Reaction of Benzylic α-Hydroxythioamides with Thionyl Chloride

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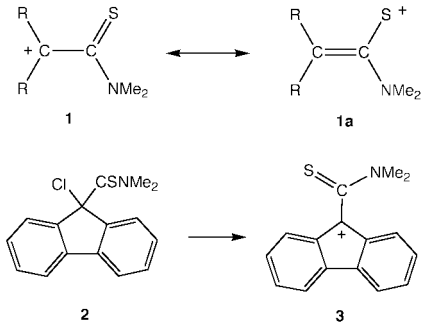
9-Hydroxy-9-(*N*,*N*-dimethylthiocarbamyl)fluorene, **4**, reacts very rapidly with 1 equiv of thionyl chloride to give the corresponding α-chlorothioamide derivative, **2**. However reaction of **4** with 2 equiv of thionyl chloride gives the desulfurized product 9-chloro-9-(*N*,*N*-dimethylcarbamyl)fluorene, **6**. This unusual desulfurization reaction, which is neither completely general nor completely understood at the present time, occurs less readily than initial formation of the α-chlorothioamide. The α-chlorothioamide **2** is highly reactive in hydroxylic solvents. The substantially less reactive α-chloroamide **6** undergoes reaction in hydroxylic solvents via the intermediacy of the 9-(*N*,*N*-dimethylcarbamyl)-9-fluorenyl cation, **15**, at rates comparable to those of the α-H analogue, 9-chlorofluorene, **14**. Computational studies indicate that the α-carbonyl cation **15** prefers a conformation in which the carbonyl group is rotated 90° with respect to the fluorenyl system. The relatively rapid rate of solvolysis of **6** is attributed to relief of ground-state strain as the cation **15** forms, as well as delocalization involving the fluorene system. Carbonyl conjugation as a cation-stabilizing feature does not appear to operate in the α-carbonyl cation **15**.

We[1] and others[2] have been interested in the chemistry of carbocations **1** substituted with the thioamide functional group, $CSNMe_2$. This interest grows out of the remarkable cation-stabilizing effect that this formally electron-withdrawing group can exert on carbocations.[1] This cation stabilizing effect has been attributed to a resonance interaction with the adjacent C=S π-bond as in **1a**. Along these lines, the generation and characterization of cation **3** from the corresponding chloride **2** has recently been reported.[3] Additionally, there has been renewed interest in fluorenyl type carbocations[4,5] and the question of antiaromaticity.[6] This prompts us to report our findings on **2** and related systems.



Results and Discussion

Thionyl Chloride Reactions. During the course of our program designed to elucidate the properties of α-carbonyl and α-thiocarbonyl cations, we have prepared the alcohols **4** and **5**. The alcohol **5** has been converted to the corresponding chloride by treatment with $SOCl_2$ in ether containing Na_2CO_3 (to react with the byproduct HCl). This procedure gives a high yield of the corresponding chloride **6**. We have carried out solvolytic studies on this chloride, and these studies will be subsequently discussed in more detail. We have found the chloride **6** is quite reactive in CF_3CH_2OH, solvolyzing with a half-life of 186 min at 25 °C. Thiocarbonyl analogues ($CSNMe_2$) are usually significantly more reactive than $CONMe_2$ analogues.[1] Indeed, we have found that certain trifluoroacetate derivatives of α-hydroxythioamides are very unstable compounds. We were therefore surprised to see the report[3] that chloride **2** could be dissolved in solvents such as CH_3OH and CF_3CH_2OH and that it survives long enough to permit irradiation and photofragmentation of the C−Cl bond with generation of a transient cationic intermediate **3**. We therefore attempted to prepare chloride **2** and to confirm its reactivity.

Reaction of the α-hydroxythioamide **4** with 1 equiv of thionyl chloride in ether (with or without suspended Na_2CO_3) proceeded rapidly to give the chloride **2**. This chloride has been fully characterized by elemental analysis, mass spectrometry, ^1H NMR,[7] and low temperature ^{13}C NMR. Chloride **2** is not stable for prolonged periods in $CDCl_3$ solution at room temperature. Solutions of **2** in $CDCl_3$ begin to decompose (autocatalytically) after about 30 min at room temperature. Additionally, the NMe_2 signals of **2** are broadened at room temperature due to rotation about the C−N bond. Therefore, it is

(1) (a) Creary, X.; Aldridge, T. *J. Org. Chem.* **1988**, *53*, 3888. (b) Creary, X.; Aldridge, T. *J. Org. Chem.* **1991**, *56*, 4280. (c) Creary, X.; Hatoum, H. N.; Barton, A.; Aldridge, T. *J. Org. Chem.* **1992**, *57*, 1887. (d) Creary, X.; Zhu, C. *J. Am. Chem. Soc.* **1995**, *117*, 5859.

