

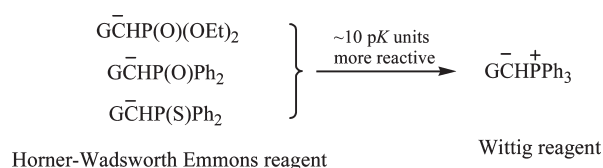
## Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C–H Bonds in Phosphonates and Related Phosphorus Containing Compounds

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Received June 14, 2009



The homolytic bond dissociation enthalpies (BDEs) of the acidic C–H bonds in a series of phosphonates and related phosphorus-containing compounds have been determined by a combination (eq 3) of their equilibrium acidities ( $\text{p}K_{\text{HA}}^{\ominus}$ 's) and the oxidation potentials [ $E_{\text{ox}}(\text{A}^{\ominus})$ 's] of their conjugate anions, which were measured in DMSO solution. The equilibrium acidity increases by 15.5, 14.9, and 10.9 pK units for the introduction of an  $\alpha$ -P(O)(OEt)<sub>2</sub> group into toluene, acetonitrile, and ethyl acetate, respectively. Comparison with the published equilibrium acidity increases by 25.6, 24.4, and 21.0 pK units for the introduction of an  $\alpha$ -<sup>+</sup>PPh<sub>3</sub> group into the same series of substrates indicates that the phosphoryl carbanions (Horner–Wadsworth–Emmons reagents) are about 10 pK units more reactive than the corresponding triphenylphosphonium ylides (Wittig reagents). However, both  $\alpha$ -P(O)(OEt)<sub>2</sub> and  $\alpha$ -<sup>+</sup>PPh<sub>3</sub> groups have negligible effects on the adjacent C–H BDEs, indicating that there is no resonance delocalization into the 3d vacant orbitals of phosphorus and that their acidifying effects are exclusively associated with the field/inductive (electrostatic) and polarizability effects. The acidifying effect of an  $\alpha$ -CO<sub>2</sub>Et group is shown to be ca. 3.5 pK units stronger than that of an  $\alpha$ -P(O)(OEt)<sub>2</sub> group in the same substrates, suggesting that the larger acidifying effect of the  $\alpha$ -CO<sub>2</sub>Et group is predominantly associated with the resonance delocalization rather than with the field/inductive (electrostatic) and polarizability effects.

### Introduction

Because of its effectiveness, reliability, and wide applicability, the triphenylphosphonium ylide ( $\text{Ph}_3\text{P}^+\text{CHR}^-$ ) (Wittig reagent) has become a common synthon to convert the carbonyl group of aldehyde and/or ketone into the corresponding olefinic carbon–carbon double bond in synthetic organic chemistry.<sup>1,2</sup> However, the Wittig reaction is slow, and the yield is poor for the sterically hindered and/or stabilized ketones. The low reactivity for the sterically hindered and/or stabilized ketones could be significantly improved

by employing more basic and nucleophilic phosphoryl carbanions known as the Horner–Wadsworth–Emmons (HWE) reagents, including those derived from phosphonates, phosphine oxides, phosphoramides, phosphine sulfides, etc.<sup>2</sup> Moreover, the Horner–Wadsworth–Emmons reaction could occur at relatively lower temperatures but with much higher stereoselectivity.<sup>3</sup>

In 1955, Doering and Hoffmann found that tetramethylphosphonium cation had much faster deprotonation rate constants than tetramethylammonium cation in aqueous solution.<sup>4</sup> Recently, Richard et al. reported that the  $\text{p}K_{\text{HA}}$

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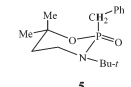
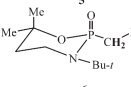
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TABLE 1. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Benzylic C–H Bonds in  $\alpha$ -Substituted Toluenes

Substrate	$pK_{HA}^a$	$E_{ox}(A^\cdot)^b$	$BDE_{HA}^c$
PhCH <sub>3</sub>	43 <sup>d</sup>	-1.935 <sup>e</sup>	88.0–89.5 <sup>f</sup>
PhCH <sub>2</sub> <sup>+</sup> NMe <sub>3</sub>	31.9 <sup>g</sup>	-1.143 <sup>g</sup>	90.6
PhCH <sub>2</sub> <sup>+</sup> PPh <sub>3</sub>	17.4 <sup>h</sup>	-0.381 <sup>h</sup>	88.3
PhCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	27.5	-0.925	89.6
PhCH <sub>2</sub> <sup>+</sup> AsPh <sub>3</sub>	22.7 <sup>h</sup>	-0.558 <sup>h</sup>	91.5
PhCH <sub>2</sub> <sup>+</sup> P( <i>t</i> -Bu) <sub>3</sub>	21.9 <sup>i</sup>	-0.620 <sup>i</sup>	89.0
	29.75	-1.057	89.6
	29.9	-1.055	89.9

<sup>a</sup>Equilibrium acidities (in pK units) determined in DMSO solution by the indicator overlapping titration.<sup>7</sup> The acidic protons are labeled in bold. <sup>b</sup>Oxidation potentials (in volts) measured in DMSO solution by cyclic voltammetry.<sup>8</sup> <sup>c</sup>Determined using eq 3 unless otherwise indicated. <sup>d</sup>Reference 7. <sup>e</sup>Reference 8a. <sup>f</sup>Reference 20. <sup>g</sup>Reference 6. <sup>h</sup>Reference 8. <sup>i</sup>Reference 9.

value of tetramethylphosphonium cation is 29.4, and the lower limit of the  $pK_{HA}$  value of tetramethylammonium cation was estimated to be 32.8 from the kinetic measurements in the aqueous solution.<sup>5</sup> Although it is too weak to be experimentally measured, the  $pK_{HA}$  value of tetramethylammonium cation was estimated at  $\sim 42$  in dimethyl sulfoxide (DMSO) solution.<sup>6</sup> The  $pK_{HA}$  values for a series of *P*-substituted triphenylphosphonium cations have been determined in DMSO solution.<sup>7,8</sup> For example, when introduced into ethyl acetate, acetonitrile, and toluene, the acidifying effect of an  $\alpha$ -triphenylphosphonium ( $\alpha^+$ PPh<sub>3</sub>) group is 21.0, 24.4, and 25.6 pK units, respectively.<sup>8</sup> Similarly, larger acidifying effects have also been observed for other onium cations, including arsonium,<sup>8b,9</sup> sulfonium,<sup>10</sup> selenium,<sup>11</sup> and niobium cations.<sup>12</sup> In a sharp contrast to the tremendous acidifying effects, these onium groups have negligible effects on the adjacent carbon radical stabilities.<sup>8–11</sup>

