

## <sup>31</sup>P NMR Study on Some Phosphorus-Containing Compounds

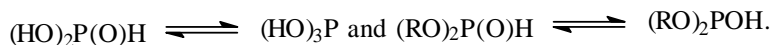
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**Abstract:** <sup>31</sup>P NMR has become a widely applied spectroscopic probe of the structure of phosphorus-containing compounds. Meanwhile, the application of <sup>31</sup>P NMR has been rapidly expanded to biochemistry and medicinal chemistry of phosphorus-containing compounds because the growing importance of the phosphorus compounds is now widely realized. We report here the results of <sup>31</sup>P NMR study on some phosphorus-containing compounds, namely, O-alkyl O-4-nitrophenyl methyl phosphonates with different alkyl chain-length (**MePO-n**), 4-nitrophenyl alkylphenylphosphinates with different alkyl chain-length (**PhP-n**), diethyl phosphono- acetonitrile anion and diethyl phosphite anion. Our results indicate that <sup>31</sup>P NMR can not only be applied to not only the study of the hydrolytic reactions of MePO-8 and PhP-8 but also be applied to the study of the presence of the anions of diethylphosphonoacetonitrile and diethyl phosphite in nucleophilic reactions.

**Keywords:** <sup>31</sup>P NMR, phosphorus-containing compounds, nucleophilic reaction.

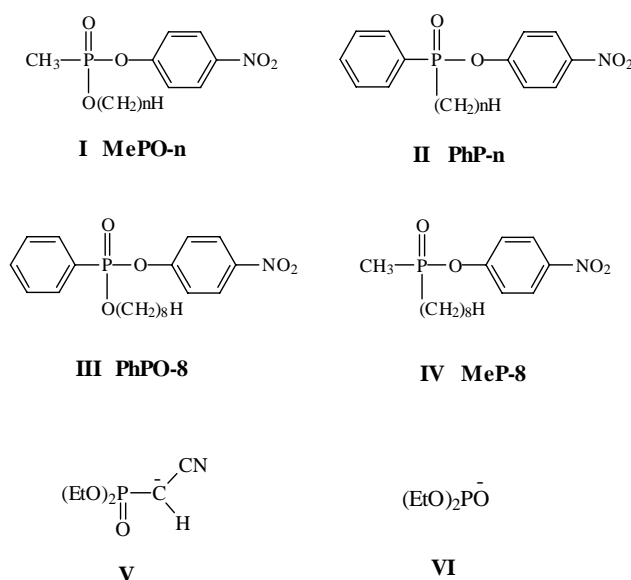
In view of the facts that the phenomena of aggregation are inseparably related to life processes and that phosphorus-containing compounds are one of the essential building blocks of life, we have studied the aggregation behavior of some phosphonates and phosphinates<sup>1</sup>. The application of NMR to the problems in chemistry has become rather popular. In phosphorus-containing compounds, phosphorus is a central or backbone atom in molecular structures. <sup>31</sup>P NMR is of importance and special value in phosphorus chemistry. But, <sup>31</sup>P NMR of phosphorus-containing compounds is very complicated<sup>2</sup> because in these compounds, phosphorus is multivalent *etc.*. Normally, phosphorus has two stable valence states, *i.e.*, trivalent and pentavalent. Besides that, in phosphorus acid and its monoalkyl ester and dialkyl ester, there are tautomerization equilibriums, *i.e.*,