(2) (a) Ablenas, F. J.; George, B. E.; Maleki, M.; Jain, R.; Hopkinson, A. C.; Lee-Ruff, E. *Can J. Chem.* **1987**, 65, 1800. (b) Richard, J. *J. Am. Chem. Soc.* **1996**, *118*, 12603.

(3) Lew, C. S. Q.; Wong, D. F.; Johnston, L. J.; Bertone, M.; Hopkinson, A. C.; Lee-Ruff, E. *J. Org. Chem.* **1996**, *61*, 6805.

(4) For a recent report on the solvolytic generation of CF_3-substituted fluorenyl cations, see Allen, A. D.; Colomvakos, J. D..; Tee, O. S..; Tidwell, T. T. *J. Org. Chem.* **1994**, *59*, 7185.

(5) For a report on the generation of CO_2CH_3 substituted fluorenyl cations under stable ion and laser flash conditions, see Johnston, L. J.; Kwong, P.; Shelemay, A.; Lee-Ruff, E. *J. Am. Chem. Soc.* **1993**, *115*, 1664.

(6) For a discussion of so-called "antiaromaticity" in fluorenyl carbocations, see Amyes, T. L.; Richard, J. P.; Novak, M. *J. Am. Chem. Soc.* **1992**, *114*, 8032.

(7) The ^1H NMR spectrum of **2** reported in ref 3 (δ 2.9 (br s, 3 H), 2.05 (br s, 3 H)) does not agree with our results.

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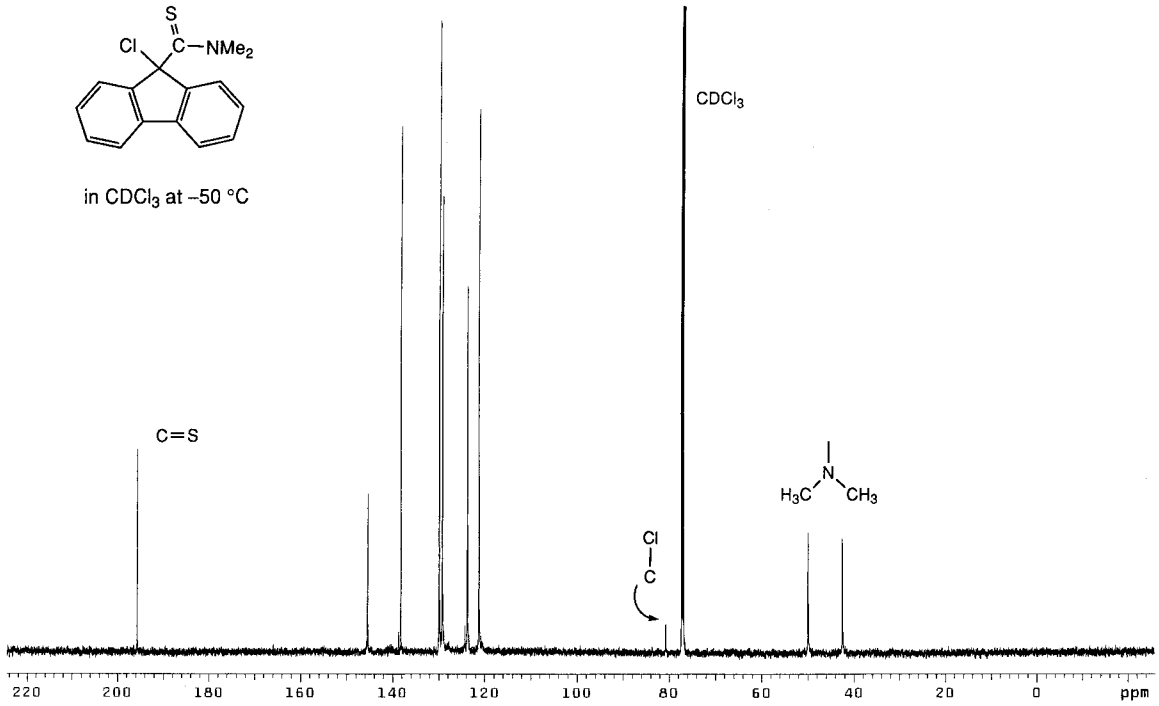
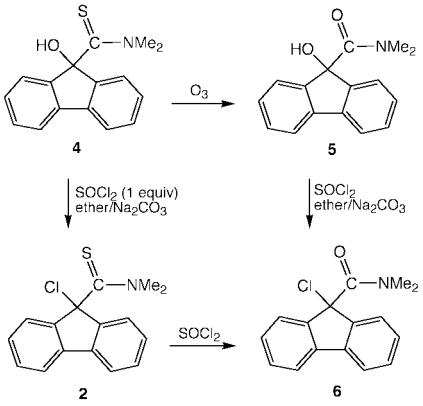


