3060 J. Org. Chem. 1993, 58, 3060–3066

Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in *N*-Substituted Trimethylammonium and Pyridinium Cations

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Received December 1, 1992

Equilibrium acidities (pK_{HA}s) of the cations in sixteen *N*-substituted trimethylammonium salts, one *N*-phenacylquinuclidinium salt, eight *N*-substituted pyridinium salts, and *N*-(ethoxycarbonyl)isoquinolinium bromide, together with the oxidation potentials of their conjugate bases, have been determined in dimethyl sulfoxide (DMSO) solution. The acidifying effects of the α-trimethylammonium groups (α-Me_3N^+) and the α-pyridinium groups (α-PyN^+) on the adjacent acidic C–H bonds in these cations were found to average about 10 and 18 pK_{HA} units, respectively, in DMSO. The homolytic bond dissociation energies of the acidic C–H bonds in these cations, estimated by the combination of the equilibrium acidities with the oxidation potentials of their corresponding conjugate bases (ylides), show that the α-trimethylammonium groups *destabilize* adjacent radicals by 2–6 kcal/mol, whereas α-pyridinium groups *stabilize* adjacent radicals by 3–6 kcal/mol. The effects of α-pyridinium groups on the stabilization energies of the radicals derived from these cations were found to be ca. 4–10 kcal/mol smaller than those of the corresponding phenyl groups, whereas their effects on the equilibrium acidities of the cations were 5.4–13.1 pK_{HA} units larger. The pK_{HA} value of tetramethylammonium cation (Me_4N^+) was estimated by extrapolation to be about 42 in DMSO.

Introduction

Ylides formed by removal of a proton from the carbon–hydrogen bond next to an atom bearing a positive charge are important synthons in the conversion of aldehydes and ketones to alkenes. Most familiar are the triphenylphosphonium ylides (Wittig reagents).[1] The nitrogen analogues, trimethylammonium and like ylides, are more reactive due to the lack of available low-lying d-orbitals to stabilize the negative charge. The more basic types often undergo rearrangement or elimination reactions.[2,3] For example, a recent study of the heat of deprotonation of benzyltrimethylammonium bromide by CH_3SOCH_2Li in DMSO has shown that the rearrangement starts within a few minutes of the addition of the base.[2c]

N-Substituted trimethylammonium or pyridinium salts are readily prepared by reactions of trimethylamine or pyridine with alkyl, phenacyl, (ethoxycarbonyl)methyl, or like halides. The cations in the resulting salts can be deprotonated to form ylides by using appropriate bases.[4] Powerful bases such as alkyllithiums in tetrahydrofuran are often used to form ylides from *N*-tetraalkylammonium cations for synthetic purposes, but cation salts such as *N*-phenacylpyridinium chloride are acidic enough to form an ylide even in methanol solution.[2b] The pK_{HA} value of this cation was determined to be 9.7 in methanol solution, and the acidities of a large number of its derivatives and of the related cations have been determined.[2b] The ylides derived from phenacylpyridinium cations have been isolated and characterized.[2d]

We found some time ago that the equilibrium acidities of $Me_3N^+CH_2COPh$, $Me_3N^+CH_2SO_2Ph$, and $Me_3N^+CH_2CN$ cations could be measured in DMSO.[5a] More recently we have found that the pyridinium group, c-$C_5H_5N^+$ (PyN^+), is considerably more acid strengthening (heterolytically bond weakening) than the Me_3N^+ group when substituted for an α-C–H bond in $PhCOCH_3$, CH_3CO_2Et, or CH_3CN. Also, the PyN^+ groups in these substrates were found to weaken the acidic α-C–H bonds toward homolytic cleavage, whereas the α-Me_3N^+ groups are bond strengthening.[5b] In the present paper we extend our studies of the effects of the α-Me_3N^+ and α-PyN^+ groups on equilibrium acidities and homolytic bond dissociation energies (BDEs) to additional carbon acid substrates, including acetone, diethyl malonate, fluorene, 2-(phenylsulfonyl)fluorene, toluene, *p*-(phenylsulfonyl)toluene, *p*-cyanotoluene, phenyl methyl sulfide, phenyl methyl sulfone, and *N,N*-diethylacetamide. The effects of the α-PyN^+ groups are then compared with those of the corresponding α-Ph groups.

Results and Discussion

Equilibrium Acidities. The equilibrium acidities of the 16 cations containing α-Me_3N^+ groups, 8 containing α-PyN^+ groups, 1 containing an α-quinuclidinium group, and 1 containing an α-isoquinolinium group, were measured in DMSO solution by the overlapping indicator method.[6] The results are summarized in Table I. All of the conjugate bases (ylides) appeared to be stable under the conditions of the measurements (three-point titrations)

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

(2) (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.

(3) (a) Bunting, J. W.; Toth, A.; Heo, C. K. M.; Moorse, R. G. *J. Am. Chem. Soc.* 1990, *112*, 8878. (b) Bunting, J. W.; Ranter, J. P. *J. Am. Chem. Soc.* 1991, *113*, 6950.

(4) Kröhnke, F. *Ber.* 1935, *68B*, 1177.

(5) (a) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* 1976, *41*, 1883. (b) Bordwell, F. G.; Zhang, X.-M. *J. Org. Chem.* 1990, *55*, 6078.

(6) Bordwell, F. G. *Acc. Chem. Res.* 1988, *21*, 456.

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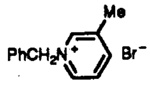
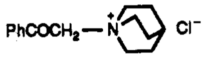
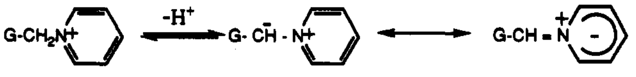
Table I. Equilibrium Acidities of α-Substituted Trimethylammonium and α-Substituted Pyridinium Salts in DMSO

