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Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in *As*-Substituted Triphenylarsonium and Related Cations[1]

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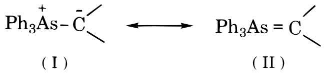
Equilibrium acidities ($\mathrm{p}K_{\mathrm{HA}}$s) of *As*-fluorenyltriphenylarsonium, *As*-phenacyltriphenylarsonium, six *As*-(*para*-substituted benzyl)triphenylarsonium $[p\text{-}\mathrm{GC_6H_4CH_2{}^+AsPh_3}]$ (G = H, Me, $\mathrm{CF_3}$, $\mathrm{CO_2Me}$, CN, and $\mathrm{NO_2}$), and six *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium $[p\text{-}\mathrm{GC_6H_4CH_2{}^+P}(n\text{-}\mathrm{Bu})_3]$ (G = H, Me, $\mathrm{CF_3}$, $\mathrm{CO_2Me}$, CN, and $\mathrm{NO_2}$) bromide salts, together with the oxidation potentials $[E_{\mathrm{ox}}(\mathrm{A}^-)]$ of their conjugate bases (ylides) have been determined in dimethyl sulfoxide (DMSO) solution. Introduction of an α-triphenylarsonium (α-$\mathrm{Ph_3As^+}$) group was found to increase the adjacent C−H bond acidities by 13−20 p*K* units (18−27 kcal/mol). The equilibrium acidities for the two series $p\text{-}\mathrm{GC_6H_4CH_2{}^+AsPh_3}$ and $p\text{-}\mathrm{GC_6H_4CH_2{}^+P}(n\text{-}\mathrm{Bu})_3$ cations were found to be nicely correlated with the Hammett σ^- constants of the corresponding *para*-substituents (G) (Figures 1 and 2). The homolytic bond dissociation enthalpies (BDEs) of the acidic C−H bonds determined by using eq 1 reveal that an α-$\mathrm{Ph_3As^+}$ group increases the BDE value of the adjacent acidic C−H bond by 2−5 kcal/mol, whereas the substituent effects for an α-$\mathrm{Ph_3P^+}$ or α-$(n\text{-}\mathrm{Bu})_3\mathrm{P^+}$ group was found to be dependent on the nature of the substituents attached to the α-carbon atom. Good linear correlations were obtained for the equilibrium acidities of *As*-(*para*-substituted benzyl)triphenylarsonium and *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium cations with the oxidation potentials of their conjugate bases (ylides) as shown in Figures 3 and 4, respectively.

Introduction

Although there are oceans of research papers about the phosphonium ylides (Wittig reagents) primarily used as reactive intermediates (synthons) to convert the carbonyl double bonds (>C=O) of aldehydes and ketones into the corresponding olefinic carbon−carbon double bonds (>C=C<),[2] relatively little attention has been paid to the arsonium ylides presumably due to the psychological barrier in that the word arsenic has been associated with poisoning for many centuries.[3,4]

Introduction of an α-triphenylarsonium group is known to significantly increase the equilibrium acidity of the adjacent C−H bond. For example, the $\mathrm{p}K_{\mathrm{HA}}$ value of *As*-phenacyltriphenylarsonium cation was found to be 8.25 in 95% ethanol solvent,[5] and the $\mathrm{p}K_{\mathrm{HA}}$ value of *As*-fluorenyltriphenylarsonium cation was reported to be 7.8 in 31.7% water−dioxane.[6] The large acidifying effects of the α-triphenylarsonium groups were believed to be caused by a combination of the Coulombic effects of the positive charge on the arsenic atom and the resonance delocalization of the negative charge into the available 4d vacant orbitals of arsenic as shown in Scheme 1.[4] The postulated resonance delocalization (covalent structure) (II) seems to be supported by the near planar carbanion structure of the stabilized arsonium ylides as obtained from X-ray diffractions.[7] The As−C bond length of the arsonium ylides was found to be shorter than the sum of the singly covalent bonded radii of carbon and arsenic.[4,7]

Scheme 1



Recently, we[8] have found that the acidifying effects of an α-triphenylphosphonium group are about 9∼20 p*K* units stronger than those of an α-trimethylammonium group on the related adjacent C−H bonds. The larger acidifying effects of the α-triphenylphosphonium than those of the α-trimethylammonium group were attributed to the larger polarizability effects rather than the resonance delocalization of the negative charge into the vacant 3d orbitals of phosphorus.[8a,b] The latter is very unlikely because the α-triphenylphosphonium groups

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[1] J.P.C. and X.M.Z. would like to dedicate this paper to Professor F. G. Bordwell for his pioneering work to determine the BDEs of the acidic H−A bonds from the acidity and oxidation potential measurements.