Furthermore, there are three-, four-, five- and six- coordinated phosphorus compounds, *i.e.*,  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{PCl}_5$ ,  $\text{PCl}_6^-$ . In addition, there is the polyphosphate, in which phosphorus appears in the molecular backbone, *etc.* However, there is also no convenient quantitative correlation between the chemical shift of <sup>31</sup>P NMR and the nature of the atoms or groups bonded to phosphorus atom. Meanwhile, it is interesting to note that in the Horner-Emmons modification of the Wittig reaction<sup>4</sup> and the nucleophilic reaction<sup>5,6</sup>, the anions of some phosphorus-containing compounds, namely, diethyl phosphonoacetonitrile anion and diethyl phosphite anion, play important roles in the

reactions. The Horner-Emmons modification of the Wittig reaction of aldehydes and ketones with the anions of substituted diethyl phosphonoacetonitrile to synthesize  $\alpha$ ,  $\beta$ -unsaturated nitriles can be accomplished in excellent yields<sup>4</sup>. Aryl iodides react rapidly with potassium dialkyl phosphates,  $(RO)_2POK^+$  in liquid ammonia under 350 nm irradiation to form dialkyl arylphosphonates in 87-96% yield<sup>5,6</sup>. Dialkyl phosphite anion is an excellent nucleophile. Consequently, it is necessary to accumulate empirical data on  $^{31}P$  NMR chemical-shifts of phosphorus-containing compounds. The structures of some phosphorus-containing compounds used in present work are shown in **Scheme 1**.

Scheme 1



## Experimental

**MePO-n**, **PhP-n**, **PhPO-8** and **MeP-8** have been synthesized in our laboratory and reported elsewhere<sup>1</sup>. Diethyl phosphonoacetonitrile was purchased from Aldrich Co. and used without further purification. Diethyl phosphite was obtained from the Department of Heteroatom Chemistry of Shanghai Institute of Organic Chemistry as a gift.

## Physical measurements

$^{31}P$  NMR spectra were obtained on a Varian FX-90Q or DRX 400 Bruker Co. spectrometer with 85%  $H_3PO_4$  as the external standard. Chemical shifts ( $\delta$ ) are expressed in ppm.  $^1H$  NMR was measured with Bruker AM 300 NMR spectrometer. The experimental uncertainty is less than 2%. The measurements of hydrolytic rate constants of **PhP-8** and **MePO-8** in DX- $H_2O$  buffer (which is a 0.064 M NaOH + 0.05 M KCl) at  $\Phi=0.05$  were performed on Perkin-Elmer 559 or Perkin-Elmer Lambda 5 UV-Vis spectrometers equipped with a thermostated cell holder at 35°C by monitoring the formation of the *p*-nitrophenol anion at 410nm, as previously described<sup>7</sup>.  $\phi$  is the

volume fraction of the organic solvent in the binary aquiorghano solvent.

### Results and Discussion

In <sup>31</sup>P NMR, a more positive chemical shift corresponds to a upfield shift<sup>2,8</sup>, and corresponds to a higher charge density on phosphorus atom. **Table 1** indicates <sup>31</sup>P chemical shifts of **MePO-n**, **PhP-n**, **PhPO-8** and **MeP-8** in CDCl<sub>3</sub>. From these data, the following conclusions might be deduced:

- 1) The <sup>31</sup>P chemical shifts for **MePO-n** and **PhP-n** are independent of the alkyl chain-length within experimental uncertainty.
- 2) The relative effects of Me and Ph can be found by comparing **MePO-8** ( $\delta=28.24$ ) with **PhPO-8** ( $\delta=15.80$ ), or **MeP-8** ( $\delta=63.37$ ) with **PhP-8** ( $\delta=50.16$ ). These results show that the electron-pair donating ability of the methyl group is larger than that of phenyl group.
- 3) Although the donating ability of the methyl group is larger than that of the phenyl group, the  $\delta$ -value ( $\approx 28$ ) of MePO-n is still smaller than that ( $\delta \approx 50$ ) of the PhP-n. This indicates that their chemical shift depends mainly on the nature of the atom directly bonded to the phosphorus atom, in other words, the electron-pair accepting ability of the alkoxy group is much larger than that of the alkyl group.