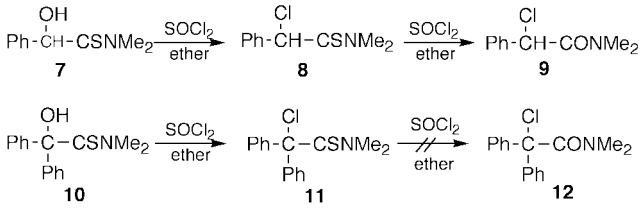
Figure 1. ^{13}C NMR spectrum of chloride **2** at −50 °C.



necessary to record ^{13}C NMR spectra (Figure 1) at low temperature. At −50 °C all carbons are visible, including the characteristic thiocarbonyl carbon at δ 195.69.

When excess thionyl chloride is used in the synthesis of **2**, the α-chlorothioamide is readily converted to the α-chloroamide **6**. This process can be easily observed when the reaction is monitored by NMR and the conversion of **2** to **6** is slower that the original formation of **2**. Figure 2 shows the low temperature ^{13}C NMR spectrum of **6**, with the characteristic amide carbonyl signal at δ 165.97. The benzylic α-hydroxythioamide **7** also undergoes an analogous transformation to the α-chloroamide **9** with 2 equiv of thionyl chloride, and the intermediate α-chlorothioamide **8** can be isolated only when 1 equiv of thionyl chloride is used. By way of contrast, the diphenyl analogue **10** can be readily converted to the α-chlorothioamide **11** with 1 equiv of thionyl chloride. This product is not further oxidized by a second equivalent of $SOCl_2$ to the α-chloroamide **12**.

These conversions of α-hydroxythioamides **4**, **7**, and **10** to α-chlorothioamides with $SOCl_2$ are all extremely rapid reactions. For example, NMR analysis within a few minutes of mixing $SOCl_2$ with **10** shows no remaining unreacted **10**. In contrast to this, the reactions of the



α-hydroxyamide **5** as well as the α-hydroxyamide analogue of **10** ($Ph_2C(OH)CONMe_2$) with thionyl chloride are relatively slow reactions at room temperature, requiring an excess of $SOCl_2$ and extended reaction times for conversion to the α-chloroamides.

The oxidation of the α-chlorothioamides **2** and **8** to α-chloroamides by excess thionyl chloride was quite unexpected. The acetate derivative of **7** (PhCH(OAc)-$CSNMe_2$) can also be oxidized to 2-acetoxy-*N*,*N*-dimethylphenylacetamide, $PhCH(OAc)CONMe_2$. However the reaction is not completely general, and $PhCH_2CSNMe_2$ is not converted to $PhCH_2CONMe_2$. A number of methods (including nitrous acid oxidation, potassium ferricyanide oxidation, selenium dioxide oxidation, basic hydrogen peroxide oxidation, as well as various hydrolytic procedures) have been reported in the literature for the conversion of thioamides to amides, and these methods have been reviewed.[8] Ozonolysis[9] and peracid oxidations[10] have also been used to convert thioamides to amides. However, we are not aware of any literature reports on the conversion of thioamides to amides with thionyl chloride. In terms of mechanism it is reasonable to suggest that the reaction is initiated by nucleophilic attack of the thiocarbonyl sulfur atom on the electrophilic

(8) Hurd, R. N.; DeLaMater, G. *Chem. Rev.* **1961**, *61*, 45.
(9) (a) Zwanenburg, B.; Janssen, W. A. J. *Synthesis* **1973**, 617. (b) Nilsson, N. H.; Jacobsen, C.; Sørensen, O. N.; Haunsøe, N. K.; Senning, A. *Chem. Ber.* **1972**, *105*, 2854. (c) Creary, X.; Zhu, C. *J. Am. Chem. Soc.* **1995**, *117*, 5859.
(10) Kochhar, K. S.; Cottrell, D. A.; Pinnick, H. W. *Tetrahedron Lett.* **1983**, 24, 1323.