The phosphonate oxygen acidities have been examined from both theoretical and experimental studies in the aqueous solution.<sup>13</sup> However, quantitative information regarding the phosphorus-containing substituents on the adjacent carbanions and carbon radicals is scarce in the literature, although phosphonate compounds are common in biological and medicinal chemistry<sup>14,15</sup> and as organic synthetic intermediates.<sup>1–3</sup> In the present paper, we present the equilibrium

acidities and homolytic bond dissociation enthalpies (BDEs) of the acidic C–H bonds in a series of phosphonates, phosphonamides, phosphine oxides, and phosphine sulfide, precursors for the Horner–Wadsworth–Emmons reactions.

## Results and Discussion

**Equilibrium Acidity.** Equilibrium acidity provides the thermodynamic stability of the conjugate anion ( $A^-$ ) as shown in eq 1, and the equilibrium acidity is very useful for reaction mechanism studies.<sup>16</sup> The most established acidity scale has been developed by Bordwell and his co-workers in DMSO solution using the indicator overlapping titration, and the measured  $pK_{HA}$  values are believed to be accurate to  $\pm 0.1$  pK units.<sup>7</sup> Since the equilibrium acidity is free from the ion-pair effect, the  $pK_{HA}$  value can also be used to compare the relative stability of the corresponding conjugate anion ( $A^-$ ).<sup>7,17</sup>



Equilibrium acidities for a series of phosphonates, phosphonamides, phosphine oxide, phosphine sulfide, and bisphosphonates were determined in DMSO solution by the indicator overlapping titration method as described in the previous papers,<sup>7</sup> and the related results are summarized in Tables 1–4. The equilibrium acidities of the related trimethylammonium and triphenylphosphonium cations are also included in these tables for comparison.

**Homolytic Bond Dissociation Enthalpy of Acidic H–A Bond (BDE).** Homolytic bond dissociation enthalpy has long been considered as the best quantitative stability measure of the radical  $A^\cdot$  formed by homolytic H–A dissociation (eq 2).<sup>18</sup> However, the direct measurement of the H–A BDE is

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**TABLE 2. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C–H Bonds in  $\alpha$ -Substituted Acetonitriles**

substrate	$pK_{HA}^a$	$E_{ox}(A^-)^b$	$BDE_{HA}^c$
CH <sub>3</sub> CN	31.3 <sup>d</sup>	0.917 <sup>e</sup>	93.4, <sup>f</sup> 95.0 <sup>g</sup>
NCCH <sub>2</sub> <sup>+</sup> NMe <sub>3</sub>	20.6 <sup>h</sup>	−0.271 <sup>h</sup>	95.3
NCCH <sub>2</sub> <sup>+</sup> PPh <sub>3</sub>	6.93 <sup>i</sup>	0.506 <sup>i</sup>	94.5
NCCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	16.36	−0.071	94.1
NCCH <sub>2</sub> P(O)Ph <sub>2</sub>	16.8	−0.116	93.6
NCCH <sub>2</sub> P(S)Ph <sub>2</sub>	16.4	−0.126	92.9

<sup>a</sup>Equilibrium acidities (in pK units) determined in DMSO solution by the indicator overlapping titration.<sup>7</sup> The acidic protons are labeled in bold. <sup>b</sup>Oxidation potentials (in volts) measured in DMSO solution by cyclic voltammetry.<sup>8</sup> <sup>c</sup>Determined using eq 3, unless otherwise indicated. <sup>d</sup>Reference 7. <sup>e</sup>Estimated. <sup>f</sup>Reference 20a. <sup>g</sup>Reference 20b. <sup>h</sup>Reference 6. <sup>i</sup>Reference 8a.

difficult, if not impossible, for most chemical compounds because both the resultant radical (A<sup>•</sup>) and hydrogen atom (H<sup>•</sup>) are extremely reactive. Nevertheless, the homolytic bond dissociation enthalpy of the acidic H–A bond can be determined from a combination of the equilibrium acidity with the oxidation potential of its conjugate anion [ $E_{ox}(A^-)$ ] as shown in eq 3.<sup>19</sup> The oxidation potentials of the conjugate anions derived from the phosphorus-containing compounds were measured in DMSO solution by cyclic voltammetry.<sup>8</sup> The acidic C–H BDEs in these phosphorus-containing compounds were determined from their equilibrium acidities and oxidation potentials according to eq 3,<sup>19</sup> and the results are summarized in the related tables.



$$BDE = 1.37pK_{HA} + 23.1E_{ox}(A^-) + C \quad (3)$$

Equation 3 was originally derived from a thermodynamic cycle,<sup>19</sup> and the empirical constant  $C$  consists of hydrogen atom formation free energy, proton transfer free energy from water to DMSO solution, solvation free energy, and entropy change ( $T\Delta S$ ) of the homolytic dissociation.<sup>21</sup> The constant  $C$  is 73.3 when the oxidation potential of the conjugate anion is referenced to the ferrocenium/ferrocene couple in DMSO solution.<sup>19b,c</sup> Although the constant  $C$  is empirical, the BDEs obtained using eq 3 have been shown to be in agreement to  $\pm 2$  kcal/mol with the best available gas-phase experimental results.<sup>18c,d,19</sup> This unique approach makes it possible to determine the thermodynamic properties of many reactive radical intermediates, which are difficult to obtain from other experimental methods. Indeed, this approach has been successfully employed to measure the acidic H–A bond BDEs in various chemical substrates in the past two decades.<sup>6–11,18c,19,21</sup>

