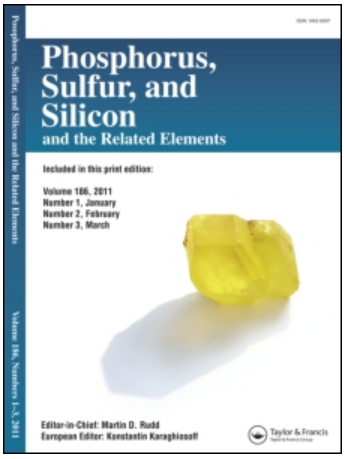


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND SUBSTITUENT EFFECT ON ^{31}P NMR CHEMICAL SHIFT OF ORTHO HYDROXYARYL DIALKYL PHOSPHINE OXIDES

Shusen Li[a]; Guoquan Wang[a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, P. R. China

To cite this Article Li, Shusen and Wang, Guoquan(1991) 'SYNTHESIS AND SUBSTITUENT EFFECT ON ^{31}P NMR CHEMICAL SHIFT OF ORTHO HYDROXYARYL DIALKYL PHOSPHINE OXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 1, 119 — 129
To link to this Article: DOI: 10.1080/10426509108027344
URL: http://dx.doi.org/10.1080/10426509108027344

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 119–129
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND SUBSTITUENT EFFECT ON ^{31}P NMR CHEMICAL SHIFT OF ORTHO-HYDROXYARYL DIALKYL PHOSPHINE OXIDES

SHUSEN LI and GUOQUAN WANG

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, P. R. China

(Received September 28, 1990; in final form December 18, 1990)

In this paper, the synthetic methods for the preparation of *o*-hydroxyaryl dialkyl phosphine oxides (**1**) are introduced. The title compounds with low bulky substituent are synthesized successfully by the reactions of the Grignard reagents with diethyl *o*-hydroxyarylphosphonates derived from the rearrangement of aryl dialkyl phosphates in good yields. The title compounds with high steric hindered alkyl groups can be prepared by the reaction of dialkyl *o*-chlorophenylphosphinate with sodium. Whether the dialkyl aryl phosphates on treatment with LDA undergo a rearrangement reaction is mainly determined by the nature of the substituents on the phenyl ring. If the substituent is en electron-donating group, the rearrangement reaction is predominant. If it is an electron-withdrawing one, the nucleophilic substitution reaction takes place.

The steric and polar effects of substituents on ^{31}P NMR chemical shifts for the title compounds are well described by the intramolecular local van der Waals interaction energy ($E_{VDW\text{-}P}$) and local dipole interaction energy ($E_{dip\text{-}P}$), which were calculated by MM2(85) program.

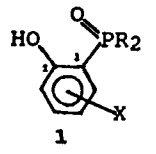
Key words: Synthesis *o*-hydroxyaryl dialkyl phosphine oxides; substituent effect; ^{31}P NMR chemical shifts; molecular mechanics.

INTRODUCTION

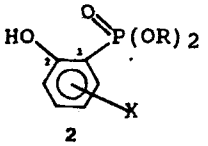
o-Hydroxyphenyl dialkyl phosphine oxides (**1**), may be reviewed as analogues of salicylic aldehyde. They may be potentially bioactive, and can be used as chelating agents. So, the investigation on the synthetic method of these compounds and the study on the relationship between structure and biochemical activity, the strength of intramolecular hydrogen-bond or substituent effect on their chelating ability are important and interesting. So far, there have been no reports on preparing such kinds of substance. We report here various methods for the preparation of these compounds and their derivatives.

In order to compare the properties of compounds **1** with dialkyl *o*-hydroxyaryl-phosphonates (**2**), a series of **2** are also synthesized by Melvin's method,[1] and obvious substituent effects on the Melvin's method are observed.

In order to estimate the substituent effects on ^{31}P NMR chemical shift in these compounds, molecular mechanics calculations are carried out and the intramolecular local dipole interaction energy of phosphorus atom ($E_{dip\text{-}P}$) was proposed to represent the polar effect of the substituents and intramolecular local van der Waals interaction energy of phosphorus atom ($E_{VDW\text{-}P}$) to serve as the steric effect. A good correlation of δ ^{31}P with $\Delta E_{dip\text{-}P}$ and $E_{VDW\text{-}P}$ is observed.