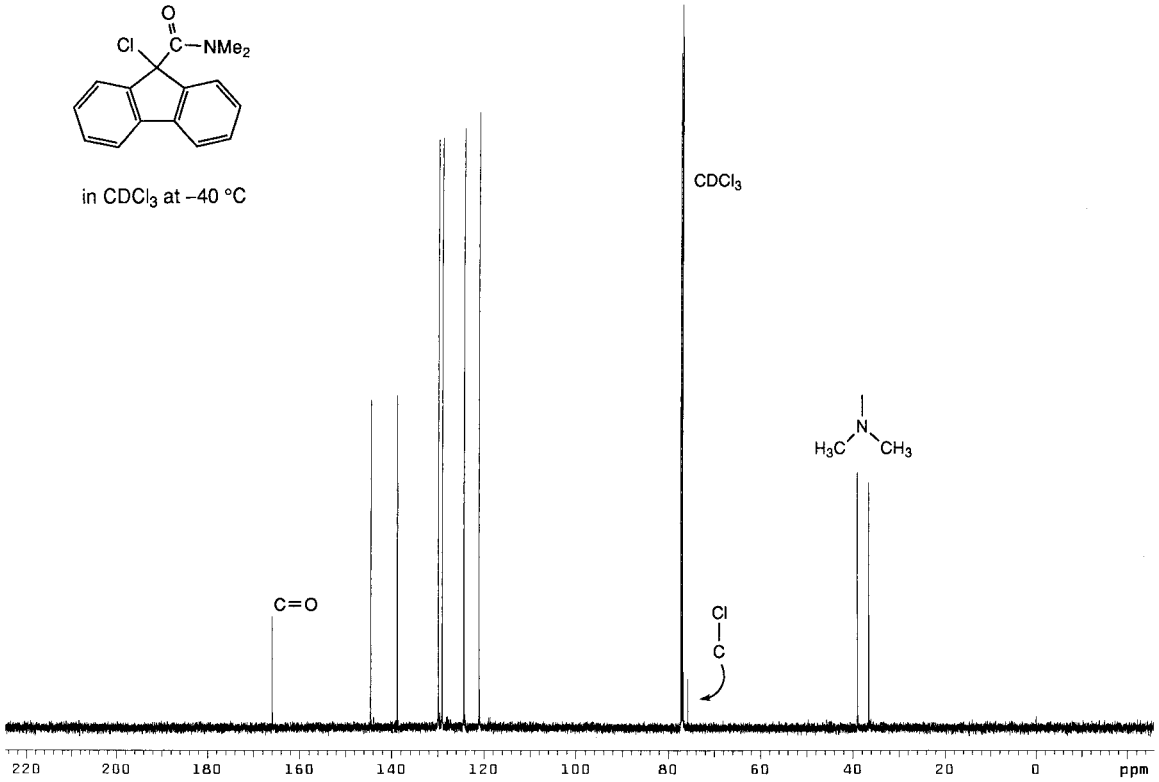


Figure 2. ^{13}C NMR spectrum of chloride **6** at −40 °C.

Table 1. Solvolysis Rates of Chlorides 6 and 14 at 25 °C

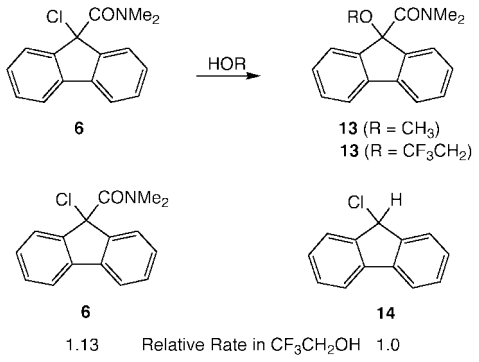
substrate	solvent	k (s^{-1})
6	CH_3CH_2OH[a]	1.10×10^{-7} [b]
6	CH_3OH[a]	5.93×10^{-7}
6	CF_3CH_2OH[c]	7.10×10^{-5}
6	$(CF_3)_2CHOH$[c]	3.94×10^{-3}
14	CF_3CH_2OH[c]	6.28×10^{-5}

[a] Determined by ^1H NMR. [b] Extrapolated from higher temperatures. $k_{(80\ °C)} = 7.58 \times 10^{-5}$. $k_{(60\ °C)} = 9.02 \times 10^{-6}$. [c] Determined by UV spectroscopy.

sulfur of the thionyl chloride. The lack of reactivity of **11** suggests that the reaction is quite subject to steric effects. The scope, mechanism, and generality of this oxidation remains under investigation.

