

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, ^1H - ^{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.

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- (7) Schaefer and Stejskal⁶ 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.
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A Phosphoranoxide¹ 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 $\text{P}=\text{O}$ 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 oxyanion, has remained an elusive goal.^{3b} We here report such an observation.

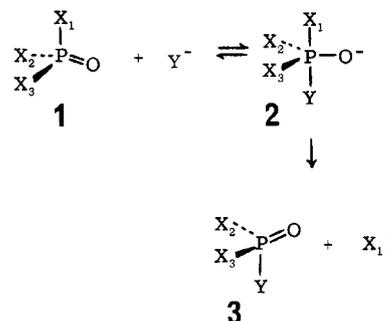
Only recently have reports appeared of compounds whose solution spectra³ and reaction products⁴ suggest that they belong to the class of hydroxyphosphoranes, conjugate acids of **2**. One such compound has been isolated as a crystalline solid.⁵

The hydroxyphosphoranes for which evidence has been reported all have alkoxy or carboxy ligands to phosphorus which

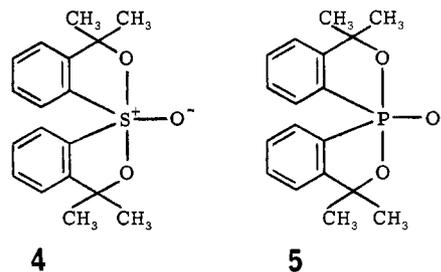
Table I. ^{31}P NMR of Mixtures of **6** and **7**

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	
$\text{C}_5\text{H}_5\text{N}$	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

are easily eliminated to generate a $\text{P}=\text{O}$ bond (vide infra). These hydroxyphosphoranes are destroyed (as in **2** \rightarrow **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.



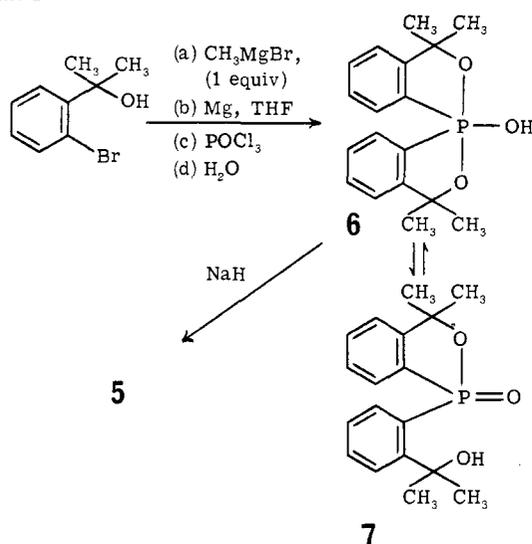
Our observation of stability in sulfurane oxides,⁶ such as **4**,⁶ suggested to us that isoelectronic phosphoranoxide anions, such as **5**, having all the structural features⁷ responsible for the stability of the analogous **4**, might be sufficiently stabilized by these structural features to allow their direct observation. We report evidence confirming this view.



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 ^1H 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

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

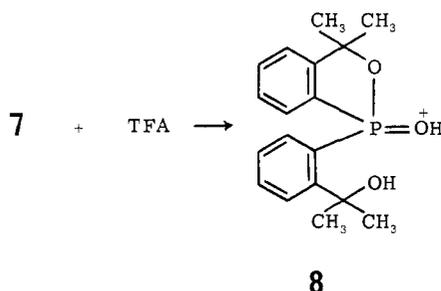
NaOCH_3 , M	$\delta_{31\text{P}}$, ppm	Line width, Hz
0	+51.0	220
0.006	+32.0	55
0.027	+12.5	35
0.046	0.0	30
0.074	-15.1	16
0.126	-22.2	7

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**.



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 $\text{CH}_3\text{OH}-\text{CH}_3\text{ONa}$ (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 phosphoroxide anion **5**. Further work will be directed toward a more quantitative assessment of the acidity of **6**.

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References and Notes

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- (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_6) 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_6) 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**.

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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**) cation⁴ 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 insulators¹¹ with structures that do not exhibit the "infinite chains" of NMP-TCNQ⁵ 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-