1



2

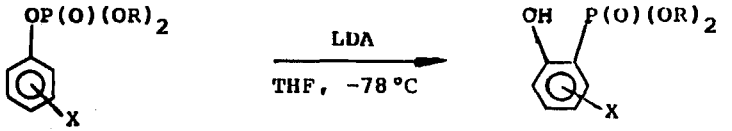
R	C_2H_5	C_2H_5	C_2H_5	C_2H_5	C_2H_5	$n\text{-}C_3H_7$	$i\text{-}C_3H_7$	$n\text{-}C_4H_9$	$i\text{-}C_4H_9$
X	H	3-CH_3	4-CH_3	5-CH_3	5-OCH_3	H	H	H	H
No.	1a	1b	1c	1d	1e	1f	1g	1h	1i
	2a	2b	2c	2d	2e	2f	2g	2h	

R	$i\text{-}C_4H_9$	$s\text{-}C_4H_9$	$n\text{-}C_5H_{11}$	$n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}$	$n\text{-}C_8H_{17}$
X	6-OCH_3	H	H	H	5-CH_3	H
NO.			1j	1k		1l
	2i	2j			2k	

RESULTS AND DISCUSSION

I. Synthesis and Reactions

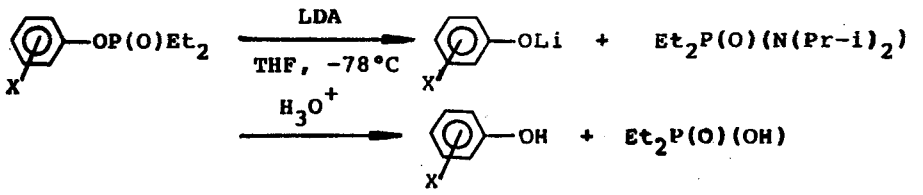
1. *The Reactions of aryl dialkylphosphinates with LDA.* Melvin reported that dialkyl aryl phosphates on treatment with lithium diisopropylamide (LDA) underwent rearrangement to yield dialkyl *o*-hydroxyphenylphosphonates.[1]



(1)

Since then, many papers have appeared on this kind of reaction.[2-12] If a similar rearrangement occurs for aryl dialkylphosphinates, it will be a good method for the preparation of *o*-hydroxyaryl dialkyl phosphine oxides.

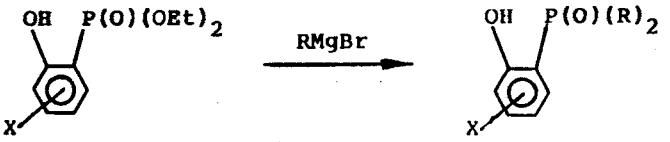
We carried out the reactions of aryl dialkylphosphinates with LDA under the same condition as Melvin did (−78°C, THF as solvent). Unfortunately, no rearrangement products were found, while phenol and dialkylphosphinic acids were identified as the main products by UV, ^1H and ^{31}P NMR methods, probably resulting from a nucleophilic substitution reaction:



(2)

An electron-withdrawing or -donating group on the phenyl ring did not change the reaction route and synthesis of the title compounds through the proposed rearrangement reaction was unsuccessful.

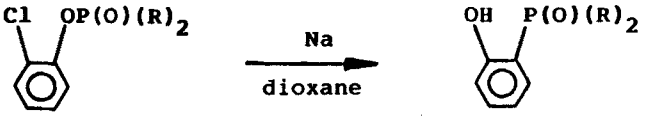
2. *The reaction of diethyl o-hydroxyarylphosphonates with Grignard reagents (method A).* A series of compounds **1** were synthesized by using the reaction of Grignard reagents with diethyl *o*-hydroxyarylphosphonates:



(3)

This method gave good yields for the compounds with normal alkyl groups (see Table I), but for those with secondary or tertiary alkyl groups, the yields were poor.

3. *The reaction of o-chlorophenyl dialkylphosphinates or diethyl o-chlorophenyl phosphate with sodium (method B).* The following method is useful for the synthesis of **1** with bulky R-groups.



(4)

For example, the formation of **1g** was achieved successfully by the reaction of *o*-chlorophenyl diisopropylphosphinate with sodium. When this method was used to prepare compounds **1a** and **2a**, we found that the yields of reaction (4) were much lower than those of reactions (3) and (1). Also, the isolation and purification of the products were much more difficult.