compounds	pK_{HA}[b]	ΔpK_{HA}[g]	$\Delta\Delta$pK_{HA}[h]
$PhCH_3$	(43)[c]	(0.0)	
$PhCH_2{}^+NMe_3\ Cl^-$	31.9[d]	11.3	(0.0)
	20.5	22.7	11.4
$PhSCH_3$	(39)[c]	(0.0)	
$PhSCH_2{}^+NMe_3\ Cl^-$	28.0[d]	11.2	(0.0)
$PyN^+CH_2SPh\ Cl^-$	17.7[d]	21.5	10.3
CH_3CONEt_2	(35)[c,e]	(0.0)	
$Me_3N^+CH_2CONEt_2\ Cl^-$	24.9	10.3	
CH_3CN	31.3	(0.0)	
$CNCH_2{}^+NMe_3\ Cl^-$	20.6	10.9	(0.0)
$PyN^+CH_2CN\ Cl^-$	16.5[d]	15.0	4.1
p-$CNC_6H_4CH_3$	30.8[f]	(0.0)	
p-$CNC_6H_4CH_2{}^+NMe_3\ Br^-$	27.1	3.9	
p-$PhSO_2C_6H_4CH_3$	29.8[f]	(0.0)	
p-$PhSO_2C_6H_4CH_2{}^+NMe_3\ Br^-$	26.7	3.3	
CH_3CO_2Et	(29.5)[c]	(0.0)	
$Me_3N^+CH_2CO_2Et\ Cl^-$	20.0	9.7	(0.0)
$PyN^+CH_2CO_2Et\ Cl^-$	14.10	15.6	5.9
iso-$QuN^+CH_2CO_2Et\ Cl^-$ [a]	13.5	16.2	6.5
$PhSO_2CH_3$	29.0	(0.0)	
$PhSO_2CH_2{}^+NMe_3\ Cl^-$	19.4	9.8	
CH_3COCH_3	26.5	(0.0)	
$CH_3COCH_2{}^+NMe_3\ ClO_4{}^-$	16.3	10.4	(0.0)
$PyN^+CH_2COCH_3\ Br^-$	11.77	14.9	4.5
$PhCOCH_3$	24.7	(0.0)	
$PhCOCH_2{}^+NMe_3\ Br^-$	14.6	10.4	(0.0)
$PhCOCH_2{}^+NMe_3\ Cl^-$	14.6	10.4	
$PhCOCH_2{}^+NMe_3\ NO_3{}^-$	14.6	10.4	
	14.6	10.4	
$PyN^+CH_2COPh\ Br^-$	10.7	14.2	3.8
fluorene (FlH_2)	22.6	(0.0)	
9-$Me_3N^+FlH\ Cl^-$	17.8	5.1	(0.0)
9-$PyN^+FlH\ Br^-$	11.8	11.1	6.0
2-$PhSO_2FlH_2$	18.1	(0.0)	
9-Me_3N^+(2-$PhSO_2$)$FlH\ Br^-$	13.9	4.5	
$CH_2(CO_2Et)_2$	16.4	(0.0)	
$Me_3N^+CH(CO_2Et)_2\ Br^-$	11.8	4.9	(0.0)
$Me_3N^+CH(CO_2Et)_2\ NO_3{}^-$	11.8	4.9	(0.0)
$PyN^+CH(CO_2Et)_2\ ClO_4{}^-$	5.6	11.1	6.2

[a] *N*-[(Ethoxycarbonyl)methyl]isoquinolinium chloride. [b] In pK_{HA} units; equilibrium acidities measured in DMSO solution against two indicators with three-point titrations by the overlapping indicator method described previously,[6,25] unless otherwise indicated. Numbers in parentheses signify the reference point. [c] Estimated by extrapolation. [d] Estimated by one-point titration. [e] Estimated; see Bordwell, F. G.; Algrim, D. *J. Org. Chem.* **1976**, *41*, 2507. [f] Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817. [g] In pK_{HA} units; equilibrium acidities, statistically corrected, relative to the parents. [h] In pK_{HA} units; equilibrium acidities of the α-substituted pyridinium substrates relative to the corresponding α-substituted trimethylammonium substrates.

except those derived from the least acidic cations, $PhCH_2{}^+NMe_3$ and $PhSCH_2{}^+NMe_3$, where the instability of the ylide[2c] allowed only a one-point titration.

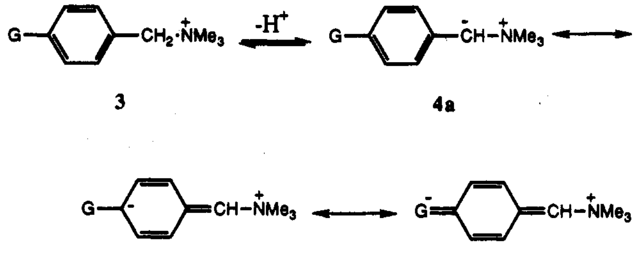
Examination of Table I shows that the α-Me_3N^+ groups acidify the adjacent acidic C–H bonds by about 10 pK_{HA} units in most of the substrates (ΔpK_{HA} in Table I), whereas the acidifying effects of the α-PyN^+ groups are ca. 4–11 pK_{HA} units greater than those of the α-Me_3N^+ groups in these substrates ($\Delta\Delta$pK_{HA} in Table I). The acidifying effects of α-Me_3N^+ groups are associated solely with the coulombic stabilization of the negative charge by the positive charge on the nitrogen atom (field/inductive or F effects). The larger acidifying effects of α-PyN^+ groups than α-Me_3N^+ groups are due to a combination of the coulombic effect of the positive charge and the resonance delocalization effects of the aromatic ring (**2a**,**2b**).[5b]



1 **2a** **2b**

Inspection of the data in Table I for the eight cations of the type $GCH_2NMe_3{}^+$, where G is Ph, PhS, Et_2NCO, CN, EtOCO, $PhSO_2$, CH_3CO, and PhCO, shows that the acidifying effects (ΔpK_{HA}) are remarkably constant, 10.5 ± 0.8 pK_{HA} units, despite the variation of the parent pK_{HA} values over about 18 pK_{HA} unit (25 kcal) range. The reason is that the center of negative charge in these ylides evidently remains essentially constant with respect to interaction with the positive charge. On the other hand, the effects of the α-PyN^+ groups vary over a 14–22 pK_{HA} unit range for these substrates. Here, where the electrostatic effects on anion stability are augmented by delocalization effects, the ΔpK_{HA} values are larger for the first two weakly acidic entries and smaller for the final two more strongly acidic entries, suggesting some leveling.

Introduction of a Me_3N^+ group at the acidic sites in *p*-$CNC_6H_4CH_3$ and *p*-$PhSO_2C_6H_4CH_3$ substrates causes only 3.9 and 3.3 pK_{HA} unit increases in acidity, respectively, compared to 11.3 pK_{HA} units for toluene and 10.9 and 9.8 pK_{HA} units for the related substrates CH_3CN and $PhSO_2CH_3$, respectively, which have only slightly different pK_{HA} values (Table I). Clearly, the smaller acidifying effects are associated in this instance with a diminution of the negative charge adjacent to the Me_3N^+ group by delocalization into the benzene ring and the substituents (G), as depicted in **4b** and **4c**. The coulombic effect of the Me_3N^+ group on the stability of the anion is diminished accordingly. (Coulombic interactions are known to decrease exponentially as the distance between the positive and negative charges increases.) The situation is somewhat similar to the progressive diminution of the acidifying effects of the phenyl group from ΔpK_{HA} = 10.6 to 7.3 to 4.5 pK_{HA} units in $PhCH_2G$ as the negative charge in the $PhCHG^-$ anions becomes more delocalized, as G is changed in the series CN, $COCH_3$, and NO_2.[7a] A similar trend was also observed for the acidifying effects of the cyano group in the series *p*-$GC_6H_4CH_2CN$, as G is changed from H (ΔpK_{HA} ≃ 21 units) to CN or $PhSO_2$ (ΔpK_{HA} = 14 units) to NO_2 (ΔpK_{HA} = 8.1 units).[6,7b,8]



3 **4a** **4b** **4c**

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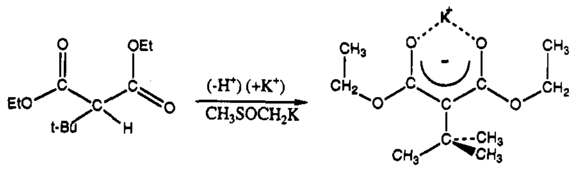
(7) (a) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321. (b) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209. (c) Bordwell, F. G.; Gallagher, T.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 3495. (d) Abbotto, A.; Bradamante, S.; Pagani, G. A. *J. Org. Chem.* **1993**, *58*, 444.

