Anal. Calcd for $C_{33}H_{22}Cl_2O_2$: C, 75.85; H, 4.30; Cl, 13.46. Found: C, 75.88; H, 4.29; Cl, 13.53.

Methanolysis of Lactone 2. A solution of 1.65 g (0.01 mole) of lactone **2** and 0.5 ml of concentrated sulfuric acid in 100 ml of methanol was refluxed for 40 hr. The solution was concentrated to 25 ml, neutralized with sodium bicarbonate, and extracted with ethyl ether. The ether extract was decolorized, dried over magnesium sulfate, and evaporated to give about 2 ml of a light yellow oil. Vaccuum distillation afforded about 1 ml of methyl 5,5-dichloro-4-oxo-2-pentenoate (**8**), bp 100° (1.5 mm).

Anal. Calcd for $C_6H_6Cl_2O_3$: C, 36.54; H, 3.07; Cl, 36.05. Found: C, 36.45; H, 3.34; Cl, 36.18.

Bromination of Lactone 2. A solution of 0.825 g (0.005 mole) of lactone **2** and 0.275 ml (0.005 mole) of bromine in 30 ml of anhydrous carbon tetrachloride was stirred and refluxed for 3 days. The solvent was evaporated and the oily residue was sublimed to give 1.22 g (75%) of white crystals of the *trans*-2,3-dibromo-5,5-dichloro-4-hydroxy-4-pentenoic acid γ-lactone (**9**), mp 59°.

Anal. Calcd for $C_5H_2Br_2Cl_2O_2$: C, 18.48; H, 0.64; Br, 49.18; Cl, 21.88. Found: C, 18.67; H, 0.53; Br, 48.99; Cl, 21.53.

Acknowledgment. The authors are indebted to Dr. Willaim J. Pace and Dr. Melvin L. Farmer of the Union Carbide Corp., Charleston, W. Va., and to Mr. Robert Smith for recording the nmr spectra, to Dr. Robert G. Burrell of the Department of Microbiology, West Virginia University, for the biological testing, and to Mr. Ray Wilkins, undergraduate chemistry major, for some purifications. Partial support by the West Virginia University Cancer Research Committee and the American Cancer Society is greatly appreciated.

Mesomeric Phosphonium Dications

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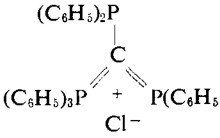
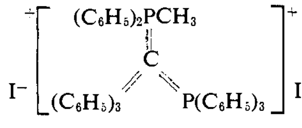
Contribution from the Monsanto Company Central Research Department, St. Louis, Missouri 63166. Received May 26, 1966

Abstract: Mesomeric phosphonium monocation salts, $(C_6H_5)_2PC[P(C_6H_5)_3]_2{}^+X^-$ (**1**), and dication salts, $\{R(C_6H_5)_2PC[P(C_6H_5)_3]_2\}^{2+}2X^-$ (**2**), in which three phosphorus atoms are bonded to a single carbon atom have been synthesized. An unusual possibility of delocalization of two positive charges over three pentavalent phosphorus centers exists in **2**. Support for such charge distribution was provided by nmr measurements and by absence of evidence of formation of triphosphonium salts when various derivatives of **2** were treated with strong acids. Reactions accomplished at the trivalent phosphorus atom of **1** include addition of active halogen compounds, complexing with heavy metal salts, oxidation, and thiolation. An unusual case of spin coupling of phosphorus and hydrogen through intervening carbon and phosphorus atoms was observed in nmr studies on a solution of **2** (R = H) in trifluoroacetic acid.

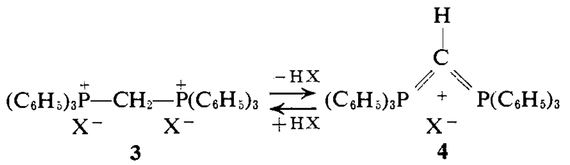
As part of an investigation of mesomeric phosphonium chemistry we have synthesized compounds in which three phosphorus atoms are bonded to a single carbon atom. The prototypes of these mesomeric compounds are the monocation salt **1a** and the dication salt **2a**. The monocation of **1a** is structurally related to the mesomeric cation of the known [(triphenylphosphoranylidene)methyl]triphenylphosphonium salts **4**[1-3] derived from diphosphonium salts **3**. The dication of **2a** has an unusual structure in which two positive charges can be delocalized over three pentavalent phosphorus centers.



1a



2a



3 **4**

The essential precursor for the synthesis of these mesomeric salts is hexaphenylcarbodiphosphorane **5** which is prepared by the dehydrobromination of **4** (X = Br).[1-3] Reaction of **5** with chlorodiphenylphosphine yielded **1a**,[4] which was converted to the diiodide **2a** by treatment with excess methyl iodide.[5] Other

$$\underset{\mathbf{5}}{(C_6H_5)_3P{=}C{=}P(C_6H_5)_3} + (C_6H_5)_2PCl \longrightarrow \mathbf{1a}$$

$$\mathbf{1a} + 2CH_3I \longrightarrow \mathbf{2a} + CH_3Cl$$

salts[6] such as **1b–e** (see Table I) and **2b–e** (see Table II) were obtained from **1a** and **2a**, respectively, by metathesis.

Evidence for structure **1** is provided by elemental analyses (Table I) and nmr spectra of several representative salts. Proton nmr spectra of **1a** contain two complex multiplets, centered at about −7.5 and −7.2 ppm in a 3:1 area ratio, characteristic of aryl protons.

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(1) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

(2) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962).

(3) J. S. Driscoll, D. W. Grisley, Jr., J. E. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964).

(4) D. Seyferth and K. A. Brändle, *J. Am. Chem. Soc.*, **83**, 2056 (1961), have reported that bromodiphenylphosphine reacts with triphenylphosphinemethylene to produce diphenylphosphinemethyltriphenylphosphonium bromide.