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were found to have no stabilizing effects on the adjacent radicals.[8] In the present paper, we extend our studies to examine the effects of α-triphenylarsonium groups on the equilibrium acidities and the BDEs of the adjacent acidic C−H bonds. Effects of α-tri(*n*-butyl)phosphonium and α-triphenylphosphonium groups have also been compared on the equilibrium acidities and BDEs.

Results and Discussion

Equilibrium Acidities. *As*-Fluorenyltriphenylarsonium, *As*-phenacyltriphenylarsonium, six *As*-(*para*-substituted benzyl)triphenylarsonium (p-$GC_6H_4CH_2{}^+AsPh_3$) (G = H, Me, CF_3, CO_2Me, CN, and NO_2), and six *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium [p-GC_6H_4-$CH_2{}^+P(n\text{-}Bu)_3$] (G = H, Me, CF_3, CO_2Me, CN, and NO_2) bromide salts were synthesized according to the literature or modified literature procedures.[8] The equilibrium acidities of these salts were measured in dimethyl sulfoxide (DMSO) solution by the overlapping indicator titration method.[9] All of the conjugated bases (ylides) derived from these salts were found to be stable enough to allow three-point titrations to be made under the experimental conditions of measurement. The counterion (Br^-) was shown to have no effects on the equilibrium acidity measurement.[8a] The related equilibrium acidities, together with those for the related parent compounds are summarized in Tables 1∼3.

Table 1. Comparison of Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in Different Onium Cations

acids	pK_{HA}^{a}	$E_{ox}(A^-)$^{e}	BDE_{HA}^{h}
$PhCH_3$	(43)^{b}		88−89^{i}
$PhCH_2{}^+NMe_3$	31.9^{c}	−1.143^{c}	90.5
$PhCH_2{}^+PPh_3$	17.4^{d}	−0.381^{d,f}	89.3
$PhCH_2{}^+AsPh_3$	22.7	−0.558	91.5
Fluorene (FlH_2)	22.6^{b}	−1.060^{b}	79.5
9-Me_3N^+FlH	17.8^{c}	−0.563^{c}	84.6
9-Ph_3P^+FlH	6.6^{d}	−0.044^{d,g}	81.3
9-Ph_3As^+FlH	9.8	−0.191	82.3
$PhCOCH_3$	24.7^{b}	−0.609^{b}	93.0
$PhCOCH_2{}^+NMe_3$	14.6^{c}	0.141^{c}	96.5
$PhCOCH_2{}^+PPh_3$	6.0^{d}	0.639^{d}	96.2
$PhCOCH_2{}^+AsPh_3$	8.6	0.450	95.5

[a] Equilibrium acidities (in p*K* units) measured in DMSO by the overlapping indicator titrations.[9] This study unless otherwise indicated. [b] Reference 16. [c] Reference 23. [d] Reference 8a. [e] Irreversible oxidation potentials (in volts) of the onium ylides measured in DMSO by conventional cyclic voltammetry. This study unless otherwise indicated. [f] The reversible oxidation potential is −0.339 V, which was measured by fast-scan CV.[8b] [g] The reversible oxidation potential is −0.021V, which was measured by fast-scan CV.[8b] [h] Homolytic bond dissociation enthalpies (in kcal/mol) of the acidic C−H bond determined by using eq 1. [i] Reference 22.

Examination of Table 1 shows that the acidifying effects of the α-triphenylarsonium group are about 6∼9 p*K* units stronger than those of the α-trimethylammonium group, but about 2∼5 p*K* units *weaker* than those of the α-triphenylphosphonium group. The equilibrium acidities of *As*-(*para*-substituted benzyl)triphenylarsonium cations (Table 2) were also found to be about 5 p*K* units weaker than those of the corresponding *P*-(*para*-substituted benzyl)triphenylphosphonium cations.[8b] The weaker acidifying effects of α-triphenylarsonium than those of the α-triphenylphosphonium groups are consistent with the relatively higher reactivities of the triphenylarsonium ylides than those of the analogous triphenylphosphonium ylides in the related Wittig reactions.[3c,4−6,10]

Table 2. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Benzylic C−H Bonds in *As*-(*Para*-substituted benzyl)triphenylarsonium Cations

acids	pK_{HA}^{a}	$E_{ox}(A^-)$^{b}	BDE_{HA}^{c}
$PhCH_2{}^+AsPh_3$	22.7	−0.558	91.5
4-$MeC_6H_4CH_2{}^+AsPh_3$	23.8	−0.630	91.4
4-$CF_3C_6H_4CH_2{}^+AsPh_3$	18.4	−0.290	91.8
4-$CH_3OCOC_6H_4CH_2{}^+AsPh_3$	18.2	−0.276	91.9
4-$NCC_6H_4CH_2{}^+AsPh_3$	17.6	−0.221	92.3
4-$O_2NC_6H_4CH_2{}^+AsPh_3$	16.1	−0.062	93.9

[a] Equilibrium acidities (in p*K* units) measured in DMSO by the overlapping indicator titrations.[9] [b] Irreversible oxidation potentials (in volts) of the triphenylarsonium ylides measured in DMSO solution by conventional cyclic voltammetry. [c] Homolytic bond dissociation enthalpies (in kcal/mol) of the benzylic C−H bonds determined by using eq 1.

