thioformate esters were prepared by reaction of formyl fluoride with the appropriate mercaptan in ether solution at 0°.[22] Fluorosulfonic acid and antimony pentafluoride were distilled prior to their use.

Nmr Spectra.—Varian Associates Model A-56/60A and HA 100 nmr spectrometers were used for all spectra. Chemical shifts are reported in parts per million (δ) from external (capillary) tetramethylsilane.

Preparation of Solutions and Kinetic Measurements.—The procedure used for the preparation of solutions of the protonated thioacids and thioesters was identical with that described previously.[14] The same procedure as was used in studies of the cleavage of protonated carboxylic acid esters[14] was used in the present work to determine rate constants for the cleavage reactions studied.

Registry No.—Fluorosulfonic acid, 7789-21-1; antimony pentafluoride, 7783-70-2.

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

[22] G. A. Olah and S. J. Kuhn, *ibid.*, **82**, 2380 (1960).

Organophosphorus Compounds. XI.[1a] ^{1}H and ^{31}P Nuclear Magnetic Resonance Study of the Protonation of Phosphines

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Received October 16, 1968

Symmetrical trialkyl (triaryl) phosphines, as well as diphenylphosphine and phosphine itself were protonated in fluorosulfuric acid. ^{1}H and ^{31}P nmr spectra of the phosphines and the corresponding phosphonium ions were studied. The one-bond coupling constant, J_{PH}, is inversely related to the bulkiness of the alkyl substituents. J_{PH} and the three-bond coupling constant, J_{HPCH}, are directly related. An empirical correlation of the phosphorus chemical shifts of the protonated phosphines with substituent constants was found.

A long-recognized characteristic of phosphines is their basicity, analogous to the basicity of amines. Although many phosphines have been studied by nuclear magnetic resonance (nmr) spectroscopy,[2] only a few protonated phosphines (which are phosphonium ions containing one or more hydrogen atoms attached directly to phosphorus) have been similarly examined. The trimethylphosphonium ion has been investigated thoroughly.[3] A pmr study of other methylphosphonium ions and the triethylphosphonium ion has been published.[3d] The unsubstituted phosphonium ion (PH_4^+) has only recently been observed spectrally.[4] Phosphorus chemical shifts have also been reported for the tributylphosphonium ion[5a] and the triphenylphosphonium ion.[5b]

We undertook a systematic nmr study of a series of alkyl- (aryl-) phosphines and the protonation of these phosphines in strong acid solution. Eight symmetrically trisubstituted alkyl- (aryl-) phosphines, diphenylphosphine, and phosphine itself (PH_3) were used in our studies. We found that neat fluorosulfuric acid served well both as a proton donor to the phosphines and as a solvent for the phosphonium ions which were formed. ^{1}H and ^{31}P nmr spectra of the phosphines and their corresponding phosphonium ions in excess fluorosulfuric acid were obtained. We were particularly interested in the effect of protonation on the phosphorus chemical shifts, and in the nmr spectral parameters of the proton which became bonded to the phosphorus atom. We also wanted to investigate the possible empirical correlations of phosphorus shifts in phosphonium ions with substituent constants.

Results

The phosphines and phosphonium ions which were studied, their phosphorus chemical shifts, and nmr spectral parameters of the proton(s) bonded directly to phosphorus are listed in Table I. Except where otherwise noted, the phosphines were examined as neat liquids. Each phosphine (except PH_3), when mixed with a fivefold molar excess of fluorosulfuric acid, yielded a stable solution of the corresponding phosphonium ion. A concentration of 1 mol of PH_3 in 31.5 mol of fluorosulfuric acid was sufficient for obtaining nmr spectra. The excess fluorosulfuric acid appeared in each proton spectrum as a sharp singlet at δ 11.1 to 12.6 (parts per million (ppm) downfield from external tetramethylsilane). The proton(s) attached to phosphorus appeared as widely separated doublets; each component had additional fine structure in those cases where three-bond coupling with other protons was possible. In the 60-MHz proton spectra of the trialkylphosphonium ions, the upfield component of the doublet due to the phosphonium proton was always hidden under peaks due to the alkyl protons. Taking spectra at 100 MHz usually separated this upfield component from the interfering peaks. In the two cases (triisopropylphosphonium ion and tricyclohexylphosphonium ion) where the upfield component remained hidden, the change in position of the downfield component upon switching from 60 to 100 MHz permitted calculation of the proton shift of the phosphonium proton and the one-bond coupling constant, J_{PH}. The trisubstituted phosphines all showed a change in the 24.3 MHz phosphorus spectra from a single broad peak to two widely separated components

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[1] (a) Part X: S. J. Kuhn and G. A. Olah, *Can. J. Chem.*, **40**, 1951 (1962); (b) National Institutes of Health Predoctoral Research Fellow, 1968.

