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SYNTHESIS AND MAGNETIC RESONANCE STUDIES OF SOME PHOSPHINOUS ACIDS, PHOSPHORYLACETIC ACIDS, AND SOME OF THEIR COORDINATION COMPOUNDS†

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Abstract—The synthesis of phosphorylacetic acids, $RR'P(O)CH_2COOH$, where $R = C_6H_5$ and $R' = OC_2H_5$, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $sec\text{-}C_4H_9$, and C_6H_5, from the appropriate phosphinous acids, several of which are previously unreported, is discussed. ^{31}P nuclear magnetic resonance spectra are reported for the phosphinous acids, RR'P(O)H, the phosphorylacetic acids and the metal derivatives of the phosphinous acids, RR'POM, where M in Na or MgBr, which are intermediates in the synthesis. The diastereoisomers of Ph*sec*-BuP(O)H exhibit different ^{31}P NMR spectra. Diastereotopic protons of the phosphinous acids and phosphorylacetic acids do not exhibit complex PMR spectra, whereas the diastereotopic methyl groups of the isopropyl compounds do. Some metal complexes of the phosphorylacetic acids are reported.

INTRODUCTION

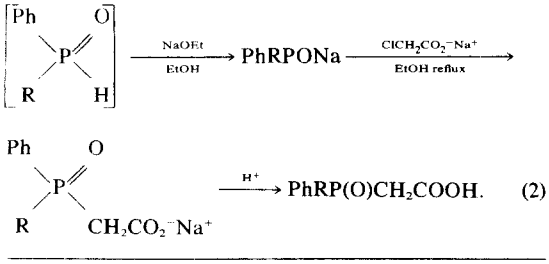
Although a few diorganophosphorylacetic acids, $RR'P(O)CH_2\text{–}COOH$, have been reported previously[2], neither their coordination chemistry nor NMR spectra had been investigated. In addition, although the coordination chemistry of the phosphoryl group is well known for simple compounds[3–5], very little has been reported for multidentate ligands in which the phosphoryl group is a potential donor[6, 7]. This research extends both of these areas. We report here the synthesis of some previously unreported[8] phosphinous acids[9], RR'P(O)H, precursors of the phosphorylacetic acids, $RR'P(O)CH_2COOH$; the isolation of some of these new phosphorylacetic acids and metal derivatives thereof; and some ^{31}P and proton magnetic resonance spectra of appropriate compounds.

DISCUSSION

It has previously been reported that an attempt to form phosphorylacetic acids by the following sequence of reactions failed, yielding only PhRP(O)OH upon hydrolysis of the reaction mixture[2]:

(1)

However, when crude PhRP(O)H was treated in the following sequence by the previous authors[2], the expected product was obtained:



(2)

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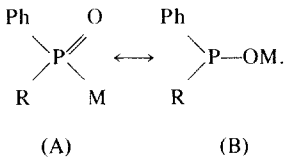
Thus, it appears that the species, PhRPOM, where M is MgBr or Na, behaves differently in modes of reaction as well as structurally, i.e. as is commonly observed in phosphorus chemistry, tautomeric structures can exist[8].



Information on these structures can be obtained from ^{31}P NMR spectra. Issleib *et al.*[10] have investigated the solution reaction products of alkali metals with $Ph_2P(O)H$ in tetrahydrofuran (THF). They conclude that the structure of the product in solution is best represented by structure (B), since the observed ^{31}P chemical shifts are in the range normally found for trivalent R_2POR type compounds (generally $\delta < -80$ ppm vs 85% H_3PO_4) rather than in the range $(-20 < \delta < -50$ ppm) for quadruply connected phosphorus compounds such as phosphine oxides or those structures represented by (A)[11].

Table 1 lists some ^{31}P chemical shifts observed for solutions after the first step of both Sequence I and Sequence II. From the chemical shift assumption, it appears that the reactions in Sequence I yield products whose structures are of type B. Hays[12] has also suggested that the reaction of $(EtO)_2\overset{O}{\overset{\|}{P}}\text{–}H$ with EtMgBr yields a phosphorus compound of the structure $Et_2P\text{–}O^{\ominus}Mg^{\oplus}Br$ (type B) on the basis of ^{31}P NMR spectroscopy. The reaction in Sequence II, however, yields a product more aptly described by structure A. Even this does not completely describe the situation as Table 2 and Fig. 1 demonstrate. The addition of less than stoichiomet-

Table 1. Chemical shifts and structures of R_2POM

Reaction		Structure[a]	δ_P (ppm)[b]
Ph(EtO)P(O)H	NaOEt/EtOH →	Ph(EtO)P(O)Na	- 26.8
$Ph_2P(O)H$	NaOEt/EtOH →	$Ph_2P(O)Na$	- 32.3
PhEtP(O)H	NaOEt/EtOH →	PhEtP(O)Na	- 31.7
Phs-BuP(O)H	NaOEt/EtOH →	Phs-BuP(O)Na	- 37.3
$(EtO)_2P(O)H$	PhMgBr(xs)/THF →	Ph_2P-O-MgBr	- 90.0
$(EtO)_2P(O)H$	MeMgBr/THF →	$(EtO)_2P$-O-MgBr	-137[c]
$(EtO)_2P(O)H$	EtMgBr(xs)/THF →	Et_2P-O-MgBr	-108[c]
Ph(EtO)P(O)H	EtMgBr/THF →	PhEtP-O-MgBr	-103
$Ph_2P(O)H$	Na/THF →	Ph_2P-O-Na	- 90.5[d]

[a]Based on the assumption from Reference 10.

[b]Negative values are downfield from 85% H_3PO_4.

[c]Ref. 12.

[d]Ref. 10.

Table 2. Exchange data for PhEtP(O)H in NaOEt/EtOH

Ratio $\frac{\text{moles NaOEt}}{\text{moles PhEtP(O)H}}$	δ^a (ppm)	Comments
0	-32.2	doublet, J_{PH}= 460 Hz
0.2	Ca.-31	very broad (800 Hz)
0.4	-30.3	singlet
0.6	-32.0	singlet
1.0	-32.0	singlet
2.0	-31.7	singlet

[a]Negative values are downfield from 85% H_3PO_4.

ric amounts of NaOEt to PhEtP(O)H in ethanol clearly shows that an equilibrium situation exists as the ^{31}P NMR signal for PhEtP(O)H (a doublet) is destroyed upon addition of some NaOEt, but appears again as a singlet upon further addition of some NaOEt. Exchange of a proton directly bonded to phosphorus has been previously observed[12].

Considering the significant differences in the structures of the salts in solution suggested by these data, it is not surprising that the reaction follows different paths and suggests that monitoring of ^{31}P NMR may be a useful technique in determining reaction intermediates and mechanisms of these compounds under varying conditions.

^{31}P NMR data for the phosphinous acids appear in Table 3. The ^{31}P NMR signal is a simple doublet due to the splitting by the proton directly bonded to phosphorus. The $^1J_{PH}$ values are obtained from PMR spectra.

