at 329 (M^+, 3.48), 328 ($M^+ - 1$, 15.68), 220 ($CHCMe_3CONHC_6H_4$-4-OMe^+, 6.43), 150 ($CONHC_6H_4$-4-OMe^+, 8.34), 109 ($C_6H_5CH^{18}OH^+$, 25.17), 108 ($C_6H_5CH^{18}O^+$, 54.67), and 107 ($C_6H_5C^{18}O^+$, 10.58). The relative ratio of $C_6H_5CH^{18}OH^+$, $C_6H_5CH^{18}O^+$, and $C_6H_5C^{18}O^+$ was 0.46:1:0.193. **Reaction of Oxetane (*Z*)-16 with $H_2{}^{18}O$.** The reaction of oxetane (*Z*)-16 (0.050 g, 0.15 mmol) and $H_2{}^{18}O$ (0.08 mL) in 1.5 mL of anhydrous dioxane containing 0.007 mL of H_2SO_4 gave a 54:48 erythro/threo mixture of amides **34**. They were separated by thick-layer chromatography. The mass spectrum of *threo*-**34** had a pattern similar to that of *erythro*-**34** formed in the reaction of (*E*)-**16** with $H_2{}^{18}O$, since the stereochemical relationship between *threo*-**34** and (*Z*)-**16** was that of inversion. Relevant peaks, together with their relative abundances, were at 329 (5.98), 328 (26.23), 220 (5.64), 150 (5.54), 109 (15.3), 108 (41.0), and 107 (8.96). The relative ratio of the intensity of the peaks at 109, 108, and 107 was 0.37:1:0.21. The relevant masses of *erythro*-**34**, which retains the stereochemistry of (*Z*)-**16**, can be attributed to the amides deriving from an attachment of $H_2{}^{18}O$ at both C4 and C2 of (*Z*)-**16**. Relevant ion masses were at 329 (M^+, 13.99), 222 ($CHCMe_3C^{18}ONHC_6H_4$-4-OMe^+, 1.24), 220 ($CHCMe_3CONHC_6H_4$-4-OMe^+, 5.05), 207 ($CHCMe_3C^{18}ONHC_6H_4$-4-OMe^+ - Me, 3.76), 205 ($CHCMe_3CONHC_6H_4$-4-OMe^+ - Me, 13.02), 109 (14.23), 108 (42.00), and 107 (23.13). The relative ratio of masses at 109, 108, and 107 was 0.34:1:0.56. This isomer revealed an abnormally high 107/108 ratio (0.56) with respect to that observed in the first two cases (0.19 and 0.21). The conclusion is that C_6H_5CHOH rather than $C_6H_5C^{18}O$ contributed to the intensity of this mass.

Supplementary Material Available: Table V, containing reaction conditions, isomer distributions, and microanalytical, MS, IR, and ^1H NMR ($CDCl_3$) data of 2-iminooxetanes **5**, **10**, **14**, **15**, and **16**, and Table VI, containing reaction conditions, isomer distributions, and microanalytical, MS, IR, ^1H NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) data of β-hydroxyamides **17**, **18**, **19**, **21**, **22**, **26**, **27**, **28**, **29**, **30**, **31**, and **33** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current mastehead page for ordering information.

Preparation and Characterization of Crystalline *N*-Acylammonium Salts

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The reaction of a tertiary amine with an acid chloride or chloroformate followed by anion exchange with either sodium tetraphenylborate or silver tetrafluoroborate provides stable, nonhygroscopic, crystalline acylammonium salts.

Introduction

Acylammonmium species have been widely invoked as intermediates in organic and biological chemistry.[1-6] Although there has been wide interest in their chemistry and a number of species have been proposed as isolable materials, a convenient, general procedure for the preparation of analytically pure acylammonium salts has not been developed.

Olah used carboxonium salts in sulfur dioxide to acylate pyridine to produce the *N*-acetyl-, *N*-propionyl-, and *N*-benzoylpyridinium hexafluoroantimonates.[7] Paukstelis and Kim treated tertiary amines with acid halides in the presence of hydrogen tetrafluoroborates to yield the corresponding tetrafluoroborate salts;[8] in the course of their work, they developed a more convenient preparation of acylammonium tetrafluoroborates using triethyloxonium tetrafluoroborate. Preformed 4-(dimethylamino)-pyridinium tetrafluoroborate has been used effectively to produce pure onium salts, as well.[9] We wish to report a simple, general method for the preparation of crystalline acylammonium salts.

