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Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in *P*-Substituted Triphenylphosphonium Cations

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Abstract: Equilibrium acidities (pK_{HA} values) for the cations in 11 *P*-substituted triphenylphosphonium salts, $[Ph_3PG]^+X^-$, where G is CH_3, $(CH_3)_2CH$, CH_2Ph, CH_2CO_2Et, $CH(Me)CO_2Et$, CH_2COCH_3, CH_2CHO, CH_2CN, CH_2COPh, fluorene, and CH_2SPh, together with the oxidation potentials of their conjugate bases (ylides), have been measured in dimethyl sulfoxide (DMSO) solution. The acidifying effects of the α-triphenylphosphonium groups (α-Ph_3P^+) on the adjacent C–H bonds in these cations were found to average about 29 kcal/mol, which is about 15 kcal/mol greater than the average for the acidifying effects of α-trimethylammonium groups (α-Me_3N^+) and about 6 kcal/mol greater than the acidifying effects of α-pyridinium groups (α-PyN^+) on these G functions. Evidence is presented to show that these large acidifying effects of α-Ph_3P^+ groups are caused by a combination of field/inductive and polarizability effects. The homolytic bond dissociation energies (BDEs) of the acidic C–H bonds in these cations estimated by combining their equilibrium acidities with the oxidation potentials of their conjugate bases (ylides) show that α-Ph_3P^+ groups increase the BDEs in most of these cations by 0–3 kcal/mol, i.e., they slightly destabilize the corresponding radicals. These effects on BDEs are similar to those of α-Me_3N^+ groups but opposite to the effects of α-PyN^+ groups, which usually decrease the BDEs by about 4–6 kcal/mol as a consequence of their ability to delocalize odd electrons present on adjacent atoms into the aromatic ring.

Introduction

P-Alkyl-substituted triphenylphosphonium salts, $[Ph_3PCH_2R]^+X^-$, are readily prepared by reactions of triphenylphosphine with alkyl halides, RCH_2X, and the like. The triphenylphosphonium ylides, $Ph_3P^+CH^-R$ (Wittig reagents), formed by removal of a proton from the C–H bond next to the positively charged phosphorus atom in the $[Ph_3PCH_2R]^+$ cations are commonly used synthons for the conversion of carbonyl (C=O) groups in aldehydes or ketones to the corresponding olefinic (C=C) bonds.[1]

It is known that *N*-substituted trimethylammonium cations,[2] *N*-substituted pyridinium cations,[2] as well as *P*-substituted triphenylphosphonium cations,[1] can be deprotonated in suitably basic media to form the corresponding ylides.[3] The strongly basic ylides derived from *N*-substituted trimethylammonium cations often undergo rearrangement and/or elimination reactions, however. For example, a recent study of the heat of deprotonation of *N*-benzyltrimethylammonium bromide, $[Me_3N^+CH_2Ph]Br^-$, by CH_3SOCH_2Li in DMSO has shown that rearrangement starts within a few minutes after addition of the base,[3c] but the corresponding $Ph_3P^+CH^-Ph$ ylide is stable in solution.[4]

Phosphonium cations of the type $Ph_3P^+CH_2G$, where G is an electron-withdrawing group such as CN, COPh, or CO_2Et, differ from their $Me_3N^+CH_2G$ analogues in being strong enough acids to be deprotonated in aqueous solution by sodium carbonate.[5] The cations where G = COPh and $COCH_3$ have been shown to have pK_{HA}s of 6.0 and 6.5, respectively, in 80% $EtOH/H_2O$.[6] Similarly, the pK_{HA} value for the 9-Ph_3P^+-fluorenyl cation has been found to be 7.5 in 31% water–dioxane,[7] and pK_{HA} values for these cations and for the $Ph_3P^+CH_2CO_2Et$ cation have been measured in various ethanol–water mixtures.[8] The ylides formed from these cations are stable enough to be isolated and characterized by ordinary methods.[5] They react slowly with aldehydes at room temperature to form alkenes where the *E* conformation is favored.[1] On the other hand, when G is an alkyl group the corresponding ylides are very reactive and are destroyed by oxygen or moisture, even at low temperatures.[1]

The much greater stability of the ylides derived from acidic $Ph_3P^+CH_2G$ cations than the ylides derived from their nitrogen analogues was at one time attributed to stabilization by a (p–d) π interaction as represented by the canonical covalent formula **1b**. This formulation was supported by an X-ray crystal structure

$$\underset{\textbf{1a}}{Ph_3P^+{-}^-CR_2} \leftrightarrow \underset{\textbf{1b}}{Ph_3P{=}CR_2}$$

analysis that showed a 0.09–0.17 Å shortening of the usual C–P bond length and a planar geometry for the stabilized carbanionic center.[9] The appreciable shortening of the C–P bond was believed to be associated with d-orbital participation which was optimized by a planar carbanionic center.[9] The geometry of nonstabilized

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(1) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989,** *89,* 863–927 and references cited therein.

(2) (a) Bordwell, F. G.; Zhang, X.-M. *J. Org. Chem.* **1990,** *55,* 6078–6079. (b) Zhang, X.-M.; Bordwell, F. G.; Van Der Puy, M.; Fried, H. E. *J. Org. Chem.* **1993,** *58,* 3060–3066.