Reactivity of Chlorides 2 and 6. While the α-chlorothioamide **2** is stable indefinitely in ether solution and for shorter periods of time in $CDCl_3$, in our hands **2** is highly reactive in hydroxylic solvents. This substrate undergoes "instantaneous" reaction upon dissolution in methanol or in trifluoroethanol, and no trace of **2** can be detected in NMR spectra recorded immediately after mixing with methanol or trifluoroethanol. Unfortunately, no products can be characterized when **2** reacts in these solvents. Only intractable material remains after standard workup procedures. These findings are in stark contrast to the reported behavior[3] of chloride **2** and the suggestion that **2** survives long enough in CH_3OH and CF_3CH_2OH to permit laser flash photolytic studies.

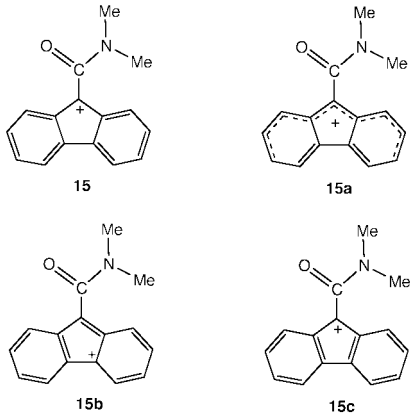
In contrast to the behavior of α-chlorothioamide **2**, the α-chloroamide **6** undergoes smooth reaction in a variety of solvents to give the simple substitution products **13**. The reaction rate increases substantially as the solvent becomes more highly ionizing (Table 1). A Winstein−Grunwald plot using Y_{OTs} values[11] is linear ($r = 0.999$) with an m value of 0.83. These reactions undoubtedly occur via the intermediacy of the α-carbonyl cation **15**. Rate data show that the α-chloroamide **6** is slightly more reactive than the α-H analogue **14** despite the presence of the electron-withdrawing $CONMe_2$ group in the cationic intermediate **15**. This result is in line with our previous findings that α-carbonyl cations can be formed relatively easily (compared to α-H analogues) under solvolytic conditions.[12]



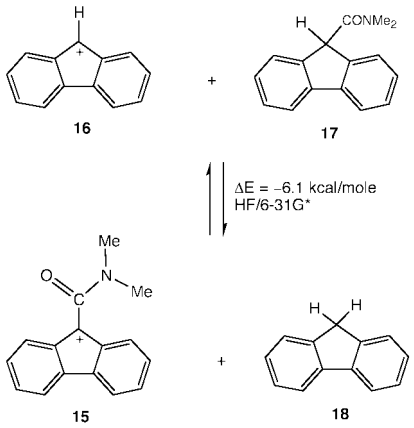
Computational Studies. Ab initio molecular orbital calculations[13] have been carried out at the HF/6-31G* level on the α-carbonyl cation **15**. These studies suggest that **15** is not a planar molecule, but that the amide group is twisted 90° out of planarity with the fluorene system due to steric effects. A substantial part of the high reactivity of **6** can therefore be attributed to relief of strain with the departure of the chloro leaving group, i.e.,

(11) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. J. *Am. Chem. Soc.* **1976**, 98, 7667.

(12) (a) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151. (b) Creary, X.; McDonald, S.; Eggers, M. D. *Tetrahedron Lett.* **1985**, 26, 811. (98) Creary, X. *J. Am. Chem. Soc.* **1984**, *106*, 5568. For a further discussion, see (d) Creary, X. *Chem. Rev.* **1991**, 91, 1625.



a ground-state effect often referred to as B-strain.[14] Carbonyl conjugation in **15** as a cation-stabilizing mechanism is precluded due to steric factors. An isodesmic calculation (Table 2) also allows a comparison of stabilities of cation **15** and the unsubstituted fluorenyl cation **16**. The cation **15**−fluorene pair are favored by 6.1 kcal/mol. This suggests that the α-carbonyl cation **15** is not an exceptionally destabilized system. This is completely consistent with our solvolytic rate data on chlorides **6** and **14**.



Computational studies also give insight into the stabilization mode for **15**. The charge in this cation is delocalized into the fluorene ring system. However, the alternating long (1.418 Å), short (1.360 Å), and long (1.412 Å) bond distances in the six-membered rings (Figure 3) suggest that charge is not uniformly delocalized throughout the ring system. The cation is best represented by the incompletely delocalized form **15a**. In valance bond terms, contributions of forms such as **15b** and **15c** (antiaromatic) are of less importance. The calculated structure of the unsubstituted 9-fluorenyl cation **16** has similar bond lengths and suggests a similar charge delocalization mechanism involving the aromatic rings of the fluorene system (Figure 3).