(5) We have found that phosphonium chlorides and bromides are readily converted by methyl iodide to the corresponding iodides.

(6) A convenient systematic way of naming these and related compounds is to regard them as derivatives of **4**, *i.e.*, as substituted [(triphenylphosphoranylidene)methyl]triphenylphosphonium salts, so that **1a** is [(diphenylphosphino)(triphenylphosphoranylidene)methyl]triphenylphosphonium chloride, and **2a** is (diphenylmethylphosphoranylidene)methylenebis(triphenylphosphonium iodide).

Table I. [(Diphenylphosphino)(triphenylphosphoranylidene)methyl]triphenylphosphonium Salts (**1**)

			C, %		H, %		P, %		B, %		X,[b] %	
Compound	Anion	Mp,[a] °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1a	Cl	251–254	77.72	77.12	5.32	5.37	12.27	12.34	...	...	4.68	4.54
1b	I	264–267	69.35	69.17	4.76	4.64	10.96	10.69	...	...	14.96	14.83
1c	PF_6	264–265	67.89	67.65	4.65	4.65	14.30	14.35	...	...	13.15	13.20
1d	BF_4	261–263	72.77	72.60	4.98	4.84	11.50	11.40	1.34	1.50	9.40	9.71
1e	$B(C_6H_5)_4$	252–254	84.22	84.04	5.81	5.98	8.93	9.04	1.04	1.21	...	...

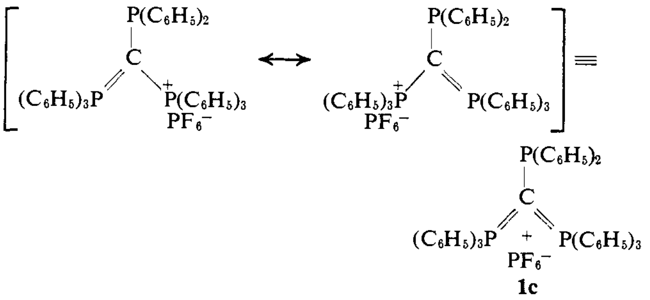
[a] Decomposition occurs at these temperatures. [b] X values are for the halogen present in the anion.

Table II. (Diphenylmethylphosphoranylidene)methylenebis(triphenylphosphonium) Salts (**2**)

			C, %		H, %		P, %		B, %		X,[b] %	
Compound	Anion	Mp,[a] °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
2a	I	293–295	60.62	60.46	4.37	4.40	9.33	9.19	...	...	25.62	25.55
2b	I_3	127–129	40.15	40.12	2.89	3.02	6.21	6.07	...	...	50.77	50.48
2c	PF_6	310–313	58.48	58.53	4.22	4.41	15.09	15.19	...	...	22.20	22.45
2d	BF_4	306–309	65.96	65.73	4.76	4.90	10.20	9.98	2.37	2.35	16.69	16.67
2e	$B(C_6H_5)_4$	228–230	85.65	85.43	6.08	6.18	6.77	6.72	1.57	1.84	...	...

[a] Decomposition occurs at these temperatures. [b] X values are for the halogen present in the anion.

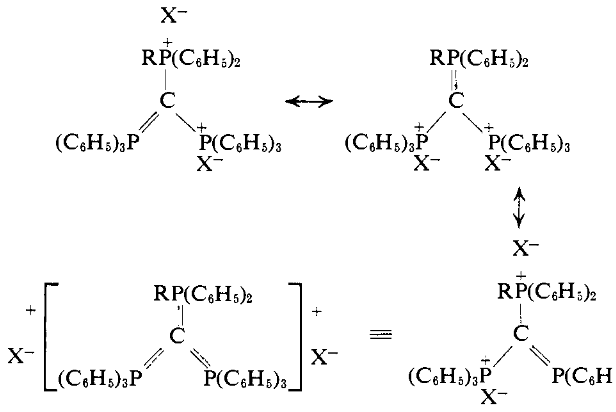
Phosphorus nmr spectra contain characteristic multiplets for spin coupling of two equivalent phosphorus atoms with an unlike phosphorus atom, *i.e.*, a doublet at −26.0 ppm representing the two equivalent phosphorus atoms and a 1:2:1 triplet at +1.5 ppm representing the single trivalent phosphorus atom. The area ratio of doublet to triplet is 2:1 and the coupling constant is about 75 cps as measured at both 24.3 and 40.5 Mc. These nmr results show that the cation **1** contains only two types of phosphorus atoms and must therefore be mesomeric. The fluorophosphate salt **1c**, for example, is better represented by the symmetrical structure shown than by classical structures in which each of its four phosphorus atoms has different covalent character.



1c

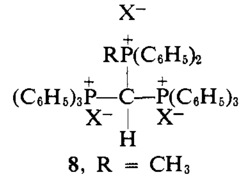
Infrared spectra of **1** are characterized by strong absorption bands of about equal intensity at 9.1, 10.1, and 11.4 μ, the latter two bands merging into a broad band in the region 10.4 to 10.8 μ on conversion of **1** to **2**.

For the dication salts **2** elemental analyses (Table II) and nmr spectra are consistent with the proposed structures. Phosphorus nmr for **2a** show two moderately broad peaks at −25.1 and −22.0 ppm in a 2:1 area ratio. Multiplets of spin coupling could not be resolved. Proton nmr spectra show two peak areas centered at −7.8 and −7.6 ppm corresponding to aryl protons and a doublet for the three methyl protons at about −2.8 ppm, with the three areas approximating the theoretical 30:10:3 ratio. The doublet was converted to a singlet by phosphorus decoupling. The benzyl homolog **6**, formed from **1a** by reaction with benzyl bromide, had phosphorus nmr peaks at −27.0 and −28.5 ppm in a 2:1 area ratio, again as expected for a mesomeric compound with two almost equivalent phosphorus environments. The nmr results therefore suggest that the dications are better represented by mesomeric structures in which two positive charges are delocalized over three pentavalent phosphorus centers than by classical diphosphonium structures.



