 cm.$^{-1}$ [ν(C:N)], as does the covalent intermediate $Ph_2C{:}NCClPh_2$. The only absorption near 1600 cm.$^{-1}$, however, was that attributable to a C–C stretching vibration of the benzene rings at 1590—1600 cm.$^{-1}$, common to all the compounds. Weak absorptions at *ca.* 1660 cm.$^{-1}$ appeared to be the result of contamination by hydrolysis products containing C=O groups; benzophenone and di-*p*-tolyl ketone have ν(C:O) near 1660 cm.$^{-1}$. Other significant features of the i.r. spectra of the dialkylideneammonium salts were the absence of the C–Cl stretching absorptions at *ca.* 730 cm.$^{-1}$, and the presence of new absorptions assignable to vibrations of the anions. The compound $Ph_2C{:}N{:}CPh_2{}^+ BCl_4{}^-$ for example had an intense broad absorption in the region 630—750 cm.$^{-1}$ of a shape typical of tetrachloroborates,[10]

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and $Ph_2C:N:CPh_2^+ SbCl_6^-$ absorbed at 339 cm.$^{-1}$; hexachloroantimonates typically absorb at *ca.* 349 cm.$^{-1}$.[11]

The skeletal stretching frequency $\nu(C=N=C)$ of the dialkylideneammonium salts, though lower than the stretching frequencies $\nu(X=Y=Z)$ of such isoelectronic substances as carbodi-imides,[12] enimines,[13] and allenes [14] (Table 3), is nevertheless higher than $\nu(C=N\hat{=}B)$ [15] and $\nu(C=N\hat{=}Be)$ [16] of $Ph_2C:NBPh_2$ and $[(Ph_2C:N)_2Be]_n$, in which the N=M bond order (M = B or Be) is likely to be lower than the C=N bond order of $Ph_2C:N:CPh_2^+$.

TABLE 3

Skeletal stretching frequencies of some cumulatively π-bonded systems

Compound	$\nu(X=Y=Z)$ (cm.$^{-1}$)	X=Y=Z
$RN:C:NR$ [12]	*ca.* 2140	N=C=N
$Ph_2C:C:NMe$ [13]	1998	C=C=N
$R_2C:C:CR_2$ [14]	*ca.* 1950	C=C=C
$Ph_2C:N:CPh_2^+MX_n^-$	*ca.* 1845	C=N=C
$Ph_2C:NBPh_2$ [15]	1786	$C=N\hat{=}B$
$[(Ph_2C:N)_2Be]_n$ [16]	1732	$C=N\hat{=}Be$

We have also made some unsuccessful attempts to prepare the dialkylideneammonium tetraphenylborate $Ph_2C:N:CPh_2^+ BPh_4^-$. One route explored was the reaction between $Ph_2C:NCClPh_2$ and $NaBPh_4$ (4).

$$Ph_2C:NCClPh_2 + NaBPh_4 \longrightarrow Ph_2C:N:CPh_2^+BPh_4^- + NaCl \quad (4)$$

The starting materials were recovered unchanged, however, after equimolar mixtures of $Ph_2C:NCClPh_2$ and $NaBPh_4$ had been heated in boiling benzene or toluene overnight. An alternative route investigated was that represented by equations (5) and (6), analogous to a known route (7) [17] to imonium tetraphenylborates.

$$Ph_2C:NH_2^+ Cl^- + NaBPh_4 \longrightarrow Ph_2C:NH_2^+ BPh_4^- + NaCl \quad (5)$$

$$Ph_2C:NH_2^+ BPh_4^- + Ph_2C:X \longrightarrow Ph_2C:N:CPh_2^+ BPh_4^- + H_2X \quad (6)$$
$$(X = O \text{ or } NH)$$

$$Me_2NH_2^+ BPh_4^- + Me_2CO \longrightarrow Me_2C:NMe_2^+ BPh_4^- + H_2O \quad (7)$$

Sodium chloride was precipitated when $Ph_2C:NH_2^+ Cl^-$ and $NaBPh_4$ were heated together in boiling toluene, whether in the presence or absence of benzophenone or diphenylketimine. After separation of the sodium chloride by filtration, however, the only product recovered from the filtrate was $Ph_2C:NBPh_2$, previously prepared from Ph_2BCl and $Ph_2C:NLi$ [15] or $Ph_2C:NSiMe_3$.[1] Its formation in the present reaction apparently results from loss of two moles of benzene from the tetraphenylborate $Ph_2C:NH_2^+ BPh_4^-$ (8), presumably *via* $Ph_2C:NH,BPh_3$. In an earlier study [18] of the system $Ph_2C:NH-Ph_3B$, $Ph_2C:NBPh_2$ was not detected.