(3) (a) Chantrapromma, K.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1983,** 1049 and references cited therein. (b) Phillips, W. G.; Ratts, K. W. *J. Org. Chem.* **1970,** *35,* 3144. (c) Arnett, E. M.; Wernett, P. C. *J. Org. Chem.* **1993,** *58,* 301–303. (d) Henrick, C. A.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1967,** *20,* 2441 and references cited therein. (e) Bunting, J. W.; Toth, A.; Heo, C. K. M.; Moorse, R. G. *J. Am. Chem. Soc.* **1990,** *112,* 8878. (f) Bunting, J. W.; Ranter, J. P. *J. Am. Chem. Soc.* **1991,** *113,* 6950.

(4) Bergelson, L. D.; Barsukov, L. I.; Shemyakin, M. M. *Tetrahedron* **1967,** *23,* 2709.

(5) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966.

(6) Fliszar, S.; Hudson, R. F.; Salvadori, G. *Helv. Chim. Acta* **1963,** *46,* 1580.

(7) Johnson, A. N.; LaCount, R. B. *Tetrahedron* **1960,** *9,* 130.

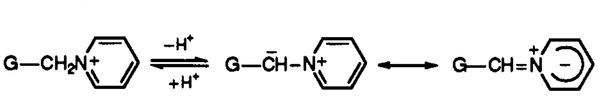
(8) Aksnes, G.; Songstad, J. *Acta Chem. Scand.* **1964,** *18,* 655–661.

(9) (a) Mak, T. C. W.; Trotter, J. *Acta Crystallogr.* **1965,** *18,* 81–88. (b) Stephens, F. S. *J. Chem. Soc.* **1965,** 5640–5650. (c) Stephens, F. S. *J. Chem. Soc.* **1965,** 5658–5678. (d) Schmidbaur, H.; Jeong, J.; Schier, A.; Graf, W.; Wilkinson, D.; Müller, G.; Krüger, K. *New J. Chem.* **1989,** *13,* 341. (e) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987,** S1.

0002-7863/94/1516-0968$04.50/0

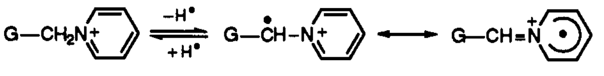
ylides, such as the *P*-cyclopropyltriphenylphosphonium ylide,[10a] has been shown, however, to be pyramidal, not planar,[10] and low-temperature NMR experiments have shown that rotation around the C–P bond is virtually unrestricted. The activation barrier for bond rotation was estimated to be less than 8 kcal/mol.[11] Furthermore, *ab initio* calculations indicated that the negative charge in phosphonium ylides is essentially localized on the carbon atom[12] and suggested that the C–P bond shortening can be accounted for as a polarization effect.[13] It would appear, then, that both experimental and theoretical evidence indicate that the most accurate description of these ylides is one in which an easily pyramidalized carbanion is stabilized by an adjacent tetrahedral phosphonium center.[14]

Recently, we have measured the equilibrium acidities of 17 *N*-substituted trimethylammonium cations and nine *N*-substituted pyridinium cations in DMSO solution.[2] The acidifying effects of α-Me_3N^+ groups in cations of the type $Me_3N^+CH_2G$, where G is CN, COPh, CO_2Et, and the like were large (ΔpK_{HA} values of about 10 units), because of the large field/inductive (electrostatic) effect of the positively charged nitrogen atom. The acidifying effects of the α-PyN^+ groups were about 6 pK_{HA} units larger because the electrostatic effect of the positively charged nitrogen atom was augmented by delocalization of the negative charge on the carbon atom of the ylide into the pyridinium ring (**3a** ↔ **3b**).



2 **3a** **3b**

The net effects of α-Me_3N^+ and α-PyN^+ groups on the homolytic bond dissociation energies (BDEs) of the acidic C–H bonds are opposite to one another. For example, whereas the presence of the α-Me_3N^+ group in the $PhCOCH_2NMe_3^+$ cation *strengthens* the acidic C–H bond by about 3.5 kcal/mol, the presence of the α-PyN group in $PhCOCH_2NPy^+$ *weakens* the acidic C–H bond by about 6 kcal/mol (henceforth kcal/mol will be abbreviated as kcal). The reversal in the latter case is attributed to the stabilizing effect of delocalizing the odd electron in the corresponding radical into the pyridinium ring (**5a** ↔ **5b**), which more than compensates for the destabilizing effect of the positive charge on the radical. It is important, therefore, to compare the effects on acidities and BDEs of α-Ph_3P^+ groups with those of α-Me_3N^+ and α-PyN^+ groups.



4 **5a** **5b**

Results and Discussion

Equilibrium Acidities. The equilibrium acidities of the cations in eleven *P*-substituted triphenylphosphonium salts were determined in dimethyl sulfoxide (DMSO) solution by the overlapping indicator method.[15] The results, together with the equilibrium acidities of the corresponding cations in *N*-substituted trimethylammonium cations, are summarized in Table 1. The conjugate bases (ylides) derived from most *P*-substituted triphenylphosphonium cations were stable under the conditions of the measurements, allowing three-point titrations to be made. The ylides derived from $Ph_3P^+CH_3$ and $Ph_3P^+CH(CH_3)_2$ cations were unstable, however, and only one-point titrations were possible.

