Table I. Rate Constants for Hydrolysis of Substrates[a]

Salt[f]	k_{H_2O}, sec^{-1} [b] ($\times 10^3$)	pK_a (amide-NH^+)[d]	k_{H^+},[c] M^{-1} sec^{-1} (A; $\times 10^9$) (calcd)	k_{H^+},[e] M^{-1} sec^{-1} (B; $\times 10^8$)	A/B	F[g]
I. BF_4^-	2.3	−7.18	0.15	2.9	0.0052	0.52
II. BF_4^-	31	−7.16	2.1	3.8	0.055	0.55
III. BF_4^-	22	−6.93	2.6	81	0.0032	0.32

[a] Ionic strength made up to 1 M with NaCl; 25°. [b] Measured spectrophotometrically: I, 235 nm; II, 235 nm; III, 250 nm. Maximum uncertainty in rate constants is ±5%. [c] Calculated from k_{H_2O}/K_a(amideNH$^+$). [d] Calculated from the equation in ref 1d; see ref 9. [e] Rate constants are extrapolated from measurements at higher temperatures; rates were followed using an NMR technique. N,N-Diethylacetamide, $\Delta H^\ddagger$, 15.1; $\Delta S^\ddagger$, −41.4; N-methyl-N-cyclohexylacetamide, $\Delta H^\ddagger$, 16.3; $\Delta S^\ddagger$, −30.7; N-acetylpiperidine, $\Delta H^\ddagger$, 18.3; $\Delta S^\ddagger$, −32 ($\Delta H^\ddagger$ and $\Delta S^\ddagger$ are in kcal/mol and entropy units per mole, respectively, and the values are for 84.3°). [f] We were unable to entirely remove the amine hydrochloride impurity from the salt; we estimated molarity and hence purity of the stock solutions in acetonitrile by reaction with acetate buffers and allowing the product acetic anhydride to hydrolyze. Purities up to 70% were estimated from the extinction change of the anhydride at 250 nm. [g] This represents the fraction of the reaction passing through the N-protonated intermediate and is derived from A/B by correcting for steric factors (see text).

We may calculate the acid-catalyzed rate constant for the N-protonation path for the secondary amides N,N-diethylacetamide, N-methyl-N-cyclohexylacetamide, and N-acetylpiperidine knowing the pK_a of the N-protonated amide[9a] and using the rate constant for hydrolysis of I, II, and III, respectively, as a model for the hydrolysis of the intermediate. The ratio of the value so obtained to the observed acid-catalyzed rate constant (A/B) gives a lower limit to the fraction of the reaction proceeding via N protonation as the prior step. The true fraction is obtained from this ratio after correcting for the steric effect of methyl or ethyl compared with hydrogen; if we assume a Taft delta of unity for the selectivity to E_s (this is a reasonable value since a delta of unity is defined for the sterically similar addition of water to ethyl esters of carboxylic acids in acid hydrolysis)[9b] then replacing hydrogen in tertiary carbon by methyl or ethyl should decrease the reactivity by 1 or 2 logarithmic units, respectively.[9b] By analogy the same effect should be expected when nitrogen is the central atom. The values represented by F in the table are probably *upper* limits for the fraction of reaction passing through the N-protonation path because there is evidence that the steric hindrance is not as pronounced as is to be expected from the delta values: for example 2-methylpropionyl chloride is only fourfold more reactive to water than is pivaloyl chloride.[12]

There will be a difference in solvation between (for example) the N-protonated form of N-acetylpiperidine and III. The former will be more strongly solvated, through specific hydrogen bonding to water molecules, because of its NH^+ group. Thus in going from cation to transition state the N-protonated amide should start off lower in energy and tend to react more slowly indicating that the value F may be too high an upper limit. It is difficult to estimate how far below F this upper limit should be: the Bronsted α for solvation by water of NH^+ must be less than unity (which represents complete proton transfer) and a reasonable value seems to be close to 0.2.[14] If we may assume the transition state approximates an N-protonated carbinolamine then a ΔpK_a of about 15 for NH^+ will reduce the ratio F to 0.32×10^{-3} as the upper limit for the fraction of the N-protonation pathway.

