Photosensitized Oxidation. A. Of 3,5-Diiodophloretic Acid (I).—A solution of 2.09 g (5 mmoles) of 3,5-diiodophloretic acid[30] and 0.16 g of erythrosin in 180 ml of 0.05 *M* phosphate buffer, pH 7.60, was irradiated for 6.5 hr with a 500-w tungsten lamp which was placed at a distance of 2 cm from the reaction vessel. During irradiation, oxygen was bubbled through the solution which was cooled with ice water by means of a cold finger so that the reaction temperature was kept between 21 and 23°. The reaction mixture (pH 7.47) was acidified with 6 *N* hydrochloric acid and extracted with 150 ml of ether. The ethereal extracts were washed with aqueous bicarbonate solution to separate acidic products. The ethereal layer was evaporated to give a small amount of a light brown oil, in which the spirolactone VII could not be detected by chromatographic fractionation on silica gel. The bicarbonate extracts were acidified with 6 *N* hydrochloric acid and extracted with 200 ml of ether. After evaporation of the ethereal layer, the residual oil (1.67 g) was chromatographed on 35 g of silica gel. Elution with chloroform–acetone (99:1) yielded 0.37 g (18%) of the crude spirolactone VII. The crude product was digested with ether and the crystals thus obtained were recrystallized from aqueous acetonitrile to yield needles, mp 214–216°, whose infrared spectrum was identical with that of an authentic specimen.

A solution of 2.09 g of I in 200 ml of phosphate buffer, pH 7.6, was irradiated without erythrosin for 8 hr as described above. After working up the reaction mixture, 1.83 g (88%) of I was recovered.

B. Of 3,5-Dibromophloretic Acid (V).—A solution of 1.20 g (3.7 mmoles) of 3,5-dibromophloretic acid and 0.16 g of erythrosin in 200 ml of 0.05 M phosphate buffer, pH 7.6, was irradiated for 10 hr under similar conditions to those described under A. The acidic products were chromatographed on 35 g of silica gel. Elution with chloroform–ether (50:1) yielded 0.28 g (24%) of the crude spirolactone VI which, after digestion with ether, gave needles, mp 170–173° (lit.[20] mp 174–176°), whose infrared spectrum was identical with that of an authentic specimen.[20]

7,9-Diiodo-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (VII). A. With N-Bromosuccinimide.—3,5-Diiodophloretic acid (I, 4.18 g) was treated with N-bromosuccinimide according to the procedure described by Schmir, *et al.*[20] The spirolactone VII was obtained as needles (from acetone): mp 225–226° dec; yield, 24%; $\nu_{\max}^{\text{Nujol}}$ 1790, 1688, and 1608 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 263 mμ (ε 2800) and 295 (2400).

Anal. Calcd for $C_9H_6O_3I_2$: C, 25.97; H, 1.45. Found: C, 26.20; H, 1.65.

B. With Hypochlorite and Hydrogen Peroxide.—The procedure was essentially the same as that described by Foote and Wexler.[27a] In a typical run, 13 ml (17 mmoles) of 10% aqueous sodium hypochlorite was added below 10° to a solution of 2.1 g (5 mmoles) of 3,5-diiodophloretic acid and 2 ml (18 mmoles) of 30% hydrogen peroxide in 50 ml of methanol in the course of 30 min. Inorganic salts deposited were filtered off and the filtrate was acidified with dilute hydrochloric acid containing a small amount of sodium bisulfite and concentrated under reduced pressure. The mixture was extracted with ether and the ethereal extract was washed with aqueous bicarbonate, then with water, and evaporated. Chromatographic separation of the residue on silica gel yielded 0.25 g (12%) of the spirolactone VII. Several modifications of this reaction were carried out under similar conditions as summarized in Table II.

C. With Persulfate.—A solution of 1.37 g (6 mmoles) of ammonium persulfate in 10 ml of water was aded to a solution of 1.28 g (3 mmoles) of 3,5-diiodophloretic acid in 26 ml of 0.25 *N* potassium hydroxide. The mixture was stirred under nitrogen for 50 min, during which period aqueous potassium hydroxide was added from time to time in order to keep the pH of the mixture between 7.7 and 7.9. The reaction mixture was separated into a neutral and an acidic fraction. From the neutral fraction 0.10 g of the spirolactone VII was isolated and from the acidic fraction 0.23 g of the acid I was recovered. The total yield of VII was 10% on the basis of the reacted I.

7,9-Dichloro-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione.—This compound was prepared by a procedure similar to that for the preparation of the diiodospirolactone VII (method B). The results are summarized in Table II: mp 155–157°; $\nu_{\max}^{\text{Nujol}}$ 1790, 1687, and 1610 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 248 mμ (ε 12,800).

Anal. Calcd for $C_9H_6O_3Cl_2$: C, 46.38; H, 2.60. Found: C, 46.34; H, 2.82.

Oxidation of 3,5-Diiodophloretic Acid (I).—The reaction conditions and the results are summarized in Table I. From 1 to 10 mmoles of 3,5-diiodophloretic acid was dissolved in the minimum amount of 1 *N* potassium hydroxide required for complete dissolution. The solution was adjusted to the desired pH by the addition of alkali or acid and to a molarity of 0.10–0.15 by dilution with water; then the oxidizing agent was added. During the reaction period, the pH of the mixture was kept constant by the addition of alkali or acid. In those cases in which the oxidizing agent was completely consumed in the course of the reaction, the reaction mixture was extracted with 1-butanol after the addition of enough sodium hydroxide to make the mixture about 1 *N* with respect to sodium hydroxide. In other cases, the reaction mixture was acidified with hydrochloric acid, then extracted with 1-butanol, and the butanol extracts washed with 1 *N* sodium hydroxide. After evaporation of the butanol, acidification of the residue yielded 3,5,3′,5′-tetraiodothyropropionic acid (II) whenever it was formed in the reaction. The aqueous layer was acidified with hydrochloric acid and extracted with ether. The ethereal extract was evaporated to give a residue, from which 3,5-diiodophloretic acid (I) was recovered by recrystallization. Intractable material obtained in the course of the oxidation was regarded as polymers and was not further investigated.