**Thermodynamic Stabilities of Phosphoryl Carbanions and Triphenylphosphonium Ylides.** Examination of Tables 1–3 shows that the introduction of an  $\alpha$ -P(O)(OEt)<sub>2</sub> group increases the equilibrium acidities of ethyl acetate, acetonitrile, and toluene by 10.9, 14.9, and 15.5 pK units respec-

tively; i.e., the average acidity increase is  $13.8 \pm 1.4$  pK units. The average acidifying effect for the introduction of an  $\alpha$ -<sup>+</sup>PPh<sub>3</sub> group into ethyl acetate, acetonitrile, and toluene is  $23.7 \pm 1.4$  pK units,<sup>8</sup> indicating that the carbanions derived from phosphonates are ca. 10 pK units more basic (or nucleophilic) than those derived from the corresponding triphenylphosphonium cations. Intriguingly, the carbanions derived from phosphoramides, diphenylphosphine oxide, and diphenylphosphine sulfide are also about 10 pK units more basic than the corresponding triphenylphosphonium ylides. These results clearly indicate that the Horner–Wadsworth–Emmons reagents are about 10 pK units (14 kcal/mol) more reactive than the corresponding Wittig reagents,<sup>22</sup> and it explains why the Horner–Wadsworth–Emmons reagents could react with the carbonyls of the sterically hindered and/or stabilized ketones, but the Wittig reagents usually fail to form the corresponding carbon–carbon double bonds.<sup>1,23</sup>

**Acidifying Effect of  $\alpha$ -<sup>+</sup>PPh<sub>3</sub>,  $\alpha$ -P(O)(OEt)<sub>2</sub>, and  $\alpha$ -P(O)-Ph<sub>2</sub> Groups.** The acidifying effect of the  $\alpha$ -<sup>+</sup>PPh<sub>3</sub> group is generally attributed to the field/inductive and polarizability effects since the resonance delocalization into the 3d vacant orbitals of phosphorus is negligible.<sup>8</sup> The theoretical calculations show that the 3d orbitals of phosphorus are both too big in size and too high in energy for any effective overlapping with the p orbitals of the adjacent carbanions derived from the phosphonium cations.<sup>24,25</sup> In addition, ESR studies of various phosphonium radical cations show that the unpaired electron is essentially localized on the carbon atom and has no resonance delocalization into the adjacent phosphonium groups.<sup>26</sup>

Examination of Tables 1–3 shows that the acidic C–H BDEs of PhCH<sub>2</sub>P(O)(OEt)<sub>2</sub>, NCCH<sub>2</sub>P(O)(OEt)<sub>2</sub>, and EtO<sub>2</sub>CCH<sub>2</sub>P(O)(OEt)<sub>2</sub> are essentially identical with those of their precursors, i.e., toluene, acetonitrile and ethyl acetate, respectively. Similarly, the phosphoryl groups of phosphoramides, phosphine oxide, and phosphine sulfide also have no effects on the adjacent C–H BDEs. These results indicate that there is no resonance delocalization of the unpaired electron into the 3d vacant orbitals of the  $\alpha$ -phosphoryl groups. This conclusion is consistent with the relatively lower phosphorus–carbon bond rotation energy ( $\sim 7$  kcal/mol) of the phosphoryl-stabilized carbanions.<sup>27</sup> Moreover, the theoretical calculations show that the overlapping between the 3d vacant orbitals of phosphorus with the p orbitals of the adjacent carbanions derived from phosphonates is also negligible.<sup>28</sup> In summary, these

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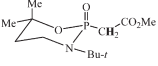
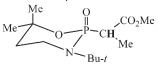
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TABLE 3. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C–H Bonds in  $\alpha$ -Substituted Alkyl Esters

Substrate	$pK_{HA}^a$	$E_{ox}(A^-)^b$	$BDE_{HA}^c$
$CH_3CO_2Et$	29.5 <sup>d</sup>	-0.767 <sup>c</sup>	96.0 <sup>f</sup>
$EtO_2CCH_2^+NMe_3$	20.0 <sup>e</sup>	-0.141 <sup>e</sup>	97.4
$EtO_2CCH_2^+PPh_3$	8.50 <sup>h</sup>	0.553 <sup>h</sup>	97.7
$EtO_2CCH_2P(O)(OEt)_2$	18.6	-0.035	98.0
	21.5	-0.240	97.2
	22.9	-0.563	91.7

<sup>a</sup>Equilibrium acidities (in pK units) determined in DMSO solution by the indicator overlapping titration.<sup>7</sup> The acidic protons are labeled in bold. <sup>b</sup>Oxidation potentials (in volts) measured in DMSO solution by cyclic voltammetry.<sup>8</sup> <sup>c</sup>Determined using eq 3, unless otherwise indicated. <sup>d</sup>Reference 7. <sup>e</sup>Estimated. <sup>f</sup>Reference 20c. <sup>g</sup>Reference 6. <sup>h</sup>Reference 8a.

TABLE 4. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C–H Bonds in Bisphosphonates and Bisphosphine Oxide

substrate	$pK_{HA}^a$	$E_{ox}(A^-)^b$	$BDE_{HA}^c$
$CH_2[P(O)(OMe)(OPr-i)_2]$	23.4	-0.252	99.5
$CH_2[P(O)Ph_2]_2$	23.7	-0.289	99.1
$CH_2[P(O)(Me)(OPr-i)_2]$	25.2	-0.360	99.5

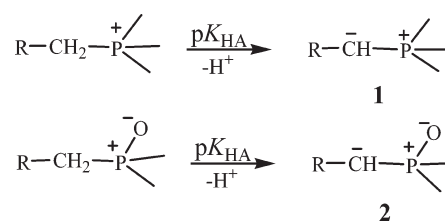
<sup>a</sup>Equilibrium acidities (in pK units) determined in DMSO by the indicator overlapping titration.<sup>7</sup> The acidic protons are labeled in bold. <sup>b</sup>Oxidation potentials (in volts), determined in DMSO by cyclic voltammetry. <sup>c</sup>BDE (in kcal/mol) determined using eq 3.

results lead to the conclusion that the acidifying effect of the  $\alpha$ -phosphoryl group is caused primarily by the field/inductive and polarizability effects rather than by the resonance delocalization into the 3d vacant orbitals of phosphorus.

