Lithium in Ammonia Reduction of 1-Bromonorbornane with Inverse Addition. A solution of 134.8 mg (19.5 mmol) of lithium metal in 60 ml of twice-distilled ammonia[31] was added dropwise to a rapidly stirred solution of 351.1 mg (2.00 mmol) of 1-bromonorbornane in 50 ml of doubly-distilled ammonia and 10 ml of dry diethyl ether. The characteristic blue color of lithium in ammonia was immediately discharged upon addition to the halide solution. Following the addition, excess lithium was destroyed with solid ammonium chloride as described above. GLC analysis of the ethereal residue revealed 90.6% norbornane and 9.4% 1,1′-binorbornane.

Lithium in Ammonia Reduction of 1-Bromonorbornane at High Dilution. A solution of 500 mg (2.86 mmol) of 1-bromonorbornane in 50 ml of dry diethyl ether was diluted with 150 ml of twice-distilled ammonia[31] and added dropwise to a rapidly stirred solution of 250 ml (35.7 mmol) of lithium in a mixture consisting of 500 ml of twice-distilled ammonia[31] and 100 ml of dry diethyl ether at reflux. Following the addition, the reaction mixture was allowed to stir for 1 h at reflux and was then quenched with solid ammonium chloride as described above. GLC analysis of the ethereal residue revealed 99.2% norbornane and 0.8% 1,1′-binorbornane.

Registry No.—**4**, 59219-48-6; *cis*-cyclopentane-1,3-dicarboxylic acid, 876-05-1; *cis*-cyclopentane-1,3-dicarboxylic acid chloride, 59219-49-7; *cis*-cyclopentane-1,3-bis(*N,N*-dimethylcarboxamide), 59219-50-0; *trans*-cyclopentane-1,3-bis(*N,N*-dimethylcarboxamide), 59219-51-1; 1,3-bis(dimethylamino)cyclopentane, 59219-52-2; *N*-methyl-*N*-(1-norbornylmethyl)formamide, 59219-53-3; lithium, 7439-93-2; ammonia, 7664-41-7.

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(31) Ammonia was first distilled from the tank into a flask containing lithium metal and then from the lithium metal into the reaction vessel.

Displacement of an Alkyl Group from Quaternary Ammonium Chlorides by Certain Neutral Nucleophiles

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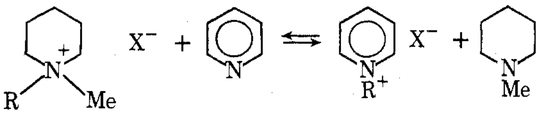
Heating $(Me_3SiO)_3Si(CH_2)_3Cl$ with excess trimethylamine caused almost quantitative yields of $(Me_3SiO)_3Si(CH_2)_3NMe_2$ and $Me_4N^+Cl^-$. Some conditions influencing the yields of products from alkyl chlorides and tertiary amines were studied. One alkyl group can be displaced from quaternary salts easily at 100 °C in nonpolar media by neutral nucleophiles with the following approximate order of reactivity: $NH_3 \leqslant RSH < HOAc < RNH_2 < R_2NH < R_3N$.

Recently we heated 3-[tris(trimethylsiloxy)silyl]propyl chloride (I) with an excess of trimethylamine expecting to obtain 3-[tris(trimethylsiloxy)silyl]propyltrimethylammonium chloride (III),[1] but obtained instead 3-[tris(trimethylsiloxy)silyl]propyldimethylamine (II) and tetramethylammonium chloride in almost quantitative yield. Dr. C. L. Frye of this laboratory suggested that these products might be an example of a type IV, SN2 reaction, the first example of which was described by Hughes and Whittingham[2] in 1960:

$$Ph_2MeNMe^+ + Me_3N \rightarrow Me_3NMe^+ + Ph_2MeN$$

This type of reaction had been predicted in 1935[3] and many examples have been found since 1960 in which an alkyl group is transferred to an uncharged nucleophile from an onium ion, including ions such as sulfonium, oxonium, or halonium ions.