Registry No.—I, 13811-11-5; V, 13811-12-6; VII, 13811-13-7; 7,9-dichloro-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione, 13811-15-9; 3,5-dichlorophloretic acid, 13811-16-0.

Acknowledgment.—The authors wish to express their hearty thanks to Dr. H. J. Cahnmann, National Institutes of Health, Bethesda, Md., for his discussion throughout this work.

[30] J. H. Barnes, E. T. Borrows, J. Elks, B. A. Hems, and A. G. Long, *J. Chem. Soc.*, 2824 (1950).

The Preparation and Properties of Bis(phosphoranylidene)ammonium Chlorides

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Methods have been developed for the preparation of both symmetrical and unsymmetrical bis(phosphoranylidene)ammonium chlorides. The former compounds were synthesized by the pyrolysis of aminophosphonium chlorides, whereas the unsymmetrical compounds were prepared from the reaction of N-lithiophosphinimines with tertiary phosphine dichlorides. Other reactions of the N-lithiophosphinimines are reported. The spectral characterization and the thermal and hydrolytic stabilities of the bis(phosphoranylidene)ammonium chlorides are also discussed.

In recent years considerable attention has been directed toward saltlike compounds containing a $[{>}P{=}N{=}P{<}]^+$ moiety in which the positive charge is distributed over all three atoms. Nearly all of the work has centered on compounds (*e.g.*, Ia–d) which appear to be intermediates in the syntheses of phosphoni-

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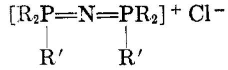
trilic trimers, tetramers, and polymers.[2] For example, Ia has been isolated from the low-temperature reaction



$$[R_2\underset{|}{\overset{}{P}}\underset{R'}{}{=}N{=}\underset{|}{P}R_2]^+\,Cl^- \quad (R' \text{ on each } P)$$

Ia, R, R′ = Cl
b, R = C_6H_5; R′ = Cl
c, R = C_6H_5; R′ = NH_2
d, R = C_2H_5; R′ = NH_2

of phosphorus pentachloride and ammonium chloride.[3] At higher temperatures, however, Ia presumably reacts further with the starting materials or with another intermediate, $Cl_3P{=}NH$, to yield eventually the cyclic or polymeric phosphonitrilic compounds.[2]

Similarly, the reaction of trichlorodiphenylphosphorane with ammonium chloride at 130° gave Ib,[4] but at 175° the tetramer $(C_6H_5)_8P_4N_4$ was obtained.[5] At the higher temperature a second compound was also obtained which was shown to be Ic. This same substance has been prepared by Sisler[6] from the reaction of chlorodiphenylphosphine with an ammonia–chloramine mixture. In addition, he applied the chloramine method to the preparation of analogous alkyl compounds such as Id and has shown that pyrolysis of either Ic or Id leads to a mixture of phosphonitrilic trimer and tetramer.

Concurrently with the investigations mentioned above, Appel and his collaborators synthesized the closely related salts IIa–c. These bis(triphenylphosphoranylidene)ammonium salts[7,8] were prepared by the methods illustrated in eq 1–4.[8–10]

$$[(C_6H_5)_3P{=}N{=}P(C_6H_5)_3]^+\,X^-$$

IIa, X = Br
b, X = Cl_3
c, X = N_3

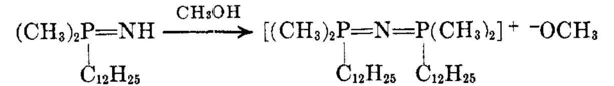
$$(C_6H_5)_3P{=}NBr + (C_6H_5)_3P \longrightarrow \text{IIa} \quad (1)$$

$$(C_6H_5)_3PBr_2 + 2(C_6H_5)_3P{=}NH \longrightarrow \text{IIa} + (C_6H_5)_3P^+NH_2\;Br^- \quad (2)$$

$$2(C_6H_5)_3P + NCl_3 \longrightarrow \text{IIb} \quad (3)$$

$$(C_6H_5)_3P^+NH_2\;N_3^- + (C_6H_5)_3P \xrightarrow{\Delta} \text{IIc} + (C_6H_5)_3P{=}NH + N_2 \quad (4)$$

Recently, the first example of a bis(trialkylphosphoranylidene)ammonium salt, namely III, was re-



$$\underset{\substack{|\\C_{12}H_{25}}}{(CH_3)_2P}{=}NH \xrightarrow{CH_3OH} [\underset{\substack{|\\C_{12}H_{25}}}{(CH_3)_2P}{=}N{=}\underset{\substack{|\\C_{12}H_{25}}}{P(CH_3)_2}]^+\;{}^-OCH_3$$

III

ported.[11] This compound, which was slowly destroyed by hydroxylic solvents, arose from the controlled methanolysis of dimethyldodecylphosphinimine.

We wish to report herein the preparation of several bis(trialkylphosphoranylidene)ammonium chlorides which are quite stable thermally and hydrolytically. Furthermore, new methods have been devised for the preparation of both symmetrical and unsymmetrical compounds. The synthesis of the unsymmetrical compounds involves the use of novel N-lithiophosphinimine intermediates.