**Polarizability Effects of  $\alpha^+PPh_3$ ,  $\alpha-P(O)(OEt)_2$  and  $\alpha-P(O)Ph_2$  Groups.** Since the carbon–nitrogen bond length (1.50 Å)<sup>29a</sup> is shorter than the carbon–phosphorus bond length (1.80 Å),<sup>29b</sup> the field/inductive effect of the  $\alpha^+NMe_3$  group is expected to be considerably larger than that of the  $\alpha^+PPh_3$  group, but the acidifying effect of the  $\alpha^+NMe_3$  group is ca. 13 pK units weaker than that of the  $\alpha^+PPh_3$  group.<sup>8,30</sup> These results suggest that the polarizability is predominant for the acidifying effect of the  $\alpha^+PPh_3$  group. Polarizability effect is a collective electrostatic interaction of a charge or dipolar moment with the substituent,<sup>31</sup> and it increases drastically with size of the substituent, especially with the bonded atom. For example, the dipole polarizability parameter (in atomic units) of the third row phosphorus (24.5) is over three times larger than that of the second row nitrogen (7.2).<sup>32</sup> Acidity enhancement by substituent polarizability effect has been well documented both in the gas phase<sup>33</sup> and in DMSO solution.<sup>34</sup>

The  $pK_{HA}$  values (Table 2) of  $NCCH_2P(O)(OEt)_2$  and  $NCCH_2P(O)Ph_2$  are 16.4 and 16.8, respectively. The  $pK_{HA}$

SCHEME 1



values (Table 4) of  $CH_2[P(O)(OPr-i)_2]$  and  $CH_2[P(O)Ph_2]_2$  are 23.4 and 23.7, respectively. These data clearly indicate that the acidifying effects of the  $\alpha-P(O)(OPr-i)_2$ ,  $\alpha-P(O)(OEt)_2$  and  $\alpha-P(O)Ph_2$  groups are comparable to each other. Since the resonance effects for all these groups are negligible, their field/inductive effects are expected to be similar due to the same semipolar phosphorus–oxygen structure for  $\alpha-P(O)(OEt)_2$ ,  $\alpha-P(O)(OPr-i)_2$  and  $\alpha-P(O)Ph_2$  groups, it follows that also the polarizability effects should be similar for  $\alpha-P(O)(OEt)_2$ ,  $\alpha-P(O)(OPr-i)_2$  and  $\alpha-P(O)Ph_2$  groups. Furthermore, the polarizability effects of the  $\alpha^+PPh_3$  group should be also comparable to  $\alpha-P(O)(OEt)_2$ ,  $\alpha-P(O)(OPr-i)_2$  and  $\alpha-P(O)Ph_2$  groups because of the similar size and chemical structure.

**Field/Inductive Effects of  $\alpha^+PPh_3$ ,  $\alpha-P(O)(OEt)_2$ , and  $\alpha-P(O)Ph_2$  Groups.** If the polarizability effects of  $\alpha^+PPh_3$  and  $\alpha$ -phosphoryl groups are comparable, the significant difference of their acidifying effects must be associated with their different field/inductive effects, but one would wonder why the field/inductive effect of the  $\alpha^+PPh_3$  group is about 10 pK units larger than that of the  $\alpha$ -phosphoryl group even though the semipolar phosphorus–oxygen structure of the  $\alpha$ -phosphoryl group is similar to that of the  $\alpha^+PPh_3$  group as shown in Scheme 1.<sup>25,28</sup> As can be seen from Scheme 1, both carbanions (**1** and **2**) are stabilized by a positively charged phosphorus atom in addition to which the carbanion **2** bears an additional negative charge on the adjacent oxygen atom.

The negative charge on the adjacent oxygen atom will certainly reduce the Coulombic attraction between the positively charged phosphorus with the carbanion center, resulting in relatively smaller acidifying effects of the  $\alpha$ -phosphoryl groups. As a result, the phosphoryl carbanion seems to be stabilized only by a partial positive charge rather than

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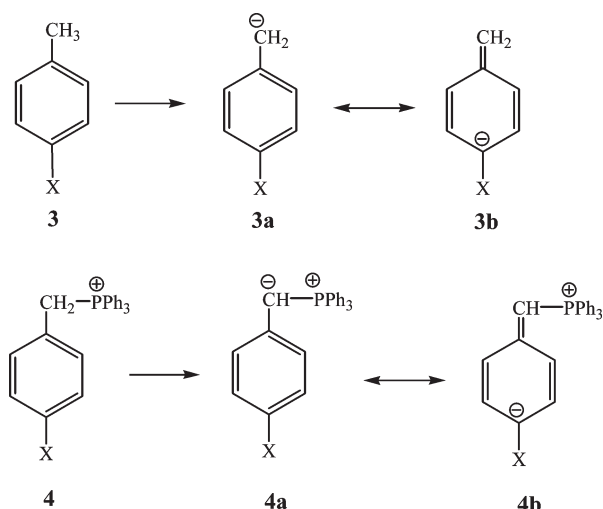
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SCHEME 2



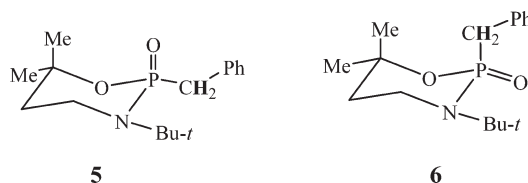
by a unity positive charge on the phosphorus atom (Scheme 1).<sup>26a,35</sup> Similar reduction of the acidifying effects has been observed for the *para* substituents when an  $\alpha$ -onium group was introduced into *para*-substituted toluenes as shown in Scheme 2. For example, the Hammett correlation slopes for *N*-benzyltrimethylammonium cations, *P*-benzyltriphenylphosphonium cations, and *As*-benzyltriphenylarsonium cations are 4.4,<sup>6</sup> 4.8,<sup>8</sup> and 5.4 p*K* units,<sup>8b,9</sup> respectively, whereas the Hammett correlation slope is ca. 12.0 p*K* units for the *para*-substituted toluenes (*p*-GC<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>) (**3**).<sup>36</sup> Attenuation of Hammett slopes for the introduction of an  $\alpha$ -onium group could be attributed to the Coulombic attraction of the carbanion center with the positive charge on  $\alpha$ -onium groups, resulting in a reduction of resonance delocalization of the carbanion negative charge into the aromatic system (**4**). Consequently, the *para* substituents (X) have less influence on the benzyl carbanion stabilities.