Table 1. Equilibrium Acidities of *N*-Substituted Trimethylammonium Cations and *P*-Substituted Triphenylphosphonium Cations and Their Corresponding Parents

compd	pK_{HA}[a]	ΔpK_{HA}[e]	$\Delta\Delta pK_{AHA}$[h]
CH_4	(56)[b]	(0.0)	
$Me_3N^+CH_3$	(42)[b]	14	(0.0)
$Ph_3P^+CH_3$	22[c]	33.5	19.5
$Ph_3P^+CH(CH_3)_2$	21[c]	35[f]	21[f]
$PhCH_3$	(43)[b]	(0.0)	
$Me_3N^+CH_2Ph$	31.9	11.1	(0.0)
$Ph_3P^+CH_2Ph$	17.4	25.6	14.5
CH_3SPh	(39)[b]	(0.0)	
$Me_3N^+CH_2SPh$	28.0	11	(0.0)
$Ph_3P^+CH_2SPh$	14.86	24	13.1
CH_3CO_2Et	(29)[b]	(0.0)	
$Me_3N^+CH_2CO_2Et$	20.0	9.0	(0.0)
$Ph_3P^+CH_2CO_2Et$	8.50	20.5	11.5
$Ph_3P^+CH(Me)CO_2Et$	9.25	19.75[g]	10.75[g]
CH_3COCH_2–H	26.5	(0.0)	
$Me_3N^+CH_2COCH_3$	16.3	10.2	(0.0)
$Ph_3P^+CH_2COCH_3$	7.1	19.4	9.2
CH_3CHO	24.5[d]		
$Ph_3P^+CH_2CHO$	6.09	18.4	8.2[i]
H–CH_2CN	31.3	(0.0)	
$Me_3N^+CH_2CN$	20.6	10.7	(0.0)
$Ph_3P^+CH_2CN$	6.93	24.4	13.4
CH_3COPh	24.7	(0.0)	
$Me_3N^+CH_2COPh$	14.6	10.1	(0.0)
$Ph_3P^+CH_2COPh$	6.0	18.7	8.6
H_2Fl	22.6	(0.0)	
9-Me_3N^+FlH	17.8	4.8	(0.0)
Ph_3P^+FlH	6.6	16.0	11.2

[a] In pK_{HA} units; equilibrium acidities measured in DMSO solution against two indicators with three-point titration by the overlapping indicator method described previously[15] unless otherwise indicated. [b] Estimated by extrapolation. [c] Estimated by one-point titration. [d] Estimated. See ref 15. [e] In pK_{HA} units; equilibrium acidities of *P*-substituted triphenylphosphonium cations and *N*-substituted trimethylammonium cations relative to the corresponding parents. [f] Relative to methane and $Me_3N^+CH_3$. [g] Relative to CH_3CO_2Et and $Me_3N^+CH_2CO_2Et$. [h] In pK_{HA} units; equilibrium acidities of *P*-substituted triphenylphosphonium cations relative to those of the corresponding *N*-substituted trimethylammonium cations. [i] Relative to $Me_3N^+CH_2COCH_3$.

The most striking feature of Table 1 is the much greater acidifying effect of an α-Ph_3P^+ group than an α-Me_3N^+ group as brought out by the equilibrium acidities of *P*-substituted triphenylphosphonium cations relative to the like *N*-substituted trimethylammonium cations ($\Delta\Delta pK_{HA}$ in column 4). We see from column 4 that as the group bearing the acidic C–H bond is changed from CH_3 or $CH(CH_3)_2$ to CH_2Ph the $\Delta\Delta pK_{HA}$ values decrease from about 20 to 14.5 pK_{HA} units (27 to 20 kcal) and then, as more strongly acidifying groups are introduced, $\Delta\Delta pK_{HA}$ decreases to an average of 10.7 pK_{HA} units (15 kcal) for the cations giving more stabilized ylides on deprotonation (1 pK_{HA} unit = 1.37 kcal). One might be tempted to attribute at least part of these large acidifying effects to p–d orbital overlap in the $Ph_3P^+CH^-G$ ylides, but the compelling evidence presented in the introduction excludes this possibility. It would appear that the effects must be associated instead with the much larger polar-

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(10) (a) Schmidbaur, H.; Schier, A. S.; Milewski-Mahrla, B.; Schubert, U. *Chem. Ber.* **1982,** *115,* 722–731. (b) Schmidbaur, H.; Schier, A. S.; Frazao, C. M. F.; Müller, G. *J. Am. Chem. Soc.* **1986,** *108,* 976. (c) Schmidbaur, H.; Schier, A. S.; Neugebauer, D. *Chem. Ber.* **1983,** *116,* 2173.

(11) Schlosser, M.; Liu, Z. *Tetrahedron Lett.* **1990,** *31,* 5753.

(12) (a) Streitwieser, A.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987,** *109,* 4184–4188 and references cited therein. (b) Frand, M. M.; Pellow, R. C.; Allen, L. C. *J. Am. Chem. Soc.* **1988,** *110,* 3723. (c) Bachrach, S. M. *J. Org. Chem.* **1992,** *57,* 4367–4773 and references cited therein.

(13) Whangbo, M.-H.; Wolfe, S.; Bernardi, F. *Can. J. Chem.* **1975,** *53,* 3040–3043.