2, R = CH_3
6, R = $CH_2C_6H_5$
7, R = H

Further evidence for mesomeric structures possessing maximum delocalization of charge lies in the stability of the dications in strongly acid solutions. In trifluoroacetic acid, nmr spectra of **2a** gave no indication that triphosphonium salts **8** were present. The dication could be dissolved in solutions containing hydriodic acid or fluoroboric acid and then recovered unchanged. When **1a** was dissolved in trifluoracetic acid, nmr spectra showed that a proton had been taken up readily to form the dication **7**, but there was no evidence that further protonation had occurred to give the triphosphonium salt **9**. The phosphorus nmr

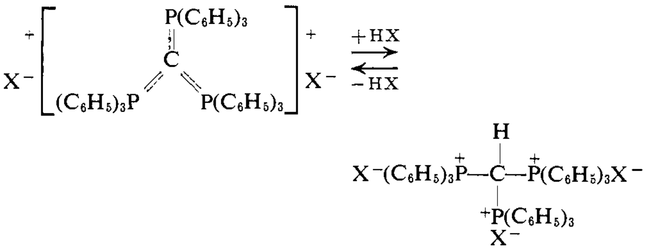


8, R = CH_3
9, R = H

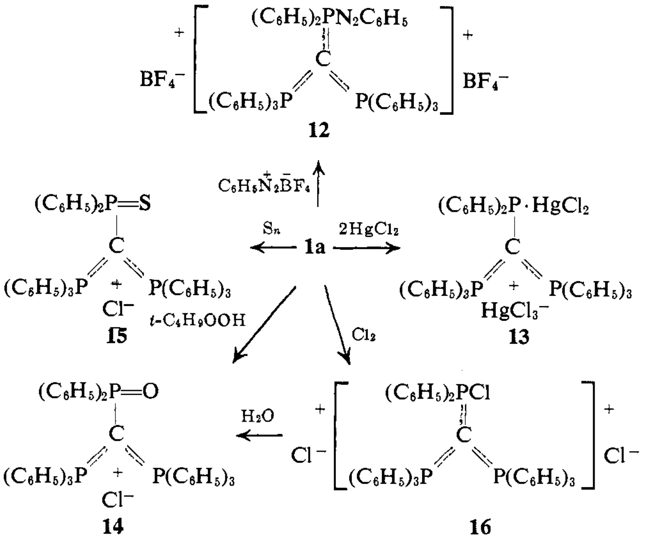
spectrum at 40.5 Mc showed a peak at -25.4 ppm for the two identical phosphorus atoms and a doublet at -8.6 ppm ($J_{PH} = 497$ cps) indicating spin coupling of the third phosphorus atom with the attached proton.[7] In addition to aryl proton multiplets, the proton nmr spectrum at 100 Mc contained a doublet centered at -8.4 ppm ($J_{HP} = 486$ cps), each leg of which was a triplet ($J_{HP'} = 4.3$ cps). Partial phosphorus decoupling converted each triplet to a singlet; the resulting doublet was converted to a singlet by complete phosphorus decoupling. The triplets appear to represent an unusual occurrence of spin coupling of phosphorus and hydrogen through intervening carbon and phosphorus atoms.

The inertness of mesomeric dications in strong acids contrasts with the behavior of mesomeric monocations **4**. Protonation of **4** to give diphosphonium salts **3** occurs readily as shown by equilibrium studies (pK_a = 4.5),[1] by isolation of diphosphonium salts in high yield (from hydrochloric acid),[8] and by nmr spectral evidence (in trifluoroacetic acid). The dication **2** apparently possesses considerably more resonance stabilization than the monocation **4**, as would be expected if **2** had the extensively delocalized structure shown. As a result of this stabilization it seems likely that triphosphonium salts—if they can exist at all—would be among the strongest of organic acids.

Further reactions with the tertiary phosphine **1a** were attempted in order to synthesize the symmetrical mesomeric dication **10** related to the hypothetical triphosphonium salt **11**. While alkyl halides and benzyl halides react readily with **1a** to give mesomeric dications, as already described, it was found that aryl halide reactions did not yield **10**. For example, iodobenzene and **1a** under various conditions gave complex mixtures in which the cleavage product **4** could be detected. Reaction of **1a** with diphenyliodonium chloride also yielded uncharacterized mixtures containing **4**. Addition of benzenediazonium fluoroborate[9] to **1a** led to the formation of a red salt, **12**, which decomposed at 220° to yield **1d** instead of **10**, presumably through elimination of nitrogen, boron trifluoride, and fluorobenzene. Other tertiary phosphine reactions carried out on **1a** included complex formation, as with mercuric chloride to give **13**; oxidation by *t*-butyl hydroperoxide to give the phosphine oxide **14**; reaction with elemental sulfur to give the phosphine sulfide **15**; and addition of chlorine to give the dichlorophosphine **16** which is readily hydrolyzed to **14**. Attempts to convert some of these compounds to **10** by applying known methods[10] of phosphonium salt synthesis have so far been unsuccessful. A possible explanation of the difficulty in obtaining **10** by the above methods is that the crowded phosphorus functional groups of the mesomeric precursors are sterically shielded from attack by the various bulky phenylating agents used.