4 *The influence of the phenyl ring substituents on the rearrangement of dialkyl aryl phosphates.* In order to synthesize compounds **1** with various substituent on the phenyl ring, a series of dialkyl *o*-hydroxyaryl-phosphonates (**2**) were prepared. It was found that the substituents on the phenyl ring had a great influence on the rearrangement reaction (1) of diethyl aryl phosphates. When X were electron-donating groups (e.g., Me, MeO), the rearrangement takes place as the main reaction. But when X were electron-withdrawing groups, for example, *o*-nitrophenyl, no rearrangement product was found; instead *o*-nitrophenol was formed quantitatively. Similarly, for dialkyl 1- or 2-naphthyl phosphate, the rearrangement product was formed only in low yield, and naphthol was the main product. It shows that the rearrangement of $(RO)_2P(O)OAr$ induced by LDA will compete with the

TABLE I

Synthesis and the date of elemental analyses of compounds 1 and 2

compd	Method	Yield (%)	mp(°C) or bp(°C)/mm Hg	calculated C	calculated H	calculated P	found C	found H	found P
1a	A(B)	80(60)	135-136	60.60	7.63	15.63	15.64	7.75	15.14
1b	A	77	88-89	62.25	8.07	14.59	62.21	8.32	14.10
1c	A	85	81-82	62.25	8.07	14.59	62.03	8.28	14.13
1d	A	87	83-85	62.25	8.07	14.59	-----	----	-----
1e	A	82	49-50	57.89	7.51	13.57	57.60	7.79	13.11
1f	A	65	118-120	63.70	8.46	13.69	63.27	8.42	13.20
1g	B	40	82-84	63.70	8.46	13.69	63.41	8.59	13.23
1h	A	85	105-106	66.12	9.12	12.18	65.87	9.06	11.71
1i	A	45	129-130	66.12	9.12	12.18	65.86	8.91	11.64
1j	A	66	86-88	68.06	9.64	10.97	67.81	9.90	10.49
1k	A	78	72-73	69.65	10.07	9.98	69.37	10.32	9.53
1l	A	75	51-52	72.09	10.72	8.45	71.80	11.02	7.96
2a	ref. 1(B)	95(45)	93-95/0.05 (92-97/0.05)	52.28	6.57	13.46	52.02	6.42	13.39
2b	ref. 1	90	98-100/0.05 (97-101/0.06)	54.10	7.02	12.68	53.86	7.17	12.20
2c	ref. 1	91	97-100/0.05 (97-102/0.05)	54.10	7.02	12.68	53.84	7.13	12.76
2d	ref. 1	94	100-102/0.05	54.10	7.02	12.68	53.88	7.10	12.44
2e	ref. 1	95	115-118/0.05	50.77	6.58	11.90	50.73	6.69	11.54
2f	ref. 1	90	109-112/0.1	55.81	7.42	11.99	55.85	7.45	11.78
2g	ref. 1	88	90-93/0.1	55.81	7.42	11.99	55.54	7.33	11.65
2h	ref. 1	83	113-116/0.1	58.73	8.10	10.82	58.39	8.31	10.57
2i	ref. 1	80	106-108/0.1	56.95	7.97	9.79	56.67	8.26	9.31
2j	ref. 1	95	108-111/0.1	58.73	8.10	10.82	58.45	8.37	10.35
2k	ref. 1	90	140-142/0.1	64.02	9.33	8.69	-----	----	-----

* The bp values in the parentheses are from Reference 1.

nucleophilic substitution (S_N) reaction of $(i\text{-Pr})_2N^-$. The reaction products are mainly controlled by the leaving ability of aryloxy groups.

The spectroscopic data for all compounds are summarized in Table II, the MS data have been reported by us.[13]

