excitations are produced by the same transmitter coil to keep the ratio of the two rf fields constant everywhere within the active sample volume.[7]

With careful consideration to the experimental details, $^{1}H-^{13}C$ cross-polarization of liquid samples can be an effective technique for determining ^{13}C NMR spectra. Further time savings may be realized by reducing T_1 of the coupled protons with a paramagnetic reagent, without significantly affecting carbon line widths. Analysis of the periodicity of the carbon magnetization in the JCP experiment can be used to assign ^{13}C resonances from J_{CH} values under conditions of proton decoupling. The JCP method should be useful in obtaining the NMR spectra of other low γ nuclei in natural abundance such as ^{15}N. The predicted enhancement factor is 9.9 at the maxima of the cross-polarization signals for NH and NH_2 groups, ideally yielding a time saving of ~100 over conventional FT spectroscopy (6.3 if full NOE is realized). Because of the negative magnetogyric ratio of ^{15}N, a diminution of intensity is possible for ordinary proton-decoupled FT experiments when nondipolar mechanisms contribute to longitudinal relaxation. This difficulty is avoided in the JCP experiment.

References and Notes

(1) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.*, **1973**, 59, 569.
(2) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules*, **1977**, 10, 384.
(3) Garroway, A. N.; Moniz, W. B.; Resing, H. A. *Prepr., Div. Org. Coatings Plastics Chem., Am. Chem. Soc.*, **1976**, 36, 133.
(4) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.*, **1962**, 128, 2042.
(5) Maudsley, A. A.; Müller, L.; Ernst, R. R. *J. Magn. Reson.*, **1977**, 28, 463.
(6) Stejskal, E. O.; Schaefer, J. *J. Magn. Reson.*, **1975**, 18, 560.
(7) Schaefer and Stejskal[6] have reported a JCP experiment under somewhat different conditions and with separate transmitter coils. For a cross-polarization time of 10 ms in neat toluene, they observed the JCP signal-to-noise ratio *reduced* by about $\sqrt{20}$ from the comparable FT result, rather than the predicted enhancement of 4. This result may reflect the criticality of matching the rf fields.
(8) On sabbatical leave from Department of Natural Sciences, University of Michigan—Dearborn, Dearborn, Mich. 48128.
(9) Department of Mechanical and Industrial Engineering, University of Utah, Salt Lake City, Utah 84112.

R. D. Bertrand,*[8] W. B. Moniz
A. N. Garroway, G. C. Chingas[9]
Code 6110, Chemistry Division, Naval Research Laboratory
Washington, D.C. 20375
Received April 12, 1978

A Phosphoranoxide[1] Anion—Direct Observation and Isolation of a Stable Model for the Postulated Intermediate in Nucleophilic Substitution at Tetracoordinated Phosphinoyl Phosphorus

Sir:

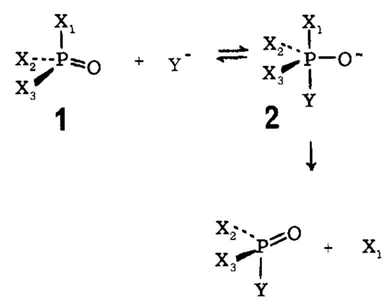
The most thoroughly studied reaction of tetracoordinated phosphorus compounds, such as **1**, which contain a P=O bond, is nucleophilic substitution at phosphorus.[2] It is generally accepted that a reaction of this type involves apical approach of the nucleophile and formation of a trigonal bipyramidal (TBP) intermediate, or transition state, such as **2**. The direct observation of such a TBP intermediate, with an equatorial oxy anion, has remained an elusive goal.[3b] We here report such an observation.

Only recently have reports appeared of compounds whose solution spectra[3] and reaction products[4] suggest that they belong to the class of hydroxyphosphoranes, conjugate acids of **2**. One such compound has been isolated as a crystalline solid.[5]

The hydroxyphosphoranes for which evidence has been reported all have alkoxy or carboxy ligands to phosphorus which are easily eliminated to generate a P=O bond (vide infra). These hydroxyphosphoranes are destroyed (as in **2** → **3**) by treatment with base,[5] even bases as weak as pyridine or dimethyl sulfoxide.[3d] The conversion of these hydroxyphosphoranes to observable phosphoranoxide anions has therefore not been accomplished.

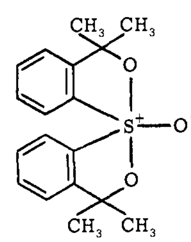
Table I. ^{31}P NMR of Mixtures of **6** and **7**

Solvent	temp, °C	chemical shift, ppm	line width, Hz	rel concn
10% TFA in $CDCl_3$	28	+81.9	5	
CH_3OH	28	+50.9	220	
$CDCl_3$	28	+45.6	140	
C_5H_5N	28	−12.4	320	
CH_3OD	28	+54.9	54	
CH_3OD	5	+54.2	24	~50
		−26.3	100	1
CH_3OD	−10	+53.7	20	8.5
		−26.3	40	1
CH_3OD	−30	+52.7	8	3.3
		−26.7	15	1
CH_3OD	−50	+52.7	5	2.5
		−27.0	5	1



1 **2** **3**

Our observation of stability in sulfurane oxides,[6] such as **4**,[6] suggested to us that isoelectronic phosphoranoxide anions, such as **5**, having all the structural features[7] responsible for the stability of the analogous **4**, might be sufficiently stabilized by these structural features to allow their direct observation. We report evidence confirming this view.