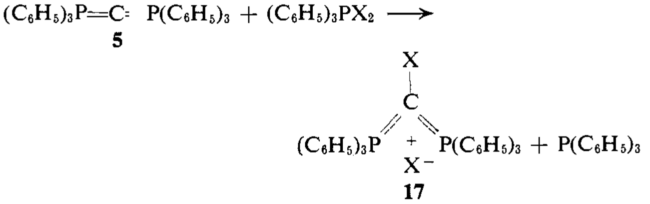


10 **11**



12 **15** **13** **14** **16**

Direct approaches not involving **1**, for example, addition of dihalotriphenylphosphines to **5** to form **10**, could perhaps be more effective. In such reactions,[11] however, it was found instead that nucleophilic attack of **5** on positive halogen occurred to yield triphenylphosphine and halogen-substituted mesomeric salts **17** (X = Cl, Br, and I). Another direct approach, displacement of halogen of trihalomethanes by excess triphenylphosphine, might be expected to yield **10** by spontaneous dehydrohalogenation of initially formed triphosphonium salts **11**. In past research on the reactions of triphenylphosphine with polyhalomethanes[12–15] however, no evidence of triphosphonium salt formation has been reported. In some cases major products obtained were diphosphonium salts **3** and mesomeric salts **4** which presumably resulted from nucleophilic attack of triphenylphosphine on the positive halogen centers of dihalomethyltriphenylphosphonium intermediates.[8,15,16] Since the analogous



5 **17**

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[7] The comparable phosphorus nmr spectrum of triphenylphosphine in trifluoroacetic acid showed a single broad peak centered at -5.4 ppm instead of a doublet. A possible explanation is that protons of the solvent exchange more slowly with 7 than with triphenylphosphine, as would be expected if 7 had a structure stabilized by electron delocalization.

[8] D. W. Grisley, Jr., J. C. Alm, and C. N. Matthews, *Tetrahedron*, 21, 5 (1965).

[9] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 295.

[10] Houben-Weyl, "Methoden der Organische Chemie," Band 12/1, "Organische Phosphorverbindungen," Part 1, Georg Thieme Verlag, Stuttgart, 1963, p 79.

[11] We are indebted to D. W. Grisley, Jr., and J. S. Driscoll for carrying out some reactions of this type with dichlorotriphenylphosphine and dibromotriphenylphosphine

[12] W. M. Dehn and R. B. Conner, *J. Am. Chem. Soc.*, 34, 1409 (1912).

[13] F. Ramirez and N. McKelvie, *ibid.*, 79, 5829 (1957).

[14] R. Rabinowitz and R. Marcus, *ibid.*, 84, 1312 (1962).

[15] F. Ramirez, N. Desai, and N. McKelvie, *ibid.*, 84, 1745 (1962).

[16] H. Hoffmann and H. J. Diehr, *Angew. Chem. Intern. Ed. Engl.*, 3, 737 (1964).

reactions of triethylphosphine with haloforms would similarly be expected to yield diphosphonium salts and related compounds, it is probable that the triphosphonium structures originally proposed[17] for the reaction products are incorrect.

Experimental Section

Melting points were obtained in a Thomas-Hoover Unimelt instrument and are corrected. Infrared spectra were determined in potassium bromide disks on a Beckman IR4 spectrophotometer. Proton nuclear magnetic resonance (nmr) spectra were obtained at 60.0 or 100.0 Mc on Varian A-60 or HR-100 spectrometers with tetramethylsilane as an internal standard. Phosphorus nmr spectra were determined at 24.3 or 40.5 Mc on Varian HR-60 or HR-100 instruments and are reported with respect to 85% H_3PO_4 contained in a capillary. The nmr measurements were generally made on saturated solutions. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

Hexaphenylcarbodiphosphorane (5).[1-3] A 1-l. flask equipped with a stirrer, thermometer, and condenser was flamed out under a stream of dry nitrogen, cooled in a drybox, and charged with 79.5 g (0.129 mole) of [(triphenylphosphoranylidene)methyl]triphenylphosphonium bromide (**4**, X = Br), 450 ml of dry diglyme, and 5.8 g (0.148 g-atom) of potassium metal. The flask was removed from the drybox and the mixture was stirred under nitrogen and warmed at 145–150° for 0.75 hr. The hot reaction mixture was then filtered (suction) in the drybox to remove KBr. The product crystallized as the filtrate was cooled to room temperature. Filtration and washing of the yellow solid with diglyme and ether and drying in a vacuum desiccator gave 51 g (74% yield) of hexaphenylcarbodiphosphorane (**5**), mp 198–201°. The P^{31} nmr spectrum showed a signal at +4.3 ppm in chlorobenzene (+4.6 ppm for another batch).

Anal. Calcd for $C_{37}H_{30}P_2$: C, 82.82; H, 5.64; P, 11.55. Found: C, 83.21; H, 5.70; P, 11.64.

[(Diphenylphosphino)(triphenylphosphoranylidene)methyl]triphenylphosphonium Chloride (1a). Hexaphenylcarbodiphosphorane (**5**), 21.4 g (0.04 mole), and 200 g of dry diglyme were stirred under nitrogen as 9.5 g (0.043 mole) of freshly distilled chlorodiphenylphosphine was added dropwise at 75–80° during 0.2 hr. A white solid began separating early in the addition, and the yellow color of **5** disappeared near the end of the addition. Stirring was continued at 70–75° for a further 0.25 hr. The reaction mixture was filtered (suction) under nitrogen while still warm and the product was washed with ether and dried at 60° (0.1 mm) to give 28.9 g (96% yield) of an off-white solid, **1a**, mp 251–254° dec.

Anal. Calcd for $C_{49}H_{40}ClP_3$: C, 77.72; H, 5.32; Cl^-, 4.68; P, 12.27. Found: C, 77.12; H, 5.37; Cl^-, 4.54; P, 12.34.