Results and Discussion

The formation of acylammonium salts in acetonitrile solution in the presence of either sodium tetraphenylborate

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Table I. Acylammonium Salt Carbonyl Data

amine[a]	acyl group	anion[b]	N–C_{CO} (Å)	C=O (Å)	C=O[c] (cm^{-1})
pyridine	carbophenoxy	TPB			1831
TEA	carbophenoxy	TFB	1.497[d]	1.180	1829
	phosgene			1.180[e]	1827[f]
3-picoline	carbomethoxy	TPB[g]	1.474	1.171	1827
3-picoline	carbomethoxy	TPB[g]	1.470	1.188	1827
3-picoline	carboisopropoxy	TPB			1819
isoquinoline	carbobenzoxy	TPB	1.477 (7)	1.172 (7)	1817
N-EPIP	acetyl	TFB			1817[h]
TEA	acetyl	TFB			1814[h]
TMA	acetyl	Br^-			1814[i]
TMA	acetyl	Cl^-			1812[i]
	CH_3COCl				1807[j]
pyridine	acetyl	TFB			1806[h]
pyridine	acetyl	Cl^-			1804[i]
DMAP	carbophenoxy	Cl^-	1.430[k]	1.187	1801
DMAP	carbophenoxy	TFB			1800
	CH_3COCl				1799[j]
	$C_6H_5O_2CCl$				1788[m]
	CH_3O_2CCl			1.190[n]	1782[m]
	$C_6H_5CH_2O_2CCl$				1780[m]
TEA	benzoyl	TPB	1.548[d]	1.186	1778
	$(CH_3)_2CHO_2CCl$				1776[m]
	C_6H_5COCl				1776[m]
pyridine	benzoyl	$SbCl_6^-$			1771[o]
DMAP	*t*-BOC	TFB			1770[p]
DMAP	benzoyl	TPB	1.456[k]	1.204	1742

[a] TEA = triethylamine, DMAP = (dimethylamino)pyridine, TMA = trimethylamine, *N*-EPIP = *N*-ethylpiperidine. [b] TFB = tetrafluoroborate anion and TPB = tetraphenylborate anion. [c] Infrared data were measured in an acetonitrile solution at rt. [d] Crystal data reported in ref 10c. [e] 1.180 Å (1.166 Å) in ref 14c. [f] Reference 6d. [g] Two crystalline polymorphs are obtained.[10e] [h] Reference 8. [i] Reference 12. [j] Reference 14e. [k] Crystal data reported in ref 10d. [l] Reference 14a. [m] Spectra measured and reported for comparative purposes. [n] Reference 13. [o] Reference 15. [p] Reference 9.

or silver tetrafluoroborate leads to the formation of the corresponding soluble acylonium borate species in essentially quantitative yield. The reaction proceeds with concomitant precipitation of either NaCl or AgCl (eq 1).

$$\text{acyl halide} + \text{amine} + MBPh_4 \rightleftharpoons [\text{acylammonium}]^+BPh_4^- + MCl\downarrow \quad (1)$$

$$M = Na, Ag$$

The acylammonium borate salts are completely soluble in the acetonitrile solution under the reaction conditions. The desired salts are isolable as stable solids following their separation from the halide salt and subsequent solvent removal. Recrystallization of the isolated borate salts from nonpolar media yields pure, crystalline compounds.

In general, the tetraphenylborate is the preferred anion for acylonium salt isolation. The tetraphenylborates crystallize readily and prove to be nonhygroscopic in the cases studied. In a number of our early attempts, we found the tetrafluoroborates to produce many glassy materials; a few of the tetrafluoroborates were observed to be hygroscopic as well. The acylonium chloride salts proved even more problematic. The chlorides prove susceptible to thermal decomposition via decarboxylative dealkylation[4] under relatively mild conditions (10–50 °C in acetonitrile solution). Furthermore, they tended to be extremely hygroscopic. Both manipulation and storage of the acylonium chlorides were substantially more difficult than for either of the borate anions.