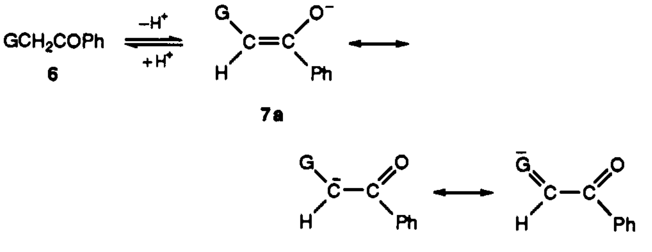
(14) (a) Vincent, M. A.; Schaefer, H. F.; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1983,** *105,* 3806–3811. (b) Vedejs, E. *Topics in Stereochemistry,* in press. The authors are also grateful to Professor E. Vedejs for providing a copy of this manuscript prior to publication.

(15) Bordwell, F. G. *Acc. Chem. Res.* **1988,** *21,* 456 and references cited therein.

izability of phosphorus, relative to nitrogen. Polarizability effects have been shown to increase dramatically on proceeding from first- to second-row elements. For example, the dipole polarizabilities (in atomic units) of phosphorus (24.5) and sulfur (19.6) are much greater than those of nitrogen (7.4) and oxygen (5.4), respectively.[16]

The polarizability of phosphorus in the Ph_3P^+ group, together with its field/inductive effects, causes this group to have an acidifying effect that rivals that of the strongest electron-withdrawing groups, such as NO_2, SO_2CF_3, PhCO, and CN, as judged by the acidities (pK_{HA} values) of the CH_3G acids in DMSO: CH_3NO_2 (17.2) > $CH_3SO_2CF_3$ (18.7) > $CH_3Ph_3P^+$ (~22) > CH_3COPh (24.7) > CH_3CN (31.3). Furthermore, the α-Ph_3P^+ group exerts its acidifying effect in a relatively constant manner (20.7 ± 5 pK_{HA} units) for the substrates in Table 1 that vary in acidity over a range of about 20 pK_{HA} units (from 22.6 for fluorene to about 43 for toluene). This suggests that the effects are not subject to large steric, stereoelectronic, or saturation (leveling) effects. This view is consistent with the observation (Table 1) that the ΔpK_{HA} for introducing an α-Ph_3P^+ group into CH_3CO_2Et is essentially the same (~20 pK_{HA} units) as introducing it into the more sterically demanding $MeCH_2CO_2Et$ substrate. Also, the effect on ΔpK_{HA} of introducing a Ph_3P^+ group into the 9-position of fluorene, although diminished, remains large (16 pK_{HA} units) despite the crowded nature of the 9-position of the fluorenide ion. For example, the pK_{HA} of 9-pivaloylfluorene is 14,[15] compared to 6.6 for 9-Ph_3P^+-fluorene, despite the much larger size of the Ph_3P^+ group than the Me_3CCO group. The CN group is unique among the strong electron-withdrawing groups in being able, because of its linear nature, to fit into the 9-position of the fluorenide ion. Yet its pK_{HA} is 1.7 pK_{HA} units *higher* than that of 9-Ph_3P^+-fluorene.[15]

The relative insensitivity of the polarizability effect of the Ph_3P^+ group to structural changes in the substrate is brought out further by a comparison of the effects of groups α-G on the acidity of acetophenone. The acidities in DMSO (pK_{HA} values) increase in the following order: H (24.7) < Me_3N^+ (14.6) < PhCO (13.1) < CH_3CO (12.7) < $PhSO_2$ (11.4) < CN (10.2) < NO_2 (7.7) < Ph_3P^+ (6.0).[15] In this series we see that again the Ph_3P^+ group is more acidifying than the CN group and even the NO_2 group. In the acid–base equilibrium for GCH_2COPh substrates the enolate ions are likely to exist in conformation **7a** with the large Ph group on the same side as the hydrogen atom. This tends to maximize the electrostatic attraction between the positive charge on the phosphorus atom and the negative charge on the oxygen atom.[17] At the same time groups that stabilize the negative charge by delocalization, like nitro, are minimized because they tend to undergo steric inhibition of resonance.

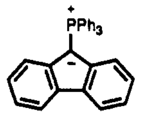


Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in *P*-Substituted Triphenylphosphonium Cations. The homolytic bond dissociation energies (BDEs) of the acidic C–H bonds in a large variety of weakly acidic substrates have been estimated during the past 6 years by eq 1,[18] including, as we have seen, the BDEs of acidic C–H bonds in *N*-substituted Me_3N^+ and PyN^+

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

cations.[2] We have now extended these studies to $Ph_3P^+CH_2G$ cations. The pK_{HA} values have been reported in Table 1. The evaluation of oxidation potentials for the conjugate bases (ylides) of these cations posed somewhat of a problem because the Br^- and Cl^- counterions in the $[Ph_3PCH_2G]^+X^-$ salts have oxidation potentials that could interfere with the measurements of the oxidation potentials of the ylides generated by addition of base. In order to avoid possible interference these halide counterions were therefore replaced by nitrate ions (see the Experimental Section). In addition, the oxidation potentials measured for six of the *in situ* generated ylides were checked by using isolated ylides (Table 2).