A portion of the solid was recrystallized from diglyme–acetonitrile to give colorless crystals containing occluded acetonitrile. The crystals were pulverized, and then freed of acetonitrile by warming at 100° (0.1 mm) for 16 hr to give a white powder, mp 253–256° dec. The P^{31} nmr spectrum of a methanol solution at 24.3 Mc had a doublet at −26.0 and a triplet at +1.5 ppm, J_{PP} = 75 cps, in a 2:1 area ratio. At 40.5 Mc the observed peaks were a doublet at −26.5 and a triplet at +1.4 ppm, J_{PP} = 76 cps, in a 2:1 ratio. The H^1 nmr spectrum of a saturated $CDCl_3$ solution showed two complex multiplets corresponding to aryl regions centered at approximately −7.5 and −7.2 ppm in a 3:1 area ratio.

Anal. Found: C, 77.62; H, 5.31; Cl^-, 4.57; P, 12.22.

No significant changes in the nmr and infrared spectra resulted from recrystallization of the initial product. Unrecrystallized material was used in the preparation of derivatives.

When **1a** was dissolved in trifluoroacetic acid, the characteristic P^{31} nmr doublet and triplet were replaced by three new peaks. At 24.3 Mc these were a singlet at −25.2 and a doublet at −8.3 ppm (J_{PH} = 502 cps) in approximately a 2:1 ratio; at 40.5 Mc, the peaks observed were a singlet at −25.4 and a doublet at −8.6 ppm (J_{PH} = 497 cps). Proton nmr measurements at 100 Mc in trifluoroacetic acid showed a complex multiplet centered at about −7.7 ppm corresponding to aryl protons and a doublet at −8.4 ppm (J_{HP} = 486 cps) approximating a 40:1 ratio. Each leg of the doublet was a triplet ($J_{HP'}$ = 4.3 cps). Partial phosphorus decoupling converted each triplet to a singlet, and the resulting doublet was converted to a singlet by complete phosphorus decoupling. Addition of ether to the trifluoroacetic acid solution caused a white solid to precipitate. The P^{31} nmr spectrum of this solid in methanol showed the doublet at −26.7 ppm and triplet at +2.4 ppm (J_{PP} = 76 cps) characteristic of **1**.

[(Diphenylphosphino)(triphenylphosphoranylidene)methyl]triphenylphosphonium Hexafluorophosphate (1c). A mixture of 2.7 g of **1a**, 1.8 g of potassium hexafluorophosphate (KPF_6), and 30 ml of methanol was stirred and warmed to reflux. The reactants dissolved, and then a white solid separated after a few minutes at reflux. The reaction mixture was filtered hot, and the salt was washed with distilled water, methanol, and ether to give 2.5 g of white powder. This was recrystallized from ethanol–acetonitrile, washed with methanol and ether, and dried for 8 hr at 120° (0.1 mm) to give 1.2 g (38%) of white solid, **1c**, mp 264–265° (an additional 1.1 g, mp 263.5–265°, crystallized from the filtrate). P^{31} nmr spectra showed a doublet at −26.5 and a triplet at +1.4 ppm (J_{PP} = 70 cps) and a heptet at +144.2 ppm (J_{PF} = 712 cps); H^1 nmr peaks for aryl regions were centered at about −7.5 and −7.2 ppm in a 3:1 area ratio.

Anal. Calcd for $C_{49}H_{40}F_6P_4$: C, 67.89; H, 4.65; F, 13.15; P, 14.30. Found: C, 67.65; H, 4.65; F, 13.20; P, 14.35.

Similar metathesis reactions were carried out to obtain **1b**, **1d**, **1e**, and other salts possessing the same mesomeric cation.

(Diphenylmethylphosphoranylidene)methylenebis(triphenylphosphonium iodide) (2a). A solution of 15.1 g (0.02 mole) of **1a** in 65 g of ethanol was stirred as 17 g (0.12 mole) of methyl iodide[5] was added. The flask was stoppered and stirring was continued at room temperature overnight. About 40% of the solvent was then distilled, the remainder was allowed to cool to room temperature with stirring, and the precipitate was separated by filtration, washed with ethanol and with ether, and dried for 8 hr at 100° (0.1 mm) to give 18.5 g (93.5% yield) of a white solid, **2a**, mp 293–294.5° dec.

Anal. Calcd for $C_{50}H_{43}I_2P_3$: C, 60.62; H, 4.37; I^-, 25.62; P, 9.38. Found: C, 60.27; H, 4.39; I^-, 25.43; P, 9.33.

In another run the product was recrystallized three times from ethanol to give a 90% yield of **2a**, mp 293–295° dec.

Anal. Found: C, 60.46; H, 4.40; I^-, 25.55; P, 9.19.

The P^{31} nmr spectrum at 24.3 Mc in methanol had signals at −25.6 and −22.6 ppm in a 2:1 area ratio; at 40.5 Mc in pyridine the signals were at −25.1 and −22.0 ppm; and in trifluoroacetic acid peaks were observed at −25.6 and −22.1 ppm in a 2:1 ratio. Multiplets from phosphorus–phosphorus and phosphorus–hydrogen coupling could not be resolved. Proton nmr measurements at 60 Mc in CH_3OD showed peaks for aryl hydrogen centered at about −7.8 and at −7.6 ppm and a doublet at −2.76 ppm (J_{HP} = 12 cps) in approximately a 30:10:3 ratio; in trifluoroacetic acid the aryl multiplets were centered at −7.8 and −7.6 ppm and the doublet at −2.47 ppm (J_{HP} = 12 cps); in pyridine the doublet was at −3.13 ppm (J_{HP} = 12 cps). In pyridine at 100 Mc the doublet was converted to a singlet by phosphorus decoupling. The H^1 and P^{31} nmr measurements in trifluoroacetic acid gave no indication of the addition of a proton to the central carbon atom of **2a**.