Scheme I



5 6

The acidifying effects of the α-Me_3N^+ groups in 9-Me_3N^+FlH, 2-($PhSO_2$)-9-Me_3N^+FlH, and $Me_3N^+CH(CO_2Et)_2$ (ΔpK_{HA} = 5.1, 4.5, and 4.9 units, respectively) are about one-half the size of those in most other substrates. Steric inhibition of solvation and resonance are no doubt the principal factors responsible for the smaller acidifying effects. The effects of introducing an α-*tert*-butyl group into fluorene and diethyl malonate can serve as a model to assess the importance of these steric effects. In fluorene, introduction of a 9-Me group causes an increase in acidity of 0.6 pK_{HA} units (statistically corrected), which is believed to be the result of a polarizability effect of the Me group stabilizing the 9-$MeFl^-$ anion. The *tert*-butyl group has a much larger polarizability effect, but 9-*tert*-butylfluorene is a weaker acid than fluorene by 1.8 pK_{HA} units.[6] Here, steric hindrance to solvation overshadows the polarizability effect. The decrease in acidity is much larger on introducing an α-*tert*-butyl group into diethyl malonate (8.3 pK_{HA} units) because the *tert*-butyl group causes very strong inhibition of solvation in the anion and perhaps steric inhibition of resonance, as well (Scheme I).

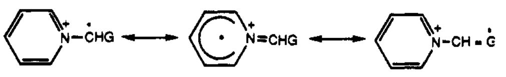
Conformation **5** in Scheme I is one of several that the undissociated acid can assume. Loss of proton and addition of a K^+ ion gives the chelate ion pair **6** (log K_{as} 2.3).[9b] In **6**, the bulky *tert*-butyl group forces the ethyl groups to be in the vicinity of the carbonyl oxygen atoms where they interfere with solvation and perhaps with chelation.

Equilibrium Acidity of the Tetramethylammonium Cation in DMSO. Quaternary ammonium salts have been widely used as the supporting electrolytes in electrochemical measurements. This is due, at least in part, to their weak acidities, since some electrochemical measurements are carried out in strongly basic media.[9a,10] The equilibrium acidity of tetramethylammonium cation Me_4N^+, the simplest quaternary ammonium cation, is too weak to be measured in DMSO solution by the titration method.[6] An estimate of its acidity can be made, however, by extrapolation based on the equilibrium acidities of its Ph and CN derivatives. (The values in parentheses are in pK_{HA} units.) The acidifying effect of the phenyl group in Ph_2CH_2 (~32) relative to toluene (~43) is about 11 pK_{HA} units. Assuming that the phenyl group in the $PhCH_2{}^+NMe_3$ cation (~32) has the same acidifying effect, the pK_{HA} value of the Me_4N^+ cation in DMSO is estimated to be about 11 + 32 $\cong$ 43. If we use the acidifying effect of the cyano group in $PhCH_2CN$ (21.9) relative to toluene (~43) as a model, the pK_{HA} value of the Me_4N^+ cation in DMSO is estimated to be about 21 + 20.6 $\cong$ 42 since the pK_{HA} value of $Me_3N^+CH_2CN$ is 20.6 (Table I). Therefore, these estimates place the pK_{HA} value of the Me_4N^+ cation at about 42 in DMSO, indicating that it will not be deprotonated appreciably even by the $CH_3SOCH_2{}^-$ anion.[10]

Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in Cations Containing α-Trimethylammonium and α-Pyridinium Groups and the Dual Role (Stabilizing–Destabilizing) of Most Substituents on Radical Stabilities. The oxidation potentials of the conjugate bases (ylides) of 22 cations containing α-trimethylammonium and α-pyridinium groups listed in Table I have been measured in DMSO by cyclic voltammetry.[9a] The homolytic bond dissociation energies (BDE_{HA}s) of the acidic C–H bonds in these cations were estimated by the combination of the equilibrium acidities with the oxidation potentials of the corresponding ylides, $E_{ox}(N^+C^-)$, eq 1.[9a] The results obtained are summarized in Table II.

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

Examination of Table II shows that the α-Me_3N^+ groups increase the BDE_{HA} values of the adjacent acidic C–H bonds in 12 substrates by ca. 2–6 kcal/mol, relative to the corresponding parents. (Henceforth, kcal/mol will be abbreviated as kcal.) The quinuclidinium group has an effect similar to Me_3N^+ group on both equilibrium acidity and BDE, indicating that the steric effects in the latter are not important. Note also that the nature of the negative counterion is not important. Radical destabilization by α-Me_3N^+ groups has been observed previously and has been attributed to strong field/inductive (F) effects.[5b] According to our rationale, radicals are electron deficient and are destabilized by electron-withdrawing groups.[5b,11] Theoretical calculations by Pasto and his colleagues also indicate that the corresponding α-H_3N^+ groups destabilize adjacent radicals (or strengthen the acidic C–H bonds) by ca. 2–5 kcal.[12] On the other hand, α-PyN^+ groups in nonsterically congested substrates stabilize adjacent radicals by 3–6 kcal (Table II). The bond-weakening effects of the α-PyN^+ groups, which contrast with the bond-strengthening effects of the α-Me_3N^+ groups, have been attributed to the resonance delocalization of the odd electron into the aromatic ring (R effect) (**7b**).[5b] This radical stabilization by the R effect overshadows the radical destabilization by the F effect of the positive charge on the nitrogen atom.



7a 7b 7c

The behavior of the α-PyN^+ group provides a good model to illustrate the dual role of most substituents on radical stabilities, i.e., destabilizing by F effects and stabilizing by R effects.[5b] On the basis of hyperfine ESR coupling constants, Wayner and Arnold suggested that meta substituents in benzyl radicals are generally destabilizing, but that these substituents usually exert net stabilizing interactions when substituted in the para positions.[13] The observation of negative ΔBDE values, relative to the BDE

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(8) Pagani, Bradamante, and their students have presented evidence to show that very little of the negative charge in substrates such as these resides on the nitrogen atom of the cyano group.[7d] We are indebted to Professor Pagani for sending us a preprint prior to publication.

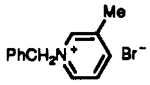
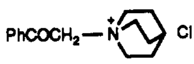
(9) (a) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* 1991, *113*, 9790. (b) Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* 1980, *45*, 3299.

(10) The base used for generating carbanions in DMSO is potassium dimsyl ($CH_3SO_2CH_2{}^-K^+$).[6,9a] The pK_{HA} of DMSO is estimated to be 35 in DMSO.[6]

(11) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* 1991, *113*, 1736.

(12) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* 1987, *52*, 3062.