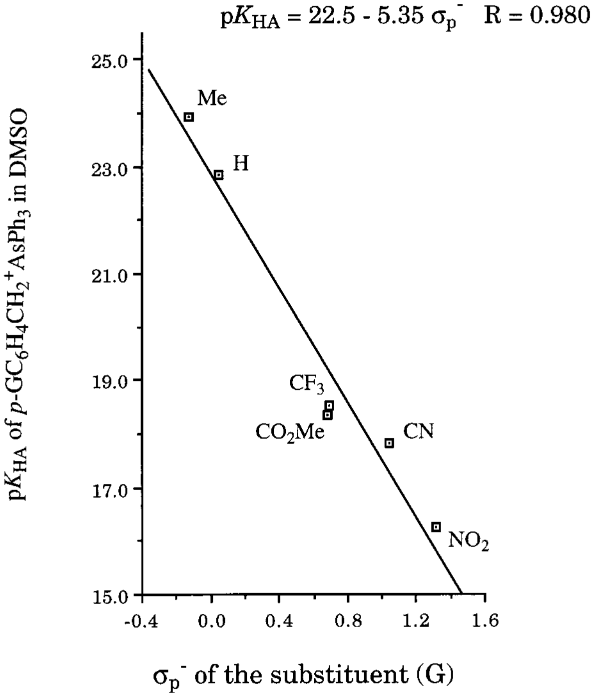

Figure 1. Correlation of the equilibrium acidities of *P*-(*p*-substituted benzyl)triphenylarsonium cations measured in DMSO solution against the Hammett $\sigma_p{}^-$ constants of the *para* substituents (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−169).

In an earlier paper,[8b] we have reported that the equilibrium acidities of *P*-(*para*-substituted benzyl)triphenylphosphonium cations were well correlated with the Hammett σ^- constants of the *para*-substituents. Not surprisingly, the equilibrium acidities of the *As*-(*para*-substituted benzyl)triphenylarsonium and *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium cations can also be well correlated with the Hammett σ^- constants of the *para*-substituents (Figures 1 and 2). Similar linear correlations of the equilibrium acidities with the Hammett σ^- constants have been observed for many other families of weak acids such as phenols,[11] thiophenols,[12]

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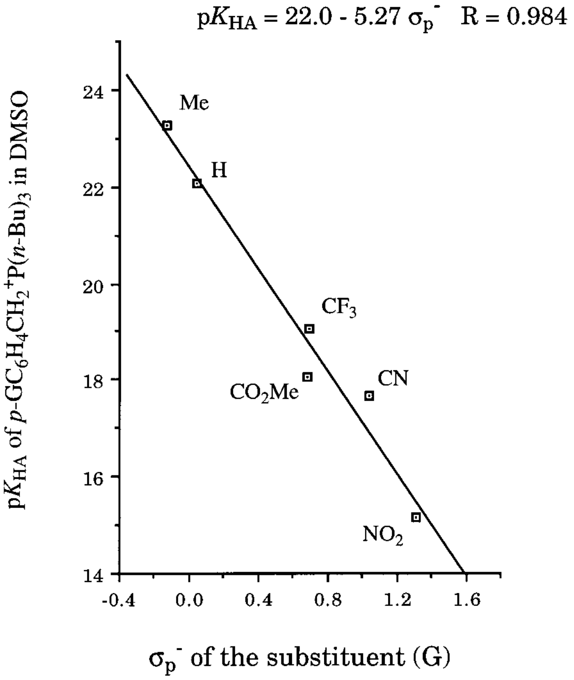

Figure 2. Correlation of the equilibrium acidities of *P*-(*p*-substituted benzyl)tri(*n*-butyl)phosphonium cations measured in DMSO solution against the Hammett σ_p^- constants of the *para* substituents (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−169).

anilines,[13] 10-substituted-9-methylanthracenes,[14] and toluenes.[15] But the Hammett correlation slopes for the *As*-(*para*-substituted benzyl)triphenylarsonium, *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium, and *P*-(*para*-substituted benzyl)triphenylphosphonium cations[8b] were found to be only about 5 p*K* units, which are much smaller than those for the *para*-substituted toluenes (12 pK_{HA} units)[15] and 10-substituted-9-methylanthracenes (10 pK_{HA} units).[14] The diminution of the Hammett correlation slopes for the *para*-substituted benzylic onium cations is clearly associated with the strong stabilization of the onium groups on the adjacent negative charge (Scheme 1), which in turn decreases the influence of the *para* substituent G.[8b]

Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds. The homolytic bond dissociation enthalpies of the acidic C−H BDEs in eight *As*-substituted triphenylarsonium cations and six *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium cations have been determined from the equilibrium acidities and the oxidation potentials of their conjugate bases (ylides) according to eq 1.[16] The calculated C−H BDEs together with those for the parent compounds and few *N*-substituted trimethylammonium and *para*-substituted triphenylphosphonium cations are also summarized in Tables 1∼3 for comparison.