In summary, reaction of the 9-hydroxyfluorene derivative **4** with a limited amount of $SOCl_2$ produces the highly reactive α-chlorothioamide **2** whose properties do not correspond to those previously reported. When excess $SOCl_2$ is employed in the preparation of **2**, facile conversion to the α-chloroamide **6** occurs. Under solvolytic conditions this chloride **6** readily forms an α-carbonyl cation in which nonuniform charge delocalization occurs into the aromatic rings of the fluorene system. Computational studies suggest that the $CONMe_2$ group of this cation is rotated 90° out of conjugation with the fluorene system.

Table 2. HF/6-31G* Energies of Molecules 15−18[a]

molecule	HF energy (au)	ZPE (au)
15	−743.13396	0.27799
16	−497.29754	0.18901
17	−743.96093	0.29159
18	−498.13321	0.20159

[a] The isodesmic energy includes the zero-point correction.

Experimental Section

Preparation of Chloride 2. A solution of 88.6 mg of alcohol **4**[3] (0.329 mmol) in 5 mL of dry ether was stirred at room temperature as a solution of 42.7 mg of $SOCl_2$ (0.359 mmol) in 200 μL of ether was added dropwise via pipet. After stirring for 30 min at room temperature, 4 mL of hexane was added to the solution and most of the solvent was then removed using a rotary evaporator. About 1 mL of hexane was then added, and the mixture was then cooled to −20 °C. The solvent was decanted from the solid residue and the chloride **2** was further washed with a small amount of hexanes and then dried under vacuum, leaving 93.2 mg of chloride **2** (98%). ^{1}H NMR of **2** ($CDCl_3$) δ 7.732 (d of m, J = 7.3 Hz, 1 H), 7.562 (d of m, J = 7.3 Hz, 1 H), 7.455 (t of d, J = 7.3, 1.3 Hz, 1 H), 7.374 (t of d, J = 7.3, 1.3 Hz, 1 H), 2.87 (br, 3 H), 2.01 (br, 3 H). ^{13}C NMR of **2** ($CDCl_3$ at −50 °C) δ 195.69, 145.41, 138.22, 129.87, 129.19, 123.71, 121.24, 80.75, 49.88, 42.43. Exact mass calcd for $C_{16}H_{14}ClNS$: 287.0535, found 287.0522. Anal. Calcd for $C_{16}H_{14}ClNS$: C, 66.77; H, 4.90; Cl, 12.32; S, 11.14. Found: C, 66.57; H, 5.50; Cl, 11.94; S, 10.85.

Preparation of α-Hydroxyamide 5. A solution of 328 mg of the α-hydroxythioamide **4** in 5 mL of methylene chloride was cooled to −78 °C, and the solution was exhaustively ozonized. The mixture was then warmed to room temperature, and the solvent was removed using a rotary evaporator. The gummy residue was extracted with ether, and the ether extract was filtered through a small amount of silica gel. The solvent was removed using a rotary evaporator to give 200 mg (65% yield) of α-hydroxyamide **5**. Recrystallization from 90% hexane−10% ethyl acetate gave an analytical sample, mp 119−120 °C. ^{1}H NMR of **5** ($CDCl_3$) δ 7.680 (d of t, J = 7.2 Hz, 1 H), 7.44−7.28 (m, 6 H), 6.172 (s, 1 H), 3.013 (s, 3 H), 2.109 (s, 3 H). ^{13}C NMR of **5** ($CDCl_3$) δ 172.50, 145.50, 140.82, 129.54, 128.70, 124.01, 120.53, 81.43, 38.36, 36.27. Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97. Found: C, 75.86; H, 6.10.

Preparation of Chloride 6 from Alcohol 5. A solution of 56.0 mg of alcohol **5** in 3 mL of ether containing 119 mg of Na_2CO_3 was stirred at room temperature, and 28 mg of $SOCl_2$ was added. After 3.5 h NMR analysis of a small portion showed only about 10% reaction. An additional 88 mg of $SOCl_2$ was added, and after 4 days the ether was decanted from the Na_2CO_3. Most of the solvent was removed using a rotary evaporator, and a small amount of hexane was added to the mixture. The mixture was cooled to −20 °C, and the solvent was decanted from the solid residue. The chloride **6** was further washed with a small amount of hexanes and then dried under vacuum, leaving 43.4 mg (72%) of chloride **6**, mp 163−165 °C. ^{1}H NMR of **6** ($CDCl_3$) δ 7.723 (d of m, J = 7.5 Hz, 1 H), 7.584 (d of m, J = 7.5 Hz, 1 H), 7.450 (t of d, J = 7.5, 1.3 Hz, 1 H), 7.366 (t of d, J = 7.5, 1.3 Hz, 1 H), 3.48 (br, 3 H), 2.36 (br, 3 H). ^{13}C NMR of **6** ($CDCl_3$ at −40 °C) δ 165.97, 144.53, 138.77, 129.89, 129.06, 124.31, 121.04, 75.78, 38.97,