Table II. Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in α-Substituted Trimethylammonium and α-Substituted Pyridinium Salts

compounds	$E_{ox}(N^+C^-)$[b]	BDE[h]	ΔBDE[n]
$PhCH_3$	−1.935[c]	87.5	(0.0)
$PhCH_2{}^+NMe_3\ Cl^-$	−1.143	90.5	−3.0
	−0.722	84.7	2.8
$PhSCH_3$		93[i]	(0.0)
$PyN^+CH_2SPh\ Cl^-$	−0.357	89	4
CH_3CONEt_2		95[j]	(0.0)
$Me_3N^+CH_2CONEt_2\ Cl^-$	−0.383	98.5	−3.5
CH_3CN		93[k]	(0.0)
$Me_3N^+CH_2CN\ Cl^-$	−0.271	95	−2
$PyN^+CH_2CN\ Cl^-$	−0.360	87.5	5.5
p-$PhSO_2C_6H_4CH_3$		88[l]	(0.0)
p-$PhSO_2C_6H_4CH_2{}^+NMe_3\ Br^-$	−0.698[d]	93.7	−5.7
CH_3CO_2Et		95[j]	(0.0)
$Me_3N^+CH_2CO_2Et\ Cl^-$	−0.141[d]	97.5	−2.5
$PyN^+CH_2CO_2Et\ Cl^-$	−0.112	90	5
iso-$QuN^+CH_2CO_2Et\ Cl^-$ [a]	−0.188	87.4	7.6
CH_3COCH_3	−0.674[e]	94	(0.0)
$CH_3COCH_2{}^+NMe_3\ ClO_4{}^-$	0.047	96.5	−2.5
$PyN^+CH_2COCH_3\ Br^-$	−0.021	89	5
$PhCOCH_3$	−0.609[e]	93	(0.0)
$PhCOCH_2{}^+NMe_3\ Br^-$	0.141[d]	96.5	−3.5
$PhCOCH_2{}^+NMe_3\ Cl^-$	0.137	96.5	−3.5
$PhCOCH_2{}^+NMe_3\ NO_3{}^-$	0.167	97	−4
	0.107	96	−3
$PyN^+CH_2COPh\ Br^-$	−0.036	87	6
fluorene (FlH_2)	−1.070[f]	79.5	(0.0)
9-$Me_3N^+FlH\ Cl^-$	−0.563[f]	84.6	−5.1
9-$PyN^+FlH\ Br^-$	−0.370	80.8	−1.3
2-$PhSO_2FlH_2$	−0.792[g]	79.7	(0.0)
9-$Me_3N^+(2\text{-}PhSO_2)FlH\ Br^-$	−0.284	85.7	−6.0
$CH_2(CO_2Et)_2$	−0.022	95[m]	(0.0)
$Me_3N^+CH(CO_2Et)_2\ NO_3{}^-$	0.401	98.7	−3.7
$PyN^+CH(CO_2Et)_2\ ClO_4{}^-$	0.638	95.6	−0.6

[a] *N*-[(Ethoxycarbonyl)methyl]isoquinolinium chloride. [b] In volts; irreversible oxidation potentials of the ylides and some of the conjugate bases of the parent weak acids measured by the cyclic voltammetry and referenced to the Fc^+/Fc couple as described previously.[9a] [c] Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. This value was estimated from measurements in THF–HMPA (v:v, 9:1). [d] Measured by Harrelson, J. A., Jr. [e] Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714. [f] Bordwell, F. G.; Cheng, J. P.; Seyedrezai, S. E.; Wilson, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 8178. [g] Bordwell, F. G.; Bausch, M. J.; Branca, J. C.; Harrelson, J. A., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 225. [h] In kcal/mol; estimated by using of eq 1 unless otherwise indicated. [i] Assumed to be the same as that of $RSCH_3$ (Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623). [j] Estimated.[5b] [k] McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. [l] Assuming that the BDE_{C-H} in *p*-$PhSO_2C_6H_4CH_3$ is equal to that (90 kcal/mol) in $PhCH_2SO_2Ph$ (Bordwell, F. G.; Bausch, M. J.; Branca, J. C.; Harrelson, J. A., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 225). [m] Harrelson, J. A., Jr., unpublished result. [n] In kcal/mol; homolytic bond dissociation energies relative to the parents.

of the O–H bond in phenol, for most meta substituents also indicates bond strengthening effects and destabilizing effects in the corresponding phenoxyl radicals.[11] Here too para donor substituents, such as *p*-Me, *p*-MeO, or *p*-NH_2, are bond weakening (radical stabilizing) because of their delocalizing effects, as illustrated in **8a–c**. But para acceptor substituents that are strongly electron withdrawing, such as *p*-CN, *p*-$PhSO_2$, *p*-NO_2, or *p*-RCO, are radical destabilizing because their F effects overshadow their delocalizing effects.[11] (The Me_3N^+ group is one of the few electron-withdrawing groups that does not play a dual role on adjacent radical stabilities.)

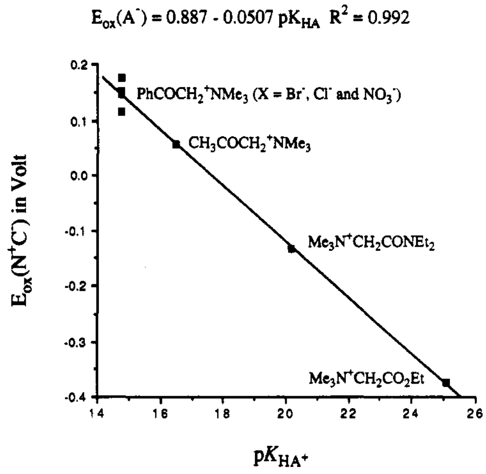
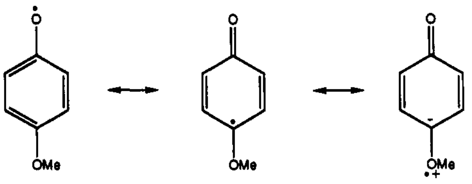


Figure 1. Plot of the oxidation potentials of ylides, i.e., the conjugate bases of cations bearing α-Me_3N^+ versus their equilibrium acidities in DMSO.



8a **8b** **8c**

Correlation of the $E_{ox}(N^+C^-)$ Values of Ylides with the pK_{HA^+} Values of the Corresponding α-Substituted Trimethylammonium Salts ($Me_3N^+CH_2G\ X^-$). In an earlier section we saw that for eight $Me_3N^+CH_2G\ X^-$ salts the ΔpK_{HA} values were surprisingly constant (10.5 ± 0.8 pK_{HA} units), indicating that the interaction of the electrostatic effects between the positive and negative charge in the correspondingly ylides, $Me_3N^+CH^-G$, were nearly constant. It follows that the $\Delta E_{ox}(A^-)$ values, which should also be controlled by these electrostatic effects, should also be constant, and that the combination of the pK_{HA} and $E_{ox}(A^-)$ values in eq 1 should lead to a nearly constant BDE value for the acidic C–H bonds in these salts. When BDEs in families of carbanions are constant, plots of $E_{ox}(A^-)$ versus pK_{HA} have been found to be linear with slopes near unity.[14] Examination of the six BDEs available in Table II revealed the $PhCH_2{}^+NMe_3$ cation to be ca. 5 kcal lower than the others. (The pK_{HA^+} value was measured from a one-point titration because of the instability of the anion, and the pK_{HA} of the parent ($PhCH_3$) was estimated by extrapolation. The ΔpK_{HA} value is therefore subject to considerable uncertainity. So it isn't surprising that it does not belong to this family.) A plot of $E_{ox}(A^-)$ versus pK_{HA^+} for the remaining five cations gave a fair linear correlation (R^2 = 0.967). An excellent correlation was obtained, however, when only the four cations containing carbonyl groups were included (R^2 = 0.992). The slope is 0.85 when both of the axes are expressed in kcal (Figure 1). (Since pK_{HA}s for the salts are independent of the nature of the counterion, pK_{HA} = pK_{HA^+}). The average of the BDE values for these four