It should be noted that our value for $^1J_{PH}$ is somewhat different than those values previously reported for $Ph_2P(O)H$ (487 Hz vs 481[13], 490[11], 513[8]). Routine monitoring of the various phosphinous acids during the work up procedure indicates that the value of $^1J_{PH}$ is dependent on the purity of the compound, in general, decreasing from about 500 Hz. The reasons for this variation are not completely understood, but it is possible that the presence of small quantities of H_2O, a protonic solvent, or some other Lewis acid might affect the phosphorus hybridization by forming a bond with the phosphoryl oxygen. Recently, it has been shown[14] that the previously reported preparative routes to $Ph_2P(O)H$ results in an impurity of $Ph_2P(O)OH$. We have observed that compounds containing a phosphoryl group and a hydrogen atom directly attached to the phorphorus atom have large changes in $^1J_{PH}$ when treated with 100% sulfuric acid[15]. Furthermore, $^1J_{PH}$ for $Me_2P(O)H$ is

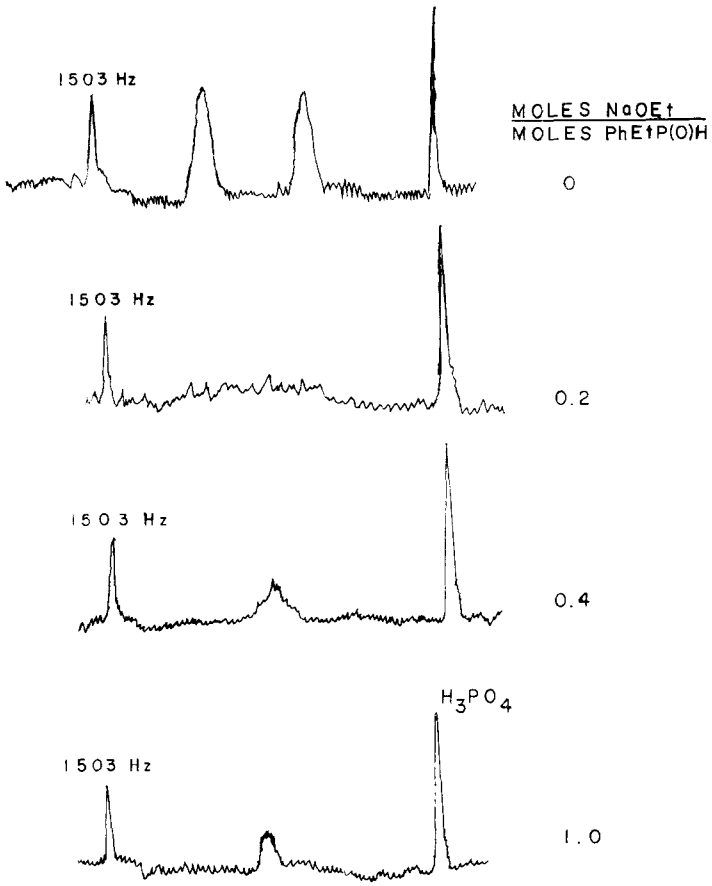


Fig. 1. ^{31}P NMR spectra of PhEtP(O)H upon addition of NaOEt.

Table 3. ^{31}P data for phosphinous and phosphorylacetic acids

Compound	δ^a	$^1J_{PH}{}^b$
Ph(EtO)P(O)H	-23.7[c]	557 [c]
$Ph_2P(O)H$	-23.1	487 [d]
PhEtP(O)H	-32.3	458
Ph(i-Pr)P(O)H	-36.1	458
Ph(n-Bu)P(O)H	-29.0	467 [e]
Ph(s-Bu)P(O)H	-34.3,-32.2	457.5,458.2
$Ph(EtO)P(O)CH_2CO_2H$	-30.9	
$Ph_2P(O)CH_2CO_2H$	-36.9	
$PhEtP(O)CH_2CO_2H$	-42.3	
$Ph(i\text{-}Pr)P(O)CH_2CO_2H$	-46.9	
$Ph(n\text{-}Bu)P(O)CH_2CO_2H$	-40.4	
$Ph(s\text{-}Bu)P(O)CH_2CO_2H$	-45.9	

[a] ppm relative to 85% H_3PO_4.

[b] Obtained from pmr data.

[c] -23.5 ppm, 565 Hz (Ref. 11).

[d] 481 Hz (Ref. 13), 490 Hz (Ref. 11), 513 Hz (Ref. 8).

[e] 461 Hz (Ref. 13).

456 Hz in dioxane and 490 Hz in D_2O, while the phosphorus chemical shifts changes from −18.6 ppm (dioxane) to −33 ppm (D_2O)[12].

The lone exception to the simple doublet spectrum is Ph(*sec*-Bu)P(O)H. This compound exhibits two doublets of nearly equal intensity (Fig. 2). Since the methine carbon of the *sec*-Bu group and the phosphorus atom are both chiral, a pair of diastereoisomers is formed with each compound having its own chemical shift and coupling constant. This phenomenon has been previously observed in the ^{31}P NMR spectrum of menthyl methylphosphinate and its thio analog[16], but appears not to have been previously observed with other classes of phosphorus compounds. Attempts to separate the two compounds by distillation failed, probably because of the conditions needed to purify these compounds (see Experimental).

The general PMR data of the phosphinous acids appear in Table 4. However, three of these compounds exhibited unusual PMR spectra which were investigated further by double resonance techniques and these will be discussed in turn.

PhEtP(O)H

The large doublet ($^1J_{PH}$) is split into triplets by the methylene protons ($^3J_{HPCH}$). Although the methylene protons are diastereotopic, there are no extra lines observed in either the methyl group or the phosphine proton resonances, indicating that the difference in chemical shifts of the two methylene protons is small. (This is also observed for PhBuP(O)H, both in this work and earlier[13].

It has been demonstrated[17], that $^1J_{PH}$ and $^2J_{PH}$ in

Table 4. PMR data for phosphinous acids

Compound	Pattern	Integration (theory)	δ (ppm)	Assignment	J (Hz)
Ph(EtO)P(O)H	doublet	0.89 (1)	7.63	PH	$J_{\underline{PH}}$= 557.4
	multiplet	5.00 (5)	8.04-7.14	phenyl	
	multiplet	1.95 (2)	4.80	CH_2	$J_{\underline{POCH}}$= 9.2
	triplet	2.80 (3)	1.24	CH_3	$J_{\underline{HCCH}}$= 7.0
$Ph_2P(O)H$	doublet	0.91 (1)	8.36	PH	$J_{\underline{PH}}$= 487.2
	multiplet	10.0 (10)	7.6	phenyl	
PhEtP(O)H	doublet of triplets*	0.84 (1)	7.34	PH	$J_{\underline{PH}}$= 458.4, $J_{\underline{HPCH}}$= 3.4
	multiplet	5.45 (5)	7.80-7.10	phenyl	
	doublet of triplets	(3)	1.13	CH_3	$J_{\underline{HCCH}}$= 7.0
	multiplet*	5.00 (2)	2.20-1.60	CH_2	$J_{\underline{PCCH}}$= 20.0
Ph(i-Pr)P(O)H	doublet of doublets	0.82 (1)	7.22	PH	$J_{\underline{PH}}$= 458.4 $J_{\underline{HPCH}}$= 2.1
	multiplet	5.25 (5)	7.96-7.05	phenyl	
	multiplet*	(1)	2.41-1.75	PCH	
	multiplet*	7.00 (6)	1.75-0.80	CH_3	
Ph(n-Bu)P(O)H	doublet of triplets	0.89 (1)	7.77	PH	$J_{\underline{PH}}$= 467.4 $J_{\underline{HPCH}}$= 3.2
	multiplet	4.85 (5)	8.25-7.40	phenyl	
	multiplet	(2)	7.6-9.0	PCH_2	
	multiplet	6.00 (4)		$C\underline{H}_2C\underline{H}_2CH_3$	
	triplet	2.94 (3)	0.80	CH_3	$J_{\underline{HCCH}}$= 6.8
Ph(s-Bu)P(O)H	six peaks*	0.95 (1)	*	PH	
	multiplet	4.85 (5)	8.2-7.5	phenyl	
	multiplet	(1)	2.4-2.2	PCH	
	multiplet	9.00 (2)	2.1-1.7	CH_2	
	multiplet	(6)	1.7-0.8	CH_3	

*See text for discussion of decoupling experiments.