Table 2. Oxidation Potentials Determined from the Ylides Derived from Deprotonation of the Corresponding Cations by Addition of Bases (Method A) and the Isolated Ylides (Method B)

ylides	method	$E_{ox}(A^-)$[c]	$\Delta E_{ox}(A^-)$[e]
$Ph_3P^+CH^-COPh$	A[a]	0.639	
	B[b]	0.633	0.006
$Ph_3P^+CH^-COCH_3$	A	0.571	
	B	0.551	0.020
$Ph_3P^+CH^-CO_2Et$	A	0.553	
	B	0.549	0.004
$Ph_3P^+C^-(Me)CO_2Et$	A	0.174	
	B	0.156	0.018
$Ph_3P^+CH^-CHO$	A	0.655	
	B	0.675	−0.018
	A	−0.044	
	B	−0.041[d]	−0.003

[a] Method A: the ylides were formed *in situ* from the corresponding *P*-substituted triphenylphosphonium cations by addition of suitable bases. [b] Method B: commercial ylides. [c] In volts; irreversible oxidation potentials of the ylides measured by cyclic voltammetry at a scan rate of 100 mV/s and referenced to the Fc^+/Fc couple.[18] [d] At a scan rate of 500 V/s, this potential is completely reversible. The $E_{1/2}$ value is −0.012 V. [e] The difference of the oxidation potentials of the ylides measured by the two different methods. $\Delta E_{ox}(A^-) = E_{ox}(A^-)$(method A) − $E_{ox}(A^-)$(method B).

Estimates of the BDEs for the acidic C–H bonds in seven substrates ($PhCH_3$, $PhSCH_3$, CH_3CO_2Et, CH_3COCH_3, CH_3CN, $PhCOCH_3$, and fluorene) where an acidic hydrogen atom has been replaced by an α-Me_3N^+ or an α-Ph_3P^+ are shown in Table 3.

Examination of the relative BDE estimates for the $GCH_2NMe_3^+$ and $GCH_2PPh_3^+$ cations where G is CO_2Et, $COCH_3$, CN, and COPh reveals a remarkable agreement between the BDEs. In all four cases the estimated BDEs for the acidic C–H bonds in the $GCH_2NMe_3^+$ and $GCH_2PPh_3^+$ cations are within 0.5 kcal of one another. This is at first sight amazing since it requires the large differences in pK_{HA} values to be almost exactly compensated by the large differences in $E_{ox}(A^-)$ values. For example, the $PhCOCH_2PPh_3^+$ cation is more acidic than the $PhCOCH_2NMe_3^+$ cation by 11.8 kcal, which will tend to lower the BDE by this amount, but the oxidation potential of the corresponding triphenylphosphonium ylide is 11.5 kcal more positive than that of the corresponding trimethylammonium ylide. The data require that a plot of $\Delta E_{ox}(A^-)$ vs ΔpK_{HA} for these eight points be linear with a slope near unity. The plot is shown in Figure 1, the slope of which is 0.94 (R^2 = 0.996). The point for

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[16] Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.

[17] Bordwell, F. G.; Gallagher, T.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 3495–3497.

[18] Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790–9796 and references cited therein.

Table 3. Homolytic Bond Dissociation Energies of the Acidic C-H Bonds in *P*-Substituted Triphenylphosphonium Cations

compd	pK_{HA}[a]	$E_{ox}(A^-)$[c]	BDE[e]
$PhCH_3$	(43)[b]	−1.935[d]	87.5
$PhCH_2{}^+NMe_3$	31.9	−1.143	90.5
$Ph_3P^+CH_2Ph$	17.4	−0.381	88.3
CH_3SPh	(39)[b]		(93)[b]
$Me_3N^+CH_2SPh$	28.0		
$Ph_3P^+CH_2SPh$	14.86	−0.245	88.0
CH_3CO_2Et	(29.5)[b]		(95)[b]
$Me_3N^+CH_2CO_2Et$	20.0	−0.141	97.5
$Ph_3P^+CH_2CO_2Et$	8.50	0.553	97.7
$Ph_3P^+CH(Me)CO_2Et$	9.25	0.174	90.0
CH_3COCH_3	26.5	−0.674	94
$CH_3COCH_2{}^+NMe_3$	16.3	0.047	96.5
$Ph_3P^+CH_2COCH_3$	7.1	0.571	96.2
$Ph_3P^+CH_2CHO$	6.09	0.655	96.7
CH_3CN	31.3		93[f]
$Me_3N^+CH_2CN$	20.6	−0.271	95
$Ph_3P^+CH_2CN$	6.93	0.506	94.5
$PhCOCH_3$	24.7	−0.609	93
$PhCOCH_2{}^+NMe_3$	14.6	0.141	96.5
$PhCOCH_2{}^+PPh_3$	6.0	0.639	96.2
fluorene (FlH_2)	22.6	−1.060	79.5
9-Me_3N^+FlH	17.8	−0.563	84.6
9-Ph_3P^+FlH	6.6	−0.044	81.3

[a] In pK_{HA} units; equilibrium acidities measured in DMSO solution against two indicators with three-point titrations by the overlapping indicator method described previously,[15] unless otherwise indicated. [b] Estimated by extrapolation. [c] In volts; irreversible oxidation potentials of the conjugate anions measured by the cyclic voltammetry and referenced to the Fc/Fc^+ couple as described previously.[18] [d] Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. This value was estimated from the measurements in THF–HMPA (v/v, 9:1) but is consistent with the reduction potential of the benzyl radical [Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635]. [e] In kcal/mol; estimated by using eq 1 unless otherwise indicated. Since eq 1 is empirical and the oxidation potentials are irreversible, the BDE values are subject to errors of as much as ±2 kcal/mol. The relative BDEs are much more accurate, as demonstrated by the good correlation found in Figure 1. [f] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

$Ph_3P^+CH_2CHO$ fits the line, which suggests that the $Ph_3P^+CH^-CHO$ ylide has properties close to those of the $Ph_3P^+CH^-COPh$ and $Ph_3P^+CH^-COCH_3$ ylides. The point for $Me_3N^+CH_2CONEt_2$[2] also fits the line.