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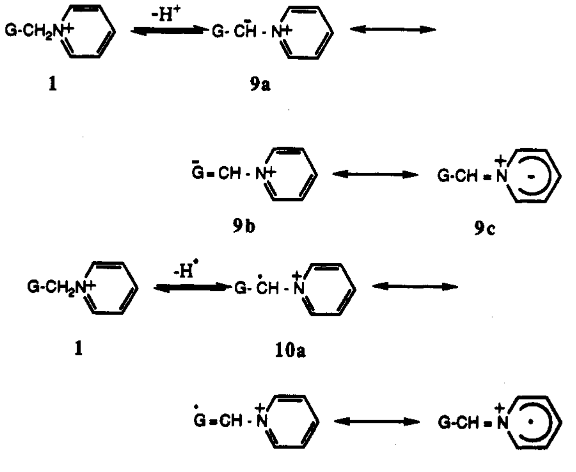
(13) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164.

(14) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979. (b) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2872–2877. (c) Bordwell, F. G.; Cheng, J.-P.; Satish, A. V.; Twyman, C. L. *J. Org. Chem.* **1992**, *57*, 6542–6546. (d) Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.*, in press. (e) Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448.

cations is 97 ± 1.5 kcal. The results show that this seemingly disparate family of carbanions also follow the rule that when BDE values are constant an inherent linear relationship between the basicities of carbanions and their oxidation potentials holds.[14d]

Comparison of the Effects of α-PyN$^+$ and α-Me$_3$N$^+$ Groups on Equilibrium Acidities and Homolytic Bond Dissociation Energies. Ordinarily, structural changes that increase acidities do so primarily by stabilizing the conjugate anions, and structural changes that weaken bonds do so primarily by stabilizing the corresponding radicals. In the present instance, however, the conjugate anions are zwitterions (**9**) and the radicals are positively charged, i.e. they are radical cations (**10**).



Stabilizing effects on anions are usually much smaller than analogous stabilizing effects on radicals because they are leveled by solvation effects.[15,17] The relative stabilizing effects are moderated for ylides and radical cations, however, because the adjacent positively charged nitrogen atom has a powerful stabilizing effect on the anion and a powerful destabilizing effect on the radical. For example, the equilibrium acidity of the 9-Me$_3$N$^+$FlH cation is 5.1 pK_{HA} units (7 kcal) greater than that of fluorene (ΔpK_{HA} in Table I), and the stability of the 9-Me$_3$N$^+$Fl$^•$ radical (ΔBDE in Table II) is about 5 kcal smaller than that of the fluorenyl radical. For comparison, the acidity of the 9-PyN$^+$FlH cation is 15 kcal greater than that of fluorene and the stability of the 9-PyN$^+$Fl$^•$ radical is only about 1 kcal smaller. Here the larger acidifying effect for the 9-PyN$^+$ vs the 9-Me$_3$N$^+$ substituent stems from the combination of its delocalizing effect (**9a–c**) with its F effect. In the radical the delocalizing (stabilizing) effect of the PyN$^+$ group (**10a–c**) almost counteracts the destabilizing F effect. Additional comparisons of ΔpK_{HA} and ΔBDE values in Tables I and II for α-Me$_3$N$^+$ and α-PyN$^+$ substituents reveal similar differences.

Table III. A Comparison of the Effects of α-Phenyl and α-Pyridinium Substituents on Equilibrium Acidities and Homolytic Bond Dissociation Energies

compounds	ΔpK_{HA}[a]	BDE[b]	(ΔBDE)$_I$[c]	(ΔBDE)$_{II}$[d]	ΔΔBDE[e]
$PhCH_3$	(0.0)	87.5	(0.0)	(0.0)	
PyN^+CH_2Ph	22.5	84.7	2.8		
$PhCH_2Ph$	11	81.8		5.7	
	11.5				2.9
$PhSCH_3$	(0.0)	93.0	(0.0)	(0.0)	
PyN^+CH_2SPh	21.3	89.2	3.8		
$PhCH_2SPh$	8.2	84.2		8.8	
	13.1				5.0
CH_3CN	(0.0)	93.0	(0.0)	(0.0)	
PyN^+CH_2CN	14.8	87.2	5.5		
$PhCH_2CN$	9.4	82.2		10.8	
	5.4				5.3
CH_3CO_2Et	(0.0)	95.0	(0.0)	(0.0)	
$PyN^+CH_2CO_2Et$	15.4	90.0	5.0		
$PhCH_2CO_2Et$	6.9	83.9		11.1	
	8.5				6.1
FlH_2	(0.0)	80.0	(0.0)	(0.0)	
9-PyN$^+$FlH	10.8	80.8	–0.8		
9-PhFlH	4.7	74.0		6.0	
	6.1				6.8
CH_3COCH_3	(0.0)	94.0	(0.0)	(0.0)	
$PyN^+CH_2COCH_3$	14.7	88.7	6.3		
$PhCH_2COCH_3$	6.6	83.2		11.8	
	8.1				5.5
CH_3COPh	(0.0)	93.0	(0.0)	(0.0)	
PyN^+CH_2COPh	14.0	87.1	5.9		
$PhCH_2COPh$	7.0	83.1		9.9	
	7.0				4.0
$CH_2(CO_2Et)_2$	(0.0)	95.0	(0.0)	(0.0)	
$PyN^+CH(CO_2Et)_2$	10.8	95.6	–0.6		
$PhCH(CO_2Et)_2$	0.1	85.3		9.7	
	10.7				10.3

[a] In pK_{HA} units. [b] In kcal/mol; values summarized by Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623. [c] (ΔBDE)$_I$ = BDE – BDE(PyN$^+$CH$_2$G). [d] (ΔBDE)$_{II}$ = BDE – BDE(PhCH$_2$G). [e] ΔΔBDE = (ΔBDE)$_{II}$ – (ΔBDE)$_I$.

Comparisons of the Effects of α-Pyridinium and α-Phenyl Groups on Acidities and Homolytic Bond Dissociation Energies. In earlier sections we have seen that (a) PyN$^+$ groups, by virtue of their delocalizing ability, are more effective than Me$_3$N$^+$ groups at stabilizing either a negative charge or an odd electron on an adjacent carbon atom, and (b) PyN$^+$ groups often exert a net stabilizing effect on adjacent carbon-centered radicals despite the destabilizing effect of the positive charge on the nitrogen atom. In this section we will compare the effects of α-PyN$^+$ groups with α-Ph groups in stabilizing adjacent negative charges and odd electrons as indicated by their relative effects on acidities and BDEs. The equilibrium acidities and BDEs of the α-PyN$^+$ substrates and the corresponding α-Ph analogues are summarized in Table III.