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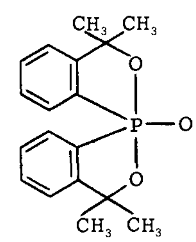

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A crystalline compound[8,9] having either structure **6** or **7** was prepared by the indicated route (Scheme I). Examination of the ^{31}P NMR spectrum of the reaction mixture in tetrahydrofuran (THF) prior to hydrolysis (aqueous ammonium chloride) reveals a sharp signal at −20.8 ppm, attributable to the magnesium salt of **5**. Solution ^{1}H and ^{31}P NMR spectra of **6**, or **7**, show clear evidence for a dynamic equilibrium between **6** and **7**, present in ratios dependent on solvent and temperature (Table I). The intermediate rate of **6**–**7** exchange evidenced by the single broad ^{31}P peak seen at room temperature is slowed at lower temperatures, to give separate sharp peaks for **6** and **7**. Peak area ratios show increasing amounts of the ring tautomer, hydroxyphosphorane **6** (ca. −27 ppm) relative to open-chain tautomer **7** (ca. +52 ppm) in CH_3OD

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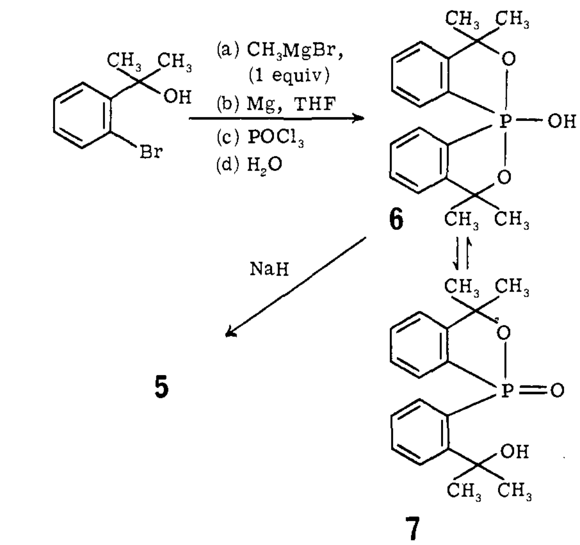
Table II. ^{31}P NMR of **6** (0.026 M in CH_3OH) with Added Sodium Methoxide

$NaOCH_3$, M	$\delta_{^{31}P}$, ppm	Line width, Hz
0	+51.0	220
0.006	+32.0	55
0.027	+12.5	35
0.046	0.0	30
0.074	−15.1	16
0.126	−22.2	7

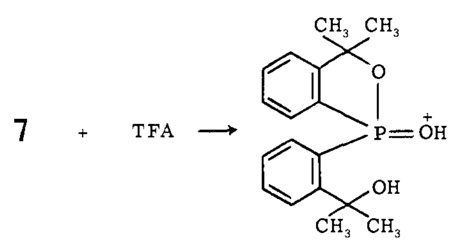
Scheme I



solution as the temperature is decreased from +5 to −50 °C.

More basic solvents, such as pyridine, increase the relative amounts of **6** in the equilibrium mixture as evidenced by the upfield chemical shift (−12.4 ppm) of the single peak seen at 28 °C relative to that seen at the same temperature in less basic solvents such as $CDCl_3$ (+45.6 ppm). The further downfield shift (+81.9 ppm) and sharpening of this peak upon addition of one part of trifluoroacetic acid (TFA) to nine parts of the $CDCl_3$ solution is interpreted in terms of protonation of **7**.

Most interesting is the effect of incremental addition of sodium methoxide to a methanol solution (Table II) of **6** or **7**. Progressive sharpening and shift of the ^{31}P NMR signals to higher field are observed, reflecting the formation of **5**.



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Moreover, upon addition of excess sodium hydride to THF solution of **6** (or **7**), immediate evolution of hydrogen is realized. Filtration and removal of solvent gives analytically pure sodium salt of **5**.[10] A THF solution of **5** shows a single sharp peak in its ^{31}P NMR at −26.9 ppm.