Table 3. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Benzylic C−H Bonds in *P*-(*Para*-substituted benzyl)tri(*n*-butyl)phosphonium Cations

acids	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE_{HA}[c]
$PhCH_2^+P(t-Bu)_3$	21.9	−0.620	89.0
$4-MeC_6H_4CH_2^+P(t-Bu)_3$	23.1	−0.694	88.9
$4-CF_3C_6H_4CH_2^+P(t-Bu)_3$	18.9	−0.370	90.6
$4-CH_3OCOC_6H_4CH_2^+P(t-Bu)_3$	17.9	−0.358	89.6
$4-NCC_6H_4CH_2^+P(t-Bu)_3$	17.5	−0.292	90.5
$4-O_2NC_6H_4CH_2^+P(t-Bu)_3$	15.0	−0.127	90.9

[a] Equilibrium acidities (in p*K* units) measured in DMSO by the overlapping indicator titration.[9] [b] Irreversible oxidation potentials (in volts) of the tri(*n*-butyl)phosphonium ylides measured in DMSO solution by conventional cyclic voltammetry. [c] Homolytic bond dissociation enthalpies (in kcal/mol) of the benzylic C−H bonds determined by using eq 1.

$$BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \quad (1)$$

Deprotonation from the substituted onium cations and neutral weak acids is different; the former changes from positive to neutral species (ylide), and the latter changes from neutral to negative species. But the deviation on the equilibrium acidity measurement due to the different activity coefficients of the charged species has been shown to be smaller than the experimental error (±0.1 p*K* units) of the overlapping indicator titration.[8b,9] The oxidation potentials of the conjugate bases (ylides) [$E_{ox}(A^-)$] are readily obtained by means of conventional cyclic voltammetry (scan rate: 100 mV/s).[16] Although most oxidation potentials measured by the conventional cyclic voltammetry are irreversible, the irreversible oxidation potentials for the conjugate anions were found to agree within potentials as obtained by fast-scan cyclic voltammetry[8b,17] or second harmonic alternating current voltammetry (SHACV).[18] Nevertheless, the BDE values obtained with the irreversible oxidation potentials according to eq 1 have been shown to agree within ± 2 kcal/mol with the best literature BDE values.[16] Furthermore, the BDEs for the same family of weak acids are expected to be accurate with each other even less than 0.5∼1 kcal/mol since the oxidation potential measurement is reproducible to ±0.020 V (∼0.5 kcal/mol)[16b] and the acidity measurement is accurate to 0.15 kcal/mol.[9]

Examination of the column 4 of Table 2 shows that the benzylic C−H BDEs of the six *As*-(*para*-substituted benzyl)triphenylarsonium cations average 92.7 ± 1.2 kcal/mol. Examination of Table 3 shows that the average benzylic C−H BDE of the six *P*-(*para*-substituted benzyl)-tri(*n*-butyl)phosphonium cations is 89.0 ± 0.9 kcal/mol, which is essentially same as the average benzylic C−H BDE (89.6 ± 0.3 kcal/mol) of the *P*-(*para*-substituted benzyl)triphenylphosphonium cations [$p-GC_6H_4CH_2^+-PPh_3$] (G = H, Br, CN, and NO_2) even though the equilibrium acidities of the former are about 5 p*K* unit

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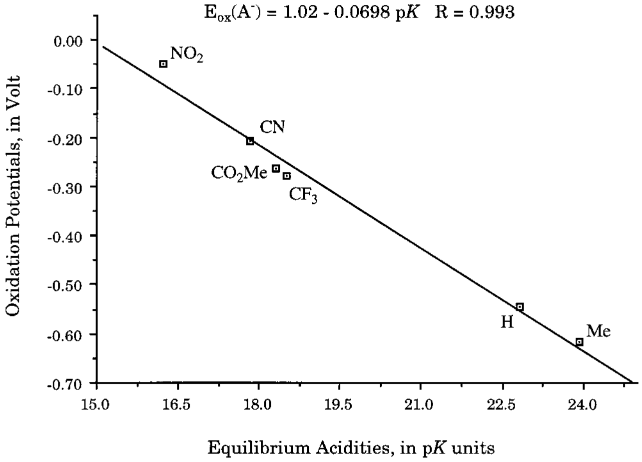