The acylonium salts can be identified by a number of spectroscopic techniques. The acylammonium salts produce a strong carbonyl absorption in their infrared spectra (Table I). The tendency of the simple tertiary amine/pyridine adducts to shift the carbonyl stretching frequency to higher energy, relative to the initial acyl halide, has been reported previously.[6] Generally, we find the same tendency of the C=O absorption to shift to higher frequency upon adduct formation. This trend holds for all but the more basic or resonance stabilized amines. Interestingly, the carbonyl shift appears more dependent on the amine moiety than on the C=O bond length. From Table I, there is no discernible trend between the measured carbon–oxygen bond length of the carbonyl and its infrared stretching frequency. The acylammonium salt carbonyl bond lengths vary between 1.204 and 1.171 Å in no consistent pattern; these bond lengths are not significantly different from those observed in simple chloroformates or phosgene.[13,14]

A number of researchers prefer NMR[2,6,9,10] or UV[1,3] methods for studies where a transient acylonium salt is generated in situ and its concentration or rate of formation–disappearance is of interest.[1] ^1H NMR is particularly well suited for structural analysis of the acylonium cations as the amine protons adjacent the appended nitrogen exhibit a characteristic 1–2 ppm downfield shift.

Using ^{13}C NMR, hindered rotation about the *N*-acyl bond is indicated in the spectrum of *N*-benzoyl-4-(dimethylamino)pyridinium tetraphenylborate; line-broadening in a number of the peaks in the proton spectrum is observed as well. The activation barrier for site-exchange within this adduct has yet to be determined. A simple steric argument seems insufficient to explain this phenomenon. Single-crystal X-ray analysis of this compound shows both the DMAP and benzene ring to be rotated out of the plane of the carbonyl group.[10d] The DMAP and the

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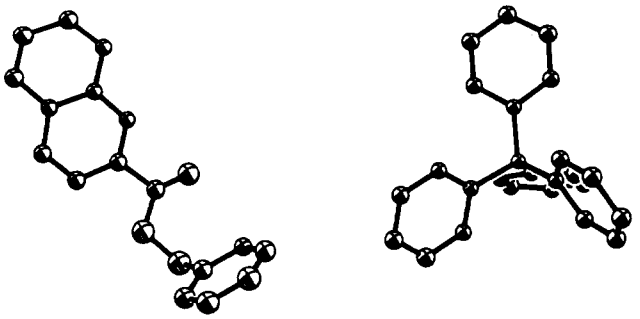

Figure 1.

benzene ring are rotated nearly perpendicular to one another, indicating little direct interaction. The corrsponding *N*-benzoyl-4-(dimethylamino)pyridinium tetrafluoroborate does not exhibit this behavior in its NMR spectra. Neither does the *N*-benzoyl-*N*-triethylammonium cation nor any of the other DMAP adducts studied. Thus, some anion-dependent aggregation phenomenon may be occurring in solution. Comparative crystallographic work for this class of onium salt cations is sparse.[10c-e]

Another unusual observation is found in the ^{13}C NMR spectrum of *N*-carboisopropoxy-3-methylpyridinium tetraphenylborate. The spectrum indicates peak doubling at the 2- (140.6 ppm), 4- (152.8 ppm), and 6- (138.7 ppm) positions of the picolinium moiety. All the other carbon atoms produce sharp absorptions. A variable-temperature ^{13}C NMR study (acetonitrile-d_3; −25 °C to +70 °C) causes only a slight peak-broadening of the doubled peaks with increasing temperature. There was no indication of the occurrence of any coalescence or exchange phenomena by NMR; hence, the doublets are assummed to result from the coupling of the carbon atoms to another atom in the system.

Color formation is characteristic of some tetraphenylborate salts. This phenomen occurs only with aromatic amines such as (alkyl)pyridine(s), DMAP, or isoquinoline. Both the solutions and isolated materials of these salts are brightly colored. Initially, it was believed that a simple anion–cation interaction was occurring. Inspection of the single X-ray crystal structure of *N*-(benzoxycarbonyl)isoquinolinium tetraphenylborate (Figure 1) indicates a marginal, if any, direct interation between the cation and anion. In the structure, the isoquinoline ring is coplanar with the carbonyl group. The arene ring of the benzyl group lies in a plane perpendicular to the plane defined by the isoquinoline moiety. Color formation appears to be unique to these tetraphenylborate anion salts. Unless the materials have degraded, color formation is not usually observed with acylonium salts containing either the tetrafluoroborate or chloride anions.[6,8-10] The cause the color formation in these acylonium tetraphenylborate salts is the subject of further investigation.