$$Ph_2C:NH_2^+ BPh_4^- \xrightarrow{-PhH} Ph_2C:NH,BPh_3 \xrightarrow{-PhH} Ph_2C:NBPh_2 \quad (8)$$

EXPERIMENTAL

Materials and Techniques.—Diphenylketimine was prepared from phenyl cyanide and phenylmagnesium bromide by Pickard and Tolbert's procedure.[19] Dichlorodiphenylmethane was prepared by the action of phosphorus pentachloride on benzophenone at 90—110° and was purified by distillation at 104—106°/0·05 mm. Manipulations were carried out in a nitrogen-filled glove box or in apparatus filled with dry nitrogen.

Spectra.—I.r. spectra in the range 2—25 μ were recorded on a Grubb-Parsons prism-grating GS2A spectrometer or Spectromaster. 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. Samples were introduced by direct insertion into the ion source.

Analyses.—Carbon and hydrogen were determined by combustion. Nitrogen was determined by the Kjeldahl method. Chlorine was determined by the sodium fusion method described by Belcher and Tatlow [20] with the modification that the aqueous sodium chloride formed was passed through an ion-exchange column and the resulting hydroxide was determined by acidimetry. Molecular weights were determined cryoscopically in benzene.

Preparation of Diphenylketiminodiphenylmethyl Chloride, $Ph_2C:NCClPh_2$.—A solution of n-butyl-lithium (50 mmoles) in hexane (25 ml.) was added by syringe to a frozen (−196°) solution of diphenylketimine (8·4 ml., 50 mmoles) in diethyl ether (80 ml.). The mixture was allowed to warm and stirred at 16° for 30 min. to ensure complete formation of diphenylketiminolithium. The solution was again cooled to −196°, and dichlorodiphenylmethane (11·8 g., 50 mmoles) in diethyl ether (30 ml.) was added. The mixture was warmed to 16°, most of the ether was removed at low pressure, and benzene (100 ml.) was added. The solution was then heated under reflux for 20 hr., during which lithium chloride separated. This was filtered off, the filtrate was concentrated by evaporation of most of the solvent, and hexane (20 ml.) was added, causing a yellow granular precipitate to separate. This after recrystallisation from benzene–hexane or toluene–hexane was identified as *diphenylketiminodiphenylmethyl chloride*, $Ph_2C:NCClPh_2$, m.p. 186—187° (Found: C, 82·0; H, 5·0; Cl, 9·5%; *M*, 390. $C_{26}H_{20}ClN$ requires C, 81·3; H, 5·2; Cl, 9·3%; *M*, 382); $\nu_{max.}$ (Nujol mull) 1620s, 1600ms, 1575ms, Nujol, 1383s, 1316w, 1282ms, 1190w, 1177w, 1163w, 1149w, 1075vw, 1031ms, 1022ms, 1010w, 998w, 980w, 917w,

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892w, 847vw, 787ms, 769ms, 752ms, 746s, 730ms, 724ms, 699vs, 680w, 667wm, 633vw, 629vw, 602s, and 592vw cm.$^{-1}$. It was readily soluble in benzene, chloroform, and toluene, moderately soluble in diethyl ether, slightly soluble in carbon tetrachloride, and effectively insoluble in pentane or hexane, and was slightly sensitive to moisture. Crystals deteriorated markedly on long exposure to moist air, but the compound could be handled briefly in the air without significant decomposition.

Preparation of Di-p-*tolylketiminodiphenylmethyl Chloride*, p-tolyl$_2$C:NCClPh$_2$.—This was prepared from p-tolyl$_2$C:NLi and Ph_2CCl_2 by the procedure described for $Ph_2C{:}NCClPh_2$. The *product*, obtained as small yellow crystals from toluene–hexane, was identified as p-tolyl$_2$C:NCClPh$_2$, m.p. 158—160° (Found: C, 82·3; H, 5·9; Cl, 9·1%; *M* (Mechrolab osmometer) 402. $C_{28}H_{24}ClN$ requires C, 82·1; H, 5·9; Cl, 8·7%; *M*, 410); $\nu_{max.}$ (Nujol mull) 1626ms, 1602s, 1563ms, 1493vs, Nujol, 1316w, 1282ms, 1196ms, 1185ms, 1163ms, 1117vw, 1087wm, 1078w, 1036s, 1005ms, 980w, 935vw, 917vw, 862vw, 847vw,sh, 840wm, 833w, 820vw, 784w, 775m, 758s, 748s, 725vs, 699vs, 641vw, 629ms, 615wm, 590w, 575vw, and 569vw cm.$^{-1}$. It was soluble in benzene, toluene, ether, and chloroform, and slightly soluble in carbon tetrachloride and hexane, and was of comparable air-stability to its diphenylketimino-analogue.