Figure 3. Plot of the oxidation potentials of the *As*-(*p*-substituted benzyl)triphenylarsonium ylides versus the equilibrium acidities of their conjugate acids in DMSO solution.

weaker than the latter.[8a,b] The weaker acidifying effects of α-tri(n-butyl)phosphonium relative to α-triphenylphosphonium groups can be attributed to the relatively smaller polarizability effects of the n-butyl than of the phenyl groups. The polarizability effects of a phenyl group are known to be larger than those of an alkyl group. For example, replacement of the alkyl group in alkylthioacetonitriles $RSCH_2CN$ (R = Me, Et, Pr, and Bu) by a phenyl group was found to increase the equilibrium acidities by 2∼4 p*K* units, but it results in negligible effects on the acidic C−H BDEs.[19] Equilibrium acidity increase accompanied with a near constant BDE has been considered as the characteristics for the polarizability effects.[19a]

Linear Correlation of Oxidation Potentials of *As*-(*Para*-substituted benzyl)triphenylarsonium and *P*-(*Para*-substituted benzyl)tri(*n*-butyl)phosphonium Ylides versus Equilibrium Acidities of Their Conjugate Acids. The near constant benzylic C−H BDEs of *As*-(*para*-substituted benzyl)triphenylarsonium (Table 2) and *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium cations (Table 3) require that the oxidation potentials of the onium ylides be linearly correlated with the equilibrium acidities of the corresponding conjugate acids. Indeed, the oxidation potentials of *As*-(*para*-substituted benzyl)triphenylarsonium and *P*-(*para*-substituted benzyl)tri(*n*-butyl)phosphonium ylides were found to be well correlated with the equilibrium acidities of their conjugate acids as shown in Figures 3 and 4, respectively. The slopes for the linear correlations are near unity when both axes are expressed in kcal/mol. Similar linear correlations of the oxidation potentials of the conjugate bases versus their equilibrium acidities have been observed in few other families of weak acids.[8a,b,14,20]

Examination of Tables 2 and 3 shows that the benzylic C−H BDEs of the $p\text{-}GC_6H_4CH_2{}^+AsPh_3$ and $p\text{-}GC_6H_4\text{-}CH_2{}^+P(n\text{-}Bu)_3$ cations (G = CN and NO_2) are about 1∼2 kcal/mol higher than those of the rest cations. The slightly higher benzylic C−H BDEs for those containing strong electron acceptors (CN and NO_2) are presumably due to the increase of the ground-state effects caused by the polar interaction of the strong electron acceptors with the weak polar C−H bonds.[21]

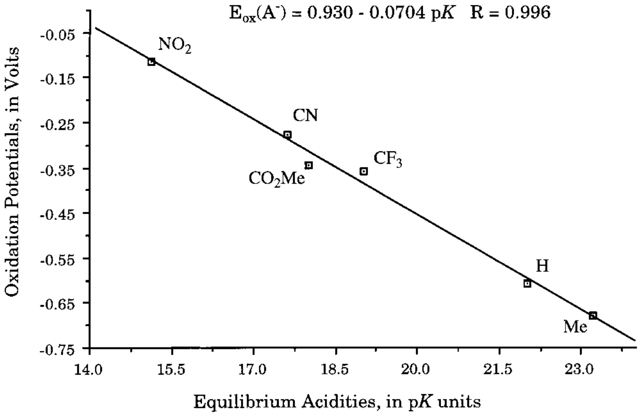

Figure 4. Plot of the oxidation potentials of the *P*-(*p*-substituted benzyl)tri(*n*-butyl)phosphonium ylides versus the equilibrium acidities of their conjugate acids in DMSO solution.

No Resonance Delocalization of the Unpaired Electron into the 4d Orbitals of Arsenic. Examination of Table 2 shows that the benzylic C−H BDEs of the *As*-(*para*-substituted benzyl)triphenylarsonium cations are in the range of 91.4−93.9 kcal/mol. This means that introduction of an α-triphenylarsonium group strengthens the benzylic C−H bond by about 2∼5 kcal/mol since the benzylic C−H BDE of toluene is well-known to be about 88∼89 kcal/mol.[22] In addition, the acidic C−H BDEs of *As*-fluorenyltriphenylarsonium and *As*-phenacyltriphenylarsonium cations (Table 1) were also found to be about 2∼3 kcal/mol higher than those of their parent compounds.

The bond-strengthening (radical destabilizing) effects of the α-triphenylarsonium group were found to be remarkably similar to those of the α-trimethylammonium (α-Me_3N^+) group.[23] The bond-strengthening effects of α-trimethylammonium groups were believed to be caused by the field/inductive effects of the positive charge on the nitrogen atom.[23] Theoretical calculations also show that an α-ammonium (α-H_3N^+) group decreases the adjacent methyl radical stability by about 4 kcal/mol.[24] Therefore, the bond-strengthening effects of the α-triphenylarsonium groups can also be attributed to the field/inductive radical destabilizing effects of the positive charge on the arsenic atom. In other words, the resonance delocalization of the unpaired electron into the related vacant 4d orbitals of arsenic is negligible as shown in Scheme 2.