In conclusion, a simple, convenient method for the preparation of crystalline acylammonium salts is demonstrated. The procedure is found to be quite general for tertiary amines. The method can be used to generate acylonium salts from either acid halides or chloroformates. Thus, this process allows the preparation of not only a convenient source of reactive carbonyl species[1-3] but also their use as a potentially new protecting group.[16]

(16) The acylammonium salts derived from aromatic tertiary amines (e.g., 3-picoline) with alkyl chloroformates can be selectively decomposed to liberate the free amine. This is accomplished by reacting the acylammonium borate in an acetonitrile solution saturated with LiCl. Depending on the acyl group substituent, the reaction temperature ranged from rt to 70 °C.

Experimental Section

All the reagents used in these experiments were obtained from Aldrich Chemical Co. Except for the benzyl and isopropyl chloroformates, all the organic reagents were purified by distillation prior to their use. The silver tetrafluoroborate and the sodium tetraphenylborate were used as obtained without further purification. The solvents were all OmniSolv grade and were used as received.

Chemical shift data for ^1H and ^{13}C NMR spectra were measured relative to a tetramethylsilane (TMS) standard in either CH_3CN-d_3 or CH_2Cl_2-d_2. Samples were transferred in a nitrogen glovebag.

The X-ray data were acquired on a Siemens R3m/V upgrade of a Nicolet P3F automated diffractometer, using a Wyckoff scan with variable scan speeds. D_m values were not determined. The structure was solved by direct methods and refined on F using the SHELXTL-Plus program package on a Micro VAX-II computer.[11] H atoms were placed in idealized positions and constrained to have C–H = 0.96 Å with isotropic thermal parameters, U = 0.08 Å. All non-H atoms were treated as anisotropic. No absorption corrections were necessary for the structure. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV).

All melting points were measured using a Thomas Hoover Uni-melt capillary melting point apparatus; the values reported are uncorrected. The elemental analyses were performed by Galbraith Analytical laboratories.

General Procedure for the Preparation of *N*-Acylammonium Tetraphenylborate Salts. An anhydrous acetonitrile solution (250 mL) containing the acid chloride or chloroformate (0.052 mol) and sodium tetraphenylborate (0.050 mol) was cooled in an ice bath (~4 °C) under a nitrogen atmosphere. The tertiary amine (0.050 mol) was added dropwise via syringe into the rapidly stirred, cooled solution over 15–20 min; during the amine addition, a white precipitate (NaCl) was formed after roughly 25% of the amine had been added. The reaction solution was stirred for another 30–45 min after the amine addition was complete. The stirring was stopped. The sodium chloride was allowed to settle and to pack at the bottom of the reactor flask. The clear supernatant was transferred from the NaCl using a cannula; the solid and liquid can be separated using filtration, but the process requires a *very* fine glass fritt. The solid acylammonium salt was collected following either solvent removal by rotary evaporation or the addition of anhydrous ether to the mother liquor. The resulting precipitate was recrystallization from either methylene chloride–ether or methylene chloride–hexane (pentane).

General Procedure for the Preparation of *N*-Acylammonium Tetrafluoroborate Salts. These salts were prepared in a manner identical to the tetraphenylborate procedure outlined above. Silver tetrafluoroborate (0.050 mol) was substituted for sodium tetraphenylborate in the initial reaction solution; the resulting white precipitate now becomes AgCl. Isolation of the acylammonium salt followed the previously outlined procedure.