TABLE II

Spectroscopic data of compounds synthesized

compd	IR (cm^{-1}) O-H	IR (cm^{-1}) P=O	IR (cm^{-1}) C-O-P	^1H NMR ($CDCl_3$/TMS)	^{31}P NMR ($CDCl_3$/ H_3PO_4 ext)
1a	3100	1115		7.6-6.7(m,4H,phenyl ring),2.0(m,4H,2xCH_2), 1.1(m,6H,2xCH_3)	59.03
1b	3050	1100		10.0(s,1H,OH),7.5-6.7(m,3H,phenyl ring), 2.4-1.6(m,7H,2xCH_2,CH_3),1.2(m,6H,2xCH_3)	66.42
1c	3120	1120		9.0(s,1H,OH),7.5-6.7(m,3H,phenyl ring), 2.4-2.0(m,7H,2xCH_2,CH_3),1.1(m,6H,2xCH_3)	65.45
1d	3100	1115		9.6(s,1H,OH),7.5-7.2(m,3H,phenyl ring), 2.6-2.0(m,7H,2xCH_2,CH_3),1.1(m,6H,2xCH_3)	60.18
1e	3050	1120		8.6(s,1H,OH),7.4-6.7(m,3H,phenyl ring), 3.8(s,3H,CH_3O),2.1(m,4H,2xCH_2),1.1(m,6H,2xCH_3)	57.75
1f	3050	1125		9.0(s,1H,OH),7.5-6.7(m,4H,phenyl ring), 2.2-0.8(m,14H,2xC_3H_7-n)	55.58
1g	3050	1115		9.1(s,1H,OH),7.5-6.9(m,4H,phenyl ring), 2.3(m,2H,2xCH),1.2(m,12H,4xCH_3)	67.21
1h	3050	1130		7.5-6.9(m,4H,phenyl ring), 2.2-0.9(m,18H,2xC_4H_9-n)	56.23
1i	3050	1140		7.5-6.8(m,4H,phenyl ring), 2.1-0.7(m,18H,2xC_4H_9-i)	55.16
1j	----	1130		7.5-6.8(m,4H,phenyl ring), 2.2-0.6(m,22H,2xC_5H_{11}-n)	56.01
1k	----	1140		7.6-6.8 (m,4H,phenyl ring), 2.2-0.8(m,26H,2xC_6H_{13}-n)	56.14
1l	----	1140		7.5-6.7(m,4H,phenyl ring), 2.3-0.7(m,34H,2xC_8H_{17}-n)	56.10
2a	3100	1250	1020	10.1(s,1H,OH),7.4-6.7(m,4H,phenyl ring), 3.9(q,4H,2xCH_2O),1.2(t,6H,2xCH_3)	22.39

TABLE II (*continued*)

compd	IR (cm^{-1}) O-H	P=O	C-O-P	^1H NMR ($CDCl_3$/TMS)	^{31}P NMR ($CDCl_3$/ H_3PO_4 ext)
2b	3080	1250	1020	10.4(s,1H,OH),7.4-6.6(m,3H,phenyl ring), 4.1(q,4H,2xCH_2O),2.2(s,3H,CH_3),1.3(t,6H,2xCH_3)	23.29
2c	3050	1255	1015	10.2(s,1H,OH),7.5-6.3(m,3H,phenyl ring), 4.1(q,4H,2xCH_2O),2.3(s,3H,CH_3),1.3(t,6H,2xCH_3)	22.92
2d	3100	1250	1020	10.0(s,1H,OH),7.3-6.7(m,3H,phenyl ring), 4.1(q,4H,2xCH_2O),2.3(s,3H,CH_3),1.3(t,6H,2xCH_3)	22.63
2e	3100	1250	1020	9.8(s,1H,OH),7.3-6.7 (m,3H,phenyl ring), 4.1(q,4H,2xCH_2O),3.8(s,3H,CH_3O),1.3(t,6H,2xCH_3)	21.99
2f	3100	1245	1000	10.2(s,1H,OH),7.6-6.9(m,4H,phenyl ring), 4.0(q,4H,2xCH_2O),1.5(m,4H,2xCH_2),0.9(m,6H,2xCH_3)	22.28
2g	3100	1295	1000	10.4(s,1H,OH),7.6-6.8(m,4H,phenyl ring), 4.6(m,2H,2xCH),1.3(q,12H,4xCH_3)	20.34
2h	3080	1245	1005	10.2(s,1H,OH),7.6-6.8(m,4H,phenyl ring), 4.1(q,4H,2xCH_2O),1.5(m,8H,4xCH_2),1.0(t,6H,2xCH_3)	22.34
2i	3050	1250	990	7.5-6.5(m,3H,phenyl ring), 4.2-3.6(m,7H,2xCH_2O,CH_3O),1.9-0.9(m,14H,2xC_3H_7-i)	22.41
2j	----	1250	995	10.4(s,1H,OH),7.6-6.8(m,4H,phenyl ring), 4.4(m,2H,2xCH),1.7-0.7(m,16H,2xCH_3,2xC_2H_5)	20.28
2k	----	1250	1000	7.3-6.8(m,3H,phenyl ring),4.1(q,4H,2xCH_2O), 2.3(s,3H,CH_3),1.7-0.9(m,11H,2xC_5H_{11}-n)	22.56