No resonance delocalization of the unpaired electron into the 4d orbitals of arsenic implies that the resonance delocalization of the negative charge in the corresponding ylides into the vacant 4d orbitals of arsenic should also

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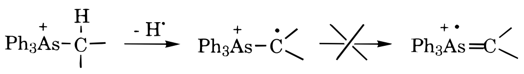
Scheme 2



be negligible.[8] Thus, the large acidifying effects of the α-triphenylarsonium groups should be caused by a combination of the polarizability effects and the field/inductive effects of the positive charge on the arsenic atom. The short ylidic As−C bond length[6,7] can be attributed to the electrostatic attraction of the opposite charge on the arsenic atom and the carbanion center.[25]

Is There Resonance Delocalization of the Unpaired Electron into the 3d Orbitals of Phosphorus? Introduction of an α-triphenylphosphonium group into the acidic sites of CH_3CN, CH_3COOEt, and CH_3COR was found to strengthen the adjacent acidic C−H bonds by 2∼3 kcal/mol, which is similar to the effects for the introduction of an α-trimethylammonium group.[8a] In other words, there is no resonance delocalization of the unpaired electron for the radical cations $Ph_3P^+CH^{\bullet}CN$, $Ph_3P^+CH^{\bullet}COOEt$, and $Ph_3P^+CH^{\bullet}COR$, formed by removal of one hydrogen atom from the corresponding precursor cations. This conclusion is in accord with the ESR studies, which showed that the majority of the unpaired electron in the radical cation ($Ph_3P^+CH^{\bullet}COOH$) is localized on the carbon atom rather than delocalized into the 3d orbitals of phosphorus.[26]

Substituent is known to have dual effects on the adjacent radical stabilities: i.e., the field/inductive effect decreases the radical stability, but the resonance delocalization will increase the radical stabiliy.[23,27] When an electron acceptor and electron donor are both attached to the same carbon radical center, the net radical stabilizing effect is usually greater than the sum of the individual substituent effects.[28] But when two electron acceptors were both introduced to the same carbon radical center, the net radical stabilizing effect will be much smaller than the sum of the individual substituent effects due to the strong polar interactions of the two electron acceptors.[20d,21] For example, introduction of a $PhSO_2$ or NO_2 group into methane decreases the C−H BDE by 6 or 7 kcal/mol respectively,[29] but no additional radical stabilizing effect was found when they were introduced into the acidic site of CH_3SO_2Ph.[20d] On the other hand, introduction of an electron donor such as a phenyl[20d] or a thiophenyl group[30] into the acidic site of CH_3SO_2Ph was found to decrease the acidic C−H BDEs by an additional 8∼10 kcal/mol.

Comparison of Tables 2 and 3 shows that the benzylic C−H BDEs of the p-$GC_6H_4CH_2{}^+P(n\text{-}Bu)_3$ cations are also about 2 ∼ 3 kcal/mol less than those of the corresponding p-$GC_6H_4CH_2{}^+AsPh_3$ cations. More significantly, the acidic C−H BDE (88 kcal/mol) of $Ph_3P^+CH_2SPh$ cation was found to be even about 5 kcal/mol *lower* than that (93 kcal/mol) of CH_3SPh.[8a] The less radical destabilizing or some radical stabilizing effects of the α-phosphonium groups are caused presumably by the radical stabilization by some resonance delocalization of the unpaired electron into the 3d orbitals of phosphorus. This is not surprising since phenyl (Ph) and thiophenyl (SPh) groups are known to be electron donating, but cyano (CN), ethoxycarbonyl (COOEt) and carbonyl (COR) are electron accepting.[29]

Lack of the resonance delocalization of the unpaired electron into the 4d orbitals of arsenic for the radical cation $Ph_3As^+CH^{\bullet}Ph$ is probably due to the greater size and diffuseness of the arsenic 4d-orbitals compared with the phosphorus 3d-orbitals, which will prevent the effectiveness of the $p\pi - d\pi$ orbital overlap.

Summary and Conclusions

The acidifying effects of α-triphenylarsonium groups (α-Ph_3As^+) are about 13 ∼ 20 pK units (18 ∼ 27 kcal/mol) and are attributed to a combination of the Coulombic and polarizable interaction on the ylide anions. Determination of the homolytic bond dissociation enthalpies reveals that introduction of an α-triphenylarsonium group decreases the adjacent radical stabilities by 2∼5 kcal/mol, which is similar to that of an α-Me_3N^+ group, indicating that there is no ($p\pi{-}d\pi$) resonance delocalization of the unpaired electron into the 4d orbitals of arsenic. But the radical stabilization effects of the α-phosphonium groups in the radical cations $R_3P^+CH^{\bullet}G$ were found to be dependent on the nature of the substituent G. The 4∼5 pK unit weaker acidifying effects of an α-tri(n-butyl)phosphonium than of an α-triphenylphosphonium group are attributed to the much larger polarizability effects of phenyl than of n-butyl groups.