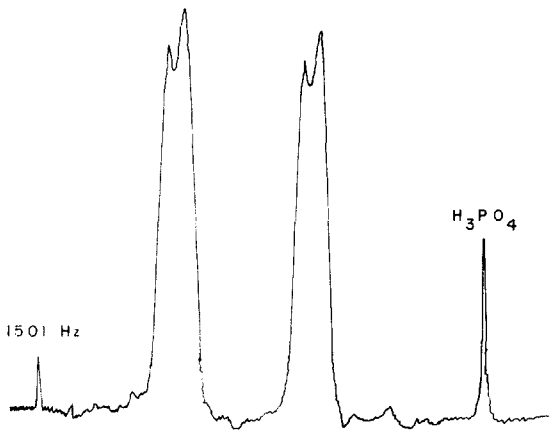


Fig. 2. ^{31}P NMR spectrum of Ph(*sec*-Bu)P(O)H.

PhMeP(O)H are of opposite signs. McFarlane [18] has also listed the sign of $^2J_{PCH}$ as negative in pentavalent phosphorus compounds, but as either positive or negative in trivalent phosphorus compounds.

PhEtP(O)H lends itself nicely to a relative sign determination study. Low intensity irradiation of one of the triplets of the $^1J_{PH}$ doublet should perturb the methylene region such that a quartet would arise from one side of the methylene multiplet. When the downfield triplet is irradiated, the quartet should arise from the downfield side of the methylene multiplet if the signs of $^1J_{PH}$ and $^2J_{PCH}$ are alike, or from the upfield side of the methylene multiplet if the signs are opposite. Figure 3 contains a diagram along with the results. It is apparent that the quartet arises from the opposite side of the methylene multiplet, confirming that $^1J_{PH}$ and $^2J_{PH}$ are of opposite signs ($^2J_{PCH}$ = 12.0 Hz).

Ph(*i*-Pr)P(O)H

This compound exhibits eight lines of equal intensity in the methyl region (Fig. 4). Since the two methyl groups are diastereotopic, each methyl group is split into a doublet by the methine proton and into another doublet by the phosphorus atom. Decoupling the methine proton collapses the eight lines into two broad lines. This leads us to conclude that lines 1 and 3, 2 and 4, 5 and 7 and 6 and 8 represent the methine proton splitting. The three possible cases of splitting patterns follow:

	δ_{CH_3}	J_{PCCH}	δ_{CH_3}	J_{PCCH}	J_{HCCH}
Case A	0.53	18.0	0.56	18.5	7.0
Case B	0.54	14.5	0.55	22.0	7.0
Case C	0.41	3.5	0.73	4.5	7.0

However, it is not clear which of the cases is correct from available data.

Ph(*sec*-Bu)P(O)H

Since this compound exhibits four lines in the ^{31}P NMR (*vida supra*), it was expected that eight lines representing

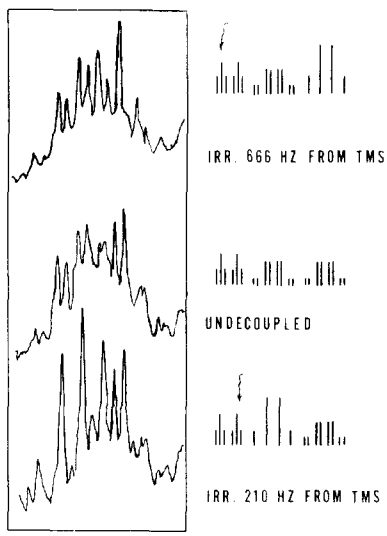


Fig. 3. Proton spectrum of the methylene region only (1.6–2.2 δ) of PhEtP(O)H (middle, undecoupled); with spin tickling of the low field PH triplet (upper spectrum); with spin tickling of the high field PH triplet (lower spectrum).

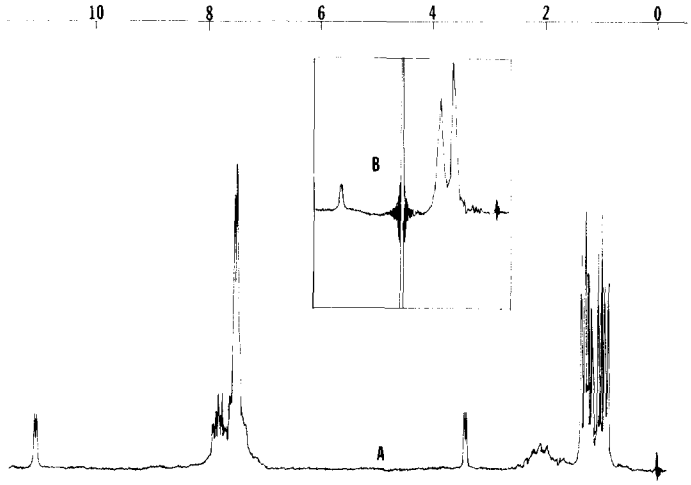


Fig. 4. Proton spectrum (1000 Hz) of Ph(*i*-Pr)P(O)H in $CDCl_3$. Spectrum A is the complete spectrum with the assignments given in Table 4. Spectrum B shows the collapse of the eight-line methyl resonance by double irradiation at the methine proton resonance.

$^1J_{PH}$ and $^3J_{HPCH}$ doublets for the phosphorus hydrogen of the two molecules would be observed in the PMR spectrum. However, as can be seen in Fig. 5, only six lines are observed in a 2:1:1 and a 2:1:1 ratio. Irradiation of the methine proton collapses the two smaller lines into a singlet ($\delta = 7.28$, $^1J_{PH} = 457.5$), leaving the larger line unchanged ($\delta = 7.35$, $^1J_{PH} = 458.2$). Thus $^3J_{HPCH}$ is 2.7 Hz for one diastereoisomer and approximately 0 Hz for the other diastereoisomer. The Table below is a summary of $^3J_{HPCH}$ values for compounds of the general formula PhRP(O)H.