Results and Discussion

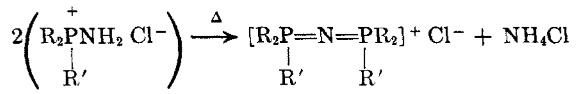
Symmetrical Bis(phosphoranylidene)ammonium Chlorides.—During the course of an investigation of trialkylphosphinimines,[11] we prepared aminodimethyldodecylphosphonium chloride (IVa) from the reaction of dimethyldodecylphosphine and chloramine. Subsequently it was found that pyrolysis of IVa in an inert atmosphere gave a substantial amount of ammonium chloride and a new substance which was identified as bis(dimethyldodecylphosphoranylidene)ammonium chloride (IVb). Because this reaction promised to be a convenient and useful preparative method for this type of compound, it seemed worthwhile to determine its generality. Therefore, five more aminophosphonium chlorides (Va–IXa) were heated *in vacuo* to temperatures at least 20° above their melting points and in each case the corresponding bis(phosphoranylidene)ammonium chloride (Vb–IXb) was obtained in good yield. The reaction times, temperatures, and yields are summarized in Table I. It is noteworthy that at times and temperatures at which the conversion of IVa to IVb had been effected completely, the corresponding reaction of the tributyl compound (VIIa) had not gone to completion. The reason for the lesser reactivity of VIIa is likely steric

TABLE I

BIS(PHOSPHORANYLIDENE)AMMONIUM CHLORIDES

Compd	Method of prepn[a]	Reaction time, hr	Reaction temp, °C	Yield, %	P^{31} nmr chemical shift,[b,c] ppm
IVb	A[d]	16	160	65	−35
Vb	A	16	170	59	−33
VIb	A	16	200	63	−32
VIIb	A	16	230	54	−35
VIIIb	A	15	245	45	−27
IXb	A	20	255	83	−21
X	B	16	25	74	−32, −36
XI	B	24	25	22[e]	−32, −36
XII	B	16	25	10	−30, −32

[a] Method A is the pyrolysis of an aminophosphonium chloride; method B is the reaction of an N-lithiophosphinimine with a tertiary phosphine dichloride. [b] Chemical shifts are reported relative to 85% H_3PO_4 as an external standard. [c] Spectra were obtained using benzene as solvent except for VIb ($CHCl_3$), VIIIb (H_2O), and IXb ($ClCH_2CH_2Cl$). [d] Compound IVb was also prepared in 17% yield using method B (see Experimental Section). [e] The low yield is believed to be due to losses during purification rather than to side reactions.



$$2\left(\underset{\substack{|\\R'}}{R_2\overset{+}{P}}NH_2\;Cl^-\right) \xrightarrow{\Delta} [\underset{\substack{|\\R'}}{R_2P}{=}N{=}\underset{\substack{|\\R'}}{PR_2}]^+\,Cl^- + NH_4Cl$$

a b

IV, R = CH_3; R′ = $C_{12}H_{25}$
V, R = CH_3; R′ = $C_{14}H_{29}$
VI, R = CH_3; R′ = $C_{16}H_{33}$
VII, R = R′ = n-C_4H_9
VIII, R = R′ = CH_3
IX, R = R′ = C_6H_5

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[2] For excellent reviews on this subject, see N. L. Paddock, *Quart. Rev* (London), **18**, 168 (1964), and R. A. Shaw, R. Keat, and C. Hewlett, *Preparative Inorg. Reactions*, **2**, 1 (1965).

[3] M. Becke-Goehring and W. Lehr, *Chem. Ber.*, **94**, 1591 (1961).

[4] E. Fluck and F. L. Goldman, *ibid.*, **96**, 3091 (1963).

[5] V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. N. Bushmarina, *Vysokomolekul. Soedin.*, **2**, 377 (1960); *Chem. Abstr.*, **54**, 24479*d* (1960).

[6] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

[7] Appel[8] called these compounds "bis(triphenylphosphine)nitride" salts; however, we prefer the nomenclature used in *Chemical Abstracts*.

[8] R. Appel and A. Hauss, *Z. Anorg. Allgem. Chem.*, **311**, 290 (1961).

[9] R. Appel and G. Büchler, *Z. Naturforsch.*, **17B**, 422 (1962).

[10] R. Appel, G. Köhnlein, and R. Schöllhorn, *Chem. Ber.*, **98**, 1355 (1965).

[11] T. W. Rave and H. R. Hays, *J. Org. Chem.*, **31**, 2894 (1966).

in nature, and this behavior is probably general for aminophosphonium salts with alkyl substituents other than methyl.

The bis(phosphoranylidene)ammonium chlorides (IVb–IXb) were identified on the basis of microanalyses and/or infrared and nmr data. The infrared spectra of all of the salts exhibited a strong, broad absorption at 8.0–8.2 μ attributable to the phosphorus–nitrogen antisymmetric stretching mode and the spectra of all except VIIb and IXb showed the characteristic PCH_3 stretching mode at about 7.7 μ.[12] The P^{31} nmr spectra consisted of a single, poorly resolved multiplet ranging from −21 to −35 ppm relative to 85% H_3PO_4; the individual values are listed in Table I.

Proton nmr analysis strongly supported the assigned structure in each case. The spectra of IVb, Vb, and VIb were practically identical and showed a doublet at τ 8.08 (J_{PCH} = 12 cps) attributable to the protons of the two methyl groups on phosphorus. Superimposed upon this doublet was a poorly resolved multiplet arising from the methylene protons adjacent to phosphorus. The remainder of the spectra consisted of a sharp signal (20, 24, or 28 protons) at τ 8.75 and a triplet (three protons) centered at τ 9.13 which were assigned to the remaining methylene protons and the methyl protons, respectively, of the long chain group.