Plots similar to that in Figure 1 have been observed in eight other studies where carbanions are being oxidized to radicals and where the substituents causing the basicity changes have little or no stabilizing or destabilizing effects on the radicals being formed.[19] In the present instance the functions COPh, $COCH_3$, CHO, CO_2Et, and $CONEt_2$ all have similar effects on the BDEs (or radical stabilities), and the Ph_3P^+ and Me_3N^+ functions tend to level the basicities without affecting the BDEs (or radical stabilities). The result is to bring out the inherent linear relationship between $E_{ox}(A^-)$ and pK_{HA} that is characteristic of carbanions.

The $E_{ox}(A^-)$ and pK_{HA} points derived from the substrates $PhCH_3$, $PhSCH_3$, and FlH_2 will not fit the line since the effects of Ph, PhS, and Fl on BDEs are different from those of the strong electron-withdrawing functions.

Table 4. Equilibrium Acidities of *P*-Substituted Triphenylphosphonium Salts Determined by the Overlapping Indicator Method[a]

acid	pK_{HA}	indicator	pK_{In}	SDV[p]	runs	selected pK_{HA}
$Ph_3P^+CH_3$	22.4[b]	TBUFH[c]	24.35		2	22.5
	22.5[b]	MFH[d]	22.34		2	
	23.0[b]	NB3923[e]	22.2		1	
$Ph_3P^+CHMe_2$	21.2[b]	MFH	22.34		2	21.3
	21.5[b]	CNAH[f]	18.9		1	
$Ph_3P^+CH_2Ph$	17.37	FMY30[g]	18.1	0.011	2	17.4
$Ph_3P^+CH_2SPh$	14.87	HZF[h]	14.95	0.010	1	14.86
	14.86	PSFH[i]	15.4	0.02	1	
$Ph_3P^+CH(Me)CO_2Et$	9.26	F79COM[j]	8.2	0.011	1	9.25
	9.25	9COMFH[k]	10.35	0.028	1	
$Ph_3P^+CH_2CO_2Et$	8.47	F79COM	8.2	0.002	1	8.50
	8.53	9COMFH	10.35	0.015	1	
$Ph_3P^+CH_2COCH_3$	7.15	F279CO	6.5	0.014	2	7.10
	7.02	F279CO[l]	6.5	0.019	2	
$Ph_3P^+CH_2CN$	7.04	FMY3Y3[m]	8.55	0.023	2	
	7.07	NTBUPH[n]	7.3	0.005	2	7.0
	6.92	F279CO	6.5	0.021	2	
Ph_3P^+FlH	6.595	NBYC2S[o]	7.1	0.000	2	6.6
$Ph_3P^+CH_2CHO$	6.09	F279CO	6.5	0.019	2	6.10
$Ph_3P^+CH_2COPh$	6.03	F279CO	6.5	0.017	3	6.10
	6.16	NTBUPH	7.3	0.002	1	

[a] See ref 15. [b] One-point titration. [c] 9-(*tert*-Butyl)fluorene. [d] 9-Methylfluorene. [e] 4,5-Methylenephenanthrene. [f] 4-Chloro-2-nitroaniline. [g] 2-(Phenylsulfonyl)fluorene. [h] 9-Fluorenone, phenylhydrazone. [i] 9-(Phenylthio)fluorene. [j] 2-Bromo-9-(methoxycarbonyl)fluorene. [k] 9-(Methoxycarbonyl)fluorene. [l] 2,7-Dibromo-9-(methoxycarbonyl)fluorene. [m] 2-(Phenylsulfonyl)-9-*p*-tosylfluorene. [n] 4-Nitro-2,6-di-*tert*-butylphenol. [o] Bis(ethylsulfonyl)penthylthiomethane. [p] Standard deviation.

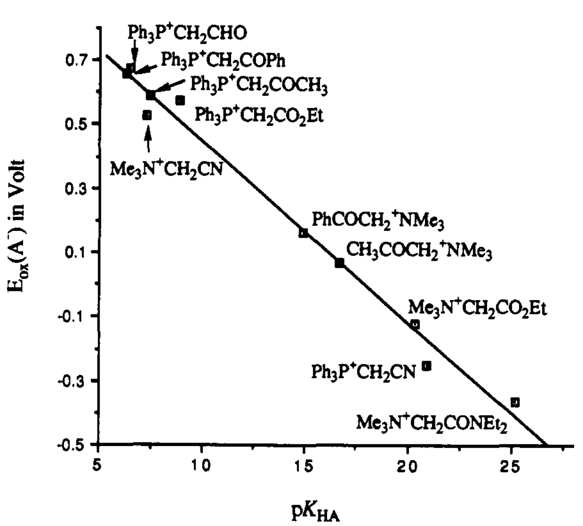

Figure 1. Plot of the oxidation potentials of the ylides $Me_3N^+CH^-G$ and $Ph_3P^+CH^-G$ versus the equilibrium acidities of their conjugate acids in DMSO solution.