Experimental Section

The ^1H NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer with tetramethylsilane as internal standard. Melting points were measured on a Yanaco apparatus and were uncorrected. The electrochemical measurements were performed on a BAS-100B electroanalytical instrument.

Materials. The synthesis of *P*-fluorenyltriphenylphosphonium and *P*-phenacyltriphenylphosphonium bromides has been described previously.[8a] *As*-Fluorenyltriphenylarsonium,[31] *As*-phenacyltriphenylarsonium,[32] and *P*-(*para*-substituted benzyl)tri(n-butyl)phosphonium bromides[33] were synthesized according to the related literature procedures. *As*-(*para*-substituted benzyl)triphenylarsonium bromides were synthesized by a modified literature procedure.[34] A solution of triphenylarsine (Ph_3As) (3.06 g, 10 mmol) in 20 mL of nitromethane was added dropwise into a solution of *para*-substituted benzyl bromide (10 mmol) in 20 mL of nitromethane. The mixture was allowed to reflux for 4∼6 h and gave a white precipitate. The crude products were purified by recrystallization from acetone/ethanol. The melting points, ^1H NMR chemical shifts, and elemental analyses (for new compounds) are summarized in Table 4.

pK_{HA} Measurement. The equilibrium acidities of the eight *As*-substituted triphenylarsonium and six *para*-substituted tri(n-butyl)phosphonium bromides were measured in DMSO solution at the room temperature by the overlapping indicator titration method as described previously.[9] The results, together with the indicator used, are summarized in Table 5.

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Table 4. Melting Points, ^{1}H NMR Chemical Shifts, and Elemental Analysis of the Onium Bromide Salts

compound	mp (°C)[a] (lit. mp)	^{1}H NMR[e] δ (CDCl$_3$)	elemental analysis (calcd)[f]
9-Ph$_3$As$^+$FlH Br$^-$	180−181 (178−179)[b]	7.01−8.12 (m, 23H), 8.62 (s, 1H)	
PhCOCH$_2$$^+$AsPh$_3$ Br$^-$	184−185 (186)[c]	6.5 (s, 2H), 7.3−8.2 (m, 20H)	
C$_6$H$_5$CH$_2$$^+$AsPh$_3$ Br$^-$	172−172.5	5.60(s, 2H), 7.11−7.52(m, 5H), 7.82(m, 15H)	C: 62.85 (62.91) H: 4.71 (4.69)
p-MeC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	161−162	2.43(s, 3H), 5.55 (s, 2H), 6.93−7.51 (m, 4H), 7.85 (s, 15H)	C: 63.53 (63.56) H: 5.02 (4.92)
p-MeO$_2$CC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	160−161	3.94 (s, 3H), 5.81 (s, 2H), 7.32−8.10 (m, 19H)	C: 60.41 (60.58) H: 4.52 (4.52)
p-NCC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	188−189	6.12 (s, 2H), 7.12−8.03 (m, 19H)	C: 62.01 (62.18) H: 4.17 (4.21) N: 2.67 (2.98)
p-CF$_3$C$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	162−163	6.02 (s, 2H), 7.11−8.12 (m, 19H)	C: 57.09 (57.27) H: 3.88 (3.88)
p-NO$_2$C$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	163−164	6.23 (s, 2H), 7.53−8.12 (m, 19H)	C: 57.29 (57.49) H: 4.13 (4.05) N: 2.57 (2.68)
C$_6$H$_5$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	148.5−150 (144−148)[d]	0.80−1.21 (m, 9H), 1.33−180 (m, 12H), 2.20−2.81 (m, 6H), 4.35 (d, 2H), 7.33−7.81 (m, 5H)	
p-MeC$_6$H$_4$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	108−110	0.80−1.12 (m, 4H); 1.22−1.81 (m, 12H), 2.34 (s, 3H); 2.45−2.85 (m, 6H), 4.25 (d, 2H), 7.13−7.64 (m, 4H)	C: 61.92 (62.02) H: 9.25 (9.35)
p-MeO$_2$CC$_6$H$_4$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	88.−89.5	0.81−1.22 (m, 9H), 1.23−1.82 (m, 12H), 2.33−3.01 (m, 6H); 4.10 (s, 3H), 4.51−5.02 (d, 2H), 7.51−8.25 (m, 4H)	C: 58.36 (58.47) H: 8.52 (8.41)
p-NCC$_6$H$_4$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	160−161.5	0.79−1.09 (m, 9H); 1.15−1.70 (m, 12H); 2.13−2.80 (m, 6H); 5.02(d, 2H), 7.42−8.13 (m, 4H)	C: 59.91 (60.30) H: 8.30 (8.35) N: 3.28 (3.52)
p-CF$_3$C$_6$H$_4$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	157−158	0.81−1.10 (m, 9H); 1.20−1.81 (m, 12 H); 2.21−2.79 (m, 6H); 4.57 (d, 2H), 7.45−8.05 (m, 4H)	C: 54.11 (54.43) H: 7.90 (7.53)
p-NO$_2$C$_6$H$_4$CH$_2$$^+$P(*n*−Bu)$_3$ Br$^-$	169−170	0.87−1.22 (m, 9H); 1.23−1.82 (m, 12H), 2.33−2.81 (m, 6H), 4.55−5.15(d, 2H), 7.84−8.45 (m, 4H)	C: 54.50 (54.55) H: 7.86 (7.95) N: 3.19 (3.35)