***N*-(Benzoxycarbonyl)isoquinolinium tetraphenylborate** (98% yield) was recrystallized from a 10:1 methylene chloride–hexane solvent by cooling the solution to −20 °C. The salt was collected as clear, orange prisms: mp 117–118 °C; IR (acetonitrile) 3059 (s), 3014 (m), 1817 (vs, C=O), 1637 (s), 1275 (s), 1215 (vs), 1168 (m), 1099 (m), 777 (m), 736 (m), 708 (s), 613 (m) cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3) δ 10.23 (t, J = 0.8 Hz, ^{14}NCH, 1 H), 8.95 (dd, J = 6.2, 1.6 Hz, 1 H), 8.55 (dd, J = 8.5, 0.7 Hz, 1 H), 8.30 (m, 4 H), 8.08 (ddd, J = 6.8, 6.8, 1.3 Hz, 1 H), 7.61 (m, 2 H), 7.49 (m, 3 H), 7.25 (m, 8 H), 6.97 (dd, J = 7.4, 7.3 Hz, 8 H), 6.81 (t, J = 7.35, 4 H), 5.74 (s, 2 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 163.5 (q, J = 49.3 Hz, ^{11}BC), 148.2, 140.9, 135.6, 134.8, 132.9, 132.7, 132.4, 130.6, 130.1, 129.8, 129.6, 128.9, 127.7, 127.6, 125.7, 125.5 (q, J = 2.6 Hz, ^{11}BC), 121.7, 74.6. Anal. Calcd for $C_{41}H_{34}O_2NB$: C, 84.38; H, 5.87; N, 2.41; B, 1.85. Found: C, 84.65; H, 5.92; N, 2.33; B, 1.76. Crystal Data: $C_{41}H_{34}BNO_2$, M = 583.5, orthorhombic, space group $Pna2_1$, a = 16.838 (6) Å, b = 9.153 (3) Å, c = 20.027 (11) Å, U = 3087 (2) Å^3, Z = 4, D_{calc} = 1.256 g cm^{-3}, T = 171 K. A total of 3994 reflections with 3.5° ≤ 2θ ≤ 55.0° were recorded using a highly oriented graphite crystal mono-

chromator and Mo Kα radiation. Of these 2437 [$F > 4.0\sigma(F)$] were judged to be observed. The data converged to give these final R indices: $R = 5.00\%$, $R_W = 6.46\%$. Atomic coordinates and parameters and bond lengths and angles are supplied as supplementary material.

***N*-Carbomethoxy-3-methylpyridinium tetraphenylborate** (76% yield) was recrystallized from a 5:2 methylene chloride–pentane solution by cooling to −20 °C. The material crystallized in two polymorphic forms: clear yellow cubes (mp 183–184 °C melts/resolidified; mp 255–257 °C dec) and light yellow prisms (mp 262–264 °C dec); IR (acetonitrile) 3059 (m), 3005 (m), 1827 (vs, C=O), 1629 (m), 1581 (m), 1481 (m), 1265 (s), 1190 (m), 758, 737 (m), 710 (s), 624 (m), 613 cm^{-1}; ^1H NMR (300 MHz; acetone-d_6) δ 9.34 (s, 1 H), 9.15 (d, J = 6.3 Hz, 1 H), 8.52 (d, J = 7.7 Hz, 1 H), 7.91 (dd, J = 7.7, 6.3 Hz, 1 H), 7.23 (m, 8 H), 6.81 (dd, J = 7.3, 7.1 Hz, 8 H), 6.67 (t, J = 7.1 Hz, 4 H), 4.21 (s, 3 H); ^{13}C NMR (75 MHz; acetone-d_6) δ 163.9 (q, J = 49.4 Hz, ^{11}BC), 153.0, 140.9, 140.7, 139.3, 139.1, 135.9, 127.3, 125.0, 121.3, 58.6, 17.3. Anal. Calcd for $C_{32}H_{30}O_2NB$: C, 81.52; H, 6.41; N, 2.98; B, 2.29. Found: C, 81.78; H, 6.48; N, 3.05; B, 2.16.