The BDE of 88 kcal estimated for the acidic C–H bond in the $Ph_3P^+CH_2Ph$ cation is within 1 kcal of the generally accepted BDE for the acidic C–H bond in toluene, and the value of 94.5 kcal estimated for the acidic C–H bond in the $Ph_3P^+CH_2CN$ cation is essentially the same as the average of the 93 and 95 kcal reported for the BDEs of the C–H bond in the gas phase[20a] and in CH_3CN,[20b] respectively. On the other hand, the 96-kcal value estimated for the acidic C–H bonds in $Ph_3P^+CH_2COPh$ and $Ph_3P^+CH_2COCH_3$ is 2–3 kcal higher than the BDEs for the acidic C–H bonds in CH_3COPh and CH_3COCH_3 estimated by eq 1.

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(19) (a) Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.* **1993**, *58*, 3051–3059. (b) Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448–4450. (c) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985. (d) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209. (e) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867. (f) Bordwell, F. G.; Cheng, J.-P.; Satish, A. V.; Twyman, C. L. *J. Org. Chem.* **1992**, *57*, 6542. (g) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101. (h) Bordwell, F. G.; Vanier, N. R.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9856–9857. (i) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510–517.

(20) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. (b) Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311–3314.

It is uncertain at this point, therefore, whether or not the Ph_3P^+ group has a small destabilizing effect on adjacent radicals comparable to that of the Me_3N^+ group or whether it has essentially no effect on adjacent radicals. But the comparison of the BDEs of the acidic C–H bonds in $[Ph_3PCH_2G]^+$ cations with those of their parent substrates, CH_3G, clearly indicates that the introduction of an α-Ph_3P^+ group does not stabilize an adjacent radical. This conclusion is consistent with various ESR data.[21–23] For example, Lucken and Mazeline[21] found that the X-ray irradiation of a single crystal of *P*-(carboxymethyl)triphenylphosphonium (**8**) yielded the corresponding radical cation (**9**) and concluded that the unpaired electron in the radical cation **9** is essentially localized on the carbon atom and is not delocalized to phosphorus. Similar results have been observed for the odd electron in the $Ph_3P^+CH_2^\bullet$ radical cation[22] and that in $R_3P^+\dot{C}R'_2$ radical cations.[23]

$$\underset{\mathbf{8}}{Ph_3P^+CH_2CO_2H} \xrightarrow[(\text{-}H^\bullet)]{h\nu} \underset{\mathbf{9}}{Ph_3P^+\text{—}\dot{C}H\text{—}CO_2H}$$

The 8 kcal lower BDE $Ph_3P^+CH(Me)CO_2Et$ than for Ph_3P^+-CH_2CO_2Et is consistent with the 7 kcal lower BDE for $MeCH_2$–H than for CH_3–H.[20]

Summary and Conclusions. The failure of the Ph_3P^+ group to exhibit a stabilizing effect on adjacent carbon-centered radicals comparable to that observed on adjacent anions (e.g., Figure 1) is consistent with the experimental and theoretical evidence indicating that anion stabilization is caused by a polarizability effect rather than a conjugative effect.[10–14] In other words, the absence of radical stabilization by (p–d) π orbital overlap is consistent with the absence of anion stabilization by (p–d) π orbital overlap. This point is emphasized by the observation that stereoelectronic effects on radicals have been shown to be much larger than those on the corresponding anions.[19h,i] Therefore, if the large stabilizing effects on anions were due to (p–d) π orbital overlap, one would expect to see even larger effects on BDEs that would be bond weakening, not bond strengthening. These polarizability effects on the anions were found to be insensitive to steric or stereoelectronic effects. The ability of the Ph_3P^+ group to promote heterolytic cleavage of the adjacent C–H bonds in a family of acids without affecting the homolytic cleavage of these C–H bonds appears to provide a characteristic model for polarizability effects in solution.

Experimental Section

The ^{1}H NMR spectra of the *P*-substituted triphenylphosphonium salts were recorded on a Varian EM-390 (90 MHz) NMR spectrometer with tetramethylsilane as internal standard. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Microelemental analyses were performed by Micro-Tech Laboratories of G.D. Searle, Skokie, IL.

Materials. *P*-Methyltriphenylphosphonium chloride, *P*-isopropyltriphenylphosphonium chloride, *P*-benzyltriphenylphosphonium chloride, *P*-acetonyltriphenylphosphonium bromide, *P*-(formylmethyl)triphenylphosphonium chloride, *P*-(1-carboethoxyethyl)triphenylphosphonium chloride, *P*-(carboethoxymethyl)triphenylphosphonium chloride, *P*-(phenylthiomethyl)triphenylphosphonium chloride, and all of the triphenylphosphonium ylides were obtained from Aldrich Chemical Co. or from Lancast Synthesis. The triphenylphosphonium salts were purified by recrystallization before use, and the ylides were used for the cyclic voltammetry measurement as received.

***P*-Phenacyltriphenylphosphonium chloride** ($Ph_3P^+CH_2COPh\ Cl^-$): A toluene solution (20 mL) containing triphenylphosphine (Ph_3P) (Aldrich) (5.25 g, 20 mmol) and phenacyl chloride (Aldrich) (3.1 g, 20 mmol) was allowed to reflux for 2 h and the 7.1 g (17 mmol) precipitate was collected from the cooled solution. The crude product was purified by recrystallization from acetonitrile; mp 250–253 °C dec. ^{1}H NMR (DMSO-d_6): 6.46 (2H, d, $-CH_2-$, J_p = 14 Hz), 7.5–8.3 (20 H, m, Ar).