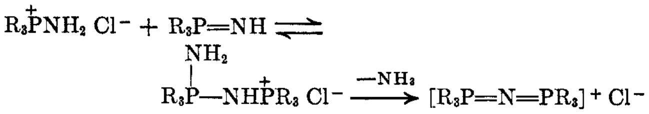
For the butyl compound VIIb, the α-methylene and remaining methylene protons appeared as multiplets centered at τ 7.98 (two protons) and 8.52 (four protons), respectively, and the terminal methyl protons appeared as a triplet at 9.05 (three protons). The spectrum of VIIIb[13] consisted of a single doublet (J_{PCH} = 12 cps) at 7.62 and that of IXb showed only a multiplet centered at 2.55 attributable to the aryl protons.

It should be noted that the PCH_3 doublets in the proton nmr spectra of IVb, Vb, and VIb appear far downfield from those of dimethyldodecylphosphine oxide (τ 8.52) and dimethyldodecylphosphinimine (8.74),[11] but they are close to those of the aminophosphonium salts IVa–VIa (8.06). This fact is indicative of the positive charge on the phosphorus atoms of the bis(phosphoranylidene)ammonium salts. Also, as has been previously pointed out for III,[11] the facts that only one PCH_3 doublet was observed and that a single peak was present in the P^{31} nmr spectra of the salts are consistent with their symmetrical structures.

$$R_3P{=}N\overset{+}{P}R_3 \longleftrightarrow R_3\overset{+}{P}N{=}PR_3 \longleftrightarrow R_3\overset{+}{P}\overset{-}{N}\overset{+}{P}R_3 \longleftrightarrow R_3P{=}\overset{+}{N}{=}PR_3$$

The mechanism of the pyrolytic conversion of an aminophosphonium chloride to a bis(phosphoranylidene)ammonium salt probably involves an equilibrium of the former compound with its conjugate base (the corresponding phosphinimine) and HCl at the high temperature. Because phosphinimines bearing hydrogen on nitrogen are very strong bases, the concentration of free $R_3P{=}NH$ at any given time must be quite small. These compounds, however, are also very reactive nucleophiles; so attack on the positively charged phosphorus atom of an aminophosphonium salt would be expected to be rapid. Loss of ammonia from the resulting intermediate would yield a bis(phosphoranylidene)ammonium chloride and the ammonia would be rapidly neutralized by the HCl liberated in the initial equilibrium.

$$R_3\overset{+}{P}NH_2\ Cl^- \rightleftharpoons R_3P{=}NH + HCl$$

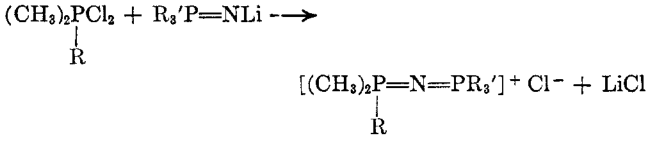


$$R_3\overset{+}{P}NH_2\ Cl^- + R_3P{=}NH \rightleftharpoons R_3\overset{NH_2}{\overset{|}{P}}{-}NH\overset{+}{P}R_3\ Cl^- \xrightarrow{-NH_3} [R_3P{=}N{=}PR_3]^+\ Cl^-$$

Evidence supporting this mechanism was provided by the fact that an equimolar mixture of the aminophosphonium chloride IVa and the corresponding phosphinimine, $(CH_3)_2P(C_{12}H_{25}){=}NH$, did indeed yield IVb upon being stirred overnight in solution *at room temperature*. Each reactant by itself was stable under the same conditions. However, this experiment, although it demonstrates that the last two steps in the mechanism outlined above are possible even at low temperatures, does not provide any information about the initial equilibrium, that is, whether any free phosphinimine could have been present at high temperatures. Thus, the possibility that the products were formed by initial attack of the nitrogen of one aminophosphonium salt on the positive phosphorus of another, as proposed by Appel for the formation of IIc (eq 4), cannot be ruled out, though we believe it to be unlikely in both his case and ours.

Unsymmetrical Bis(phosphoranylidene)ammonium Chlorides.—The pyrolytic route described above is clearly unsatisfactory for the preparation of unsymmetrical bis(phosphoranylidene)ammonium salts because pyrolysis of a mixture of two aminophosphonium salts would lead to three bis(phosphoranylidene)ammonium compounds. Therefore, a totally different synthesis of the unsymmetrical compounds was devised.

In the first step, an aminophosphonium chloride was treated with 2 equiv of *n*-butyllithium to generate an N-lithiophosphinimine.[14] This was then combined with 1 equiv of a tertiary phosphine dihalide derived from a phosphine different from that used in the preparation of the N-lithiophosphinimine. The resulting mixture was stirred for several hours at room temperature to yield the desired product. Using this method,[15] the unsymmetrical bis(phosphoranylidene)ammonium chlorides X, XI, and XII were prepared and data on these reactions and products are also recorded in Table I.



$$\underset{\underset{R}{|}}{(CH_3)_2PCl_2} + R_3'P{=}NLi \longrightarrow [\underset{\underset{R}{|}}{(CH_3)_2P}{=}N{=}PR_3']^+\ Cl^- + LiCl$$

X, R = $C_{12}H_{25}$; R′ = n-C_4H_9
XI, R = $C_{18}H_{37}$; R′ = n-C_4H_9
XII, R = $C_{12}H_{25}$; R′ = CH_3

Compound X was also prepared by treating N-lithiodimethyldodecylphosphinimine with tributylphosphine dichloride, that is, by "reversing" the phosphorus reagents. In addition, the symmetrical salt IVb was

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[12] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 321.