(13) Frisch, M, J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.3, Gaussian, Inc., Pittsburgh, PA, 1995.

(14) Brown, H. C. *The Nonclassical Ion Problem*; Plenum Press: New York, 1977; pp 21−31.

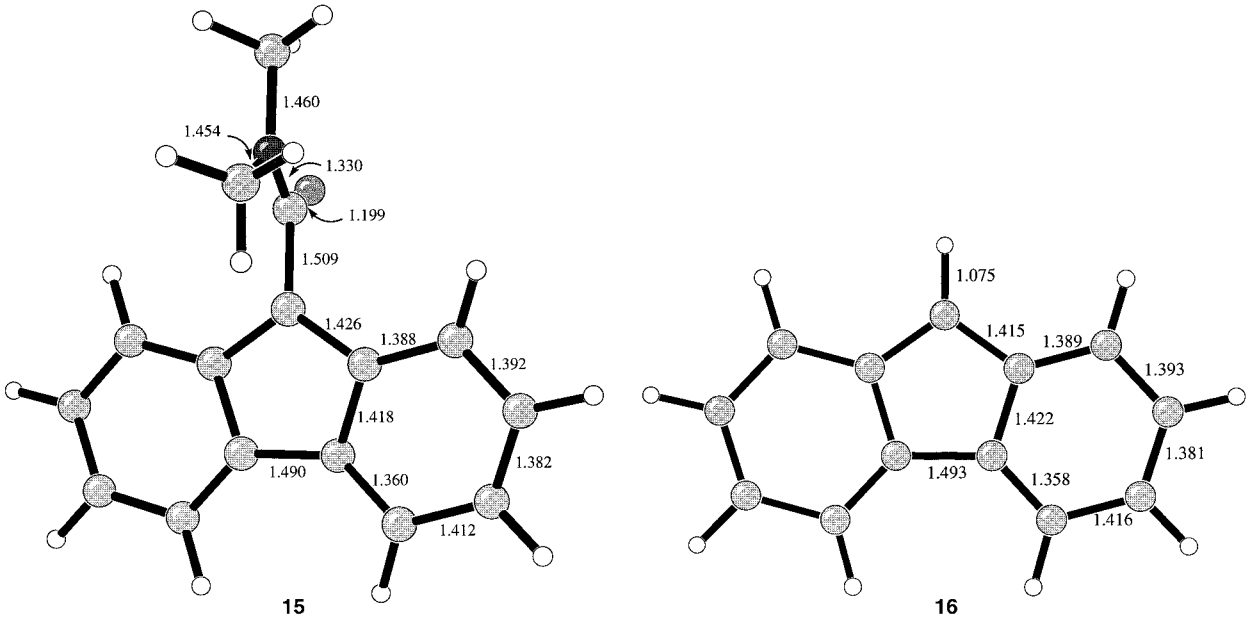


Figure 3.

36.52. Anal. Calcd for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.80; H, 5.49; N, 5.25.

Preparation of Chloride 6 from Alcohol 4. A suspension of 106.8 mg of alcohol **4** (0.397 mmol) in 5 mL of ether was stirred as 103 mg (0.866 mmol) of $SOCl_2$ in a small amount of ether was added dropwise. The mixture was stirred for 19 h at room temperature, and the ether solution of **6** was decanted from the precipitated residue. The ether was removed using a rotary evaporator, and the solid residue was slurried with a small amount of a 2:1 hexane:ether mixture. The mixture was cooled to −20 °C and the solvent was decanted from the solid residue leaving 105.8 mg (98% yield) of chloride **6**. The ^{1}H and ^{13}C NMR spectra were identical to those of an authentic sample of **6** prepared from alcohol **5** as described above.