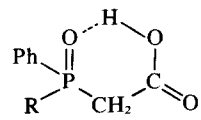
R	$^3J_{HPCH}$(Hz)
$-CH_3$	3.5[16]
$-CH_2CH_3$	3.4
$-CH_2CH_2CH_2CH_3$	3.2
$-CH_2Ph$	3.0–3.5[15]
$-CH(CH_3)_2$	2.1
$-CH(CH_3)CH_2CH_3$	2.7 and 0

There does appear to be a decrease in the magnitude of $^3J_{HPCH}$ with substitution on the alpha carbon, suggesting that this coupling constant is sensitive to steric and/or electronic effects.

IR bands[19] for the P=O stretch, usually the strongest absorption between 1100 and 1300 cm^{-1} and P–H stretch, a medium absorption from 2300 to 2400 cm^{-1}, appear in Table 5.

The ^{31}P NMR chemical shifts for the phosphorylacetic acids also appear in Table 3. Each is a singlet in the −30 to −47 ppm range. Only one peak was observed for Ph(*sec*-Bu)P(O) CH_2CO_2H. This, coupled with a relatively sharp m.p., indicates that only one of the possible diastereoisomers was isolated.

The PMR data are reported in Table 6. Each compound exhibits a very sharp carboxylic acid proton peak between 9δ and 12δ, indicative of strong hydrogen bonding, probably intramolecular as shown below.



In each of the compounds containing a chiral phosphorus atom, the diastereotopic carboxyl methylene protons (P-$\underline{CH_2}CO_2H$) give rise to only a simple sharp doublet indicating that the chemical shift differences in the two protons must be small. The ethyl methylene diastereotopic protons in PhEtP(O)CH_2CO_2H also exhibit only a simple doublet of quartets (phosphorus and CH_3

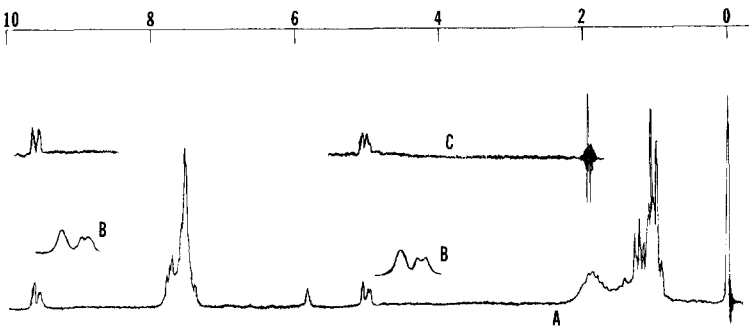


Fig. 5. Proton spectrum (1000 Hz) of Ph(*sec*-Bu)P(O)H in $CDCl_3$. Spectrum A is the complete spectrum. Spectrum B is an expanded view of the resonance due to the phosphorus proton. Spectrum C shows the phosphorus hydrogen region during double irradiation at the methine proton resonance.

Table 5. IR data for phosphinous and phosphorylacetic acids

	Stretching frequency (cm^{-1})			
Compound	P=O	P-H	C=O	C-O
PhEtP(O)H	1186	2285		
Ph(i-Pr)P(O)H	1182	2274		
Ph(n-Bu)P(O)H	1187	2296		
Ph(s-Bu)P(O)H	1176	2301		
$Ph_2P(O)CH_2CO_2H$	1164*		1699	1275
PhEtP(O)CH_2CO_2H	1142*		1705	1278
Ph(i-Pr)P(O)CH_2CO_2H	1151*		1699	1271
Ph(n-Bu)P(O)CH_2CO_2H	1148*		1689	1277
Ph(EtO)P(O)CH_2CO_2H	1177*		1712	1249
Ph(s-Bu)P(O)CH_2CO_2H	1170*		1703	1261

*Tentative assignment - see text for discussion.

Table 6. PMR data for phosphorylacetic acids

Compound	Pattern	Integration (theory)	δ (ppm)	Assignment	J (Hz)
$Ph(EtO)P(O)CH_2CO_2H$	singlet	1.06 (1)	11.15	CO_2H	
	multiplet	5.00 (5)	7.96-7.14	phenyl	
	doublet	2.08 (2)	4.09	PCH_2CO_2	J_{PCH} = 17.7
	multiplet*	2.00 (2)	3.12	$POCH_2$	
	triplet	3.00 (3)	1.28	CH_3	J_{HCCH} = 7.2
$Ph_2P(O)CH_2CO_2H$	singlet	1.17 (1)	9.81	CO_2H	
	multiplet	10.0 (10)	8.02-7.33	phenyl	
	doublet	2.02 (2)	3.54	PCH_2CO_2	J_{PCH} = 13.8
$PhEtP(O)CH_2CO_2H$	singlet	1.05 (1)	9.34	CO_2H	
	multiplet	5.00 (5)	8.23-7.38	phenyl	
	doublet	2.11 (2)	3.25	PCH_2CO_2	J_{PCH} = 13.9
	doublet of quartets	2.20 (2)	2.28	PCH_2CH_3	J_{PCH} = 13
	doublet of triplets	3.30 (3)	1.10	CH_3	J_{PCCH} = 18.9, J_{HCCH} = 7.5
$Ph(i\text{-}Pr)P(O)CH_2CO_2H$	singlet	1.16 (1)	11.72	CO_2H	
	multiplet	4.90 (5)	7.95-7.34	phenyl	
	doublet	1.98 (2)	3.22	PCH_2CO_2	J_{PCH} = 14.8
	multiplet*	0.95 (1)	2.95-2.50	$PCH(CH_3)_2$	
	multiplet*	6.00 (6)	1.56-0.88	CH_3	
$Ph(n\text{-}Bu)P(O)CH_2CO_2H$	singlet	1.00 (1)	11.95	CO_2H	
	multiplet	4.75 (5)	8.04-7.29	phenyl	
	doublet	(2)	2.75	PCH_2CO_2	J_{PCH} = 16.2
	multiplet	11.0 (6)	1.35	$CH_2CH_2CH_2CH_3$	
	triplet	(3)	0.85	CH_3	J_{HCCH} = 7.0
$Ph(s\text{-}Bu)P(O)CH_2CO_2H$	singlet	1.07 (1)	10.27	CO_2H	
	multiplet	4.70 (5)	8.05-7.40	phenyl	
	doublet	2.09 (2)	3.21	PCH_2CO_2	J_{PCH} = 13.9
	multiplet	(1)		PCH(Me)(Et)	
	multiplet	9.00 (2)	2.5-1.7	$PCH(Me)CH_2Me$	
	multiplet	(6)	1.50-0.83	CH_3	

*See text for discussion of decoupling experiments.

splittings) so that the chemical shift difference in these two protons must also be small.

Two of these compounds exhibited PMR spectra which were further investigated by double resonance studies and will be discussed in turn.

$Ph(EtO)P(O)CH_2CO_2H$

The ethoxy methylene group appears as an unsymmetrical three line pattern with small shoulders on the edge. Irradiation of the methyl group collapses the multiplet into a simple doublet (J_{POCH} = 7.0 Hz, δ = 4.14 ppm).

$Ph(i\text{-}Pr)P(O)CH_2CO_2H$

The methyl region exhibits eight lines of equal intensity, indicating that the diastereotopic methyl groups do have significantly different chemical shifts and/or coupling constants. Irradiation of the methine proton (Fig. 6) collapses the eight lines to four, indicating that lines 1 and 2, 3 and 5, 4 and 6 and 7 and 8 are paired. The three possible assignments appear below, although it is not clear from available data which of these cases is correct, although case C can probably be excluded because of the unusual magnitudes of $^3J_{PH}$.