**Substituent Effects of  $\alpha$ -P(S)Ph<sub>2</sub> and  $\alpha$ -P(O)Ph<sub>2</sub> Groups.** Replacement of the C=O bond in carboxamides by a C=S bond has a profound effect on both p*K*<sub>HA</sub> and BDE results.<sup>37</sup> For example, the p*K*<sub>HA</sub> value of thioacetamide is 7 p*K*<sub>HA</sub> units lower than that of acetamide, and the N–H BDE of thioacetamide is 16 kcal/mol lower than that of acetamide.<sup>37</sup> The larger stabilization of the thiocarbonyl group can be attributed to its more effective resonance delocalization since there is ca. 10 kcal/mol less enolization energy for the thiocarbonyl than the corresponding carbonyl group.<sup>38</sup>

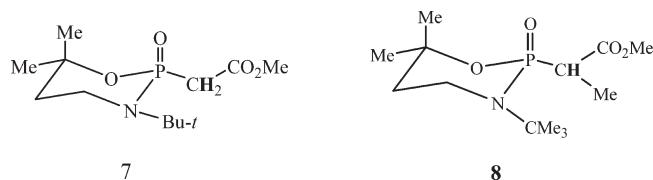
In a sharp contrast, Table 2 shows that the p*K*<sub>HA</sub> values of NCCH<sub>2</sub>P(O)Ph<sub>2</sub> and NCCH<sub>2</sub>P(S)Ph<sub>2</sub> are 16.4 and 16.8, respectively, indicating that the acidifying effects of the  $\alpha$ -P(S)Ph<sub>2</sub> and  $\alpha$ -P(O)Ph<sub>2</sub> groups are comparable. Also, the C–H BDEs are same within the experimental error. However, our experimental results are consistent with the

theoretical calculations. The calculations show that the phosphorus–sulfur bond in phosphine sulfide has a semi-polar structure similar to that of the phosphorus–oxygen bond in phosphine oxide, and there is no resonance delocalization into the vacant 3d orbitals of phosphorus.<sup>25b</sup> Furthermore, both the phosphoryl- and thiophosphoryl-stabilized carbanions have strikingly similar properties:<sup>39</sup> for example, relatively small phosphorus–carbon rotation energy was observed for both thiophosphoryl (9.8 kcal/mol) and phosphoryl carbanion (7.0 kcal/mol).<sup>28b,40</sup>

**Equilibrium Acidities and Acidic C–H BDEs of Phosphorinanes.** Table 1 shows that the two enantiomers of (2*R*)-2-benzyl-3-*tert*-butyl-6,6-dimethyl-1,3,2-oxazaphosphorinane (**5**) and (2*S*)-2-benzyl-3-*tert*-butyl-6,6-dimethyl-1,3,2-oxazaphosphorinane (**6**) have the same equilibrium acidity. However, their equilibrium acidities are 2.3 p*K* units weaker than diethyl phenylphosphonate. Similarly, the equilibrium acidity of 2-carbomethoxymethyl-3-*tert*-butyl-6,6-dimethyl-1,3,2-oxazaphosphorinane (**7**) of Table 3 is 2.9 p*K* units weaker than that of triethyl phosphonoacetate. The weaker acidities of the phosphorinane could be attributed to their smaller field/inductive effects resulting from the fact that the phosphorus–nitrogen bond in phosphorinanes is less polar than the phosphorus–oxygen bond in phosphonates. For example, the Hammett substituent constant ( $\sigma_p$ ) of P(O)(NMe<sub>2</sub>)<sub>2</sub> is 0.40, and the  $\sigma_p$  constant of P(O)(OEt)<sub>2</sub> is 0.60.<sup>41</sup> Since the field/inductive effects are dependent upon the electrostatic interaction, it is not surprising to find that the acidic C–H BDEs of the phosphorinanes and phosphonates are essentially identical (Tables 1 and 3).



Introduction of a methyl group in **8** decreases the equilibrium acidity by 1.4 p*K* units relative to **7**, presumably due to reduction of the carbanion salivation by the steric effects.<sup>7,17</sup> A similar decrease in equilibrium acidity by 0.75 p*K* units has been observed for introduction of a methyl group into *P*-(carbomethoxymethyl)triphenylphosphonium cation (EtO<sub>2</sub>-CH<sub>2</sub><sup>+</sup>PPh<sub>3</sub>).<sup>8a</sup> However, introduction of a methyl group weakens the acidic C–H bond strength of **8** by 5.6 kcal/mol and of EtO<sub>2</sub>CH(Me)<sup>+</sup>PPh<sub>3</sub> by 7.7 kcal/mol.<sup>8a</sup>



**Equilibrium Acidities and Acidic C–H BDEs of Bisphosphonates and Bisphosphine Oxides.** The p*K*<sub>HA</sub> value of methyltriphenylphosphonium cation (Ph<sub>3</sub>P<sup>+</sup>CH<sub>3</sub>) was measured to be 22.5,<sup>7</sup> and the acidifying effect of  $\alpha$ -Ph<sub>3</sub>P<sup>+</sup> is