The overall selectivity of acid hydrolysis via N-protonation to leaving group pK_a is estimated to be approximately +0.5 being composed of a selectivity of +1.04 for the N-protonation equilibrium[1d] and close to −0.5 for hydrolysis of the intermediate.[13] Since the observed selectivity for acid hydrolysis of substituted anilides is approximately zero[15] (this could be used as an argument in favor of O protonation) then the N-protonation mechanism will predominate for amides of highly basic amines.

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(8) The hydrolysis may be followed by uv absorption (Table I) or with a pH–stat; in the latter case the amount of acid released follows a logarithmic plot (vs. time) consisting of two linear phases: a high rate constant identical with that from the uv work and a smaller one equal to the rate constant for acetic anhydride hydrolysis under the same conditions. In acetate buffers the absorption at 250 nm increased and then decayed at the rate expected for acetic anhydride hydrolysis suggesting that in the pH–stat experiments acetic anhydride is formed by capture of the initial acetate product by the acetylammonium salt (present in relatively high concentrations ~10 mM).

(9)(a) Estimates of pK_a for the N-protonated amide depend on acid catalyzed proton exchange[1e,10,11] and on models of equilibria in thermodynamic cycles.[1d] The good agreement between the results gives us confidence in the equation: $pK_a = -18.6 + 1.04pK_{a\,(R_2NH)}$[1d] where R_2NH is the free amine; (b) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.

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Aromatic Radical Anions in Neat Solvents. Crown Complex Ion-Pair Formation

Sir:

Reports[1,2] of radical anion formation in neat benzene and toluene using crown ethers and alkali metals prompt us to describe our experimental results with 18-crown-6. We hope our direct observation of the role played by ion-pair formation in the case of mesitylene and toluene will assist other workers. To our knowledge this is also the first report of the preparation of the mesitylene radical anion. The observed reactivity, in contrast to the very weak electron affinity of mesitylene in other solvents and in the absence of crown ether complex, may be due to the stabilization of the anion radical by ion-pair formation.

Samples are prepared under high vacuum conditions by bringing a solution of 18-crown-6 in benzene, toluene, or mesitylene, into contact with an alkali metal mirror. The reaction begins quickly and is complete after a few hours at −20°C.

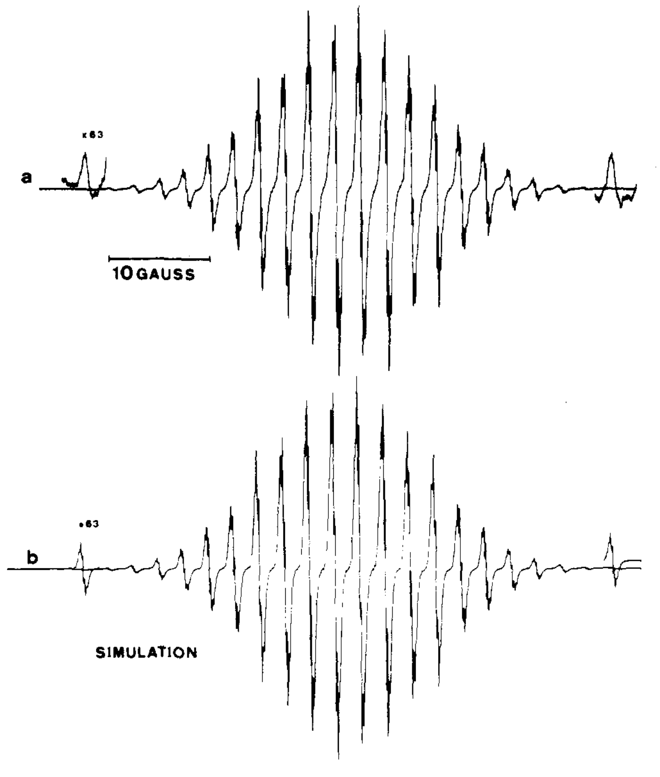

Figure 1. (a) EPR spectrum of mesitylene radical anion produced by reaction of a solution of 18-crown-6 in mesitylene upon a potassium mirror. (b) Simulated spectrum including splitting by six additional equivalent protons and three equivalent ^{13}C nuclei.