**Table 1** <sup>31</sup>P NMR chemical shift ( $\delta$ , ppm) of **MePO-n**, **PhP-n**, O-octyl O-4-nitrophenyl phenylphosphonate (**PhPO-8**) and 4-nitrophenyl octylmethylphosphinate (**MeP-8**) with 85% H<sub>3</sub>PO<sub>4</sub> as the external standard.

Phosphorus-containing compounds	Chemical shift (ppm)	Phosphorus-containing compounds	Chemical shift (ppm)
<b>MePO-4</b>	28.10	<b>PhP-4</b>	49.99
<b>MePO-8</b>	28.24	<b>PhP-8</b>	50.16
<b>MePO-12</b>	28.14	<b>PhP-10</b>	50.28
<b>MePO-16</b>	28.24	<b>PhP-16</b>	50.23
<b>PhPO-8</b>	15.80	<b>MeP-8</b>	63.37

The hydrolytic rate constants of **PhP-8** and **MePO-8** have been measured in  $\Phi=0.05$  DX-H<sub>2</sub>O, which is an aqueous buffer (0.064 M NaOH+0.05 M KCl). In these experiments, the concentration of **PhP-8** is  $9.59 \times 10^{-6}$  M and the concentration of **MePO-8** is  $9.93 \times 10^{-6}$  M. These concentrations are less than their critical aggregate concentrations (CAGC) in  $\Phi=0.05$  DX-H<sub>2</sub>O. The  $k_{ob}$  of **PhP-8** is  $7.11 \times 10^{-3}$  S<sup>-1</sup> and the  $k_{ob}$  of **MePO-8** is  $6.60 \times 10^{-2}$  S<sup>-1</sup>. The  $k_{ob}$  of **PhP-8** is less than that of **MePO-8** because the P-atom of **MePO-8** is more electron-pair deficient, thus more prone to nucleophilic attack than that of **PhP-8**. This result is consistent with the <sup>31</sup>P NMR data.

Furthermore, the existence of a carbanion intermediate **V** has been proposed<sup>4</sup> but not proven. In the reaction of diethylphosphonoacetonitrile with NaH, we have now demonstrated its presence by the observation of the <sup>31</sup>P NMR spectrum of **V**. It shows a singlet peak with  $\delta=43.413$  ppm in DMSO-d<sub>6</sub>. But, in DMSO-d<sub>6</sub> the diethylphosphonoacetonitrile has  $\delta=17.253$  ppm. Therefore, by the change of <sup>31</sup>P NMR chemical shift, the presence of this anion can be demonstrated. It is worthy to note that there is a solvent effect in the measurement of <sup>31</sup>P NMR of diethylphosphonoacetonitrile, namely, in CDCl<sub>3</sub> its  $\delta=15.027$  ppm and in DMSO-d<sub>6</sub> its  $\delta=17.253$  ppm.

J.F. Bunnett *et al.*<sup>5,6</sup> have reported diethyl phosphite anion as an excellent nucleophile in  $S_{RN}1$ . The precursor of diethyl phosphite anion is diethyl phosphite. It is well known that there is a tautomeric equilibrium for diethyl phosphite., namely ,

$(C_2H_5O)_2P(O)H \rightleftharpoons (C_2H_5O)_2POH$  . We have now demonstrated the existence of **VI** by observation of the  $^{31}P$  NMR spectrum.  $^{31}P$  NMR spectrum of diethyl phosphite shows a  $^1H - ^{31}P$  split. There are doublet-doublet peaks in  $^{31}P$  NMR spectrum . The  $\delta$  values are 5.127 ppm and 8.760 ppm . Fortunately, diethyl phosphite reacts with NaH in DMSO- $d_6$  to form the diethyl phosphite anion (**VI**).  $^{31}P$  NMR spectrum of this anion in DMSO- $d_6$  shows a singlet peak with  $\delta = -139.59$  ppm. This result indicates that the diethyl phosphite anion  $(C_2H_5O)_2PO^-Na^+$  has formed. The results may serve as useful reference data for other phosphorus-containing compounds

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