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**TABLE 5. Substituent Effects of  $\alpha$ -CO<sub>2</sub>Et and  $\alpha$ -P(O)(OEt)<sub>2</sub> on Adjacent Carbanions and Radicals**

substrates	$pK_{HA}^a$	$\Delta pK_{HA}^b$	BDE <sup>c</sup>	$\Delta BDE^d$
CH <sub>3</sub> CO <sub>2</sub> Et	29.5 <sup>e</sup>		96.0 <sup>f</sup>	
CH <sub>3</sub> P(O)(OEt) <sub>2</sub>	~32.5 <sup>g</sup>	3.0	99.0 <sup>g</sup>	3.0
PhCH <sub>2</sub> CO <sub>2</sub> Et	22.6 <sup>h</sup>		84 <sup>h</sup>	
PhCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	27.5	4.9	89.5	5.5
NCCH <sub>2</sub> CO <sub>2</sub> Et	13.1 <sup>i</sup>		91.0	
NCCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	16.4	3.3	94.0	3.0
Ph <sub>2</sub> C=NCH <sub>2</sub> CO <sub>2</sub> Et	18.7 <sup>j</sup>		79.0	
Ph <sub>2</sub> C=NCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	22.95	4.25	84.4	5.4
CH <sub>2</sub> (CO <sub>2</sub> Et) <sub>2</sub>	16.4 <sup>i</sup>		95.3	
EtO <sub>2</sub> CCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	18.6	2.2	98.0	2.7
CH <sub>2</sub> [P(O)(OMe)(OPr)] <sub>2</sub>	23.4	7.0	99.5	4.2

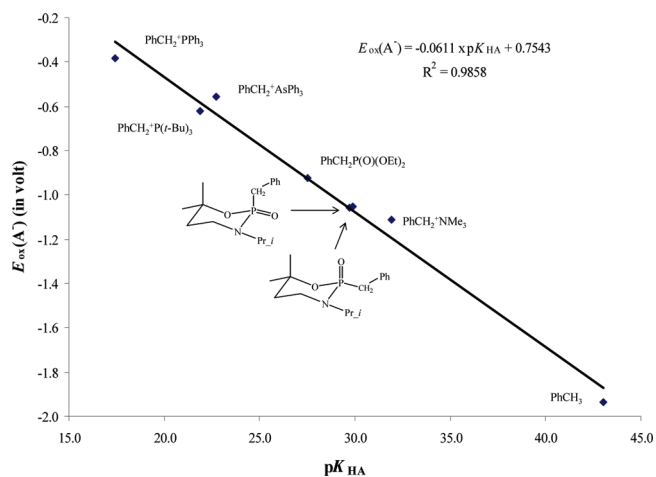
<sup>a</sup>Equilibrium acidities (in pK units) determined in DMSO.<sup>7</sup> The acidic protons are labeled in bold. <sup>b</sup>Relative pK<sub>HA</sub> values. <sup>c</sup>BDEs (in kcal/mol) determined using eq 3. <sup>d</sup>Relative BDEs. <sup>e</sup>Reference 42. <sup>f</sup>Reference 18c. <sup>g</sup>Estimated, see the text. <sup>h</sup>Reference 19a. <sup>i</sup>Zhang, X.-M. et al. *J. Phys. Org. Chem.* **1994**, *7*, 751. <sup>j</sup>Bordwell, F.G. et al. *J. Am. Chem. Soc.* **1988**, *110*, 8520.

known to be about 10 pK units larger than those of the  $\alpha$ -P(O)(OEt)<sub>2</sub> and  $\alpha$ -P(O)Ph<sub>2</sub> groups. Thus, the equilibrium acidities of diethyl methylphosphonate [CH<sub>3</sub>P(O)(OEt)<sub>2</sub>] and diphenylmethylphosphine oxide [CH<sub>3</sub>P(O)Ph<sub>2</sub>] can be estimated at ~32.5 in DMSO solution although they are too weak to be experimentally measured.<sup>7</sup>

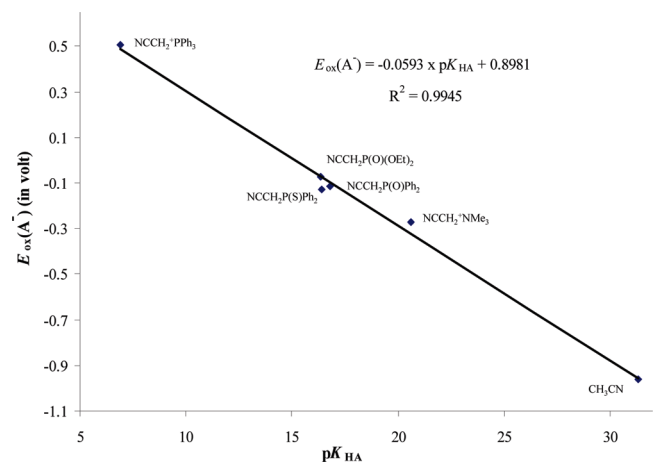
The equilibrium acidities and bond dissociation enthalpies for bisphosphonates and bisphosphine oxides are summarized in Table 4. The pK<sub>HA</sub> values of CH<sub>2</sub>[P(O)(OMe)(OPr-*i*)]<sub>2</sub> and CH<sub>2</sub>[P(O)Ph<sub>2</sub>]<sub>2</sub> are 23.4 and 23.7 respectively, indicating that the introduction of an additional electron acceptor  $\alpha$ -phosphoryl group increases the equilibrium acidity by about 9 pK units. However, introduction of an additional electron acceptor usually has negligible effects on the acidic C–H BDEs, and the BDE of the C–H bond bearing two electron acceptors approximately equals to an average of the individual C–H BDEs.<sup>42</sup> Thus, the acidic C–H BDEs of CH<sub>3</sub>P(O)(OEt)<sub>2</sub> and CH<sub>3</sub>P(O)Ph<sub>2</sub> should be about 99 kcal/mol, the acidic C–H BDEs observed for bisphosphonate and bisphosphine oxide (Table 4).

**Substituent Effects of  $\alpha$ -CO<sub>2</sub>Et and  $\alpha$ -P(O)(OEt)<sub>2</sub> Groups.** The pK<sub>HA</sub> value of ethyl acetate (CH<sub>3</sub>CO<sub>2</sub>Et) from one-point titration measurement is 29.5,<sup>42</sup> about 3.0 pK units lower than that of diethyl methylphosphonate [CH<sub>3</sub>P(O)(OEt)<sub>2</sub>]. Table 5 lists additional  $\alpha$ -substituted acetates that are more acidic than the corresponding  $\alpha$ -substituted phosphonates. The acidifying effect of the  $\alpha$ -CO<sub>2</sub>Et group is about 3.5 ± 0.5 pK units larger than that of the  $\alpha$ -P(O)(OEt)<sub>2</sub> group. Interestingly, the equilibrium acidity of diethyl malonate is 7.0 pK units stronger than that of the bisphosphonates, i.e., 3.5 pK units for each compared group.