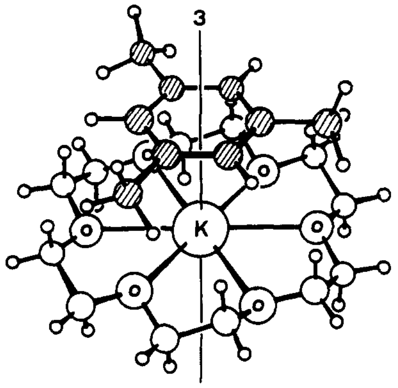

Figure 2. Proposed model for the ion pair formed between mesitylene radical anion and potassium 18-crown-6 complex. The smallest coupling constant observed is thought to couple the radical anion with the six equivalent axial protons above the plane of the crown.

The basic 22-line EPR pattern in Figure 1a obtained for mesitylene arises from the overlap of the 40 line pattern expected (a_{CH_3} = 4.91 G; a_H = 2.57 G; g = 2.0026). Additionally these lines are split by six equivalent protons ($a_{H'}$ = 0.18 G; peak-to-peak width = 0.16 G). The simulated spectrum in Figure 1b also includes ^{13}C splitting caused by three equivalent nuclei ($a_{C\text{-}13}$ = 2.2 G). The coupling constants are temperature dependent, but the basic hyperfine pattern persists even at +30°C. The spin polarizations produced by an extended-Hückel MO calculation of the lone mesitylene anion agree with the two largest hyperfine coupling constants.

The most probable explanation for the splitting pattern due to six equivalent protons involves the formation of ion pairs between the mesitylene radical anion and the potassium-crown complex cation. X-Ray structural determination in the case of potassium thiocyanate treated with 18-crown-6 reveals axial pairs of hydrogens on the crown related by a S_6 axis and three equivalent vertical mirror planes.[3] In Figure 2 is presented our proposed model for the ion pair. The crown complex is drawn from the X-ray results[3] and the mesitylene anion from nominal values of bond distances and angles. The anion is oriented with its three ring hydrogens on the three equivalent mirror planes of the crown as shown.

Further confirmation of the proposed model is obtained in the case of toluene with potassium and 18-crown-6. (See paragraph at end of paper regarding supplementary material.) The five major lines of the EPR pattern obtained at −90°C arise from the nearly equivalent toluene ortho and meta proton coupling constants ($a_{o\text{-H}}$ = 4.86 G; $a_{m\text{-H}}$ = 5.45 G; g = 2.0026). The simulation obtained through optimizing the above ion-pair model in the case of toluene anion gives not only the simplest model but also the most complete fit of the spectrum we obtained after exhausting other possible models (a_{CH_3} = 0.85 G; $a_{p\text{-H}}$ = 0.45 G; $a_{o\text{-crown}}$ = 0.12 G (four axial protons); $a_{p\text{-crown}}$ = 0.18 G (two axial protons); peak-to-peak width = 0.15 G). The 0.70 G splitting is roughly the difference between the position of the two lowest field groupings in the spectrum instead of the potassium coupling as previously assigned.[2]

The EPR spectrum in the case of benzene and 18-crown-6 with potassium is not highly resolved, with a line width of 1.6 G. In addition to the pattern caused by the six equivalent protons of the benzene (a_H = 3.49 G), there may also be unresolved hyperfine splitting of six axial crown protons or one ^{39}K nucleus.[4] Our optimization gives the same goodness of fit in both cases.