[13] Because of the insolubility of VIIIb in nearly all organic solvents, this spectrum was measured in D_2O using TMS as an external standard.

[14] Evidence for the structure of these compounds is presented in the next section.

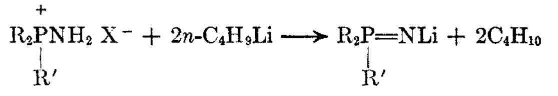
[15] A route similar to this was used for the preparation of compounds of the type $[R_3P{=}N{=}S(\rightarrow O)R_2']^+\ Cl^-$; see T. W. Rave and T. J. Logan, *J. Org. Chem.*, **32**, 1629 (1967).

synthesized by using the N-lithiophosphinimine and the phosphine dichloride both derived from dimethyldodecylphosphine. However, the pyrolytic preparation of IVb is preferable since it involves only one step and gives the product in better yield.

The structures of the unsymmetrical salts X, XI, and XII were established by infrared and nmr analyses. The infrared spectra of the three were very similar to one another and displayed the same characteristic absorptions at 7.7 and 8.1 μ as did their symmetrical counterparts. The proton nmr spectra of X and XI were identical except for the expected larger relative peak area of the methylene protons of the long chain alkyl substituent of XI. The PCH_3 doublets ($J_{PCH} = 12$ cps) were centered at τ 8.08 which is the same value as for the corresponding doublets in the spectra of the symmetrical salts. Multiplets centered at about τ 8.0 (six protons) and at 8.53 (12 protons) and a triplet at 9.05 (nine protons) were assigned to the methylene protons adjacent to phosphorus, the other methylene protons, and the methyl protons, respectively, of the butyl groups. The spectrum of compound XII showed only the usual peaks due to the protons of the dodecyl group and a doublet at τ 8.07 ($J_{PCH} = 12$ cps) attributable to the protons of the three methyl groups on one phosphorus and the two on the other.

Contrary to the P^{31} nmr spectra of the symmetrical bis(phosphoranylidene)ammonium salts which showed only one peak, the spectra of the unsymmetrical compounds displayed two resonances. This is no doubt a consequence of the different alkyl substituents on each phosphorus. As expected, the chemical shift of each of the two resonances was very similar to that of the corresponding symmetrical compound (see Table I).

N-Lithiophosphinimines.—It has already been mentioned that treatment of an aminotrialkylphosphonium salt with 2 equiv of *n*-butyllithium yields the corresponding N-lithiophosphinimine. Using this method, the dimethyldodecyl, tributyl, and trimethyl compounds XIII, XIV, and XV, respectively, were prepared in benzene solutions. Evaporation of the solvent gave in each case a gum which could neither be satisfactorily crystallized nor purified and which rapidly hydrolyzed to give ammonia and the corresponding phosphine oxide.



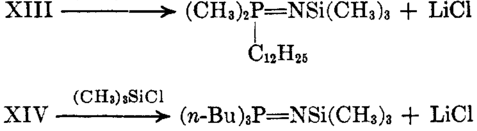
$$\underset{R'}{R_2\overset{+}{P}NH_2}\,X^- + 2n\text{-}C_4H_9Li \longrightarrow \underset{R'}{R_2P}{=}NLi + 2C_4H_{10}$$

IVa XIII, R = CH_3; R′ = $C_{12}H_{25}$
VIIa XIV, R, R′ = n-C_4H_9
VIIIa XV, R, R′ = CH_3

The infrared spectra of the three N-lithiophosphinimines showed a strong, broad band at 8.6 μ (not present in the spectra of the unsubstituted phosphinimines) which apparently arises from the $P{=}\overset{\delta-}{N}-$ moiety, and, significantly, no N–H stretching absorption was present. Compounds XIII and XIV were also subjected to nmr analyses and their proton nmr spectra were completely consistent with the assigned structures.[16] The spectrum of XIII completely eliminated the possibility that unreacted *n*-butyllithium was present because only the protons due to two methyl groups and one dodecyl group appeared. The single peaks in the P^{31} nmr spectra of XIII and XIV appeared at +10 and −10 ppm, respectively. These are far upfield from those of the corresponding unsubstituted phosphinimines [−18 ppm for $(CH_3)_2P(C_{12}H_{25}){=}NH$ and −31 ppm for $(n\text{-}C_4H_9)_3P{=}NH^{11}$] and indicate the diminished positive character of the phosphorus atoms in the N-lithio compounds.

Because of the ease with which trialkylphosphines[17] and their derivatives[18] undergo metalation on carbon when treated with organolithium compounds, it was possible that significant quantities of carbon-metalated species were present along with the N-lithiophosphinimines. To check this, the product mixture from the reaction of the aminophosphonium salt IVa and 1.9 equiv[19] of n-C_4H_9Li was quenched with D_2O and the resulting phosphine oxide was analyzed by mass spectrometry after purification. The mass spectrum showed less than 3%[20] dimethyldodecylphosphine oxide-d_1; so very little carbon metalation could have occurred.