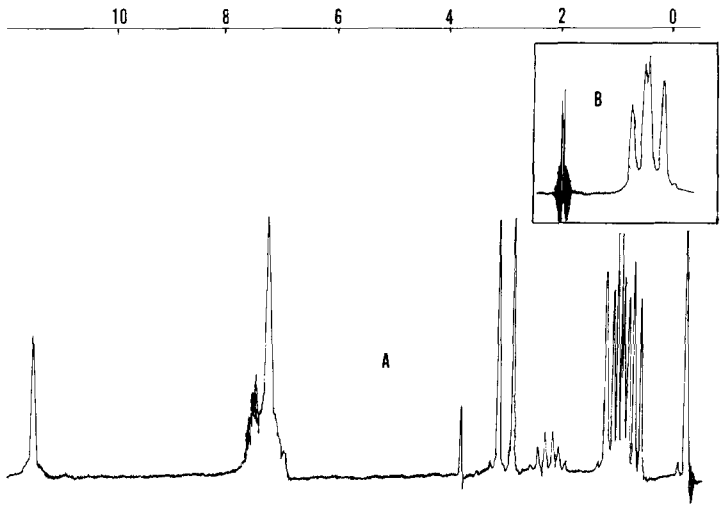


Fig. 6. Proton spectrum (1000 Hz) of Ph(*i*-Pr)P(O)CH_2COOH in $CDCl_3$. Spectrum A is the complete spectrum with assignments given in Table 6. Spectrum B shows the methyl region of the isopropyl group with double irradiation at the methine proton.

	δMe_1	J_{PCCH}(Hz)	δMe_2	J_{PCCH}(Hz)
Case A	0.73	12.4	0.49	13.2
Case B	0.61	17.0	0.50	18.0
Case C	0.54	30.8	0.56	4.4

The IR data for these compounds appear in Table 5. They support the conclusion of a strong hydrogen bond as no strongly discernible OH band present and the normally very strong P=O bond almost disappears. Two recent detailed studies[20, 21] of the IR spectra of some phosphorylacetic acids arrive at similar conclusions.

Only a few reports using ^{31}P NMR to study compounds containing a coordinated phosphoryl group have appeared[7, 22–26], primarily solution studies of ATP or ADP[22–24], or extraction studies of uranyl compounds[25, 26]. Some relatively large coordination chemical shifts (δ complex—δ free ligand) for a phosphoryl phosphorus (−30 ppm)[25, 26] have been observed.

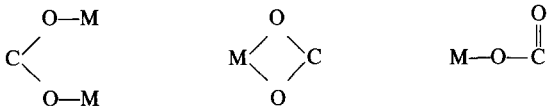
Phosphorus NMR data appear in Table 7. Several points should be noted. First, all of the UO_2^{+2} complexes have large coordination shifts compared to most other phosphoryl complexes measured[7, 27]. This effect was also noted in studies of UO_2^{+2} with phosphine oxides[25, 26]. Second, the UO_2^{+2} complexes exhibit a coordination shift of −14 to −15 ppm for the alkyl substituted compounds, −13 ppm for the phenyl substituted compound and −10 ppm for the ethoxy substituted compound. This would be expected based on the electron releasing character (alkyl > phenyl > ethoxy) of the substituted group and presumed resultant basicities of the phosphoryl groups (alkyl > phenyl > ethoxy).

Third, the nickel(II) complex did not exhibit a ^{31}P NMR signal, which indicates that it is paramagnetic and probably tetrahedral in configuration as expected.

Fourth, the addition of excess ligand to $[PhEtP(O)CH_2CO_2]_2UO_2$ demonstrates that ligand exchange, which is rapid on the NMR time scale, is occurring. A plot of the data (Fig. 7) shows a smooth curve for excess ligand added vs the change in chemical shift. A more complete study was prevented by the limited solubility of the ligand in CH_2Cl_2 as evidenced by the last point in Fig. 7.

PMR data for the complexes appear in Table 8. The Hg(II) and Pb(II) complexes exhibit the expected spectra. However, the UO_2^{+2} complexes have very broad peaks, such that many coupling constants could not be determined. In an effort to determine if ligand exchange occurs rapidly on the NMR time scale, a variable temperature study was carried out. As shown in Fig. 8, decreasing the temperature of the solution results in even poorer resolution. Upon returning the solution to ambient temperature, the initial spectrum is again observed.

Interpretation of the IR spectra of the complexes is not simple for several reasons. First, carboxylic acids are capable of coordinating three different ways to metal atoms[28].



Uranyl compounds are capable of both 6- and 7-coordination[29]. Thus, different types of carboxylic acid coordination, coupled with a variable coordination number of uranium could lead to numerous isomeric compounds of the general formula L_2UO_2. Furthermore, the difficulties encountered with the interpretation of the phosphoryl region of the free ligand's spectra and the extreme difficulties of isolating the pure alkali metal salts of the ligands (see experimental) further serve to mask analysis of the IR data.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Varian Associates DP-60 Spectrometer at 24.3 MHz on solutions as described previously[30]. Chemical shifts are accurate to ± 0.4 ppm. Proton spectra were recorded on a Varian Associates A 60A Spectrometer or a Perkin–Elmer R 20A Spectrometer at 60 MHz. The decoupling experiment on Ph(*s*-Bu)P(O)H was performed on a Varian Associates HA-100 Spectrometer at the National Institutes

Table 7. ^{31}P data for phosphorylacetic acid complexes

Compound	δ_P Ligand (ppm)	δ_P Complex (ppm)	Δ_P[a]
$[Ph_2P(O)CH_2CO_2]_2Pb$	-30.9(.2)	-34.8(.2)	- 3.9
$[Ph_2P(O)CH_2CO_2]_2Ni$	-30.9(.2)	b	--
$[Ph_2P(O)CH_2CO_2]_2Hg$	-30.9(.2)	-34.5(.2)	- 3.6
$[Ph_2P(O)CH_2CO_2]_2UO_2$	-30.9(.2)	-44.1(.2)	-13.2
$[Ph(EtO)P(O)CH_2CO_2]_2UO_2$	-36.9(.2)	-47.3(.4)	-10.4
$[PhEtP(O)CH_2CO_2]_2UO_2$	-42.3(.3)	-56.8(.2)	-14.5
$[Ph(i\text{-}Pr)P(O)CH_2CO_2]_2UO_2$	-46.0(.3)	-60.1(.3)	-14.1
$[Ph(n\text{-}Bu)P(O)CH_2CO_2]_2UO_2$	-40.4(.2)	-55.4(.3)	-15.0
$PhEtP(O)CH_2CO_2^-K^+$	-42.3(.3)	-40.1(.3)	+ 2.2
$PhEtP(O)CH_2CO_2^-Na^+$	-42.3(.3)	-41.9(.1)	+ 0.4

Exchange Study of $[PhEtP(O)CH_2CO_2]_2UO_2$

δ (ppm)	Excess Ligand (g)	Peak Width[c] (Hz)
-56.8	0	70
-55.6	0.0566	80
-54.6	0.1071	100
-54.3[d]	0.2103	120

[a] δ complex - δ ligand.