(Diphenylmethylphosphoranylidene)methylenebis(triphenylphosphonium hexafluorophosphate) (2c). A mixture of 2.0 g (0.002 mole) of **2a** and 1.5 g (0.008 mole) of KPF_6 in 30 ml of CH_3OH was stirred magnetically and warmed at reflux for 0.5 hr. The solid reactants first dissolved and then a solid again formed. The reaction mixture was filtered hot and the solid was washed with methanol and with ether to give 1.7 g of a white solid, mp 300–304° dec. This material and a further 0.5 g of KPF_6 were dissolved in 6 g of dimethylformamide and stirred as 30 ml of methanol was added. The mixture was warmed to reflux, placed in a refrigerator for 5 hr to induce crystallization, and filtered. The solid was washed with methanol and with ether, and dried for 10 hr at 120° (0.1 mm) to give 0.8 g of white crystals, **2c**, mp 310–313°; H^1 nmr spectra showed a complex multiplet centered at about −7.5 (aryl region) and a doublet at −2.30 ppm (J_{HP} = 12 cps) in approximately a 40:3 ratio; the P^{31} nmr spectrum showed singlets at −25.8 and −22.7 ppm in a 2:1 ratio and a heptet at +143.9 ppm (J_{PF} = 708 cps).

Anal. Calcd for $C_{50}H_{43}F_{12}P_5$: C, 58.48; H, 4.22; F, 22.20; P, 15.09. Found: C, 58.53; H, 4.41; F, 22.45; P, 15.19.

Similar metathesis reactions were carried out to obtain **2d**, **2e**, and other salts possessing the same mesomeric dication; **2b** was obtained by adding iodine to **2a** in methanol.

(Benzyldiphenylphosphoranylidene)methylenebis(triphenylphosphonium iodide) (6, X = I). A mixture of 8.0 g of **1a** and 30 g of benzyl bromide was stirred magnetically and warmed to 145°,

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[17] A. W. Hoffman, *Proc. Roy. Soc.* (London), **10**, 189 (1860); **11**, 290 (1862). The only published claim to the synthesis of triphosphonium salts appears to be in these pioneering papers on phosphonium chemistry.

giving a clear solution from which a solid began separating after a few minutes. About 30 ml of dry diglyme was added to facilitate stirring, and warming was continued at 140–145° for a further 0.25 hr. The reaction mixture was filtered hot, and the solid was washed with diglyme and ether to give a cream-colored powder which was dissolved in 15 ml of ethanol. Methyl iodide (15 g) was then added in order to replace bromide and chloride ions with iodide ions.[5] When the solution was distilled to a pot temperature of about 70°, a white solid separated. Another 10 g of methyl iodide was added at room temperature, and the stoppered reaction flask was allowed to stand overnight. The excess methyl iodide and about one-third of the ethanol were removed by distillation at atmospheric pressure, the mixture was filtered hot, and the solid was washed with ethanol and then recrystallized from methanol and dried for 16 hr at 120° (0.1 mm) to give 2.7 g of off-white solid, **6** (X = I), mp 230–232° (5.6 g of additional product, mp 229–232°, was isolated in three crops from the filtrate). The P^{31} nmr spectrum at 40.5 Mc showed broad signals at -27.0 and -28.5 ppm in a 2:1 area ratio; H^1 nmr aryl peaks were observed at about -7.8, -7.6, -7.0, and -6.3 ppm together with a doublet at -4.2 ppm (J_{HP} = 13 cps) in approximately a 30:10:3:2:2 area ratio.

Anal. Calcd for $C_{56}H_{47}I_2P_3$: C, 63.05; H, 4.44; I^-, 23.80; P, 8.71; Br, 0.00. Found: C, 62.67; H, 4.53; I^-, 23.81; P, 8.57; Br, 0.05.

(Benzyldiphenylphosphoranylidene)methylenebis(triphenylphosphonium tetraphenylborate) (6, X = $B(C_6H_5)_4$). A solution of 1.1 g (0.001 mole) of **6** (X = I) in methanol was added dropwise to a stirred solution of 1.0 g (0.003 mole) of sodium tetraphenylboron in warm methanol, refluxed for 0.25 hr, and filtered while still hot. The solid product was washed with methanol and then dissolved in dimethylformamide containing a further 0.5 g of sodium tetraphenylboron. Methanol was added to precipitate the product which was separated by filtration, washed with methanol and ether, and dried at 120° (0.05 mm) for 16 hr to give 1.3 g (88%) of a white solid, **6** (X = $B(C_6H_5)_4$), mp 206–211° dec.

Anal. Calcd for $C_{104}H_{87}B_2P_3$: C, 85.94; H, 6.03; B, 1.49; I^-, 0.00; P, 6.39. Found: C, 86.19; H, 5.90; B, 1.83; I^-, 0.00; P, 6.42.

[Diphenyl(phenyldiazo)phosphoranylidene]methylenebis(triphenylphosphonium tetrafluoroborate) (12, X = BF_4). A solution of 7.6 g (0.01 mole) of **1a** in 30 g of methanol was stirred magnetically as 4.2 g (0.022 mole) of freshly purified benzenediazonium fluoroborate[9] was added in small portions at room temperature. The color changed rapidly to red, and a solid separated. The reaction mixture was warmed at 40–50° for 1.5 hr and filtered while warm; the solid product was washed with warm methanol and dried to give 8.6 g (86%) of red powder. A portion was recrystallized from ethanol–acetonitrile to give red crystals, **12** (X = BF_4), which changed from red to white at 219–220°, melting at 255–258°. The P^{31} nmr spectrum showed signals at -38.9 and -24.1 ppm in about a 1:2 ratio.