In addition to the reaction of N-lithiophosphinimines with tertiary phosphine dihalides to yield bis(phosphoranylidene)ammonium salts, XIII and XIV were derivatized with chlorotrimethylsilane to yield the corresponding N-silylphosphinimines in yields of 55–60%. These experiments, besides providing more evidence for the structures,[21] suggested that a wide variety of N-substituted phosphinimines might be prepared[21a] by treating N-lithiophosphinimines with appropriate organic halides. The reaction of XIII with either p-$CH_3C_6H_5SO_2Cl$ or CH_3SO_2Cl, however, led to mixtures of products which contained only a small amount (<10%) of the desired N-sulfonylphosphinimine. An investigation of how other types of substrates, such as the less acidic alkyl halides, react with N-lithiophosphinimines was not undertaken.



$$\text{XIII} \xrightarrow{(CH_3)_3SiCl} \underset{C_{12}H_{25}}{(CH_3)_2P}{=}NSi(CH_3)_3 + LiCl$$

$$\text{XIV} \xrightarrow{(CH_3)_3SiCl} (n\text{-}Bu)_3P{=}NSi(CH_3)_3 + LiCl$$

Properties of Bis(phosphoranylidene)ammonium Chlorides.—The saltlike nature of the bis(phosphoranylidene)ammonium chlorides was confirmed by the fact that the conductance of IVb was slightly greater than that of sodium 2-dodecylbenzenesulfonate.

All of the bis(phosphoranylidene)ammonium chlorides listed in Table I with the exception of VIIIb and IXb were quite hygroscopic. The extreme hygroscopicity of VIIb, X, and XII was the main reason that adequate microanalytical data were not obtained on these compounds.

Two other properties of the bis(phosphoranylidene)-

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[16] The nmr spectra of the N-lithiophosphinimines were measured in benzene because of their reactivity with the more common nmr solvents.

[17] D. J. Peterson and H. R. Hays, *J. Org. Chem.*, **30**, 1939 (1965).

[18] J. J. Richard and C. V. Banks, *ibid.*, **28**, 123 (1963).

[19] Slightly less than 2 equiv were used so as to ensure that no metalation could occur by an excess of this reagent.

[20] This value is the upper limit for C-metalated species because the possibility that some deuterium was incorporated by base-catalyzed proton exchange of the phosphine oxide after quenching was not checked.

[21] In a separate experiment, it was shown that treatment of $(CH_3)_2P(C_{12}H_{25}){=}NH$ with $(CH_3)_3SiCl$ gave only $(CH_3)_2P^+(C_{12}H_{25})NHSi(CH_3)_3\ Cl^-$; none of the N-silylphosphinimine was observed.

[21a] NOTE ADDED IN PROOF.—After the submission of this paper, a report appeared in the literature describing the preparation of N-lithio- and N-silylphosphinimines by routes analogous to those reported herein. See H. Schmidbaur and G. Jonas, *Chem. Ber.*, **100**, 1120 (1967).

TABLE II

MELTING POINTS AND MICROANALYTICAL DATA FOR BIS(PHOSPHORANYLIDENE)AMMONIUM CHLORIDES

Compd	Mp, °C	Recrystn solvent	Calcd, %					Found, %				
			C	H	N	Cl	P	C	H	N	Cl	P
IVb	116–118	Benzene–hexane	65.91	12.25	2.76	6.95	12.14	65.59	12.26	2.75	6.85	11.91
Vb	113–116	Acetonitrile	67.86	12.46	2.40	6.26	10.94	67.65	12.45	2.48	6.27	10.96
VIb	110–113	Acetonitrile	69.47	12.63	2.25	5.68	9.95	69.96	12.48	2.39	...	10.29
VIIb	44–46	Carbon tetrachloride	63.48	11.99	3.09	7.81	13.64	60.27	11.96	3.06	7.41	...
VIIIb	249–253	Acetonitrile										
IXb	265–267[a]	Water										
X	44–46	Carbon tetrachloride	64.77	12.13	2.91	7.35	12.85	62.55	12.20	2.91	6.99	...

[a] Lit.[9] mp 269–271°.

ammonium chlorides deserve mention. The first is their thermal stability which was shown by the fact that they can be prepared in good yields by pyrolyses at quite high temperatures. The second is their resistance to hydrolysis in acidic, basic, or neutral media when compared with that of most phosphinimines. For example, IVb was removed unchanged after 2 hr treatment with warm 1.2 *N* HCl or NaOH or with hot water. It was partially destroyed, however, by treatment over a 16-hr period with 6 *N* NaOH, 90% aqueous methanol 0.6 *N* in NaOH, or boiling 2 *N* HCl. The expected products of hydrolysis, dimethyldodecylphosphine oxide and ammonia (or ammonium chloride), were obtained. The high degree of hydrolytic stability of the hexaphenyl compound IXb has been reported by Appel.[8]

Experimental Section[22]

1. **Tertiary Phosphines.**—Dimethyldodecylphosphine, dimethyltetradecylphosphine, and dimethylhexadecylphosphine were prepared by reduction of the corresponding phosphine oxides[23] with trichlorisilane.[24] Tributylphosphine and triphenylphosphine were purchased from Carlisle Chemical Works, Inc., and Matheson Coleman and Bell, respectively. Trimethylphosphine[25] was prepared from phosphorus trichloride and methyllithium (Foote Mineral Co.) and was used in ether solution without isolation.

2. **Aminophosphonium Chlorides.**—The aminophosphonium chlorides IVa–IXa were prepared from the reaction of the corresponding phosphine and gaseous chloramine using an apparatus and procedure similar to those used previously.[11,26] The chlorides Va and VIa were identified on the basis of the similarity of their infrared and nmr spectra to those of the well-characterized IVa.[11] The melting points of VIIa and IXa agreed well with those previously reported for these compounds,[26] but this was not the case for VIIIa. Although VIIIa was very difficult to purify, the melting points on samples of this compound taken from different preparations ran about 100° higher than the melting point (122°) reported by Appel.[27] Our identification was based on infrared and P^{31} ($\delta = -50$ ppm) and proton (doublet at τ 7.97, $J_{PCH} = 12$ cps) nmr spectroscopy, along with the isolation of trimethylphosphine oxide and ammonium chloride in good yields from its hydrolysis. The phosphine oxide was identical with an authentic sample.