[2] Recent summaries of nmr spectra of phosphorus compounds are by (a) G. Mavel in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. I, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Long Island City, N. Y., 1966, Chapter 4; and by (b) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance," John Wiley & Sons, Inc., New York, N. Y., 1967.

[3] (a) B. Silver and Z. Luz, *J. Amer. Chem. Soc.*, **83**, 786 (1961); (b) P. Haake, W. B. Miller, and D. A. Tyssee, *ibid.*, **86**, 3577 (1964); (c) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964); (d) H. Dreeskamp, H. Elser, and C. Schumann, *Ber. Bunsenges. Phys. Chem.*, **70**, 751 (1966); (e) K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

[4] G. M. Sheldrick, *Trans. Faraday Soc.*, **63**, 1077 (1967).

[5] (a) Reference 2b, p 197; (b) J. E. Lancaster in ref 2b, p 381.

TABLE I

NMR SPECTRAL PARAMETERS OF PHOSPHINES AND PROTONATED PHOSPHINES

No.	Phosphine	Phosphorus shift of phosphine, ppm rel to 85% H_3PO_4	Phosphorus shift of protonated phosphine, ppm	Proton shift of proton(s) bonded to phosphorus, δ	J_{PH}, Hz	J_{HPCH}, Hz
1	PH_3	+238[a]	+101.0	2.28,[b] 6.20[c]	188,[b] 548[c]	
2	$P(CH_3)_3$	+62.2	+3.2	6.36	497	5.6
3	$P(C_2H_5)_3$	+19.2	−22.5	5.97	471	5.3
4	$P(i\text{-}C_3H_7)_3$	−19.3	−44.4	5.58	448	4.2
5	$P(t\text{-}C_4H_9)_3$	−61.9	−58.3	5.46	436	
6	$P(n\text{-}C_4H_9)_3$	+32.6	−13.7	6.01	470	5.1
7	$P(n\text{-}C_8H_{17})_3$	+32.5	−13.0	6.04	465	5.0
8	$P(c\text{-}C_6H_{11})_3$	−11.3[d]	−32.7	5.48	445	3.6
9	$P(C_6H_5)_3$	+5.4[e]	−6.8	8.48	510	
10	$HP(C_6H_5)_2$	+40.7	+21.2	5.14,[f] 7.88[g]	216,[f] 519[g]	

[a] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, **78**, 5715 (1956). [b] PH_3 in CCl_4. [c] PH_4^+. [d] In $CHCl_3$. [e] In CCl_4. [f] $(C_6H_5)_2PH$. [g] $(C_6H_5)_2PH_2^+$.

upon protonation. Diphenylphosphine showed the expected change from a doublet to a more widely spaced 1:2:1 triplet upon protonation. The phosphorus spectrum of PH_4^+ was the anticipated 1:4:6:4:1 quintet. Since the proton spectra exhibited stronger and better resolved peaks than the phosphorus spectra, the values given for J_{PH} are taken from the proton spectra. The separation(s) of peaks in the phosphorus spectra of the phosphonium ions was in good agreement with these values of J_{PH}.

Discussion

The magnitude of the one-bond coupling constant, J_{PH}, has been related to the amount of s character in the phosphorus orbital used for bonding to hydrogen.[6] J_{PH} for the phosphonium ion, PH_4^+, is found to be 548 Hz. If replacement of hydrogen by an alkyl (aryl) group results in increased s character in the corresponding phosphorus orbital, this increase would be expected to be at the expense of the s character in the phosphorus bonds to the remaining hydrogen atoms. The values of J_{PH} in the phosphonium ions investigated are indicative of less than 25% s character in the phosphorus bond(s) to hydrogen. Furthermore, an inverse relationship between J_{PH} and the bulkiness of the alkyl substituents is apparent. An increase in the bulkiness of the substituents in the trialkylphosphonium ions would be expected to result in increased mutual repulsions between the substituents. These increased repulsions would be expected to result in larger C–P–C bond angles and increased s character in the phosphorus bonds to the alkyl groups (noting that 109.5° bond angles are associated with sp^3-hybridized bond orbitals and 120° bond angles are associated with sp^2-hybridized bond orbitals). Again, there should be a corresponding decrease in the s character in the phosphorus orbital to the hydrogen atom, accompanied by a decrease in J_{PH}. A direct relationship between J_{PH} and the three-bond coupling constant, J_{HPCH}, is also present.