Anal. Calcd for $C_{55}H_{45}F_8N_2P_3$: B, 2.16; Cl, 0.00; F, 15.20; N, 2.80; P, 9.29. Found: B, 2.32; Cl, 0.12; F, 15.01; N, 2.88; P, 9.35.

A 2.0-g portion of **12** (X = BF_4) was stirred in 18 g of paraffin oil and warmed to 222°. The color changed from red to light buff at 215–222°. The reaction mixture was filtered at about 175° and the solid product was washed with diglyme and ether to give 1.2 g, mp 255–260°. This material was extracted with hot methanol and dried at reduced pressure to give a white solid, **1d**, mp 257–262° dec, having infrared and P^{31} nmr spectra essentially identical with those of the product obtained by a metathesis reaction of **1a** with $NaBF_4$ or HBF_4 (see Table I).

Anal. Calcd for $C_{43}H_{40}BF_4P_3$: C, 72.77; H, 4.98; B, 1.34; F, 9.40; P, 11.50. Found: C, 72.46; H, 4.95; B, 1.58; F, 9.24; P, 11.73.

Mercuric Chloride Complex of 1a (13). A solution of 3.8 g (0.005 mole) of **1a** in 10 ml of methanol was added dropwise to a stirred solution of 4.1 g (0.015 mole) of $HgCl_2$ in 40 ml of methanol at room temperature. A white precipitate formed rapidly. The reaction mixture was warmed at 40–50° for 1 hr and filtered and the solid washed with methanol. The product was recrystallized from dimethylformamide containing an additional 1.4 g of $HgCl_2$, washed thoroughly with methanol and then with ether, and dried at 120° (0.05 mm) to give 6.1 g (theory, 6.5 g for addition of 2 equiv of $HgCl_2$). The white solid, **13**, softened at about 225° and melted at 230–234°. The infrared spectrum had a new absorption band at 11.05 μ in place of the 11.4 μ band of **1a**.

Anal. Calcd for $C_{49}H_{40}Cl_5Hg_2P_3$: C, 45.27; H, 3.10; Cl, 13.63; P, 7.16. Found: C, 44.50; H, 2.87; Cl, 13.63; P, 7.03.

In another experiment, a solution of 0.5 g (0.002 mole) of $HgCl_2$ in 5 ml of methanol was added to a stirred solution of 2.3 g (0.003 mole) of **1a** in 20 ml of methanol. The reaction mixture was refluxed for 0.25 hr, filtered hot, washed thoroughly with methanol and with ether, and dried for 20 hr at 120° (0.05 mm) to give 1.4 g of white solid (68% of the theoretical yield based on addition of 1 equiv of $HgCl_2$), mp 149–152° (cloudy melt). The infrared spectrum contained an absorption band at 11.05 μ and a band at 11.4 μ in about one-third the intensity of the similar band in **1a**. Even with a deficiency of $HgCl_2$, some reaction apparently occurred at the chloride ion of **1a** as well as at the trivalent phosphorous atom.

[(Diphenylphosphinyl)(triphenylphosphoranylidene)methyl]triphenylphosphonium Chloride (14). Method 1. A solution of 7.6 g (0.01 mole) of **1a** in 20 g of ethanol was stirred magnetically as 1.8 g (0.02 mole) of *t*-butyl hydroperoxide was added dropwise. Heat of reaction increased the temperature to 50°. Stirring was continued for 2 hr as the reaction mixture cooled. Ether (100 ml) was stirred in to precipitate a white solid which was separated by filtration, washed with ether, and redissolved in 30 ml of ethanol. Dry diglyme (30 ml) was added and the solvent was then distilled until the ethanol and about 20% of the diglyme were removed. The remainder was stirred while cooling to room temperature. The precipitate was separated by filtration, washed with ether, and dried for 20 hr at 100° (0.1 mm) to give 7.4 g (96% yield) of white solid, **14**, mp 269–270° dec, with a strong infrared absorption at 8.5 μ (P=O). P^{31} nmr signals at -23.2 and -26.9 ppm were in a 2:1 ratio.

Anal. Calcd for $C_{49}H_{40}ClOP_3$: C, 76.10; H, 5.21; Cl^-, 4.58; P, 12.02. Found: C, 76.12; H, 5.39; Cl^-, 4.58; P, 11.93.

Method 2. A solution of 7.6 g (0.01 mole) of **1a** in 65 g of methylene chloride was stirred under N_2 as anhydrous chlorine gas was added under the surface at room temperature until the color of chlorine persisted. The methylene chloride and excess chlorine were removed at reduced pressure, the residue was redissolved in methylene chloride, and ether was added slowly to precipitate a light-colored solid which after filtration, washing with ether and drying at reduced pressure weighed 9.7 g and melted at about 225–270°. The P^{31} nmr spectrum had signals at -67.9 and -25.9 ppm in about a 1:2 ratio. A 2.4-g portion of the solid, presumed to be **16**, was dissolved in 10 g of methanol with stirring, and 0.5 g of distilled water was added. After standing for 20 hr at room temperature, ether was added to precipitate a product which was separated by filtration, washed with ether, and dried at 100° (0.1 mm) to give 1.8 g of white solid, **14**, mp 259–262° dec. A portion was dissolved in warm ethanol, diglyme was added, about half of the total solvent was distilled, the remainder was cooled and filtered, and the solid was washed with diglyme and with ether and dried for 6 hr at 100° (0.1 mm) to give a white solid, mp 262–264° dec. The infrared spectrum and H^1 and P^{31} nmr spectra were essentially identical with those of the product prepared by method 1.