The other aminotrialkylphosphinium chlorides reported herein were also converted to the corresponding phosphine oxides and ammonium chloride with water, thus confirming the structural assignments.

3. **Symmetrical Bis(phosphoranylidene)ammonium Chlorides. General Procedure for Pyrolysis of Aminophosphonium Chlorides.**—The desired amount of an aminophosphonium chloride (IVa–IXa) was placed in a heavy-walled glass pyrolysis tube and the tube was evacuated to 0.1 mm and sealed at this pressure. It was then kept for several hours in an oil bath that had been preheated to a temperature at least 20° higher than the melting point of the salt being pyrolyzed. (Shorter times than those listed in Table I may be sufficient for complete reaction.) After cooling, the tube was opened under an atmosphere of argon. The white crystalline mass was partially dissolved in hot acetonitrile and filtered to remove the insoluble ammonium chloride. The solid obtained by evaporation of the solvent from the filtrate was extracted again with hot acetonitrile and then recrystallized several times to give pure bis(phosphoranylidene)ammonium chlorides (IVb–IXb). A summary of the times, temperatures, and yields of the pyrolyses is given in Table I. Melting points, recrystallization solvents, and microanalytical data are listed in Table II.

Compound IVb from IVa and Dimethyldodecylphosphinimine.—A solution of 319 mg (1.30 mmoles) of dimethyldodecylphosphinimine and 366 mg (1.30 mmoles) of the aminophosphonium chloride IVa in 10 ml of acetonitrile was stirred overnight at room temperature under an argon atmosphere. Evaporation of the solvent gave a white solid which was recrystallized several times from acetonitrile to give 250 mg (38%) of white crystals identified as IVb by infrared analysis, melting point, and mixture melting point comparison with an authentic sample.

Compound IVb from N-Lithiodimethyldodecylphosphinimine (XIII) and Dimethyldodecylphosphine Dichloride.—To a stirred mixture of 2.35 mmoles of dimethyldodecylphosphine dichloride and 20 ml of benzene under argon was added (using a syringe) a solution of 1.88 mmoles of XIII in 10 ml of benzene. Methods for the preparation of both of these reactants are given below. An exothermic reaction occurred along with slow deposition of a white solid. After the mixture was stirred 16 hr, the solvent was evaporated at 0.5 mm to yield a yellow solid which was extracted with hot acetonitrile. The extract was dried ($MgSO_4$) and evaporated to give another white solid which was recrystallized from a 1:1 benzene–hexane mixture. The resulting white crystals (166 mg, 17%) were shown to be IVb by the identity of their infrared and nmr spectra with those of an authentic sample.

4. **Unsymmetrical Bis(phosphoranylidene)ammonium Chlorides. Preparation of N-Lithiophosphinimines XIII and XIV.**—*n*-Butyllithium (2 equiv) in hexane solution was added to a benzene solution of the desired amount of the aminophosphonium chloride IVa or VIIa under argon. (The *n*-butyllithium was titrated to a known normality immediately before use.) The resulting solution was stirred 1 hr at room temperature and used without isolation or purification of the N-lithiophosphinimine XIII or XIV.

Preparation of Tertiary Phosphine Dichlorides.[28]—In a one-necked round-bottomed flask equipped with a rubber serum cap and filled with argon was placed the desired amount of the appropriate phosphine. Benzene was added and the resulting solu-

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[22] Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. The proton nmr spectra were obtained using a Varian spectrometer, Model A-60 or Model HA-100, and were measured in deuteriochloroform solutions using tetramethylsilane as an internal standard unless otherwise noted. Phosphorus nmr spectra were recorded on a Varian HR-60 spectrometer and are reported in ppm relative to 85% H_3PO_4 as an external standard. Microanalyses were carried out by the Analytical Section of Procter & Gamble's Miami Valley Laboratories and by Spang Microanalytical Laboratories. *n*-Butyllithium was purchased from Foote Mineral Co. All solvents were distilled and dried over molecular sieves. Hydrolytically unstable and hygroscopic solids were handled in glove bags purchased from Instruments for Industry and Research, Cheltenham, Pa. Melting points were determined in evacuated sealed tubes.

[23] R. G. Laughlin, *J. Org. Chem.*, **30**, 1322 (1965).

[24] H. Fritzsche, U. Hasserodt, F. Korte, G. Friese, and K. Adrian, *Chem. Ber.*, **98**, 171 (1965).

[25] C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

[26] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[27] R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).

[28] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 58.

tion was vigorously stirred while 1 equiv of chlorine gas was injected into the closed flask using a gas syringe inserted through the serum cap. The solution first became yellow and then turned viscous as the phosphine dichloride began to precipitate. The compound was used without isolation or purification after being stirred 1 hr at room temperature; the yield was assumed to be quantitative.

Compound X from N-Lithiotributylphosphinimine (XIV) and Dimethyldodecylphosphine Dichloride.—To a mixture of 30.7 mmoles of dimethyldodecylphosphine dichloride and 50 ml of benzene under argon was added 45.7 mmoles of XIV in 100 ml of benzene–hexane solution. This mixture was stirred overnight under argon without external heating and then filtered to remove the precipitated lithium chloride (identified by infrared analysis). The filtrate was evaporated to yield a yellow oil which was dissolved in 50 ml of CCl_4. Overnight cooling of this solution gave 10.88 g (74%) of a white solid. Two more recrystallizations from CCl_4 gave white crystals, mp 44–46°.