[b] Paramagnetic, no signal observed.

[c] Estimated peak width at half-height.

[d] Limit of solubility of ligand reached; not all ligand dissolved.

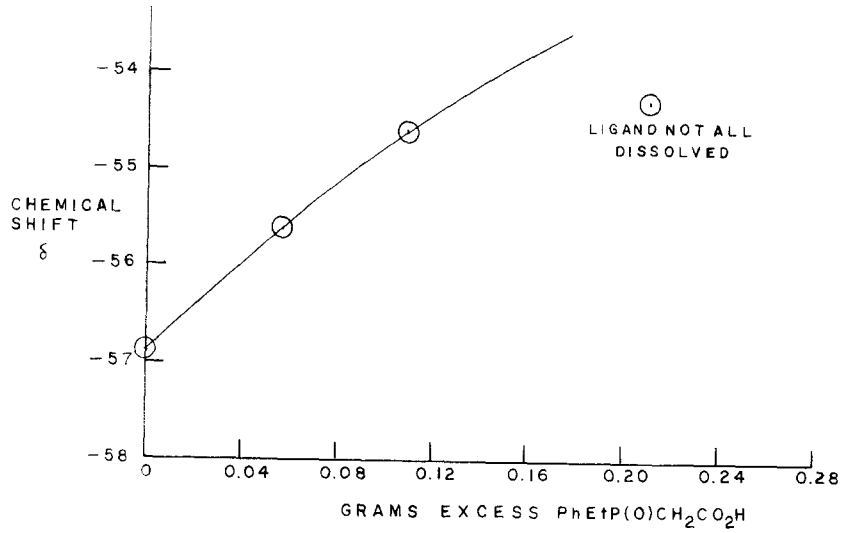


Fig. 7. The variation of the ^{31}P chemical shift of $[PhEtP(O)CH_2CO]_2UO_2$ in CH_2Cl_2 with excess phosphorylacetate ligand.

of Health, Bethesda, Maryland. M.ps were recorded on a Mel-Temp m.p. apparatus and are reported uncorrected. Microanalyses were performed by Dr. Franz Kasler, University of Maryland and by Galbraith Laboratories, Knoxville, Tennessee. IR spectra were recorded on a Perkin-Elmer Model 331 Infrared Spectrophotometer in KBr pellets.

$Ph_2P(O)H$

The syntheses of this and the other compounds, $PhRP(O)H$ and $R_2P(O)CH_2CO_2H$, roughly follow the published procedure[2]. However, when the exact procedure as given by earlier authors[2] was used, poor yields of very impure products were obtained. It appears that there exist some errors in the translated paper. Our procedure follows.

To the Grignard solution prepared from 24.3 g Mg (1.00 mole) and 157 g bromobenzene (1.00 mole) in 700 ml ether was added dropwise, 41.4 g of $(EtO)_2P(O)H$ (0.30 ml) in 150 ml Et_2O. Upon complete addition, the solution was refluxed for one hour, cooled to

Table 8. PMR data for phosphorylacetic acid complexes

Compound	Pattern	Integration (theory)	δ (ppm)	Assignment	$J_{(Hz)}$
$[Ph_2P(O)CH_2CO_2]_2Hg$	multiplet	5.00 (5)	7.95-7.09	phenyl	
	doublet	0.81 (1)	3.35	PCH_2CO_2	$J_{\underline{PCH}}$= 14
$[Ph_2P(O)CH_2CO_2]_2Pb$	multiplet	5.00 (5)	7.91-7.02	phenyl	
	doublet	1.04 (1)	3.28	PCH_2CO_2	$J_{\underline{PCH}}$= 13
$[Ph_2P(O)CH_2CO_2]_2UO_2$	multiplet	5.00 (5)	8.32-7.30	phenyl	
	doublet	0.92 (1)	3.99	PCH_2CO_2	$J_{\underline{PCH}}$= 11
$[PhEtP(O)CH_2CO_2]_2UO_2$	multiplet	1.93 (2)	8.58-7.85	o-phenyl	
	multiplet	2.88 (3)	7.68-7.30	m,p-phenyl	
	doublet of triplets	3.00 (3)	1.33	CH_3	$J_{\underline{PCCH}}$= 19
	broad	1.93 (2)	4.50-3.55	PCH_2CO_2	$J_{\underline{HCCH}}$= 7
	broad	2.14 (2)	3.17-2.30	PCH_2CH_3	
$[Ph(i\text{-}Pr)P(O)CH_2CO_2]_2UO_2$	multiplet	1.84 (2)	8.40-7.86	o-phenyl	
	multiplet	2.79 (3)	7.65-7.15	m,p-phenyl	
	broad	1.00 (1)	3.33-2.44	$PCH(Me)_2$	
	broad	1.78 (2)	4.30-3.53	PCH_2CO_2	
	multiplet	6.00 (6)	1.86-1.03	CH_3	
$[Ph(n\text{-}Bu)P(O)CH_2CO_2]_2UO_2$	multiplet	1.88 (2)	8.44-7.90	o-phenyl	
	multiplet	2.84 (3)	7.67-7.19	m,p-phenyl	
	broad		3.86	PCH_2CO_2	J_{PCH}= 11
	broad	11.0 (2)	2.18-1.02	$PCH_2CH_2CH_2CH_3$	
	broad	(4)		$PCH_2CH_2CH_2CH_3$	
	triplet	(3)	0.73	CH_3	$J_{\underline{HCCH}}$= 6.8
$[Ph(EtO)P(O)CH_2CO_2]_2UO_2$	multiplet	5.00 (5)	8.20-7.40	phenyl	
	broad	2.21 (2)	3.61	PCH_2CO_2	J_{PCH}= 16
	broad	2.14 (2)	3.65-3.15	$POCH_2$	
	triplet	3.15 (3)	1.26	CH_3	$J_{\underline{HCCH}}$= 7.1
$PhEtP(O)CH_2CO_2^-K^+$	multiplet	5.00 (5)	7.95-7.38	phenyl	
	doublet	2.18 (2)	3.06	PCH_2CO_2	$J_{\underline{PCH}}$= 15.5
	doublet of quartets	2.21 (2)	2.53-1.85	PCH_2CH_3	$J_{\underline{PCH}}$= 12
	doublet of triplets	3.18 (3)	0.99	CH_3	$J_{\underline{PCCH}}$= 18.7
					$J_{\underline{HCCH}}$= 7.3