The replacement of one of the hydrogen atoms at the acidic site of the substrates PhCH$_3$, PhSCH$_3$, CH$_3$CO$_2$Et, CH$_3$CN, CH$_3$COCH$_3$, H$_2$Fl, and CH$_2$(CO$_2$Et)$_2$ by a phenyl substituent, as shown in Table I, leads to the following compounds, which have the pK_{HA} values shown in parentheses: PhCH$_2$Ph (32.2), PhSCH$_2$Ph (30.8), PhCH$_2$CN (21.9), PhCH$_2$COCH$_3$ (19.9), 9-PhFlH (17.9), PhCOCH$_2$Ph (17.7), and PhCH(CO$_2$Et)$_2$ (16.3). The increases in acidity brought about by these structural changes are compared in the second column of Table III (ΔpK_{HA}) with those caused by analogous replacements of these hydrogen atoms by α-PyN$^+$ substituents. We see that α-PyN$^+$ groups and

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(15) We have previously observed that changes in stereoelectronic effects in radicals derived from 2-benzoylperhydropyrimidines brought about by structural changes cause a difference of 16 kcal compared to about 4 kcal for the analogous anions[16] and have suggested that stereoelectronic effects on radicals, because of the absence of solvation forces, will be much larger than analogous effects on anions.

(16) Bordwell, F. G.; Vanier, N. R.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9856.

(17) Bordwell, F. G.; Singer, D.; Satish, A. V. *J. Am. Chem. Soc.*, in press.

α-Ph groups both have strong acidifying effects. The effects for α-PyN^+ groups vary from 10.8 pK_{HA} units for the 9-PyN^+FlH and $PyN^+CH(CO_2Et)_2$ substrates, where the acidic sites are sterically congested, to ca. 22 pK_{HA} units for weakly acidic PyN^+CH_2Ph and PyN^+CH_2SPh substrates; the overall average is about 15.5 pK_{HA} units. The α-Ph acidifying effects vary from 4.7 and 0.1 pK_{HA} units for the 9-PhFlH and $PhCH(CO_2Et)_2$ substrates to ca. 11 and 9.4 pK_{HA} units for the $PhCH_2Ph$ and $PhCH_2CN$ substrates, respectively; the average is ca. 6.7 pK_{HA} units. Both Ph and PyN^+ groups have large delocalizing abilities, but the much larger F effect of the PyN^+ group gives it an appreciably larger net acidifying effect, which averages about 8.8 pK_{HA} units.

The powerful F effect of the positive charge tends to strengthen the acidic C–H bonds and destabilize the corresponding radicals for α-PyN^+CH_2G substrates. But the delocalizing effects of the α-PyN^+ moieties usually overshadow the F effects, and the net effects of the α-PyN^+ groups are usually bond weakening and radical stabilizing leading to positive $(\Delta BDE)_I$ values. The bond weakening (radical stabilizing) effects of the α-Ph groups are stronger, however, because of the absence of appreciable F effects of the positive charge.

In the 9-PyN^+FlH and $PyN^+CH(CO_2Et)_2$ substrates steric inhibition of resonance decreases the delocalizing effect of the PyN^+ moieties to the point where the $(\Delta BDE)_I$ values are slightly negative. Steric inhibition of resonance negates the acidifying effect of the Ph group in $PhCH(CO_2Et)_2$, but its bond weakening effect appears to remain intact. This is surprising, and needs to be investigated further.

Summary and Conclusions. From an examination of the effects of α-Me_3N^+, α-PyN^+, and α-Ph groups on the equilibrium acidities and BDEs of a variety of weak carbon acid substrates, we have concluded that (a) α-Me_3N^+ groups strongly stabilize on adjacent carbanion center, but destabilize an adjacent radical center, (b) α-PyN^+ groups, by virtue of their resonance delocalizing ability, are more effective than α-Me_3N^+ groups at stabilizing a negative charge on an adjacent carbon atom, and usually have a net stabilizing effect on an adjacent carbon-centered radical, (c) α-PyN^+ groups, by virtue of their combined F effect and delocalizing ability are more effective at stabilizing an adjacent carbanion center than are α-Ph groups, but are less effective at stabilizing an adjacent carbon-centered radical, (d) for the family of ylides $GCH^{-+}NMe_3$, with G equal to $CONEt_2$, CN, CO_2Et, COMe, and COPh functions, the electrostatic stabilizing effects of Me_3N^+ groups controlling the pK_{HA^+} and $E_{ox}(A^-)$ values are each nearly constant leading to a near constancy in the BDE_{HA} values; the plot of $E_{ox}(A^-)$ versus pK_{HA^+} is linear for this family, and (e) the effects of α-Me_3N^+ and α-PyN^+ groups on the adjacent carbanions and radicals are unusual in that they affect the stabilities of anions more than radicals.

Experimental Section

The ^{1}HNMR spectra of the α-substituted trimethylammonium and pyridinium salts were recorded on a Varian EM-390 spectrometer (90 MHz) or a Varian XLA-400 MHz NMR spectrometer with tetramethylsilane as internal standard. Melting points were measured on a Thomas Hoover capillary melting point apparatus and were not corrected. Microelemental analysis were performed by Micro-Tech Laboratories of G.D. Searle, Skokie, IL.

Materials. $PhCH_2{}^+NMe_3Cl^-$, a commercially available sample, was purified by recrystallization from ethanol/chloroform.

General Procedures for Preparing Ylide Precursors. The trimethylammonium (or pyridinium) salts were prepared by reactions of trimethylamine (cooled at 0 °C) (or pyridine) with appropriate alkyl, or like, chlorides or bromides in anhydrous ether or ethanol often following literature procedures. The reactions were generally allowed to reflux until appreciable quantities of salt had precipitated on the bottom of the flask. The solutions were then diluted with cold anhydrous ether and the crude products collected on a filter and purified. All purified products gave NMR spectra in agreement with the structures assigned. Nitrogen analysis on 14 of the salts was found to be satisfactory. Seven of the salts were shown to give carbon and hydrogen analysis consistent with the structures assigned. The linear correlations of the oxidation potentials of the ylides with pK_{HA} values shown in Figure 1 provide additional evidence as to the structures and purity of the salts.

***N*-Benzyl-3-methylpyridinium bromide** was prepared by reaction of benzyl bromide with 3-methylpyridine. The crude product was purified by recrystallization from ethanol/chloroform: mp 64–65 °C; NMR (DMSO-d_6) δ 2.53 (3 H, s, CH_3), 5.90 (2 H, s, CH_2), 7.3–9.4 (9 H, m, Ar).

***N*-[(Phenylthio)methyl]trimethylammonium chloride** ($PhSCH_2{}^+NMe_3Cl^-$) was prepared by reaction of trimethylamine with (phenylthio)chloromethane (Aldrich). The crude product was purified by repeated recrystallization from ethanol/chloroform: mp 90–91 °C; NMR (DMSO-d_6) δ 3.09 [9 H, s, $^+N(CH_3)_3$], 5.22 (2 H, s, CH_2), 7.3–7.8 (5 H, m, Ar).