Hutchinson and Tarbell[4] in 1969 showed that the reaction for ammonium ions was reversible and they studied the equilibrium



R = $PhCH_2$, X = Cl; R = $PhCH_2$, Me, X = Cl, Br

They found that (1) water prevented the reaction even at 140 °C; (2) bromides reacted faster than chlorides; (3) equilibria were reached most rapidly in nonpolar solvents; (4) a

Table I. Products From 3-[Tris(trimethylsiloxy)silyl]propyl Chloride and Trimethylamine

$$\mathrm{RCl(I)} + \mathrm{Me_3N} \rightarrow \mathrm{RN^+Me_3Cl^-(III)} \overset{\mathrm{Me_3N}}{\rightleftarrows} \mathrm{RNMe_2(II)} + \mathrm{Me_4N^+Cl^-}$$

$$\mathrm{R} = \mathrm{(Me_3SiO)_3SiCH_2CH_2CH_2}\text{–}$$

	Mol of NMe_3/RCl	Solvent	Time, h	Temp, °C	Mol %		
					I	III	II
1	2.4	None	129	130			>98
2	1.66	None	164	110		50	50
3	2.5	None	20	150			>95
4	1	None	1.25	150	50	25	25
5	2.2	30% Me_2CHOH by volume	3	100	61	39	
6	2.2	30% Me_2CHOH by volume	7.5	100	24	76	
7	2.2	30% Me_2CHOH by volume	69	100		21	79
8	2.2	30% Me_2CHOH by volume	144	100		21	79
9	7.5	70% heptane by volume	3	160	>97		

Table II. Ammonium Ions + Nucleophiles → Products

$$\mathrm{R_4N^+} + \mathrm{Nucl} \rightarrow \mathrm{R_3N} + \mathrm{R \cdot Nucl^+}$$

	Mol ratio of ion/nucl	Ion	Nucl	Registry no.	Time, h	Temp, °C	Products (% yield)[a]
1	3	NH_4^+	*n*-Bu_3N	102-82-9	17.5	160	No detectable change
2	1	$PhCH_2NC_5H_5^+$	*n*-Bu_2NH	111-92-2	18	155	C_5H_5N, $PhCH_2NBu_2$ (100)
3	1	$PhCH_2NC_5H_5^+$	*n*-$BuNH_2$	109-73-9	18	155	C_5H_5N, $PhCH_2NHBu$ (75)
4	1	III	*n*-Bu_2NH		18	155	$(Me_3SiO)_3Si(CH_2)_3NBu_2$ (19)[b] Me-Bu_2N (II) (81)[b]
5	1	III	*n*-$BuNH_2$		18	155	$(Me_3SiO)_3Si(CH_2)_3NHBu$ (13)[b] MeBuNH (II) (87)[b]
6	1	$PhCH_2NC_5H_5^+$	NH_3	7664-41-7	1.3	150	C_5H_5N, $PhCH_2NH_2$ (23)
7	1	$PhCH_2NC_5H_5^+$	*n*-$BuNH_2$		1.3	150	C_5H_5N, $PhCH_2NHBu$ (57)
8	1	$PhCH_2NC_5H_5^+$	*n*-Bu_2NH		1.3	150	C_5H_5N, $PhCH_2NBu_2$ (91)
9	1	$PhCH_2NC_5H_5^+$	*n*-Bu_3N		1.3	150	C_5H_5N, $PhCH_2NBu_3^+$ (100)[c]
10	1	$PhCH_2NC_5H_5^+$	$C_{12}H_{25}SH$	112-55-0	1.3	150	C_5H_5N, $PhCH_2SC_{12}H_{25}$ (33)
11	1	$PhCH_2NC_5H_5^+$	CH_3COOH	64-19-7	1.3	150	C_5H_5N, $PhCH_2OAc$ (47)

[a] % yield was calculated from GLC analysis of products (see Experimental Section). [b] Products were treated with NaOH, extracted with ether, analyzed by GLC, and identified by GLC–mass spectrometry. [c] This product was extracted with ether; C_5H_5N was identified by GLC of extract. Crystalline $PhCH_2NBu_3^+Cl^-$ was dried, weighed, titrated for Cl^- with $AgNO_3$, Cl^- equivalent 311.8 (calcd 311.94).

benzyl group exchanged more rapidly than did a methyl group; (5) equilibrium constants were nearly the same for bromides or chlorides.

The effects of such equilibria during syntheses of quaternary ammonium salts from alkyl halides and tertiary amines have not been described.

Table I shows some effects of temperature, solvents, time, and molar ratio of reagents upon the products formed from trimethylamine and I.

The products in Table I are explained as the result of two consecutive reactions, the first being practically irreversible below about 175 °C:[5] III heated in heptane above 100 °C for 48 h was recovered quantitatively and unchanged as should be expected if step 1 is irreversible under these conditions. Step 2, however, is highly reversible and leads to equilibrium mixtures of quaternary salts.