[(Diphenylphosphinothioyl)(triphenylphosphoranylidene)methyl]triphenylphosphonium Chloride (15, X = Cl). A mixture of 3.0 g (0.004 mole) of **1a** and 0.2 g (0.006 mole) of sulfur in dimethylacetamide was stirred and warmed. Most of the solid reactants dissolved after moderate warming, when a light tan solid rapidly formed. Warming was continued at 70–80° for 0.5 hr. After cooling to room temperature, the reaction mixture was filtered, and the solid was washed with dimethylacetamide and ether to give 2.8 g of white powder, presumably **15** (X = Cl). This was recrystallized twice from ethanol and dried at 100° (0.1 mm) for 20 hr to give 1.5 g of a white solid, mp 308.5–310° (another 1.3 g, mp 304–306°, separated from the filtrate). The P^{31} nmr spectrum in $CDCl_3$ contained peaks at -24.7 and -44.0 ppm in approximately a 2:1 area ratio. The H^1 nmr spectrum contained two aryl proton regions centered at -7.4 and -7.0 ppm, a singlet at -4.32 ppm, a quartet at -3.80 ppm (J_{HH} = 7 cps), and a triplet at -1.28 ppm (J_{HH} = 7 cps), the areas approximating the theoretical ratio for a 1:1 complex of ethanol with **15** (X = Cl). The infrared spectrum contained a medium band centered at 15.6 μ (P=S).

Anal. Calcd for $C_{51}H_{46}ClP_3SO$: Cl^-, 4.24; P, 11.13; S, 3.84. Found: Cl^-, 4.52; P, 10.81; S, 3.75.

[Iodo(triphenylphosphoranylidene)methyl]triphenylphosphonium Iodide, 17 (X = I). A solution of 3.3 g (0.012 mole) of recrystallized triphenylphosphine in 60 g of chlorobenzene was stirred at 50° as 2.5 g (0.01 mole) of iodine was added in portions. After a few minutes at 40–50° the iodine color disappeared and an orange solid, diiodotriphenylphosphine, separated. Stirring was continued as 5.4 g (0.01 mole) of **5** was added in portions. The orange color of the reaction mixture changed to yellow during this addition. The mixture was warmed at reflux for 1 hr and filtered hot; the solid product was washed with chlorobenzene and with ether and dried at 90° (0.1 mm) to give 7.4 g (94% yield) of yellow powder, **17** (X = I), mp 300–304° dec.

Anal. Calcd for $C_{37}H_{30}I_2P_2$: C, 56.22; H, 3.83; I, 32.11; P, 7.84. Found: C, 56.57; H, 4.16; I, 31.77; P, 7.65.

Evaporation of the filtrate to dryness gave 3.3 g of slightly yellow triphenylphosphine, mp 78–80°, having a P^{31} nmr signal at +6.3 ppm (an authentic sample of triphenylphosphine melted at 80–81° and had a P^{31} nmr signal at +6.0 ppm).

Compound **17** (X = I) was also prepared by addition of I_2 to a solution of **5** in chlorobenzene. Working-up of the product gave a 99% yield of yellow solid, mp 302–304°, having an infrared spectrum essentially identical with that obtained for the product prepared from diiodotriphenylphosphine and **5**.

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Solvation of Anilinium Salts

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Abstract: Nuclear magnetic resonance spectra have been obtained for several anilinium salts in a variety of solvents. It has been found that the charge on nitrogen in quaternary anilinium salts reduces the electron densities around the rings, the effect decreasing with distance, and it is concluded that pure inductive effects decrease with distance. For primary anilinium salts in polar media, the spectra are nearly independent of the anion and the NH_3^+ substituent has an influence on the ring carbon densities comparable to that of hydrogen. In nonpolar media the nmr spectra of primary anilinium salts vary with the nature of the accompanying anion, and NH_3^+ has a small deshielding effect on the ring hydrogens. The addition of exactly 4 equiv of methanol to a $CDCl_3$ solution of *p-n*-butylanilinium salt changes the nmr spectrum to that observed in pure methanol. Salts of secondary and tertiary anilines behave in a manner intermediate between the primary and quaternary salts described above. The effects which most satisfactorily account for these results are: (1) hydrogen bonding of solvent molecules to ammonium groups; and (2) in nonpolar media, formation of intimate ion pairs in which the *centers of charge are juxtaposed.* Investigation of the nmr spectra of model systems for intimate ion pairs such as aniline oxides and BF_3 adducts of anilines reveals that substituent dipoles which are not in conjugation with aromatic rings exert only a small effect on the ring electron densities.

The chemical shift of hydrogen has been ascribed to a sum of terms each arising from a different effect: electron currents on atoms,[1,2] in bonds,[3-8] and around rings.[1,2,4] Solvent effects in chemical shifts have been treated by various workers in terms of anisotropic shielding[9] by solvents, dispersion forces,[10] and electric fields.[11]

The idea that charge influences chemical shift originally came from electronegativity correlations by Dailey and Schoolery[12] and by Narasimhan and Rogers.[13] It was suggested on the basis of ring hydrogen shifts observed in cyclic aromatic species that in systems which have the same ring current and a common solvent for all substances studied, the differences in chemical shifts observed for the ring protons are probably chiefly caused by the charge distribution around the ring.[14] The shifts due to charge among the ring hydrogens are given by eq 1, where z is the charge on

$$\delta(H_i) - \delta(H_{C_6H_6}) = 10z(C_i) \qquad (1)$$

carbon i and $\delta(H_i)$ and $\delta(H_{C_6H_6})$ are shifts of hydrogen on carbon i and in benzene, respectively, both in the same medium. This idea was tested by several workers,[15-17] and the general conclusion is that although π-electron densities dominate the chemical shifts, other effects contribute also and care should be exercised to take account of them. Relationships similar to (1) for aromatic ^{13}C[18] and ^{19}F[19] shifts have also been reported.

It was of interest to measure charge distributions with the nmr method in compounds whose ring carbon

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