II. The Substituent Effect on ^{31}P NMR Chemical Shift in o-Hydroxyphenyl Dialkyl Phosphine Oxides and Dialkyl o-Hydroxyphenylphosphonates

The data in Table II indicate that the δ ^{31}P are influenced by both steric and polar effects of the substituents. Especially, the influence of the ring-substituents on δ ^{31}P can not be illustrated by only its polar effect. For example, the 3-methyl group in **1b** and 5-methyl group in **1d** are both located in meta position to the phosphorus atom. But they give large different influences on ^{31}P NMR chemical shift. The difference of δ ^{31}P between **1b** and **1d** (Δδ ^{31}P) is 6.24 ppm. Therefore, for compounds **1** and **2**, besides the steric effect of alkyl or alkoxy groups on the phosphorus atom, the influences of ring-substituents can not be described by only its polar effect. On the other hand, due to the fact that the ring substituents give their

influence on both hydroxyl and phosphoryl groups, there are no sets of polar parameters to be suitable for this kind of substituent effects.

In general, charge distribution which is calculated by quantum mechanical methods can be used to estimate the polar effect of the substituents. However, for heavy nuclei, in many cases, the charge is not the main factor to control the shielding effect. We tried to use MNDO method[14] to get the charge distribution of the molecules or to calculate the difference of the summation of the charge of each two substituents on the phosphorus atom (Δq). In some cases the Δq may be correlated with δ ^{31}P.[15] But no correlation between δ ^{31}P and q_P or Δq was found for compounds **1** and **2** (see Table III).

In recent years, molecular mechanics has been used to study steric and polar effects of substituents on NMR chemical shift of various nuclei.[16–21] Pachter *et al.*[22,23] suggested that intramolecular local charge interaction energy calculated by MM2 method when combined with intramolecular local van der Waals interaction energy could be used to illustrate polar and steric effects of polar substituents on NMR chemical shift, such as the effect of hydroxy group on δ ^{13}C NMR; however, Pachter's treatment is very tedious and time consuming. In our opinion, for compounds **1** and **2**, the resonant nucleus of the phosphorus atom is located in polar bonds. We propose that the polar effect of the substituents on ^{31}P NMR chemical

TABLE III

Charge distribution of compounds **1a–1e** and **2a–2e**

entry	q_P	$q_{C_{sp^2}}$	q_{C_1} (q_{O_1})	q_{C_2} (q_{O_2})	$q_{=O}$	Δq	$\delta^{31}P$
1a	0.646	-0.275	-0.129	-0.128	-0.628	0.646	59.03
1b	0.649	-0.279	-0.129	-0.128	-0.627	0.649	66.42
1c	0.642	-0.271	-0.129	-0.128	-0.627	0.649	66.45
1d	0.650	-0.278	-0.127	-0.129	-0.627	0.650	60.18
1e	0.621	-0.248	-0.128	-0.127	-0.626	0.621	57.75
2a	1.222	-0.331	-0.476	-0.476	-0.714	0.384	22.39
2b	1.222	-0.333	-0.476	-0.476	-0.714	0.381	23.29
2c	1.222	-0.328	-0.476	-0.476	-0.714	0.387	22.92
2d	1.223	-0.334	-0.476	-0.476	-0.741	0.380	22.63
2e	1.226	-0.304	-0.474	-0.474	-0.713	0.409	21.99

Δq(**1a–1e**) = $(q_{=O} + q_{C_{sp^2}}) - (q_{C_1} + q_{C_2})$.
Δq(**2a–2e**) = $(q_{=O} + q_{O_1}) - (q_{O_2} + q_{C_{sp^2}})$.

shift may be represented by their dipole interactions which can be evaluated by the dipole interaction energy (E_{dip}) easily. Therefore, the change of the dipole interaction energy for the phosphorus atom ($\Delta E_{dip\text{-}P}$) referred to the parent compound may be used to measure the polar effect of the substituents. The steric effect of the substituents on the NMR chemical shift of the phosphorus nucleus can be estimated by $E_{VDW\text{-}P}$ well.[16,17] Therefore, the polar and steric effect of substituents on ^{31}P NMR chemical shift may be described by $E_{dip\text{-}P}$ and $E_{VDW\text{-}P}$, which are given in Table IV.