Although precipitation of $Me_4N^+Cl^-$ can drive these reactions to completion in nonpolar media, the use of a polar solvent in which $Me_4N^+Cl^-$ remains dissolved afforded the expected equilibrium mixtures. Thus, in 30% by volume 2-propanol, an equilibrium was reached with 21% III and 79% II at a Me_3N/RCl ratio of 2.2 at 100 °C. The high concentration of III at 7.5 h indicates that step 1 was much faster than step 2 in this solvent. In 70% by volume heptane almost no reaction took place in 3 h at 160 °C.

Benzylpyridinium chloride and III were found to be of approximately the same reactivity toward *n*-butyl- and di-*n*-butylamines. Benzylpyridinium chloride was heated with various nucleophiles to gain some qualitative data about the relative effectiveness of nucleophiles. See Table II.

Apparently an amine hydrochloride will not transfer an alkyl group. In our brief study the quaternary ammonium salts transferred an alkyl group to uncharged nucleophiles which included ammonia, a primary, a secondary, or a tertiary amine, a thiol, and acetic acid.

Experiment 9 in Table II indicates that pyridine must be a surprisingly ineffective nucleophile judging from the near quantitative formation of $PhCH_2NBu_3^+Cl^-$.

The 4th and 5th examples of Table II demonstrate that a methyl group transfers to certain nucleophiles more readily than does a $(Me_3SiO)_3Si(CH_2)_3$– group, and both compete in these reactions.

The yields of products from benzylpyridinium chloride with a series of nucleophiles in no solvent under similar conditions would suggest the following approximate order of reactivity: $NH_3 \leqslant RSH < HOAc <$ *n*-$BuNH_2 <$ *n*-$Bu_2NH <$ *n*-Bu_3N.

Experimental Section

Reagents. 3-[Tris(trimethylsilyl)propyl] chloride (I) was prepared by a published procedure.[6] All other reagents were reagent grade commercial products.

All gas–liquid chromatographs were obtained with an F & M Model 500 gas chromatograph with a 6 ft × 0.25 in. stainless steel column packed with 5% Dow Corning 200 gum on Anakrom ABS 60–70 mesh, treated with hexamethyldisilazane and programmed from 50 to 300 °C at 30 °C/min.

All mass spectra were recorded with an AEI MS-30 dual beam mass spectrometer interfaced to an AEI DX-50 data system.

Procedures. All experiments were done with sealed containers. Large-scale experiments were done with a 1.4-l. 316 stainless steel autoclave. Others were done in sealed Pyrex glass tubes. A typical example for expt 1 and 3 in Table I follows.

The autoclave was charged with I (707.9 g, 1.9 mol) and trimethylamine (265 g, 4.5 mol) was added from a small steel sampling bottle. The mixture was heated to 130 °C for 129 h and cooled to room temperature. Trimethylamine was then permitted to escape into a trap filled with dilute hydrochloric acid. The products were vacuum filtered to yield 223.6 g of crystalline solids. These were washed with hexane, dried under vacuum, and titrated potentiometrically in water for chloride ion. Found: 109.5 mg/mequiv (calcd for $Me_4N^+Cl^-$, 109.60 mg/mequiv). The filtrate was >98 area % of one compound. The filtrate was distilled to obtain 641.1 g (88% yield), bp 106–107 °C (3 mmHg), $n^{25}{}_D$ 1.4086, neut equiv 382.2 mg/mequiv (calcd for $(Me_3SiO)_3Si(CH_2)_3NMe_2$ (II),[7] $Si_4C_{14}H_{39}O_3N$, 381.8).[7] The distilled product was one sharp peak on GLC and was taken as a standard for subsequent analyses.

The analysis of example 4 of Table I illustrates how mixtures were analyzed when they contained I, II, and III at the end of the experiment.

The product was filtered and the crystalline material was washed with dry hexane, dried, weighed, and titrated for Cl^- with $AgNO_3$. The Cl^- equivalent weight was 269.6 mg/mequiv (calcd for a 1:1 molar mixture of III and $Me_4N^+Cl^-$ 270.61 mg/mequiv). The filtrate and hexane washes were stripped of solvent under vacuum to obtain 14.5 g of a liquid residue, which by GLC was 65.25 wt % I, 0.025 mol, 0.5 of initial charges of I, and 34.7 wt % II. The liquid residue had a base neutral equivalent weight of 1097.1 mg/mequiv which independently indicated ~34.75% II or about 0.013 mol.