For 18-crown-6 as well as for cryptate(221), both with benzene and toluene, we do not observe reaction with a sodium mirror as reported in the case of dicyclohexyl-18-crown-6[1] if we use analytical grade sodium. We think one should be cautious when describing reactions of sodium under conditions where trace amounts of potassium may be present. For thiocyanate salts with 18-crown-6 the potassium ion is found to lie within the plane of the six ether oxygens, whereas the sodium ion takes its sixth oxygen above the plane in an apical position.[3] If the ions are coordinated the same way in solution, the potassium ion in the complex is more exposed, and the crown ligand is better situated, to stabilize the ion pair.

Because the rubidium and cesium ions are found to be too large to fit within the plane of the crown oxygens,[3] we feel their greater exposure to the anion may allow even the possibility of direct metal coupling. Experiments with cesium metal and solutions of 18-crown-6 can be interpreted along these lines. With benzene or mesitylene as solvent only one broad asymmetric line is obtained in the EPR spectrum, in marked contrast with the hyperfine coupling pattern observed when using potassium metal. The manifold of lines shows the asymmetric character of a second-order m_I dependence of the splitting by the larger cesium cation. In the case of toluene, however, the eight lines from the ^{133}Cs nucleus become the predominant coupling pattern (a_{Cs} = 2.65 G). It is expected that rubidium will exhibit behavior similar to cesium.

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Supplementary Material Available. EPR spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6279.

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Bis(trimethylphosphoranylidene)methane, $(CH_3)_3PCP(CH_3)_3$

Sir:

Currently there is considerable interest in the chemistry of both the bis(triphenylphosphoranylidene)ammonium cation,[1] **1**, and the isoelectronic bis(triphenylphosphoranylidene)methane molecule,[2] **2**. This interest is based on some unexpected observations. (1) The cation **1** has been found by X-ray studies to vary strongly in its structure, depending on the nature of the anion and the type of the crystal lattice.[1] The PNP bond angle may range between 134.6 and 180°, and two different bond angles may be met in one and the same unit cell (!).[1b] (2) The crystals of compound **2** were also demonstrated[2b] to contain two different types of molecules, with PCP valence angles of 143.8 and 130.1°. (3) Moreover, compound **2** is unusual in showing the rare phenomenon of triboluminescence[2a] (i.e., to emit visible light upon touching of the crystals).

$$(C_6H_5)_3P{=}N{=}P(C_6H_5)_3^{+} \qquad (C_6H_5)_3P{=}C{=}P(C_6H_5)_3$$

1 **2**

It was concluded[1a,2a] from these observations, that there should be only a delicate energy balance associated with angle deformation in these species, similar and related to the energy characteristics of bond deformations in the isoelectronic siloxanes $R_3SiOSiR_3$.[3]

To contribute to this discussion, we report here some of the properties of $(CH_3)_3P{=}C{=}P(CH_3)_3$ and its synthesis, which was impossible to accomplish via the traditional methods employed previously[2] for the hexaphenyl analog **2**. We reported earlier[4] on $(CH_3)_3P{=}N{=}P(CH_3)_3^+$.

Difluorotrimethylphosphorane[5] undergoes a smooth reaction with trimethylsilylmethylene trimethylphosphorane[6] under mild conditions, in benzene solvent, resulting in about an 80% yield of fluorotrimethylsilane and fluoro(trimethylphosphoranylidene)methyltrimethylphosphorane (**3**) (eq 1a). Alternatively, this compound is obtained in high yield from the reaction of 1:2 molar amounts of $(CH_3)_3PF_2$ and $(CH_3)_3PCH_2$ (eq 1b). This precursor, **3**, mp. 74°C, is a covalent nonsalt-like species, soluble in benzene and other nonpolar solvents. In solution it appears to be a fluxional molecule in which the fluorine atom is subject to rapid site exchange at the phosphorus atoms. This renders the ^{31}P nuclei equivalent even at temperatures as low as −90°C, and no ^{19}F-couplings are observed:[7] ^1H NMR (in benzene at 30°C) $\delta(H_3C)$ 0.93 ppm, $A_9XX'A_9'$, $N = 11.3$ Hz;[8] $\delta(HC)$ −0.14, t, $J(PCH) = 21.5$ Hz. ^{31}P NMR, $\{^1H\}$ −32.8, s.