The multiple regression analysis of $\delta\ ^{31}P$ with $\Delta E_{dip\text{-}P}$ and $E_{VDW\text{-}P}$ is carried out by Equation 1:

$$\delta\ ^{31}P = a\ \Delta E_{dip\text{-}P} + b\ E_{VDW\text{-}P} + c \qquad (1)$$

For compounds **1**: $a = 48.559$, $b = 8.017$, $c = -57.357$,
$T_a = 26.863$, $T_b = 5.718$, $T_c = -4.887$,
$r = 0.9313$, $n = 11$, CL% = 99.9
For compounds **2**: $a = -2.246$, $b = 5.030$, $c = 8.816$,
$T_a = -4.243$, $T_b = 8.107$, $T_c = 5.343$
$r = 0.9558$, $n = 11$, CL% = 99.9,

The correlation coefficient (r) indicates a good binary correlation between $\Delta E_{dip\text{-}P}$, $E_{VDW\text{-}P}$ and $\delta\ ^{31}P$ for compounds **1** and **2**. From the T-test values (T_a and T_b), it

TABLE IV

$E_{VDW\text{-}P}$, $E_{dip\text{-}P}$, $\Delta E_{dip\text{-}P}$ values for compounds **1** and **2***

entry	$E_{VDW\text{-}P}$	$E_{dip\text{-}P}$	$\Delta E_{dip\text{-}P}$	entry	$E_{VDW\text{-}P}$	$E_{dip\text{-}P}$	$\Delta E_{dip\text{-}P}$
1a	1.1795	-0.7371	0.0000	**2a**	2.7610	-5.8360	0.0000
1b	1.1867	-0.8709	-0.1338	**2b**	2.7658	-6.0340	-0.1980
1c	1.1613	-0.8086	-0.0715	**2c**	2.7382	-5.9616	-0.1256
1d	1.1500	-0.8259	-0.0888	**2d**	2.7298	-5.9980	-0.1620
1e	1.1945	-0.5634	0.1737	**2e**	2.7798	-5.4156	0.4204
1f	1.0799	-0.7373	-0.0002	**2f**	2.6913	-5.8356	0.0004
1g	2.3969	-0.7391	-0.0020	**2g**	2.4537	-5.7298	0.1062
1h	1.0182	-0.7368	-0.0003	**2h**	2.6511	-5.8421	-0.0061
1i	0.6982	-0.7687	0.0316	**2i**	2.7795	-5.5963	0.2397
1j	0.9883	-0.7368	0.0003	**2j**	2.2730	-5.7520	0.0840
1k	0.9843	-0.7352	0.0019	**2k**	2.5812	-6.0041	-0.1681

* Energy unit: kcal/mol.

can be found that the $E_{dip\text{-}P}$ and $E_{VDW\text{-}P}$ have similar important contribution to $\delta\ ^{31}P$.

It is interesting to find that although the 3-methyl group in **1b** and the 5-methyl group in **1d** are both in the meta position to the phosphorus atom, their $\Delta E_{dip\text{-}P}$ values are different (see Table III). Similar results for **2b** and **2d** are also observed. These results also indicate that the $E_{dip\text{-}P}$ or $\Delta E_{dip\text{-}P}$ can reflect the stereoelectronic interactions among the polar groups well.

In order to demonstrate the validity of our model, substituted *o*-phenyl diethylphosphinates (**3**) and substituted phenyl dihexyl phosphates (**4**) were also studied in which the steric effect could be neglected when the substituents were changed. Their $E_{VDW\text{-}P}$, $E_{dip\text{-}P}$, $\Delta E_{dip\text{-}P}$ and $\delta\ ^{31}P$ are given in Table V. Data in Table V show that the variation of $E_{VDW\text{-}P}$ of these two sets of compounds are small and have not any correlation with $\delta\ ^{31}P$. However, there exists an approximately linear correlation between $\delta\ ^{31}P$ and $\Delta E_{dip\text{-}P}$; the correlation coefficients (r) are 0.977 and 0.921 for compound **3** and **4** respectively:

$$\delta\ ^{31}P(3) = 58.96 - 5.645\ \Delta E_{dip\text{-}P}\quad n = 7,$$
$$r = 0.977,\quad \text{RMS} = 0.183,\quad \text{CL} = 99.9\% \qquad (2)$$

$$\delta\ ^{31}P(4) = -7.79 + 12.77\ \Delta E_{dip\text{-}P}\quad n = 7,$$
$$r = 0.921,\quad \text{RMS} = 0.167,\quad \text{CL} = 99.9\% \qquad (3)$$