Preparation of Bis(diphenylketimino)diphenylmethane, $(Ph_2C{:}N)_2CPh_2$.—Diphenyldichloromethane (2·3 g., 9·7 mmoles) and diphenylketiminolithium (19·5 mmoles) reacted during 24 hr. in boiling toluene to form a precipitate of lithium chloride. This was filtered off and the filtrate was concentrated by evaporation, leaving a reddish brown viscous residue from which *bis(diphenylketimino)diphenylmethane* was recovered as a yellow powder after addition of hexane (Found: C, 88·6; H, 5·5; N, 5·4. $C_{39}H_{30}N_2$ requires C, 89·0; H, 5·7; N, 5·3%); $\nu_{max.}$ (Nujol mull) 1600s, 1572s, 1316w, 1266ms, 1190w, 1176wm, 1149wm, 1070ms, 1025ms, 1000ms, 885ms, 847w, 787wm, 777wm, 758s, 746s, 719wm, 694vs, and 621s cm.$^{-1}$. When heated, it shrank perceptibility in the range 180—195°, softened at 205—210°, and ultimately melted at 230—240° to a clear yellow-brown liquid. Attempts at its recrystallisation from benzene–hexane or toluene–hexane afforded only yellow powders.

Preparation of Dialkylideneammonium Salts $R_2C{:}N{:}CPh_2^+\ MCl_n^-$.—$Ph_2C{:}N{:}CPh_2^+\ BCl_4^-$. When boron trichloride gas in dry nitrogen was bubbled through a solution of $Ph_2C{:}NCClPh_2$ (0·6 g., 1·6 mmoles) in 15 ml. of dry toluene, a dark brown oil settled. This was separated, washed with toluene, and allowed to stand under 2 ml. toluene for 2 days during which time it set to a brown hard mass. This was pumped dry and ground to a powder in the glove box, and identified as *bis-(α-phenylbenzylidene)ammonium tetrachloroborate*, $Ph_2C{:}N{:}CPh_2^+\ BCl_4^-$ (decomp. 125—140°) (Found: C, 62·0; H, 4·0; Cl, 28·0. $C_{26}H_{20}BCl_4N$ requires C, 62·4; H, 4·0; Cl, 28·4%); $\nu_{max.}$ (Nujol mull) 1845sbr, 1658w, 1593s, Nujol, 1319s, 1282vs, 1163s, 1075ms, 1028ms, 1000ms, 971w, 935ms, 917ms, 840w, 781ms, 741ms, 719ms, 690vs, 654vs, 629s, and 593ms cm.$^{-1}$.

$Ph_2C{:}N{:}CPh_2^+\ AlCl_4^-$. When aluminium chloride (0·2 g., 1·5 mmoles) was held at 150—160° for 10 min. with diphenylketiminodiphenylmethyl chloride (0·58 g., 1·5 mmoles), the product was a dark brown paste which was washed with toluene and hexane, pumped dry, and ground to a powder, which was identified as the *tetrachloroaluminate* $Ph_2C{:}N{:}CPh_2^+\ AlCl_4^-$ (decomp. 140—160°) (Found: C, 61·0; H, 4·0; Cl, 27·1%. $C_{26}H_{20}AlCl_4N$ requires C, 60·6; H, 3·9; Cl, 27·6%); $\nu_{max.}$ (Nujol mull) 1845s,br, 1655w, 1600vs, Nujol, 1330s, 1290vs, 1170vs, 1087ms, 1031s, 1003vs, 939s, 918s, 847ms, 784vs, 735vs, 694vs, 658s, 629vs, 613s, 595vs, 566ms, 521ms, 488vs, and 465vs cm.$^{-1}$. An alternative method for preparing this compound was the reaction between equimolar proportions of $Ph_2C{:}NCClPh_2$ and $AlCl_3$ in benzene or toluene at 60—70° for 1 hr.