Analysis of Examples 7 and 8 (Table I). Various standard solutions of III decomposed in a very reproducible way when injected into our GLC column. III → I + Me_3N + II + MeCl. The ratio of the peak areas of I/II was very close to 1:3.125.

The composition of mixtures that contained both II and III was determined from peak areas measured for I and II. For example, a solution of 1 equiv of I, 2.2 equiv of Me_3N, and 2-propanol, 30% by volume, was heated to 100 °C for 69 h. The tube was then cooled and opened and a sample was injected on the GLC column. The peak areas of I/II were 1/14.9 corresponding to that calculated to result from a mixture of 21% III and 79% II.

The alcohol was stripped from the sample under vacuum. The salts that precipitated were removed by filtration. The filtrate contained no I detectable by GLC. Thus, I observed above in solution had its origin in the thermal decomposition of III.

Analysis of Examples in Table II. Concentrated aqueous NaOH was added to the mixtures to free amines from their hydrochlorides. The mixtures were shaken with a weighed quantity of heptane.

The amount of each amine in the heptane was determined by GLC with heptane as an internal standard.

Registry No.—I, 18077-31-1; II, 29346-33-6; III, 29394-88-5; Me_3N, 75-50-3; $NH_4{}^+Cl^-$, 12125-02-9; $PhCH_2NC_5H_5{}^+Cl^-$, 2876-13-3.

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Nuclear Magnetic Resonance Studies. 6. Properties of Phosphorus–Nitrogen Ylides[1]

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The electronic distribution and conformation of triphenylphosphinimines and phosphinazines are discussed in the context of their ^{13}C and ^{31}P NMR parameters. CNDO/2 molecular orbital calculations on model phosphorus–nitrogen ylides are substantially in agreement with these NMR properties. It is found that the barriers of rotation about the N–C and N–N bond in *N*-vinylphosphinimine (**17**) and formylphosphazine (**18**), respectively, are small. The lone pairs of electrons on the nitrogen adjacent to phosphorus are delocalized to the methylene carbon in **17** but not in **18**. Direct evidence is found for the dissociation of a phosphinazine into triphenylphosphine and the parent diazo compound.

Phosphinimines and phosphazines have been known since 1919[3] and their synthetic utility has been extensively explored.[4] Little, however, is known about the physical properties, conformation, and electron distribution in these phosphorus–nitrogen ylides. In the present work[5] we have examined the ^{13}C and ^{31}P NMR of these ylides and by the use of CNDO/2 molecular orbital calculations[6] information concerning the conformation and electronic nature of these compounds is discussed. The ^{31}P and ^{13}C NMR parameters for a series of *N*-trimethylsilyltrialkylphosphinimines has recently been reported[7] and Hückel π-type calculations have been published with regard to the uv properties of phosphinimines and phosphazines.[8]

NMR Results. The ^{31}P, ^{13}C chemical shifts and ^{13}C–^{31}P couplings are given in Tables I–III, respectively. The ^{31}P chemical shift in Table I of *N*-phenyltriphenylphosphinimine (**1**) is shielded by 29.0 ppm from its phosphonium salt, **2**. Likewise, the phosphazines are shielded by approximately 20 ppm from their corresponding salts, i.e., compare **9** with **10**. These $\Delta\delta P$ values are somewhat larger than for the isoelectronic benzylidene or allylidenetriphenylphosphoranes (16.2 and 10.1 ppm, respectively).[1] The ^{31}P chemical shift of **1** where the excess negative charge on the nitrogen can be delocalized into the phenyl ring is not much different from that of *N*-trimethylsilyltriphenylphosphinimine (**4**). However, phosphinimines containing a strong electron-withdrawing group adjacent to the nitrogen, i.e., **5** and **6**, are deshielded by 11.6 to 17.6 ppm, respectively, from **1**. The phosphazines in Table I have ^{31}P chemical shifts that are deshielded from **1** by 15.4 to 19.4 ppm. *N*-Tosyltriphenylphosphazide (**14**) is deshielded from its phosphinimine counterpart, **6**, by 14.2 ppm.

The ^{31}P chemical shift of *N*-trityltriphenylphosphinimine (**3**) is shielded with respect to the other phosphinimines. This is presumably a result of steric interactions between the two sets of phenyl rings.[9]

The ^{13}C chemical shift for carbon 4 in *N*-phenyltriphenyl-