Although the $\Delta E_{dip\text{-}P}$ can approximately represent the polar effect of substituents on $\delta\ ^{31}P$, it can not reflect the direction of shielding effect on $\delta\ ^{31}P$. Because the shielding direction of compounds **3** and **4** are opposite to one another, i.e., the same substituent in **3** is shielding, but in **4** is deshielding. Maybe the ΔE_{dip} gives only the magnitude of the effect; the direction of shielding effect may be determined by the symmetry of the electron cloud or orbitals.[15]

EXPERIMENTS AND CALCULATIONS

IR spectra (KBr disc) were recorded on a Shimadzu 400 spectrometer. ^1H NMR spectra were obtained on a Varian EM-3601 spectrometer with $CDCl_3$ as solvent and TMS as external standard. ^{31}P NMR spectra were taken from a FX-90Q spectrometer, with $CDCl_3$ as solvent and 85% H_3PO_4 as external standard. Melting points were uncorrected. All reactions were carried out in dried glassware under nitrogen atmosphere. THF was distilled over sodium and used in situ. 1,4-dioxane, ether and benzene were dried over sodium prior to use.

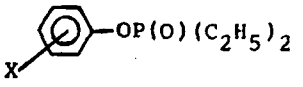
1. Dialkyl o-hydroxyarylphosphonates (**2**) *were prepared by Melvin's method.*[1]

2. Synthesis of dialkyl o-hydroxyaryl phosphine oxides (**1**). Method A: 0.03 mol **2a** in 100 ml benzene were added to 0.18 mol of Grignard reagent in ether. The mixture was boiled for 1.5 h to remove most of the ether. Then the reactants were stirred and refluxed for an additional 5–8 h, the reaction mixture was then carefully poured onto a cooled mixture of 150 ml 10% HCl and 400 ml of $CHCl_3$. The organic layer was separated, dried with anhydrous Na_2SO_4 and evaporated to give a crude product which was purified by crystallization from ethyl acetate or acetone-petroleum ether. Then the reactants were stirred and refluxed for an additional 5–8 h, the reaction mixture was then carefully poured onto a cooled mixture of 150 ml 10% HCl and 400 ml of $CHCl_3$. The organic layer was separated, dried with anhydrous Na_2SO_4 and evaporated to give a crude product which was purified by crystallization from ethyl acetate or acetone-petroleum ether.

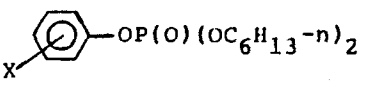
Method B: 0.05 mol of diethyl phenyl phosphate, phenyl diethylphosphinate or phenyl diisopropylphosphinate in 50 ml dioxane were added to 0.11 mol of a sodium suspension in 50 ml dioxane at 40°C. The mixture was stirred at 40°C for 5 h then kept over night at room temperature. Then 11 ml of

TABLE V

E_{dip-P}, ΔE_{dip-P}, and E_{VDW-P} values for compounds 3 and 4*



3



4

entry	X	E_{dip-P}	ΔE_{dip-P}	E_{VDW-P}	$\delta^{31}P$ [1]
3a	H	0.3472	0.0000	1.9546	58.90
3b	p-CH_3	0.3855	0.0383	1.9424	58.96
3c	p-CH_3O	0.3487	0.0015	1.9283	58.74
3d	m-CH_3O	0.3108	-0.0364	1.9680	59.03
3e	p-Cl	0.1703	-0.1769	1.9523	59.84
3f	p-Br	0.1940	-0.1532	1.9495	60.16
3g	p-NO_2	-0.0719	-0.4191	1.9577	61.28
4a	H	8.5564	0.0000	3.3470	-7.86
4b	p-CH_3O	8.5676	0.0115	3.3151	-7.40
4c	p-CH_3	8.5606	0.0042	3.3219	-7.61
4d	m-CH_3O	8.5526	-0.0038	3.3276	-7.92
4e	p-Cl	8.5425	-0.0139	3.3243	-7.97
4f	p-Br	8.5410	-0.0154	3.3184	-8.30
4g	p-NO_2	8.4689	-0.0875	3.3413	-8.81

* Energy unit kcal/mol.

concentrated hydrochloric acid was added to the mixture with stirring. The mixture was filtered and the filtrate was dried with anhydrous Na_2SO_4. Removal of solvent gave an oily residue, which was purified by distillation or recrystallization.