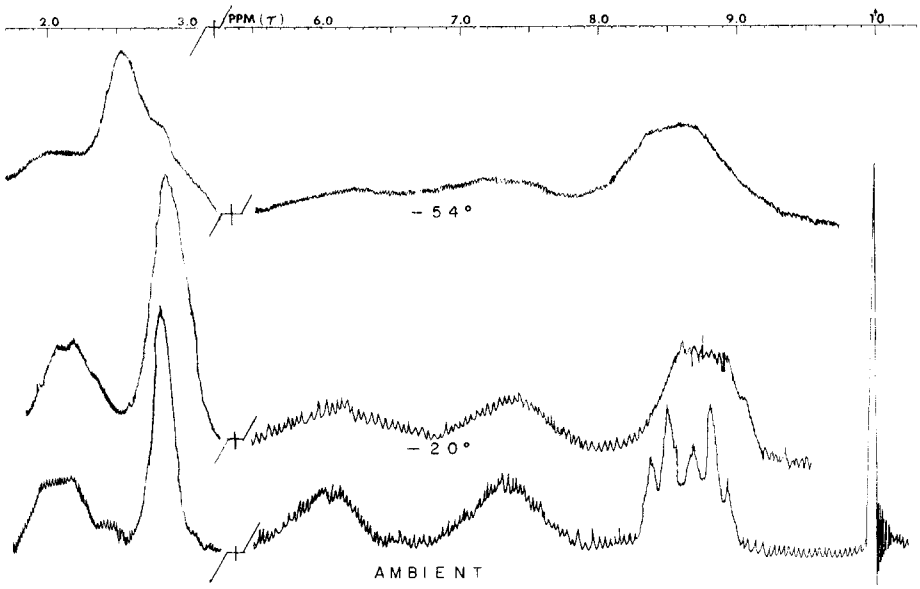


Fig. 8 Variable temperature proton spectra of $[PhEtP(O)CH_2CO_2]UO_2$ in $CDCl_3$.

room temperature and hydrolyzed with deoxygenated 8 M HCl until two layers separated. The ether layer was removed and the water layer extracted with four 150 ml portions of benzene. The combined organic fractions were then extracted with enough 75 ml portions of deoxygenated saturated $NaHCO_3$ solution until the HCl in the organic layer was neutralized. The mixture was dried over Na_2SO_4, decanted and the solvents removed with a rotary evaporator. The yields generally were about 90% (58 g) of a slightly impure (^{31}P and PMR spectra) yellow oil, $Ph_2P(O)H$. The compound was used without further purification in the synthesis of $Ph_2P(O)CH_2CO_2H$. Of five attempts to distill the compound, four led to decomposition to Ph_2PH and Ph_2PO_2H as identified by ^{31}P NMR spectra. One small sample was successfully distilled at 148–153° at 0.05 mm of Hg for spectral analysis.

Ph(EtO)P(O)H

Dichlorophenylphosphine (321 g, 1.79 mole) was added to 190 g of EtOH (4.12 mole) cooled to 0° with an ice bath. Upon complete addition, the solution was stirred for a half hour and anhydrous ether (1.5 l.) was added. The mixture was again cooled to 0° and 262 g of diethylamine (3.59 mole) was added, dropwise. (**CAUTION**, the addition of the amine results in a vigorous reaction.) When the addition was completed, the solution was stirred for one hour and filtered through a fine frit filter under N_2. The salts were washed with one liter of ether and the combined organic fractions were placed on a rotary evaporator to remove the ether. Vacuum distillation of the crude product with an oil bath (128°) yielded 258 g (83%) of the compound, b.p. 108°, 0.6 mm of Hg (lit. [13], 102–103°, 0.2 mm).

PhRP(O)H: R = Et, *i*-Pr, *n*-Bu, *sec*-Bu

To 0.6 mole of the appropriate Grignard reagent prepared in 400 ml ether and cooled to 10°, was added, dropwise, 45 g of Ph(EtO)P(O)H (0.26 mole) in 150 ml ether. Upon complete addition, the mixture was refluxed for one hour, cooled to slightly below room temperature and hydrolyzed with 25% H_2SO_4 until the solids coagulated (approx. 75 ml). Chloroform (450 ml) was added and the solids allowed to settle. The organic layer was decanted and the solids washed with four 150 ml portions of ether. The combined decantate and ether washings were extracted with 100 ml portions of a saturated deoxygenated $NaHCO_3$ solution until it was evident that the acid in the organic layer was neutralized. The organic layer was allowed to stand overnight with anhydrous sodium sulfate, then decanted and the solvents removed with a rotary evaporator. The resulting oils were generally over 90% pure when checked by ^{31}P NMR and PMR spectra and used without further purification in the synthesis of the respective phosphorylacetic acids. Small quantities were purified by molecular distillation. Attempts with normal vacuum distillation procedures resulted in the eventual decomposition to PhRPH and (probably) $PhRPO_2H$ as identified by ^{31}P NMR. It appeared that the decomposition was self-catalyzed and possibly small quantities could be distilled without large decomposition at higher pressures. However, no problems were encountered at very low pressures. The yields were R = *n*-Bu (45%), R = *sec*-Bu (55%) and R = *i*-Pr (90%). The b.ps and analysis are given below.

PhEtP(O)H, b.p. 65° at 8×10^{-5} mm of Hg (lit. [31], 117–118° at 2 mm. *Anal.* Calcd for $C_8H_{11}OP$: C, 62.30; H, 7.20. Found: C, 62.65; H, 7.19.

Ph*n*-BuP(O)H, b.p. 75° at 8×10^{-5} mm (lit. [13], 136–138° at 2.9 mm). *Anal.* Calcd for $C_{10}H_{15}OP$: C, 65.92; H, 8.30. Found: C, 66.18; H, 8.15.

Ph*sec*-BuP(O)H, b.p. 75° at 8×10^{-5} mm. *Anal.* Calcd for $C_{10}H_{15}OP$: C, 65.92; H, 8.30. Found: C, 65.65; H, 8.20.

Ph*i*-PrP(O)H, b.p. 50° 3×10^{-5} mm. *Anal.* Calcd for $C_9H_{13}OP$: C, 64.27; H, 7.79. Found: C, 63.36; H, 7.20.

$PhRP(O)CH_2CO_2H$: R = Ph, Et, *i*-Pr, *n*-Bu, -OEt, *sec*-Bu

To a 500 ml solution of absolute EtOH containing 0.48 mole of freshly prepared NaOEt cooled with an ice bath, was added rapidly 0.24 mole of the appropriate phosphinous acid in 150 ml absolute EtOH. Solid chloroacetic acid (26.8 g, 0.23 mole) was added and the mixture was stirred and refluxed for 6–10 hr. When R is Ph, it became necessary to add another 500 ml absolute EtOH to the reaction mixture to insure sufficient solvent to stir the mixture. The mixture was allowed to cool, the solvents removed by a rotary evaporator, and the residue dissolved in 200–300 ml distilled water. The solution was extracted twice with 100–200 ml portions of $CHCl_3$, and the $CHCl_3$ extracts were discarded. The pH of the aqueous solution was adjusted to 5 with 25% H_2SO_4 and extracted four times with 100–200 ml portions of $CHCl_3$. Removal of the $CHCl_3$ resulted in a gummy residue. Crystallization method, recrystallization solvent, yields, m.p. and analytical results are given below.

$Ph_2P(O)CH_2CO_2H$: 80 ml of a 1:1 methylethyl ketone–hexane solution; acetonitrile; 75%; m.p., 144–146° (lit. [2], 144–145°). *Anal.* Calcd for $C_{14}H_{13}O_3P$: C, 64.61; H, 5.00; P, 11.93. Found: C, 64.52; H, 5.04; P, 11.98.

PhEtP(O)CH_2CO_2H: 80 ml of a 1:3 MEK–hexane solution; acetonitrile; 70% m.p., 129–130° (lit. [2], 129–130°). *Anal.* Calcd for $C_{10}H_{13}O_3P$: C, 56.60; H, 6.17; P, 14.59. Found : C, 56.84; H, 5.90; P, 14.57.