***P*-(Cyanomethyl)triphenylphosphonium chloride** ($Ph_3P^+CH_2CN\ Cl^-$): An anhydrous ether solution (10 mL) of triphenylphosphine (Ph_3P) (Aldrich) (2.6 g, 10 mmol) was added dropwise to an anhydrous ether solution (15 mL) of α-chloroacetonitrile (1.51 g, 20 mmol). Then the solution was refluxed for 5 h and diluted with 30 mL of cool ether to yield 2.6 g (7.7 mmol) of precipitate. Repeated recrystallization from ethanol/chloroform gave the colorless crystal; mp 265–267 °C dec. ^{1}H NMR (DMSO-d_6): 6.13 (2 H, d, $-CH_2-$, J_p = 18 Hz), 7.95 (15 H, s, Ar).

***P*-9-Fluorenyltriphenylphosphonium bromide** (9-$Ph_3P^+FlH\ Br^-$) was synthesized following the literature method.[24] The product was purified by recrystallization from acetonitrile/ethanol; mp > 260 °C [lit.[24] mp 303 °C dec]. Calculated for $C_{31}H_{24}BrP$: C, 73.37; H, 4.77. Found: C, 73.33; H, 4.73.

General Procedures for Preparing *P*-Substituted Triphenylphosphonium Nitrates. The *P*-substituted triphenylphosphonium halides were prepared by the reactions of triphenylphosphine with appropriate chlorides or bromides in anhydrous ether or ethanol as described above or were commercial samples.

A solution of $AgNO_3$ (0.2548 g, 1.50 mmol) in 5 mL of acetonitrile was added dropwise to a solution of *P*-substituted triphenylphosphonium chloride or bromide (1.50 mmol) in 5 mL of acetonitrile. The mixture was allowed to stir for 30 min and then kept in a refrigerator over night. The precipitate (AgCl or AgBr) was collected on a filter and the solvent removed. The crude product was purified by recrystallization from ethanol/chloroform or ethanol/hexane. All of these *P*-substituted triphenylphosphonium nitrate salts are new compounds.

***P*-Acetonyltriphenylphosphonium nitrate**: mp 159–160 °C. ^{1}H NMR (D_2O) 2.65 (3H, s, $-CH_3$), 5.0 (2H, d, $>CH_2$, J_p = 13 Hz), 7.5–8.3 (15H, m, –Ar). Calculated for $C_{21}H_{20}PNO_4$: C, 66.14; H, 5.29; N, 3.67. Found: C, 65.88; H, 5.22; N, 3.66.

***P*-(Carboethoxymethyl)triphenylphosphonium nitrate**: mp 138–140 °C. ^{1}H NMR (DMSO-d_6) 1.1 (3H, t, $-CH_3$), 4.1 (2H, q, $>CH_2$), 5.45 (2H, d, $>CH_2$, J_p = 19 Hz). Calculated for $C_{22}H_{22}PNO_5$: C, 64.23; H, 5.39; N, 3.40. Found: C, 64.18; H, 5.38; N, 3.39.

***P*-(Cyanomethyl)triphenylphosphonium nitrate**: mp 181–182 °C dec. ^{1}H NMR (DMSO-d_6) 5.0 (2H, d, $>CH_2$, J_p = 11 Hz), 7.4–8.5 (15H, m, –Ar). Calculated for $C_{20}H_{18}PNO_4$: C, 65.39; H, 4.94; N, 3.81. Found: C, 65.51; H, 4.84; N, 3.78.

***P*-(Formylmethyl)triphenylphosphonium nitrate**: mp 142–143 °C dec. Calculated for $C_{20}H_{17}PN_2O_3$: C, 65.93; H, 4.70; N, 7.69. Found: C, 65.81; H, 4.64; N, 7.68.

***P*-Phenacyltriphenylphosphonium nitrate**: mp 221–223 °C dec. ^{1}H NMR (DMSO-d_6): 5.3 (2H, d, $>CH_2$, J_p = 12 Hz), 7.4–8.5 (20H, m, –Ar). Calculated for $C_{26}H_{22}PNO_4$: C, 70.42; H, 5.00; N, 3.16. Found: C, 70.41; H, 5.00; N, 3.12.

Equilibrium Acidities. The equilibrium acidities of eleven *P*-substituted triphenylphosphonium salts in DMSO were determined by the overlapping indicator method as described previously.[15] The results, together with the indicator used, are summarized in Table 4.

Oxidation Potentials. The oxidation potentials of the isolated ylides and the conjugate anions (ylides) derived from *P*-substituted triphenylphosphonium cations were determined in DMSO by conventional cyclic voltammetry as described previously.[18] The working and auxiliary electrodes are platinum. The reference electrode is Ag/AgI, and all of the reported potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple ($E_{1/2}$ = 0.875 V vs the Ag/AgI).[18]

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(21) Lucken, E. A. C.; Mazeline, C. *J. Chem. Soc. A* **1966**, 1074.

(22) Lucken, E. A. C.; Mazeline, C. *J. Chem. Soc. A* **1967**, 439.

(23) (a) Begum, A.; Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc. A* **1971**, 2388. (b) Lyons, A. R.; Neison, G. W.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. II, 1972, 68*, 807.

(24) Pinck, L. A.; Hilbert, G. E. *J. Am. Chem. Soc.* **1947**, *69*, 723.