Compound X from N-Lithiodimethyldodecylphosphinimine (XIII) and Tributylphosphine Dichloride.—A solution of 6.96 mmoles of XIII in 30 ml of benzene was prepared and then added to 6.96 mmoles of tributylphosphine dichloride in 70 ml of benzene. The resulting mixture was stirred 16 hr under argon and filtered to remove the by-product lithium chloride. Evaporation of the solvent from the filtrate yielded a yellow oil which was dissolved in CCl_4. A white solid (1.81 g, 54%) deposited from the cooled solution. An additional recrystallization from CCl_4 gave white crystals identified as X by spectral analyses, melting point, and mixture melting point comparison with an authentic sample.

Compound XI.—A solution of 48.1 mmoles of N-lithiotributylphosphinimine (XIV) in 100 ml of dry benzene was prepared and added under argon to a stirred mixture of dimethyloctadecylphosphine dichloride (48.1 mmoles) and 300 ml of benzene. After the resulting mixture was stirred for 24 hr, the precipitated lithium chloride was allowed to settle out. Evaporation of the supernatant liquid to dryness (0.5 mm) yielded a yellow gummy oil which could not be crystallized. It was therefore chromatographed on Grace silica gel, grade 923, and the column was eluted successively with carbon tetrachloride–benzene (1:1), benzene, benzene–chloroform (1:1), chloroform, chloroform–ethyl acetate (1:1), ethyl acetate, ethyl acetate–methanol (4:1), and methanol. Ethyl acetate–methanol (4:1) eluted a colorless oil which partially crystallized. The oil was dissolved in benzene; addition of an equal volume of hexane followed by overnight cooling caused a very small amount of white solid to precipitate which was shown to be dimethyloctadecylphosphine oxide by spectral analysis. The phosphine oxide no doubt was formed by inadvertent hydrolysis of unreacted phosphine dichloride. The benzene–hexane filtrate from above was evaporated (0.5 mm) to give 6.10 g (22%) of a colorless oil. This was identified as XI by spectral analyses and shown to be 95% pure by thin layer chromatography on silica gel. Microanalytical data were not obtained owing to the difficulty of achieving complete purification.

Compound XII.—N-Lithiotrimethylphosphinimine (XV) was prepared by treating 4.16 g (32.6 mmoles) of VIIIa suspended in 20 ml of benzene with 2 equiv of 1.53 *N* *n*-butyllithium. The resulting mixture was stirred under argon for 1 hr and then boiled under reflux for 2 hr because the insolubility of VIIIa prevented the usual rapid reaction with the butyllithium. (Even this treatment did not effect complete reaction, however, as some unreacted VIIIa was later detected.) Then a mixture of 32.7 mmoles of dimethyldodecylphosphine dichloride and 50 ml of benzene was added and the resulting mixture was stirred 16 hr under argon. A strong odor of dimethyldodecylphosphine was noted, which may have arisen by reduction of the phosphine dichloride by unreacted butyllithium. Evaporation of the solvent from the gummy reaction mixture gave a solid which was partially dissolved in CCl_4. The insoluble portion was removed by filtration and shown to be a mixture of lithium chloride and VIIIa by infrared analysis. The filtrate was evaporated to dryness (0.5 mm) to give a brown solid which could not be satisfactorily recrystallized. Hence it was chromatographed on 250 g of Grace silica gel, grade 923, using as eluents the same order of solvents and solvent mixtures used for XI. Pure methanol eluted a colorless oil which slowly crystallized. The solid was recrystallized from 1:1 benzene–hexane to yield 1.2 g (10%) of a white solid, mp 105–115°, which was shown to be XII by spectral analysis. Thin layer chromatography on silica gel showed it to be 90–95% pure; its hygroscopicity prevented a sample from being satisfactorily purified for microanalysis.

5. N-Trimethylsilylphosphinimines. A. N-Trimethylsilyldimethyldodecylphosphinimine from XIII.—A benzene solution of XIII was prepared as described in section 4 and then treated with 1.3 equiv of chlorotrimethylsilane (Matheson). After being stirred for 2 days, the solution contained N-trimethylsilyldimethyldodecylphosphinimine[11] as shown by gas chromatographic analysis at 220° on a 6-ft column packed with 10% Apiezon-L on Fluoropak. This identification was confirmed by infrared analysis of the trapped material corresponding to this peak. The yield (57%) was calculated by comparing the area under the peak with that of a standard solution of the N-silylphosphinimine in benzene.

B. N-Trimethylsilyltributylphosphinimine from XIV.—A benzene solution of XIV was treated with 1 equiv of chlorotrimethylsilane and analyzed by glpc in a manner analogous to that described above. The chromatogram showed a peak with retention time identical with that of N-trimethylsilyltributylphosphinimine.[29] The material corresponding to this peak was collected and its infrared spectrum was identical with that of an authentic sample of the N-silylphosphinimine. Comparison of the area under the peak with that of a standard solution allowed the yield (59%) to be calculated.

Registry No.—IVb, 13970-25-7; Vb, 13811-03-5; VIb, 13811-04-6; VIIb, 13811-05-7; VIIIb, 13970-26-8; IXb, 13811-06-8; X, 13811-07-9; XI, 13862-50-5; XII, 13811-08-0.

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[29] L. Birkofer and S. M. Kim, *Chem. Ber.*, **97**, 2100 (1964).