[a] Melting point; in °C; uncorrected. [b] Johnson, A. W. *J. Org. Chem.* **1960**, *25*, 183. [c] Aksnes, G.; Songstad, J. *Acta Chem. Scand.* **1964**, *18*, 655. [d] Ramirez, E.; Madaan, C. P.; Smith, G. P. *Tetrahedron*, **1966**, *22*, 567. [e] Chemical shifts in ppm. [f] Elemental analysis for the new compounds. The numbers in the parenthesis are calculated from the related molecular formula.

Table 5. Equilibrium Acidity Measurements for the Onium Bromides by the Overlapping Indicator Titration

cations	pK_{HA}[a]	indicator	pK_{IN}[i]	pK_{HA} (assigned)	runs[j]
9-Ph$_3$As$^+$FlH Br$^-$	9.77 ± 0.11	COMFH[b]	10.35	9.8	3
PhCOCH$_2$$^+$AsPh$_3$ Br$^-$	8.56 ± 0.02	CNFH[c]	8.3	8.6	2
PhCH$_2$$^+$AsPh$_3$ Br$^-$	22.68 ± 0.07	FH[d]	22.6	22.7	2
p-MeC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	23.83 ± 0.06	FH	22.6	23.8	2
p-MeO$_2$CC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	18.17 ± 0.06	PFH[e]	17.9	18.2	2
p-NCC$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	17.67 ± 0.15	PFH	17.9	17.6	2
p-CF$_3$C$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	18.40 ± 0.02	PFH	17.9	18.4	2
p-NO$_2$C$_6$H$_4$CH$_2$$^+$AsPh$_3$ Br$^-$	16.11 ± 0.12	J1Y300[f]	15.0	16.1	2
C$_6$H$_5$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	21.92 ± 0.12	2NPANH[g]	20.66	21.9	2
p-MeC$_6$H$_4$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	23.07 ± 0.02	FH	22.6	23.1	2
p-MeO$_2$CC$_6$H$_4$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	17.86 ± 0.04	CNAH[h]	18.9	17.9	2
p-NCC$_6$H$_4$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	17.49 ± 0.08	PFH	17.9	17.5	2
p-CF$_3$C$_6$H$_4$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	18.85 ± 0.21	CNAH	18.9	18.8	2
p-NO$_2$C$_6$H$_4$CH$_2$$^+$P(*n*-Bu)$_3$ Br$^-$	15.59 ± 0.25	J1Y300	15.0	15.6	2

[a] Equilibrium acidities measured in DMSO. [b] 9-(Methoxycarbonyl)fluorene. [c] 9-Cyanofluorene. [d] Fluorene. [e] 9-Phenylfluorene. [f] (Phenylsulfonyl)acetonitrile. [g] 2-Naphthylacetonitrile. [h] 4-Chloro-2-nitroaniline. [i] Equilibrium acidity of the indicator used. [j] Numbers of the experimental measurements.

Electrochemical Measurement. All electrochemical experiments were carried out in DMSO solution under an argon atmosphere as described previously.[16,35] *n*-Bu$_4$NPF$_6$ (0.1 M) was employed as the supporting electrolyte. A standard three-electrode cell consists of platinum disk (ø = 1 mm) as working electrode and platinum wire as counter electrode. The scan rate was 100 mV/s. AgNO$_3$/Ag (0.1 M) couple was used as the reference electrode. The reported oxidation potentials were all referenced to the ferrocenium/ferrocene couple, which was used as an internal standard. In the electrochemical cell (BAS), the conjugate bases (ylides) were generated by addition of a stock potassium dimsylate solution to a 5∼8 mL solution of the onium bromide salt to be deprotonated. The concentration of the onium ylides generated was about 2 mM.

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