***N*-Carboisopropoxy-3-methylpyridinium tetraphenylborate** (97% yield) was recrystallized from a 5:2 methylene chloride–pentane solution by cooling to −20 °C. The material crystallized as ruby-red prisms: mp 141–142 °C; IR (acetonitrile) 3059 (m), 3001 (w), 1819 (vs; C=O), 1628 (m), 1582 (m) 1481 (m), 1262 (vs), 1240 (s sh), 1096 (s), 891 (m), 835 (m), 737 (s), 710 (m), 613 cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_6) δ 9.14 (s, 1 H), 9.01 (d, J = 6.3 Hz, 1 H), 8.39 (d, J = 8.2 Hz, 1 H), 7.79 (dd, J = 8.2, 6.3 Hz, 1 H), 7.39 (m, 8 H), 7.03 (dd, J = 7.2, 6.6 Hz, 8 H), 6.87 (t, J = 6.6 Hz, 4 H), 5.49 (heptet, J = 6.3 Hz, 1 H), 2.51 (s, 3 H), 1.56 (d, J = 6.3 Hz, 6 H); ^{13}C NMR (75 MHz; acetonitrile-d_6) δ 163.8 (q, J = 49.3 Hz, ^{11}BC), 152.9 (d, J = 6.8 Hz), 146.4, 140.6 (d, J = 16.9 Hz), 139.8, 138.8 (d, J = 16.5 Hz), 135.7, 127.2, 125.6 (q, J = 2.2 Hz, ^{11}BC), 121.8, 82.5, 21.7, 18.1. Anal. Calcd for $C_{34}H_{34}O_2NB$: C, 81.75; H, 6.86; N, 2.82; B, 2.16. Found: C, 82.03; H, 6.91; N, 2.82; B, 2.04.

***N*-Benzoyl-4-(dimethylamino)pyridinium tetraphenylborate** (95% yield) was recrystallized from a 10:1 methylene chloride–ether solution. The material crystallized as light yellow prisms: mp 179–181 °C; IR (acetonitrile) 3057 (m), 3001 (w), 1790 (vw), 1742 (s; C=O), 1647 (vs), 1584 (s), 1263 (s), 1219 (vs), 1115 (vs), 735 (s), 710 (s), 613 (m) cm^{-1}; IR (CH_2Cl_2) 3051 (m), 1748 (s; C=O), 1645 (vs), 1586 (w), 1262 (vs), 1217 (vs), 1109 (s), 748 (vs), 716 cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3) δ 8.26 (bd, J = 7.2 Hz, 2 H), 7.84–7.73 (m, 3 H), 7.63 (bt, J = 7.7 Hz, 2 H), 7.29 (m, 8 H), 7.00 (dd, J = 7.3, 7.3 Hz, 8 H), 6.85 (tt, J = 7.3, 1.2 Hz, 4 H), 6.74 (d, J = 8.1 Hz, 2 H), 3.20 (s, 6 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 167.8, 163.8 (q, J = 49.3 Hz, ^{11}BC), 162.6, [158.2, 157.4], [138.4, 138.2], 135.7, [134.8, 134.5], [130.6, 130.4], [129.2, 129.1], 125.6 (q, J = 2.5 Hz, ^{11}BC), 121.8, [106.9, 106.8], [40.7, 39.5]. Anal. Calcd for $C_{38}H_{35}ON_2B$: C, 83.50; H, 6.45; N, 5.15; B, 1.98. Found: C, 83.65; H, 6.48; N, 5.37; B, 1.89.

***N*-Benzoyl-4-(dimethylamino)pyridinium tetrafluoroborate** (85% yield) was recrystallized from a 5:2 methylene chloride–ether solution by cooling to −20 °C. The material crystallized as clear prisms: mp 155–157 °C; IR (acetonitrile) 1744 (s; C=O), 1647 (vs), 1589 (m), 1263 (s), 1219 (s), 1115 (vs), 1063 cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3) δ 8.50 (d, J = 8.3 Hz, 2 H), 7.93–7.85 (m, 3 H), 7.77 (t, J = 8.3 Hz, 2 H), 3.37 (s, 6 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 168.1, 158.4, 138.9, 138.8, 134.8, 130.3, 129.6, 107.2, 41.2.