3. Molecular mechanics calculations. The MM2 force field[24] was used in this work and the program was the 1985 version.[25] In general, the most stable conformation for each molecule was selected to compare with each other. However, some of the compounds have two or more than two conformations having small difference of steric energies. In this case, the E_{dip} is taken as the Boltzmann averaged value.

The parameters for the bond length, bond angle, dihedral angle and bond moment which are not in the program are estimated by our laboratory.[17] It was found that the E_{dip} values calculated with the zero bond moment of O—Lp bond (Lp—Lone pair electrons) give better correlation results for com-

pounds **1** and **2**, but slightly poorer ones for compounds **3** and **4** than that with 0.9 Debye bond moment of O—Lp bond; therefore the $E_{dip\text{-}P}$ for **1** and **2** were evaluated without bond moment of O—Lp bond, while that for **3** and **4** with 0.90 Debye bond moment of O—Lp bond.

All of the calculations were carried on the Vax-11/780 computer at the Computer Chemistry Laboratory, Chinese Academy of Sciences, in Shanghai Institute of Organic Chemistry.

ACKNOWLEDGEMENT

This project was supported by the National Natural Science Foundation of China and the Computer Chemistry Laboratory of Chinese Academy of Sciences in Shanghai Institute of Organic Chemistry.

REFERENCES

1. L. S. Melvin, *Tetrahedron Lett.*, 3375 (1981).
2. R. C. Cambie and B. D. Palmer, *Austr. J. Chem.*, **35,** 827 (1982).
3. J. F. Koszuk, B. P. Czech, W. Walkowiak, D. A. Babb and R. A. Bartsch, *J. Chem. Soc. Commun.*, 1504 (1984).
4. B. Dhawan and D. Redmore, *J. Org. Chem.*, **49,** 4018 (1984).
5. B. Dhawan and D. Redmore, *Synth. Commun.*, **15,** 411 (1985).
6. B. Dhawan and D. Redmore, *J. Org. Chem.*, **51,** 179 (1986).
7. J. Heinicke, I. Bohle and A. Tzschach, *J. Organomet. Chem.*, **317,** 11 (1986).
8. T. Calogerapoulou, G. B. Hammond and D. F. Wiemer, *J. Org. Chem.*, **52,** 4185 (1987).
9. B. Dhawan and D. Redmore, *Synth. Commun.*, **17,** 465 (1987).
10. K. A. Petrov, S. V. Agafanov and V. P. Pokaton, *Zh. Obshch. Khim*, **57,** 98 (1987).
11. B. Dhawan and D. Redmore, *J. Chem. Research(s)*, 222 (1988).
12. B. Dhawan and D. Redmore, *Phosphorus, Sulfur and Silicon*, **42,** 177 (1989).
13. S. Li and G. Wang, *Phosphorus, Sulfur and Silicon*, **48,** 251 (1990).
14. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99,** 4897 (1977).
15. S. Li, X. Liao and C. Yuan, *Phosphorus, Sulfur and Silicon*, **48,** 69 (1990).
16. S. Li and D. B. Chesnut, *Org. Magn. Reson.*, **23,** 625 (1985).
17. S. Li, Z. Cheng and C Yuan, *Sci. China (Ser. B)*, **32,** 1172 (1989).
18. S. Li and D. B. Chesnut, *Org. Magn. Reson.*, **24,** 93 (1986).
19. S. Li and N. L. Allinger, *Tetrahedron*, **44,** 1339 (1988).
20. D. B. Chesnut and W. P. Johnson, *J. Magn. Reson.*, **65,** 110 (1985).
21. D. B. Chesnut, D. W. Wright and B. A. Krizek, *J. Mol. Struct.*, **190,** 99 (1988).
22. R. Pachter and P. L. Wessels, *J. Mol. Struct.* (THREOCHEM), **164,** 189 (1988).
23. R. Pachter and P. L. Wessels, *J. Mol. Struct.*, **178,** 323 (1988).
24. N. L. Allinger, *J. Am. Chem. Soc.*, **99,** 8127 (1977).
25. MMP2(85) version was offered by Prof. N. L. Allinger.