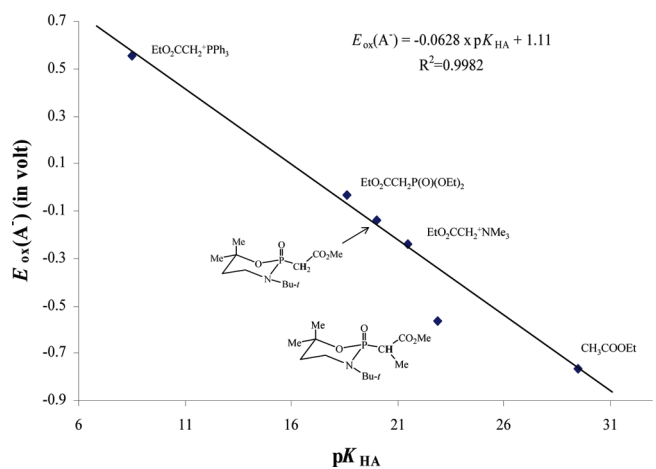
The polarizability effect of the  $\alpha$ -CO<sub>2</sub>Et group is expected to be smaller than that of the  $\alpha$ -P(O)(OEt)<sub>2</sub> group because the former size is much smaller than the latter and the dipolar polarizability parameter of carbon (11.8 atom units) is much smaller than that of phosphorus (24.5 atom units).<sup>32</sup> In addition, the field/inductive effect of the  $\alpha$ -CO<sub>2</sub>Et group is expected to be also smaller than that of  $\alpha$ -P(O)(OEt)<sub>2</sub> group due to the semipolar phosphorus–oxygen structure. Since both the field/inductive and polarizability effects of the  $\alpha$ -CO<sub>2</sub>Et group are smaller than those of the  $\alpha$ -P(O)(OEt)<sub>2</sub>



**FIGURE 1.** Linear correlation of equilibrium acidities with oxidation potentials of the conjugate anions for the  $\alpha$ -substituted toluenes.



**FIGURE 2.** Linear correlation of equilibrium acidities with oxidation potentials of the conjugate anions for the  $\alpha$ -substituted acetonitriles.

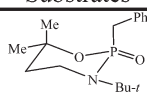
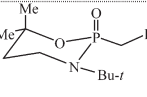
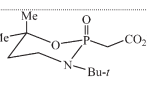
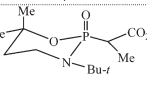


**FIGURE 3.** Linear correlation of equilibrium acidities with oxidation potentials of the conjugate anions for the  $\alpha$ -substituted alkyl esters.

group, the larger acidifying effects of the  $\alpha$ -CO<sub>2</sub>Et group must be associated with the resonance delocalization.

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TABLE 6. Equilibrium Acidity Measurements in DMSO Solution by the Overlapping Indicator Titration Method

Substrates	$pK_{HA}^a$	Indicator <sup>b</sup>	SDV <sup>c</sup>	Selected $pK_{HA}$
 5	29.74	DDH(29.4) <sup>d</sup>	0.023	29.75
	29.75	TH(30.6) <sup>e</sup>	0.131	
 6	29.94	DDH(29.4)	0.018	29.90
	29.87	TH(30.6)	0.022	
NCCH <sub>2</sub> P(O)Ph <sub>2</sub>	16.82	FMY30(18.1) <sup>f</sup>	0.022	16.8
	16.77	PSFH(15.4) <sup>g</sup>	0.018	
NCCH <sub>2</sub> P(S)Ph <sub>2</sub>	16.46	FMY30(18.1)	0.010	16.4
	16.36	PSFH(15.4)	0.020	
 7	21.41	2NPANH(20.66) <sup>h</sup>	0.024	21.45
	21.49	MFH(22.35) <sup>i</sup>	0.023	
 8	23.01	FH(22.6) <sup>j</sup>	0.016	23.0
	22.96	TNT(24.3) <sup>k</sup>	0.027	
CH <sub>2</sub> [P(O)(OMe)(OPr)] <sub>2</sub>	23.45	TNT(24.3)	0.025	23.4
	23.35	DBS (23.93) <sup>l</sup>	0.019	
CH <sub>2</sub> [P(O)Ph <sub>2</sub> ] <sub>2</sub>	23.76	TNT(24.3)	0.015	23.7
	23.62	DBS (23.93)	0.021	
CH <sub>2</sub> [P(O)(Me)(OPr)] <sub>2</sub>	25.31	TNT(24.3)	0.022	25.2
	25.14	HB1(26.1) <sup>m</sup>	0.010	
Ph <sub>2</sub> C=NCH <sub>2</sub> P(O)(OEt) <sub>2</sub>	22.98	DBS (23.93)	0.029	22.95
	22.92	BPS (21.47) <sup>n</sup>	0.011	

<sup>a</sup>Equilibrium acidities measured in DMSO solution. <sup>b</sup>Indicators used for the titration measurements. The numbers in the parentheses are the  $pK_{HA}$  values of the indicators used. <sup>c</sup>Standard deviation for three different measurements. <sup>d</sup>Biphenyldiphenylmethane. <sup>e</sup>Triphenylmethane. <sup>f</sup>2-(Phenylsulfonyl)fluorene. <sup>g</sup>9-Phenylthiofluorene. <sup>h</sup>2-Naphthylacetonitrile. <sup>i</sup>9-Methylfluorene. <sup>j</sup>Fluorene. <sup>k</sup>*N*-(Diphenylmethylene)benzenemethanamine. <sup>l</sup>Dibenzyl sulfone. <sup>m</sup>Iminostilbene. <sup>n</sup>*m*-Bromobenzyl phenyl sulfone.