***N*-[*p*-(Phenylsulfonyl)benzyl]trimethylammonium bromide** (p-$PhSO_2C_6H_4CH_2{}^+NMe_3Br^-$) was prepared by reaction of trimethylamine with p-(phenylsulfonyl)benzyl bromide. The crude product was purified by repeated recrystallization from ethanol/chloroform: mp 210–212 °C; NMR (DMSO-d_6) δ 3.20 [9 H, s, $^+N(CH_3)_3$], 4.90 (2 H, s, $>CH_2$), 7.4–8.5 (9 H, m, Ar).

***N*-[(Phenylthio)methyl]pyridinium chloride** ($PhSCH_2{}^+NPyCl^-$) was prepared by reaction of pyridine with (phenylthio)chloromethane (Aldrich). The crude product was purified by recrystallization from ethanol/chloroform, mp 153–156 °C (lit.[18] 155–157 °C).

***N*-[(Phenylsulfonyl)methyl]trimethylammonium Chloride** ($PhSO_2CH_2{}^+NMe_3Cl^-$). An amount of 0.7 g (3.2 mmol) $PhSCH_2{}^+NMe_3Cl^-$ in 50 mL of acetic acid was added dropwise into 5 mL of H_2O_2 (~30%) in 20 mL of acetic acid solution. The mixture was heated on a steam bath for 18 h. Water (50 mL) was added and the aqueous layer was extracted three times with ethyl acetate. An oily residue obtained by removal of water was purified by repeated recrystallization from acetonitrile/ethanol: mp 181.5–183.5 °C; NMR (DMSO-d_6) δ 3.35 [9 H, s, $^+N(CH_3)_3$], 5.20 (2 H, s, $>CH_2$), 7.8–8.5 (5 H, m, Ar).

***N*-Acetonyltrimethylammonium Perchlorate** ($CH_3COCH_2{}^+NMe_3ClO_4{}^-$). Chloroacetone (2 mL) (Aldrich) in 30 mL of anhydrous ether was added dropwise into ca. 15 mL of anhydrous trimethylamine (Aldrich) cooled in a flask at 0 °C and refluxed for 2 h. The crude product was dissolved in 10 mL of distilled water, and 1 equiv of 70% perchloric acid was added dropwise. Refrigeration for 1 day gave needlelike hygroscopic crystals: mp 86–87 °C; NMR (DMSO-d_6) δ 2.13 (3 H, s, $COCH_3$), 4.5 (2 H, s, CH_2), 3.23 [9 H, s, $^+N(CH_3)_3$].

***N*-Acetonylpyridinium bromide** ($CH_3COCH_2{}^+NPyBr^-$) was prepared by reaction of pyridine with α-bromoacetone. The crude violet solid was purified by recrystallization from ethanol/chloroform: mp 185–188 °C (lit.[2d] mp 185 °C); NMR (DMSO-d_6) δ 2.33 (3 H, s, CH_3), 5.88 (2 H, s, CH_2), 8.1–9.0 (5 H, m, Ar).

***N*-Phenacyltrimethylammonium chloride** ($PhCOCH_2{}^+NMe_3Cl^-$) was prepared by reaction of trimethylamine with α-chloroacetophenone (Aldrich). The crude product was purified by recrystallization from acetonitrile: mp 203–205 °C dec; NMR (DMSO-d_6) δ 3.35 [9 H, s, $^+N(CH_3)_3$], 5.48 (2 H, s, $>CH_2$), 7.5–8.2 (5 H, m, Ar).

***N*-Phenacyltrimethylammonium bromide** ($PhCOCH_2{}^+NMe_3Br^-$) was prepared by reaction of trimethylamine with

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[18] Böhme, H.; Dietz, K.; Frank, R. *Arch. Pharm.* **1954**, *287*, 524.

α-bromoacetophenone (Aldrich). The crude product was purified by repeated recrsytallization from ethanol/chloroform: mp 198–199 °C dec; NMR (DMSO-d_6) δ 3.35 [9 H, s, $^+N(CH_3)_3$], 5.48 (2 H, s, >CH_2), 7.5–8.2 (5 H, m, Ar).

***N*-Phenacyltrimethylammonium Nitrate** ($PhCOCH_2{}^+NMe_3NO_3{}^-$). An ion-exchange resin (50–100 dry mesh) was stirred with distilled water, and then the water solution was decanted to remove the small particles. The resin was mixed with water and packed into a column. The resin was washed with (a) water, (b) 1 N NaOH, (c) water, (d) 1 N HCl, (e) water, (f) 95% ethanol, and (g) water. This washing procedure was repeated three times. The resin was converted into the nitrate form by washing the resin with three bed volumes of 1 N KNO_3 and then water. $PhCOCH_2{}^+NMe_3Br^-$ was dissolved in a very small amount of water and introduced into the column and washed with water. The aqueous solution was concentrated by a rotavapor and dried in vacuum at 100 °C to give powdered solid. The crude product was purified by repeated recrystallization from ethanol/chloroform: mp 153–154 °C; NMR (DMSO-d_6) δ 3.35 [9 H, s, $^+N(CH_3)_3$], 5.48 (2 H, s, >CH_2), 7.5–8.2 (5 H, m, Ar).

***N*-Phenacylquinuclidinium chloride** was prepared by reaction of α-chloroacetophenone with quinuclidine. The crude product was purified by recrystallization from ethanol/chloroform: mp 252–253 °C dec; NMR (DMSO-d_6) δ 1.8–4.0 (13 H, m), 5.36 (2 H, s, >CH_2), 7.5–8.2 (5 H, m, Ar).

***N*-Phenacylpyridinium bromide** ($PhCOCH_2{}^+NPyBr^-$) was prepared by reaction of pyridine with α-bromoacetophenone. The crude product was purified by recrystallization from ethanol/chloroform: mp 198–199 °C (lit.[19] mp 199–200 °C, lit.[2b] mp 194.5–197 °C); NMR (DMSO-d_6) δ 6.67 (2 H, s, >CH_2), 7.5–9.2 (10 H, m, Ar).

***N*-(Cyanomethyl)trimethylammonium chloride** ($Me_3N^+CH_2CNCl^-$) was prepared by reaction of trimethylamine with α-chloroacetonitrile. The crude product (hydroscopic) was purified by repeated recrystallization from ethanol/chloroform: mp 180 °C dec; NMR (DMSO-d_6) δ 3.46 [9 H, s, $^+N(CH_3)_3$], 5.5 (2 H, s, >CH_2).

***N*-(Cyanomethyl)pyridinium chloride** ($PyN^+CH_2CNCl^-$) was prepared by reaction of pyridine with α-chloroacetonitrile. The crude product was purified by recrystallization from ethanol/chloroform: mp 172.5–173.5 °C (lit.[20] mp 178 °C); NMR (DMSO-d_6) δ 6.34 (2 H, s, >CH_2), 8.3–9.6 (5 H, m, Ar).