The possible correlation of phosphorus chemical shifts with additive group contributions has been a subject of interest for several years. Recently, it has been discovered that the phosphorus shifts of many organophosphorus compounds in several classes can be predicted quite accurately by simple linear equations. These equations utilize numerical constants which have been assigned to a number of substituents. The constants, known as σ^P constants, which have been derived for the substituents involved in the phosphonium ions that we have prepared, are listed in Table II. These σ^P constants, which were derived from tertiary phosphines,[7] have general applicability in equations which have been formulated for primary phosphines,[8] secondary phosphines,[9] and quaternary phosphonium ions.[10] We find that such an equation can also be derived for the protonated trialkylphosphines that we have prepared.

TABLE II

SUBSTITUENT CONSTANTS FOR PREDICTING PHOSPHORUS CHEMICAL SHIFTS[a]

Substituent	σ^P
CH_3	0
$n\text{-}C_nH_{2n+1}$ $(n \geq 3)$	10
C_2H_5	14
C_6H_5	18
$c\text{-}C_6H_{11}$	23
$i\text{-}C_3H_7$	27
$t\text{-}C_4H_9$	44

[a] Reference 7.

In Figure 1, the experimental phosphorus shifts of the starting tertiary phosphines and the corresponding phosphonium ions are plotted *vs.* the sums of the constants of the three substituents. The upper line is the one given by the Grim and McFarlane[9] equation for tertiary phosphines (eq 1). The lower line is the

$$\delta_{^{31}P}\ (\text{ppm from }85\%\ H_3PO_4) = 62 - \sum_{n=1}^{3} \sigma_n{}^P \qquad (1)$$

best least-squares fit to the six phosphonium ion chemical shifts which lie nearest to it. Equation 2 describes this line. We expect that it can be used to

$$\delta_{^{31}P} = 3.2 - 0.56 \sum_{n=1}^{3} \sigma_n{}^P \qquad (2)$$

predict the shifts of other tertiary phosphonium ions.

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(6) For a discussion of the possibility of a quantitative relationship, see S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

(7) S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, **32**, 781 (1967).

(8) L. Maier, *Helv. Chim. Acta*, **49**, 1718 (1966).

(9) S. O. Grim and W. McFarlane, *Nature*, **208**, 995 (1965).

(10) (a) S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, **70**, 581 (1966); (b) E. Fluck and J. Lorenz, *Z. Naturforsch.*, **22b**, 1095 (1967).

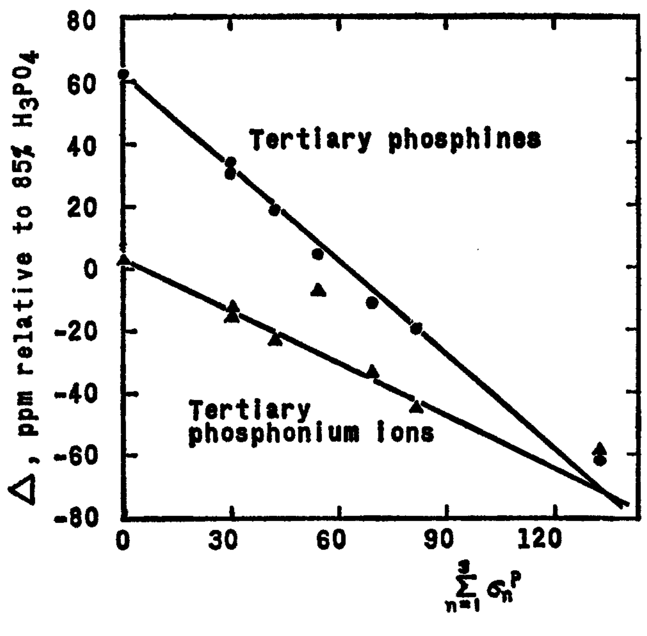

Figure 1.—Experimental phosphorus chemical shifts as functions of substituent constants.

The standard deviation of the six points used in this derivation is 1.7 ppm.

There are three experimental phosphorus shifts in Figure 1 which deviate significantly from predicted values. The phosphorus shift of the triphenylphosphonium ion

$$\left(\sum_{n=1}^{3} \sigma_n{}^{P} = 54\right)$$

is considerably higher than expected. Similar deviations of phenyl-substituted quaternary phosphonium ions were noticed by Grim, *et al.*[10a] They ascribed this behavior to the ability of phenyl groups to act as π-electron donors in phosphonium ions, thereby providing an extra amount of electronic shielding about the phosphorus nucleus.