Ph*i*-PrP(O)CH_2CO_2H: 80 ml of a 1:3 MEK–hexane solution; 1:1 MEX–hexane; 20%, m.p. 137–139°. *Anal.* Calcd for $C_{11}H_{15}O_3P$: C, 58.40; H, 6.68; P, 13.70. Found: C, 58.28; H, 6.78; P, 13.70.

Ph*n*-BuP(O)CH_2CO_2H: 80 ml of 1:3 MEK–hexane; 1:1 acetone–hexane; 53%; m.p. 95–96° (lit. [2], 95.5–96.5°). *Anal.* Calcd for $C_{12}H_{17}O_3P$: C, 59.99; H, 7.13; P, 12.90. Found: C, 59.71; H, 7.04; P, 13.20.

Ph(EtO)P(O)CH_2CO_2H: 1:1 MEK–hexane, crystals appeared after standing six months; 1:1 MEK–hexane; 40%; m.p. 92–94° (lit. [2], 92.5–93.5°). *Anal.* Calcd for $C_{10}H_{13}O_4P$: C, 52.63; H, 5.74. Found: C, 52.69; H, 5.64.

Ph*sec*-BuP(O)CH_2CO_2H: 80 ml of 1:3 MEK–hexane; crystals formed over a two week period; 1:1 MEK–hexane; 38%, m.p. 146–148°. *Anal.* Calcd for $C_{12}H_{17}O_3P$: C, 59.99; H, 7.13; P, 12.90. Found: C, 59.85; H, 7.00; P, 12.81.

Treatment of PhEtP(O)H *with* NaOEt

Solutions of NaOEt and PhEtP(O)H were prepared as above. The addition process was reversed so that the appropriate amount of NaOEt solution was added to an EtOH solution of PhEtP(O)H. After each addition, an aliquot was withdrawn and the ^{31}P NMR spectrum determined. Upon complete addition, the reaction was completed and worked up in the usual manner. No significant differences were detected in purity or yield of PhEtP(O)CH_2CO_2H.

$[Ph_2P(O)CH_2CO_2]_2UO_2$

One gram of diphenylphosphorylacetic acid (3.85 mmole) was placed in an Erlenmeyer flask. Sodium hydroxide (3.85 mmole from a 0.1000 M solution) was added from a buret. Uranyl nitrate hexahydrate (0.96 g, 1.92 mmole) was dissolved in 10 ml H_2O and added dropwise while the solution was stirred magnetically. The compound precipitated immediately as a yellow microcrystalline solid. The solid was removed by filtration, washed with cold water and dried at room temperature and 0.2 mm. Attempts to recrystallize this and all of the other analogous compounds led to partial decomposition. Prepared similarly were [Ph(*i*-Pr)P(O)$CH_2CO_2]_2UO_2$, [Ph(*n*-Bu)P(O)$CH_2CO_2]_2UO_2$, [PhEtP(O)$CH_2CO_2]_2UO_2$, [Ph(EtO)P(O)$CH_2CO_2]_2UO_2$, $[Ph_2P(O)CH_2CO_2]_2Hg$, $[Ph_2P(O)CH_2CO_2]_2Cu$, $[Ph_2P(O)CH_2CO_2]_2Pb$, $[Ph_2P(O)CH_2CO_2]_2Ni$. These were the only compounds that could be isolated as reasonably pure compounds as they precipitated immediately. Attempts to isolate complexes by extraction of the aqueous solution with chloroform and removal of the solvents with a rotary evaporator invariably resulted in solids that had low, wide (20–50°) m.ps and poor elemental analyses. Successive recrystallizations led to even poorer results. The yields, colors, m.ps, and analyses are given.

$[Ph_2P(O)CH_2CO_2]_2Ni$: 31%, green, m.p. 214–215°. *Anal.* Calcd for $C_{28}H_{24}O_6P_2Ni$: C, 58.26; H, 4.19. Found: C, 56.89; H, 4.63.

$[Ph_2P(O)CH_2CO_2]_2Pb$: 93% colorless, m.p. 149–153°. *Anal.* Calcd for $C_{28}H_{24}O_6P_2Pb$: C, 46.34; H, 3.33; P, 8.54. Found: C, 45.36; H, 3.51; P, 7.96.

$[Ph_2P(O)CH_2CO_2]_2UO_2$: 94%, yellow, m.p. 200–202°. *Anal.* Calcd for $C_{28}H_{24}O_8P_2U$: C, 42.65; H, 3.07; P, 7.86. Found: C, 41.93; H, 3.08; P, 7.70.

$[Ph_2P(O)CH_2CO_2]_2Cu$: 80%, green, m.p. 195–198°. *Anal.* Calcd for $C_{28}H_{24}O_6P_2Cu$: C, 57.78; H, 4.16. Found: C, 57.49; H, 4.72.

$[Ph_2P(O)CH_2CO_2]_2Hg$: 77%, colorless, m.p. 193–197°. Calcd for $C_{28}H_{24}O_6P_2Hg$: C, 46.77; H, 3.36. Found: C, 45.63; H, 3.60.

$[Ph(EtO)P(O)CH_2CO_2]_2UO_2$: 77%, cream, m.p. 212–215°. *Anal.* Calcd for $C_{20}H_{24}O_{10}P_2U$: C, 33.16; H, 3.34; P, 8.55. Found: C, 32.20; H, 2.84; P, 8.36.

$[PhEtP(O)CH_2CO_2]_2UO_2$: 54%, yellow, m.p. 165–170°. *Anal.* Calcd for $C_{20}H_{24}O_8P_2U$: C, 34.69; H, 3.49; P, 8.95. Found: C, 33.80; H, 3.93; P, 9.08.

[Ph*i*-PrP(O)$CH_2CO_2]_2UO_2$: 72%, yellow, m.p. 180–185°. *Anal.* Calcd for $C_{22}H_{28}O_8P_2U$: C, 36.67; H, 3.92; P, 8.60. Found: C, 34.99; H, 3.49: P, 8.10.

[Ph*n*-BuP(O)$CH_2CO_2]_2UO_2$: 92%, yellow, m.p. 130–136° *Anal.* Calcd for $C_{24}H_{32}O_8P_2U$: C, 38.51; H, 4.31; P, 8.28. Found: C, 38.42; H, 3.93; P, 8.19.

PhEtP(O)$CH_2CO_2^-Na^+$

One gram of PhEtP(O)CH_2CO_2H (4.72 mmole) was dissolved in 10 ml of EtOH and 4.72 mmole of NaOH. The solution was stirred for one hour and evaporated to dryness under a vacuum. The residue was dissolved in $CHCl_3$. Upon standing overnight, the salt crystallized. The salts proved too hygroscopic for analytical purposes. Typically, a small amount of the salt will dissolve in its water of hydration in less than one minute in moist Maryland atmosphere. Proton and ^{31}P NMR data were recorded in D_2O and H_2O respectively. IR data were recorded in KBr pellets with no effort made to eliminate water from the spectrum. Similar procedures were used to prepare PhEtP(O)$CH_2CO_2^-K^+$.

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