***N*-(9-Fluorenyl)trimethylammonium bromide** (9-$Me_3N^+FlHBr^-$) was prepared by reaction of trimethylamine with 9-bromofluorene. The crude product was purified by recrystallization from ethanol/chloromethane: mp 189–190 °C (lit.[21] mp 189–190 °C); NMR (DMSO-d_6) δ 3.16 [9 H, s, $^+N(CH_3)_3$], 6.10 (1 H, s, CH), 7.3–8.2 (8 H, m, Ar).

***N*-[9-[2-(Phenylsulfonyl)fluorenyl]]trimethylammonium Bromide** [9-(Me_3N^+)-2-($PhSO_2$)$FlHBr^-$]. Benzoyl peroxide [$(PhCO_2)_2$] (0.1 g) in 10 mL of $CHCl_3$ was added dropwise to a solution of 1.3 g of 2-(phenylsulfonyl)fluorene and 0.75 g of NBS in 20 mL of $CHCl_3$. The reaction was allowed to reflux for 4 h under nitrogen and then extracted with ether after cooling. The organic ether layer was dried over $MgSO_4$ for overnight. A yellow oil obtained by removal of solvent was treated with excess trimethylamine in ethanol without further purification. The reaction mixture was diluted with anhydrous ether at 0 °C, and the crude product was purified by recrystallization from ethanol/chloroform: mp 181–184 °C dec; NMR (DMSO-d_6) δ 3.18 [9 H, s, $^+N(CH_3)_3$], 6.06 (1 H, s, CH), 7.5–8.4 (12 H, m, Ar).

***N*-(9-Fluorenyl)pyridinium bromide** (9-PyN^+FlHBr^-) was prepared by reaction of pyridine with 9-bromofluorene. The crude product was purified by recrystallization from ethanol/chloroform: mp 204–206 °C (lit.[22] mp 209 °C); NMR (DMSO-d_6) δ 3.40 (1 H, s, CH), 7.3–9.3 (13 H, m, Ar).

***N*-[(Ethoxycarbonyl)methyl]trimethylammonium chloride** ($Me_3N^+CH_2CO_2EtCl^-$) was prepared by reaction of trimethylamine with ethyl α-chloroacetate (Aldrich). The crude product was purified by recrystallization from acetonitrile: mp 151–153 °C; NMR (D_2O) δ 1.30 (3 H, t, CH_2CH_3), 3.27 [9 H, s, $^+N(CH_3)_3$], 4.21 (2 H, q, CH_2CH_3), 4.22 (2 H, s, CH_2N^+).

***N*,*N*-[[(Diethylamino)carbonyl]methyl]trimethylammonium Chloride** ($Me_3N^+CH_2CONEt_2Cl^-$). α-Chloroacetic acid (15.7 g, 0.168 mol) and thionyl chloride (25 mL) were refluxed until the evolution of HCl ceased (~2 h). After cooling to room temperature, the thionyl chloride was distilled under reduced pressure until ca. 15 mL of solution remained. This residue was added slowly to a solution of diethylamine (30 mL) in benzene (40 mL). After stirring for 1 h, the dark brown solution was washed successively with 10% hydrochloric acid solution and 10% sodium hydroxide solution, dried ($MgSO_4$), and concentrated under reduced pressure to give 12.4 g of black oil. This oil was added directly to a solution of trimethylamine (20–30 mL) in 150 mL of absolute ethanol. The mixture was refluxed for 6 h, yielding 21.0 g brown solid. The crude product was purified by recrystallization from ethyl acetate/ethanol: mp 214.5–216 °C; NMR (D_2O) δ 1.20 (6 H, t, -CH_2CH_3), 3.24 (2 H, s, >CH_2), 3.44 [9 H, s, $^+N(CH_3)_3$], 3.44 (4 H, m, CH_2CH_3).

***N*-[(Ethoxycarbonyl)methyl]pyridinium bromide** ($PyN^+CH_2CO_2EtBr^-$) was prepared by reaction of pyridine with ethyl α-bromoacetate (Aldrich). The crude product was purified by recrystallization from ethanol/chloroform; mp 130–131 °C (lit.[23] mp 135–136 °C, lit.[2d] mp 133–135 °C); NMR (DMSO-d_6) δ 1.27 (3 H, t, CH_3), 4.22 (2 H, q, CH_2CH_3), 5.75 (2 H, s, >CH_2), 8.1–9.3 (5 H, m, Ar).

***N*-[2-(1,3-Diethoxy-1,3-dioxopropyl)]trimethylammonium bromide** [$Me_3N^+CH(CO_2Et)_2Br^-$] was prepared by reacting trimethylamine with diethyl α-bromomalonate. The crude product was purified by recrystallization from ethanol/chloroform: mp 119.5–120.5 °C; NMR (DMSO-d_6) δ 1.30 (6 H, t, CH_3), 3.53 [9 H, s, $^+N(CH_3)_3$], 4.33 (4 H, q, >CH_2), 5.97 (1 H, s, CH).

***N*-[2-(1,3-Diethoxy-1,3-dioxopropyl)]trimethylammonium Nitrate** [$Me_3N^+CH(CO_2Et)_2NO_3{}^-$]. A solution of $AgNO_3$ (0.2718 g, 0.160 mmol) in 5 mL of acetonitrile was added dropwise to a solution of $Me_3N^+CH(CO_2Et)_2Br^-$ (0.4771 g, 0.160 mmol) in 5 mL of acetonitrile. The mixture was allowed to stir for another 30 min, the precipitate (AgBr) was filtered, and the solvent was removed. The crude product was purified by recrystallization from ethanol/chloroform: mp 70–71 °C; NMR (DMSO-d_6) δ 1.31 (6 H, t, CH_3), 3.57 [9 H, s, $^+N(CH_3)_3$], 4.29 (4 H, q, >CH_2), 6.01 (1 H, s, CH).

Diethyl Pyridiniomalonate perchlorate [$PyN^+CH(CO_2Et)_2ClO_4{}^-$] was prepared according to the literature method.[24] The crude product was purified by recrystallization from ethanol to give needle-like crystals: mp 145–147 °C (lit.[23] 152 °C); NMR (DMSO-d_6) δ 6.95 (1 H, s, CH), 4.28 (4 H, q, >CH_2), 1.27 (6 H, t, CH_3), 8.3–9.3 (5 H, m, Ar).

Equilibrium Acidities. The equilibrium acidities of α-substituted trimethylammonium and α-substituted pyridinium salts were determined by the overlapping indicator method as described previously.[6,25]

Oxidation Potentials. The oxidation potentials of the conjugate anions (ylides) were determined in DMSO by cyclic voltammetry. The working and auxiliary electrodes are platinum. The reference electrode is Ag/AgI, and the reported potentials are all referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple ($E_{1/2}$ = 0.875 V vs the Ag/AgI).[9a] Checks were made to be sure that the oxidation potentials were those of the ylide rather than those of the counterions.

Acknowledgment. We are grateful to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research. We thank Dr. T.-Y. Lynch for the preparation of phenacyltrimethylammonium nitrate and the oxidation potential measurement made with this compound. We thank a reviewer for helpful comments.

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