***N*-Benzoyl-*N*-triethylammonium tetraphenylborate** (92% yield) was recrystallized from a 4:1 methylene chloride–ether solution by cooling to −20 °C. The material crystallized as clear prisms: mp 162–163 °C (resolidified/reddened; second mp 171–173 °C dec); IR (acetonitrile) 3057 (s), 2988 (m), 1778 (s; C=O), 1732 (w), 1582 (m), 1479 (m), 1211 (s), 1177 (m), 874, 737 (s), 710 (vs) cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3) δ 7.87–7.82 (m, 3 H), 7.67 (dd, J = 8.3, 7.9 Hz, 2 H), 7.31–7.26 (m, 8 H), 7.01 (dd, J = 7.3, 7.2 Hz, 8 H), 6.85 (t, J = 7.2 Hz, 4 H), 3.68 (q, J = 7.3 Hz, 6 H), 1.27 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 172.2, 163.7 (q, J = 49.2 Hz, ^{11}BC), 146.2, 135.7, 135.2, 129.8, 129.3, 125.5 (q, J = 2.6 Hz), 121.8, 52.7, 8.0. Anal. Calcd for $C_{37}H_{40}ONB$: C, 84.56; H, 7.67; N, 2.66; B, 2.06. Found: C, 84.84; H, 7.60; N, 2.62; B, 2.12.

***N*-Carbophenoxy-*N*-triethylammonium tetrafluoroborate** (87% yield) was recrystallized from a 5:2 methylene chloride–ether solution by cooling to −20 °C. The material crystallized as clear prisms; mp 103–104 °C; IR (acetonitrile) 1829 (s; C=O), 1485 (m), 1215 (s), 1188 (m), 1062 (vs) cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_6) δ 7.60 (dd, J = 7.8, 7.3 Hz, 2 H), 7.50 (t, J = 7.3 Hz, 1 H), 7.40 (d, J = 7.8, 2 H), 3.85 (q, J = 7.2 Hz, 6 H), 1.41 (t, J = 7.2 Hz, 9 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 151.6, 149.9, 130.4, 128.4, 120.1, 54.5, 7.93. Anal. Calcd for $C_{13}H_{20}O_2NBF_4$: C, 50.51; H, 6.52; N, 4.53; B, 3.50. Found: C, 50.83; H, 6.57; N, 4.48; B, 3.33.

***N*-Carbophenoxypyridinium tetrafluoroborate** (82% yield) was recrystallized from a 10:1 methylene chloride–ether solvent by cooling the solution to −20 °C. The salt was collected as clear needles: mp 138–139 °C (melts/resolidifies; second mp 143–145 °C dec); IR (acetonitrile) 3082 (m), 2947 (w), 1831 (s; C=O), 1784 (w), 1626 (m), 1479 (s), 1246 (vs), 1202 (s), 1184 (s), 1063 (vs), 756(m), 733 (m) cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3) δ 9.56 (J = 6.7 Hz, 2 H), 8.97 (t, J = 7.4 Hz, 1 H), 8.31 (dd, J = 7.4, 6.7 Hz, 2 H), 7.64–7.57 (m, 2 H), 7.53–7.46 (m, 3 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 153.5, 150.4, 146.6, 142.3, 142.2, 130.4, 128.3, 120.5. Anal. Calcd for $C_{12}H_{10}O_2NBF_4$: C, 50.21; H, 3.51; N, 4.90, B, 3.77. Found: C, 50.50; H, 3.60; N, 4.81; B, 3.78.

***N*-Carbophenoxy-4-(dimethylamino)pyridinium tetrafluoroborate** (92% yield) was recrystallized from a 5:2 methylene chloride–ether solution by cooling to −20 °C. The material crystallized as clear prisms: mp 197–198 °C; IR (CH_2Cl_2) 3069 (w), 1800 (s; C=O), 1653 (vs), 1589 (m), 1491 (w), 1277 (s), 1208 (s), 1188 (s), 1142 (m), 1101 (s), 1061 (), 719 (vs) cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_6) δ 8.65 (d, J = 8.3 Hz, 2 H), 7.55 (dd, J = 7.5, 6.9 Hz, 2 H), 7.43 (t, J = 6.9 Hz, 1 H), 7.39 (d, J = 7.5, 2 H), 7.01 (d, J = 8.3 Hz, 2 H), 3.37 (s, 6 H); ^{13}C NMR (75 MHz; acetonitrile-d_3) δ 158.7, 150.4, 148.2, 137.6, 130.3, 127.7, 121.2, 107.7, 41.1. Anal. Calcd for $C_{14}H_{15}O_2N_2BF_4$: C, 50.94; H, 4.58, N, 8.49; B, 3.27. Found: C, 51.12; H, 4.56; N, 8.51; B, 3.00.

Supplementary Material Available: X-ray data (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.