The similarity in ^{31}P chemical shifts seen (Table II) for solutions of **6** in CH_3OH-CH_3ONa (as negative as −22.2 ppm) and for the sodium derivative of **5** (−26.9 ppm) or the magnesium derivative of **5** (−20.8 ppm) in THF suggests that sodium methoxide is sufficiently basic to convert **6** to its conjugate base **5**. The detailed dependence of ^{31}P chemical shift on methoxide ion concentration revealed in the data of Table II suggests that **6** titrates as a weak acid in methanol. In particular one should note that the addition of 1 equiv of base does not produce the chemical shift characteristic of the phosphoranoxide anion **5**. Further work will be directed toward a more quantitative assessment of the acidity of **6**.

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References and Notes

(1) We suggest "phosphoranoxide anion" as a name for the type of structure which we discuss in this paper, nomenclature analogous to that used for "alkoxides".
(2) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); R. F. Hudson and C. Brown, *ibid.*, **5**, 204 (1972); S. J. Bencovic in "Comprehensive Chemical Kinetics", Vol. 10, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N.Y., 1969, pp 1–56. Another type of very stable phosphorane produced by a nucleophilic attack at phosphorus is described by D. S. Milbrath and J. G. Verkade, *J. Am. Chem. Soc.*, **99**, 6607 (1977). For a theoretical treatment see C. A. Deakyne and L. C. Allen, *ibid.*, **98**, 4076 (1976), and an earlier paper by J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
(3) (a) I. Granoth, Y. Segall, and H. Leader, *J. Chem. Soc., Chem. Commun.*, 74 (1976), and references therein; (b) F. Ramirez, M. Nowakowski, and J. F. Marecek, *J. Am. Chem. Soc.*, **98**, 4330 (1976); (c) A. Munoz, M. Gallagher, A. Klaebe, and R. Wolf, *Tetrahedron Lett.*, 673 (1976); (d) F. Ramirez, M. Nowakowski, and J. F. Marecek, *J. Am. Chem. Soc.*, **99**, 4515 (1977).
(4) G. Kemp and S. Trippett, *Tetrahedron Lett.*, 4381 (1976).
(5) Y. Segall and I. Granoth, *Abstr. 44th Annu. Meeting Isr. Chem. Soc.*, OR-10 (1977); *J. Am. Chem. Soc.*, in press.
(6) L. J. Adzima and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 1657 (1977).
(7) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974).
(8) Elemental analyses of new compounds are within 0.4% of calculated values. Chemical shifts for ^{31}P are given in parts per million downfield from 85% H_3PO_4 and H chemical shifts are in parts per million downfield from Me_4Si, in $CDCl_3$ as the solvent, unless otherwise stated.
(9) Methylmagnesium bromide (1 equiv) was added to THF solution of 2-bromophenyl-2-propanol, followed by magnesium powder (70–80 mesh). The mixture was refluxed for 1.5 h and cooled and $POCl_3$ (0.48 mol equiv) was added dropwise. The resulting mixture was boiled for 45 min, cooled, and hydrolyzed with aqueous ammonium chloride solution. The usual workup gave **6** (or **7**) in 40% yield: mp 181 °C (EtOH); ^1H NMR δ 1.74 (6 H, s, Me), 1.79 (6 H, s, Me), 5.90 (1 H, br s, HO), 7.17–7.60 (6 H, m, HAr), 7.94–8.18 (2 H, m, H ortho to P); ^1H NMR (THF-d_8) δ 1.63 (12 H, s, Me), 7.10–7.53 (6 H, m, HAr), 8.03–8.23 (2 H, m, H ortho to P).
(10) ^1H NMR (THF-d_8) of **5**: δ 1.33 (6 H, s, Me), 1.45 (6 H, s, Me), 6.90–7.31 (6 H, m, HAr), 8.20–8.41 (2 H, m, H ortho to P). The upfield and downfield shifts of the methyls and hydrogen ortho to phosphorus, respectively, as compared with the values for **6** or **7**, are also consistent with the structure shown for **5**.

Itshak Granoth*, J. C. Martin*
Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801
Received April 7, 1978

A Kinetic Model for the Formation of the Conductor *N*-Methylphenazinium Tetracyanoquinodimethanide (NMP-TCNQ)[1]

Sir:

Prior to the discovery[2,3] of the metallic tetrathiafulvalenium tetracyanoquinodimethanide (TTF-TCNQ), the best organic conductor was the 1:1 TCNQ salt of the *N*-methylphenazinium (NMP, **1a**) cation[4] which exhibits a uniform segregated stack crystal structure.[5] This 1:1 salt is unusual because at least 28 other 1:1 TCNQ salts of planar closed-shell nitrogen heterocyclic monocations[4,6-10] are insulators[11] with structures that do not exhibit the "infinite chains" of NMP-TCNQ[5] in the three reported cases.[12-14] The perspective adopted herein is that the 28 insulating salts constitute "normal" behavior for this subclass of TCNQ salts and that an explanation for the formation of NMP-TCNQ is desirable.

This communication proposes a kinetic model for the formation of NMP-TCNQ involving a donor–acceptor interaction between the acceptor **1a** and any of several donor "impurities" found in precursor salts of **1a** and which persist in NMP-