Preparation of Chloride 8. A suspension of 89.0 mg of alcohol **7** and 203 mg of Na_2CO_3 in 5 mL of ether was stirred at 15 °C as 54.4 mg of $SOCl_2$ in a small amount of ether was added. After stirring for 30 min at room temperature, the ether solution was decanted from the Na_2CO_3, and the solvent was removed using a rotary evaporator. Chloride **8** (88.9 mg, 90% yield) remained as a clear oil. ^{1}H NMR of **8** ($CDCl_3$) δ 7.59−7.51 (m, 2 H), 7.43−7.30 (m, 3 H), 6.462 (s, 1 H), 3.491 (s, 3 H), 3.183 (s, 3 H). ^{13}C NMR of **8** ($CDCl_3$) δ 196.20, 135.78, 128.71, 128.46, 126.68, 67.24, 45.92, 43.00. Exact mass calcd for $C_{10}H_{12}ClNS$: 213.0379, found 213.0385.

Reaction of $PhCH(OAc)CSNMe_2$ with $SOCl_2$. A solution of 71 mg of $PhCH(OAc)CSNMe_2$[1a] in 6 mL of ether was stirred at room temperature, and 46 mg of $SOCl_2$ dissolved in 0.3 mL of ether was added. The mixture was kept at room temperature for 13 h and the ether was then filtered through a small amount of silica gel. The ether solvent was removed using a rotary evaporator leaving 51 mg (77% yield) of $PhCH(OAc)CONMe_2$. This product was spectroscopically identical to an authentic sample.[15]

Preparation of Chloride 11. A suspension of 152.2 mg of alcohol **10** and 199 mg of Na_2CO_3 in 6 mL of ether was stirred at 15 °C as 70.8 mg of $SOCl_2$ in a small amount of ether was added. After stirring for 10 min at room temperature, the ether solution was decanted from the Na_2CO_3, and the solution was stored in a freezer at −20 °C for 12 h. The ether solvent was decanted from the solid chloride **11** which had crystallized. The solid **11** was washed with pentane and dried under vacuum to give 103.1 mg (63% yield). ^{1}H NMR of **11** ($CDCl_3$) δ 7.39−7.28 (m, 10 H), 3.544 (s, 3 H), 3.192 (s, 3 H). ^{13}C NMR of **11** ($CDCl_3$) δ 199.62, 143.51, 129.08, 128.10, 127.62, 80.94, 47.80, 46.07. Exact mass calcd for $C_{16}H_{16}ClNS$: 289.0692, found 289.0649.

Solvolysis of Chloride 6 in Methanol. A solution of 28.2 mg of chloride **6** and 17.5 mg of 2,6-lutidine in 3 mL of methanol was heated in a sealed tube at 64 °C for 24 h. The methanol was then removed using a rotary evaporator, and the residue was taken up into ether and water. The aqueous extract was discarded, and the ether was washed with dilute HCl solution. The ether extract was dried over Na_2SO_4, and the solvent was removed using a rotary evaporator leaving 25.5 mg (92% yield) of the methyl ether **13a** as an oil which solidified on standing. The solid **13a**, mp 124−126 °C, was titurated with hexanes and dried under vacuum. ^{1}H NMR of **13a** ($CDCl_3$) δ 7.688 (d of m, J = 7.4 Hz, 1 H), 7.493 (d of m, J = 7.4 Hz, 1 H), 7.432 (t of d, J = 7.3, 1.3 Hz, 1 H), 7.335 (t of d, J = 7.3, 1.2 Hz, 1 H), 2.857 (s, 3 H), 3.2−2.1 (br, 6 H). ^{13}C NMR of **13a** ($CDCl_3$) δ 169.70, 142.57, 141.58, 129.72, 128.46, 124.99, 120.40, 88.59, 51.10, 37.30 (broad, $N(CH_3)_2$). Exact mass (FAB) calcd for $C_{17}H_{18}NO_2$: 268.1338, found 268.1339.

Solvolyses of Chlorides 6 and 14. Kinetics Procedures. Solvolysis of chloride **6** in methanol was monitored by ^{1}H NMR spectroscopy using our recently described kinetic method.[16] The chloride was dissolved in a 0.025 M solution of 2,6-lutidine in methanol, and the solution was sealed in an NMR tube, which was then placed in a constant-temperature bath. At periodic time intervals the shift of the methyl signal of the 2,6-lutidine was determined by 300 MHz NMR spectroscopy. Rate constants were calculated by standard least squares procedures. Rates of solvolyses of **6** and **14** in trifluoroethanol (2.5×10^{-4} M in 2,6-lutidine) were monitored by UV spectroscopy at 240 and 235 nm, respectively, using the previously described method.[1c]

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 94 series of programs.[13] Structures were characterized as minima via frequency calculations which showed no negative frequencies.

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