Indeed, the resonance delocalization is generally believed to be responsible for the increased acidity of carboxylic acid compared to alcohol.<sup>43</sup> However, Holt and Karty recently challenged this traditional explanation from theoretical calculations and believed that the field/inductive effects account for at least two-thirds of the increased acidity of carboxylic acid than alcohol.<sup>44</sup>

$\Delta$ BDE values in Table 5 show that the introduction of an  $\alpha$ -CO<sub>2</sub>Et group decreases the adjacent C–H BDE by 3.0–5.5 kcal/mol more than the introduction of an  $\alpha$ -P(O)(OEt)<sub>2</sub> group (see Tables 1–3). These results provide additional experimental evidence to support the conclusion that the predominantly acidifying effect of the  $\alpha$ -CO<sub>2</sub>Et group is the resonance delocalization rather than the field/inductive and/or polarizability effects.

**Correlation of Equilibrium Acidities with Oxidation Potentials of the Conjugate Anions.** Table 1 shows that the benzylic C–H BDEs of diethyl benzylphosphonate and phosphorinanes **5** and **6** are the same as those of toluene, *N*-benzyltrimethylammonium cation, *P*-benzyltri(*tert*-butyl)phosphonium cation, *P*-benzyltriphenylphosphonium cation, and *As*-benzyltriphenylarsonium cation, although their

equilibrium acidities span over 25 pK units. Interestingly, there is a linear correlation between their equilibrium acidities and oxidation potentials as shown in Figure 1. A unity slope ( $\rho = 1.03$ ) is obtained for the linear correlation ( $R^2 = 0.99$ ) when both oxidation potentials and equilibrium acidities are expressed in kcal/mol.

Table 2 shows that the introduction of an  $\alpha$ -P(O)(OEt)<sub>2</sub>,  $\alpha$ -P(O)Ph<sub>2</sub>,  $\alpha$ -P(S)Ph<sub>2</sub>,  $\alpha$ -<sup>+</sup>NMe<sub>3</sub>, or  $\alpha$ -<sup>+</sup>PPh<sub>3</sub> group into acetonitrile has negligible effect on the acidic C–H BDE. The equilibrium acidities of the  $\alpha$ -substituted acetonitriles can also be linearly correlated with the oxidation potentials of their conjugate carbanions as shown in Figure 2. The slope of the linear correlation is  $\rho = 1.03$  ( $R^2 = 0.99$ ) when both oxidation potentials and equilibrium acidities are expressed in kcal/mol.

Examination of Table 3 shows that the acidic C–H BDEs of the  $\alpha$ -substituted esters are essentially identical with that of ethyl acetate. The equilibrium acidities of the  $\alpha$ -substituted esters can also be linearly correlated with the oxidation potentials of their conjugate anions as shown in Figure 3. The slope of the linear correlation is 1.06 ( $R^2 = 0.998$ ) (excluding compound **8**) when both oxidation potentials and equilibrium acidities are expressed in kcal/mol. The deviation of compound **8** from the linear correlation (Figure 3) can be attributed to the radical stabilization (5.5 kcal/mol) of the methyl group. Similar radical stabilizations were observed for

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introduction of a methyl group into diethyl malonate<sup>45</sup> and *P*-ethoxycarbonylmethyltriphenylphosphonium cation.<sup>8a</sup> Linear correlation of equilibrium acidities with the oxidation potentials of their conjugate anions has been observed in other weak acids.<sup>7,8,42,46</sup> These nice correlations further illustrate that the acidifying effects of the phosphorus-containing groups are exclusively caused by the field/inductive and polarizability effects rather than by the resonance delocalization into the 3d vacant orbitals of phosphorus. Because the field/inductive and polarizability effects are dependent upon the electrostatic interaction, they could affect the stability ( $pK_{\text{HA}}$  value) of the charged species but have no effects on the stability (BDE) of the neutral radical species.

### Experimental Section

The phosphorus-containing compounds used in this study were either commercial samples or gifts from other research laboratories such as Professor Scott Denmark from the Department of Chemistry, University of Illinois, Urbana–Champaign.<sup>3,27</sup>

**Equilibrium Acidities.** The equilibrium acidities were determined by the overlapping indicator titration method as described in the previous papers.<sup>6–8</sup> The results for equilibrium acidity measurements, together with the  $pK_{\text{HA}}$ 's for the indicators used, are summarized in Table 6.

**Oxidation Potentials.** The oxidation potentials of the conjugate anions derived from the phosphorus-containing com-

pounds were determined in DMSO solution using three-electrode cyclic voltammetry (Bioanalytical System, Inc.) as described previously.<sup>8</sup> All measurements were conducted in an airtight glass cell. Sublimed tetraethylammonium tetrafluoroborate ( $\text{Et}_4\text{N}^+\text{BF}_4^-$ ) was used as the supporting electrolyte. The working electrode consists of a 1.5 mm diameter platinum disk embedded in a cobalt glass seal. The electrode was polished with 0.05  $\mu\text{m}$  Fisher polishing aluminum or cleaned by ultrasonication and then rinsed with ethanol and dried before each run. The counter (auxiliary) electrode was a platinum wire, and a Ag/AgI electrode was used as the reference electrode. In a typical run,  $\sim 5$  mg of the weak acid and  $\sim 100$  mg  $\text{Et}_4\text{N}^+\text{BF}_4^-$  were added to a glass cell fitted with three-way stopcock.<sup>6,8</sup> The cell was purged with argon, and  $\sim 5$  mL of pure DMSO solvent was then added to the cell via airtight syringe generating about 1–3 mM solution of the weak acids. Dimsyl anion was then added dropwise to the solution via airtight syringe, providing about 1 mM solution of the desired anion, with continuous stirring and argon bubbling for maximum mixing. Voltammograms were recorded at a sweep rate of 100 mV/s using a BAS CV 27 voltammeter. An  $E_{1/2}$  of 0.875 V for the ferrocene/ferrocenium ( $F_c/F_c^+$ ) couple was used as the reference electrode in DMSO solution.

**Acknowledgment.** We greatly appreciate the kind help and stimulating discussions of Professor F. G. Bordwell of Northwestern University. We also appreciate the financial support from the Natural Science Foundation of Zhejiang province, China.

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