$Ph_2C{:}N{:}CPh_2^+\ SbCl_6^-$. Antimony pentachloride (0·20 ml., 1·6 mmoles) was added by syringe to a solution of $Ph_2C{:}NCClPh_2$ (0·60 g., 1·6 mmoles) in 15 ml. of toluene. A reddish brown oil separated but solidified rapidly on stirring. After being washed with toluene and hexane, it was identified as the *hexachloroantimonate*, $Ph_2C{:}N{:}CPh_2^+$-$SbCl_6^-$, m.p. 158—162° (decomp.) (Found: C, 45·9; H, 3·6; Cl, 31·3. $C_{26}H_{20}Cl_6NSb$ requires C, 45·8; H, 3·0; Cl, 31·3%); $\nu_{max.}$ (Nujol mull) 1845s,br, 1653w, 1600vs, 1510ms, Nujol, 1323s, 1299vs, 1190ms, 1172s, 1130w, 1087ms, 1036ms, 1005s, 980vw, 943wm, 921ms, 862ms, 847w, 800s, 787s, 735vs, 706s,sh, 694vs, 668vw, 660w, 632s, 571vw, and 465ms cm.$^{-1}$. This compound was apparently unaffected by exposure to moist air, and floated unchanged on water, but reacted with aqueous acetone. Its KBr disc spectrum, in addition to absorptions at essentially the same frequencies as those found for the Nujol mull, also contained bands at 1488w, 1447s, and 1377m cm.$^{-1}$.

p-Tolyl$_2$C:N:CPh$_2^+$ $SbCl_6^-$. This was prepared as an oil from $SbCl_5$ and a slight excess of p-tolyl$_2$C:NCClPh$_2$ in toluene. Washing with toluene and hexane converted the oil into the pale brown solid *salt* (decomp. 125—135°) (Found: C, 46·1; H, 3·9; Cl, 30·6. $C_{28}H_{24}Cl_6NSb$ requires C, 47·4; H, 3·4; Cl, 30·0%); $\nu_{max.}$ (Nujol mull) 1845s,br, 1653w, 1639w,sh, 1608vs, Nujol, 1319s, 1282vs, 1266s, 1191s, 1163vs, 1093s, 1020s, 935wm, 926w, 870w, 827s, 800s, 781s, 741s, 735s,sh, 725s, 696s, 690s, 655ms, 630ms, 575w, and 467w cm.$^{-1}$.

Reaction between $Ph_2C{:}NH_2^+Cl^-$, $NaBPh_4$, *and* $Ph_2C{:}NH$.—Diphenylketimine hydrochloride (1·20 g., 5·5 mmoles), sodium tetraphenylborate (1·82 g., 5·5 mmoles), and diphenylketimine (1·00 g., 5·5 mmoles) were heated together in boiling toluene (100 ml.) under reflux under dry nitrogen for 3 hr. The precipitate of sodium chloride was filtered off, the volume of the filtrate was reduced to about 20 ml. at low pressure, and *ca.* 8 ml. of hexane were added. Small white crystals separated slowly. These were washed with hexane, pumped dry, and identified as diphenylketiminodiphenylborane $Ph_2C{:}NBPh_2$, m.p. 138—140° (lit.,[1] 143—144°) (Found: C, 89·9; H, 6·0; N, 3·5. Calc. for $C_{25}H_{20}BN$: C, 87·0; H, 5·8; N, 4·1%). Its i.r. spectrum contained all the bands appropriate for authentic $Ph_2C{:}NBPh_2$, previously prepared from $Ph_2C{:}NSiMe_3$ and Ph_2BCl,[1] though extra bands, notably at 3230, 1600, and 1565 cm.$^{-1}$ indicated that the sample was contaminated by a little diphenylketimine.

Reaction between $Ph_2C{:}NH_2^+Cl^-$ *and* $NaBPh_4$.—When the previous experiment was repeated with only equimolar proportions of $Ph_2C{:}NH_2^+Cl^-$ and $NaBPh_4$ in an attempt at the preparation of $Ph_2C{:}NH_2^+\ BPh_4^-$, sodium chloride and diphenylketiminodiphenylborane $Ph_2C{:}NBPh_2$ were the only crystalline solid products isolated and identified.

We thank the S.R.C. for financial support (to B. S.).

[9/324 *Received, February 24th*, 1969]