Figure 1 indicates that, if a phosphine contains substituents with large enough σ^P constants, protonation would lead to an upfield change in the phosphorus shift. Tri-*t*-butylphosphine gives this interesting result—the phosphorus shift moves upfield by 3.6 ppm upon protonation. Furthermore, the shifts of both this phosphine and the corresponding phosphonium ion are somewhat higher than predicted. Van Wazer and Letcher[11] have pointed out, on the basis of quantum mechanical calculations, that the empirical linear equations which have been developed can be used successfully only because bond angles in most alkyl- and aryl-substituted phosphines tend to be the same. We suggest that the mutual repulsions of the alkyl groups in tri-*t*-butylphosphine and the corresponding phosphonium ion are extensive enough to create unusually large bond angles, sufficient to result in deviations from correlation with less crowded molecules.

Experimental Section

Materials.—Trimethylphosphine, triethylphosphine, triisopropylphosphine, tricyclohexylphosphine, and diphenylphosphine were used as obtained from Strem Chemicals, Inc. Commercially available triphenylphosphine was used without further purification. Phosphine was used as obtained from Matheson Co., Inc. Tri-*n*-butylphosphine and tri-*n*-octylphosphine, obtained from Carlisle Chemical Works, Inc., were distilled under reduced pressure before use. Tri-*t*-butylphosphine was prepared according to the procedure of Hoffmann and Schellenbeck.[12] Fluorosulfuric acid was distilled and stored in a Teflon bottle, which was kept in a desiccator until needed.

Nmr Spectra.—Pmr spectra were taken with Varian Associates Models A-60, A-56/60A, and HA-100 nmr spectrometers. Proton chemical shifts are reported in parts per million (δ) from external (capillary) tetramethylsilane. The pmr spectra were integrated, and the peak areas supported the postulated assignments of the various phosphonium ions. Phosphorus nmr spectra were taken with Varian Associates Model HA-60IL nmr spectrometer operating at 24.3 MHz and equipped with a Model V4331A probe. Samples were contained in a 12-mm-o.d. thin-walled polished spinning tube. A 5-mm-o.d. polished tube containing 85% H_3PO_4 as the reference material was inserted in the sample tube and maintained in a concentric position by two specially constructed Teflon inserts. Nearly all of the phosphorus chemical shifts were calculated from frequency sweep spectra taken under conditions of field-frequency stabilization. The phosphorus shifts of trimethylphosphine and PH_4^+ were found from field sweep spectra calibrated by audio frequency side-band modulation. Combinations of field-frequency stabilized and sideband modulated spectra provided the shifts of diphenylphosphine and the diphenylphosphonium ion. Since the peaks in many of the phosphorus spectra were broad and often showed unresolved multibond couplings, the reported phosphorus shifts are probably accurate to about ±0.5 ppm.

Protonation of Phosphines.—Except in the case of phosphine, itself (PH_3) each phosphine were added dropwise (or otherwise slowly added, with the solid phosphines) to a fivefold molar excess of fluorosulfuric acid with stirring and cooling. Clear yellow solutions quickly formed. In some cases, an ice bath provided sufficient cooling for the exothermic reactions. The protonation of the more reactive phosphines (trimethyl-, triethyl-, triisopropyl-, and tri-*t*-butyl-) was vigorous enough that cooling in a Dry Ice–acetone bath was found to be necessary. The protonation of phosphine was accomplished by condensing PH_3 in a liquid nitrogen cooled tube and adding dropwise a large excess of fluorosulfuric acid. Allowing the tube to warm to room temperature yielded a stable solution of the phosphonium ion.

Registry No.—**1,** 7803-51-2; **1** (protonated), 19287-78-6; **2,** 594-09-2; **2** (protonated), 19287-79-7; **3,** 554-70-1; **3** (protonated), 19287-80-0; **4,** 6476-36-4; **4** (protonated), 19287-81-1; **5,** 13716-12-6; **5** (protonated), 19287-82-2; **6,** 998-40-3; **6** (protonated), 19287-83-3; **7,** 4731-53-7; **7** (protonated), 19287-84-4; **8,** 2622-14-2; **8** (protonated), 19287-85-5; **9,** 603-35-0; **9** (protonated), 19287-86-6; **10,** 829-85-6; **10** (protonated), 19287-87-7.

Acknowledgments.—Support of this work by a grant from the National Institutes of Health and by a Public Health Service Fellowship from the National Institute of General Medical Sciences (to C. W. M.) is gratefully acknowledged.

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(11) J. R. Van Wazer and J. H. Letcher in ref 2b, p 212.

(12) H. Hoffmann and P. Schellenbeck, *Chem. Ber.*, **100,** 692 (1967).