Anal. Calcd for $C_7H_{19}FP_2$: C, 45.65; H, 10.40. Found: C, 45.31; H, 10.57.

$$(CH_3)_3P{=}CH{-}Si(CH_3)_3 + (CH_3)_3PF_2 \xrightarrow[78^\circ C]{\text{benzene}} (CH_3)_3P{=}CH{-}P(CH_3)_3F + (CH_3)_3SiF \quad (1a)$$

3

$$2(CH_3)_3P{=}CH_2 + (CH_3)_3PF_2 \longrightarrow (CH_3)_3P{=}CH{-}P(CH_3)_3F + [(CH_3)_4P]F \quad (1b)$$

3

With methylene dichloride, an instantaneous reaction (eq 2) was observed, even at −80°C, which converted **3** into the corresponding chloride, **4**, mp 168°C dec.[9] This chloride is salt-like in character and therefore differs in all its physical and spectral properties from the fluoride (**3**): ^1H NMR (in CH_2Cl_2 at 30°C): $\delta(H_3C)$ 2.0, $A_9XX'A_9'$, $N = 12.8$;[8] $\delta(HC)$ 0.65, t, $J(PCH) = 5.0$ Hz; ^{31}P NMR, $\{^1H\}$ 10.5, s.

Anal. Calcd for $C_7H_{19}ClP_2$: C, 41.91; H, 9.55. Found: C, 42.37; H, 9.79.

$$(CH_3)_3P{=}CH{-}P(CH_3)_3F \xrightarrow[-CH_2F_2]{CH_2Cl_2} [(CH_3)_3P{=}CH{-}P(CH_3)_3]Cl \quad (2)$$

4

When an intimate mixture of **3** and sodium hydride is heated to the melting point of **3**, hydrogen is rapidly evolved and a colorless liquid can be distilled from the reaction mixture under vacuum. This product ($bp_{0.1}$ 41°C, mp ca. 0°C), **5**, which is extremely reactive, was identified as **5** by elemental analysis, ^1H, ^{13}C, and ^{31}P NMR, and mass spectra: ^1H NMR (in benzene) $\delta(H_3C)$ 1.21, $A_9XX'A_9'$, $N = 11.3$; ^{31}P NMR, $\{^1H\}$ −29.6, s; ^{13}C NMR, $\{^1H\}$ $\delta(CH_3)$ 23.9, AXX′, $N = 52$;[10] $\delta(C)$ 10.8, t, $J(PC) = 32$ Hz.

Anal. Calcd for $C_7H_{18}P_2$: C, 51.21; H, 11.05. Found: C, 50.84; H, 11.02. Parent ion mass: calcd 164.2, found 164 (MS, M^+).[11]

$$(CH_3)_3P{=}CH{-}P(CH_3)F + NaH \xrightarrow[\Delta]{\text{neat}} (CH_3)_3P{=}C{=}P(CH_3)_3 + H_2 + NaF \quad (3)$$

The compound **5** is one of the most air-sensitive compounds of the whole ylide series. Traces of air will immediately turn samples brown. Strict adherence to inert gas methods is necessary. The general chemical behavior of the ylide is characterized by a very strong basicity, which makes it a powerful deprotonating agent and a good nucleophile, and exceeds both the hexaphenyl analog and the simple monoylides.

Although there is no ambiguity about the structure of the hexaphenyl analog, in the case of **5** three isomers must be considered (**5, 5a, 5b**). The magnetic resonance spectra clearly indicate only the presence of **5**. Since prototropy has been demonstrated to be facile in ylide systems,[12] it follows that the "cumulated" (allene-type) ylide **5** is more stable than both the "conjugated" and the "isolated" double ylides **5a, b.**

Our results do not yet provide information on the valence angle at the central carbon atom in **5**, but a large angle