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Effect of oxime substituents on 9-fluorenyl carbocations

Xavier Creary* and Allison Wolf

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA

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ABSTRACT: 9-Fluorenyl carbocations substituted with the oxime functional groups $CH{=}NOCH_3$, $CH_3C{=}NOCH_3$, and *i*-$PrC{=}NOCH_3$ were generated by solvolyses of the corresponding chlorides in methanol. These cations form at rates which greatly exceed those of formation of the parent 9-fluorenyl cation. Relative rate data suggest that stabilization of 9-fluorenyl cations by $CH{=}NOCH_3$ is greater than stabilization by $CH_3C{=}NOCH_3$, which is in turn greater than that by *i*-$PrC{=}NOCH_3$. Computational studies on these cations show that the oxime group is progressively rotated out of conjugation with the cationic center as the oxime group becomes larger. These rate and computational studies also suggest that 9-fluorenyl cations are not antiaromatic. They are essentially delocalized 'nonatetraenyl' cations, where formally antiaromatic resonance forms contribute little to the overall structure. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: fluorenyl carbocation; antiaromatic; solvolysis; oxime; conjugation

INTRODUCTION

Carbocations **1** bearing a directly attached oxime substituent are of interest owing to the dual electronic properties of the oxime functional group.[1,2] This group is inductively electron withdrawing as reflected by a σ_I value of 0.14. However, our studies have shown that the oxime group can be an effective cation stabilizing group and this is attributed to charge delocalization utilizing the oxime group as represented by **1a** and **1b**. The extent of this stabilization is dependent on the ability of the C=N to interact with the cationic center. Twisting the oxime out of conjugation results in destabilization of the cation.[2]

There has been renewed interest in 9-fluorenyl carbocations.[3,4] For an interesting metal cluster stabilized 9-fluorenylcation, see Dunn *et al.*[4] Traditionally, this cation has been considered a 4π electron formally antiaromatic cation and attempts by Olah and Schleyer to generate the parent unsubstituted cation under stable ion conditions were unsuccessful.[5] More recent work by Richard and Novak disputes the claim of antiaromaticity.[6] The Tidwell group has successfully generated a CF_3-substituted 9-fluorenyl cation **2** and suggested that this cation is 'doubly destabilized' by incorporation of the potent electron-withdrawing CF_3 group.[7] In a related studies, the carbonyl substituted cations **3** have been studied by Lee-Ruff and Johnston under laser flash photolytic conditions.[8,9] Recent computational studies by Schleyer and Tidwell suggest that the parent 9-fluorenyl cation is non-aromatic (as opposed to antiaromatic).[10]

Our recent experimental and computational studies on fluorene system **4** suggests that the carbonyl group in this cation is rotated 90° out of conjugation with the cationic center.[11] This is attributed to unfavorable steric effects which outweigh any cation stabilizing conjugative effects. We were therefore interested in the ability of the oxime group ($RC{=}NOCH_3$) to interact with 9-fluorenyl carbocations of type **5**. Will oxime steric effects dominate or will conjugative effects be of greater importance? Reported here are the results of these studies.

RESULTS AND DISCUSSION

Syntheses

The chlorides **15, 16** and **17** are potential precursors to cations **5**. These chlorides were prepared from the corresponding alcohols which were in turn available as shown in Scheme 1. Ozonolysis of 9-vinylfluorenol, **6**, followed by reaction with O-methylhydroxylamine gave the oxime derivative **8**. Addition of ethoxyvinyllithium[12] to fluorenone followed by hydrolysis and reaction with O-methylhydroxylamine gave oxime **11**. Reaction of the silylated cyanohydrin of fluorenone with *i*-PrMgBr followed by hydrolysis and oxime formation led to **14**. The *E*-sterochemistry of this oxime was confirmed by an x-ray structure determination. These alcohols were in turn converted to chlorides **15, 16** and **17** by reaction with $SOCl_2$.

**Correspondence to:* X. Creary, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA.
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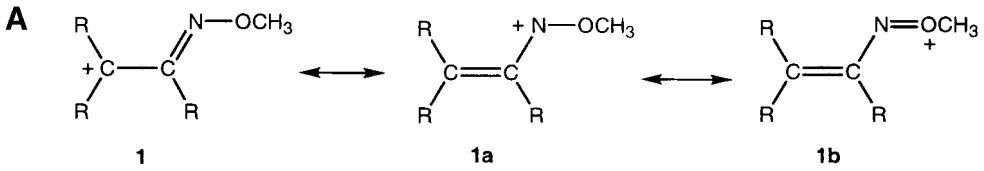
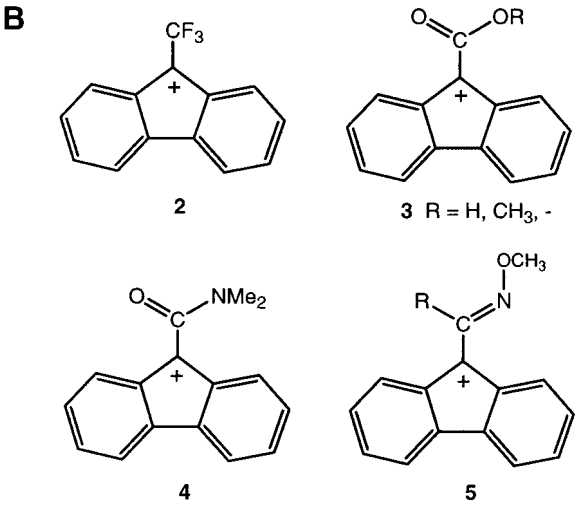
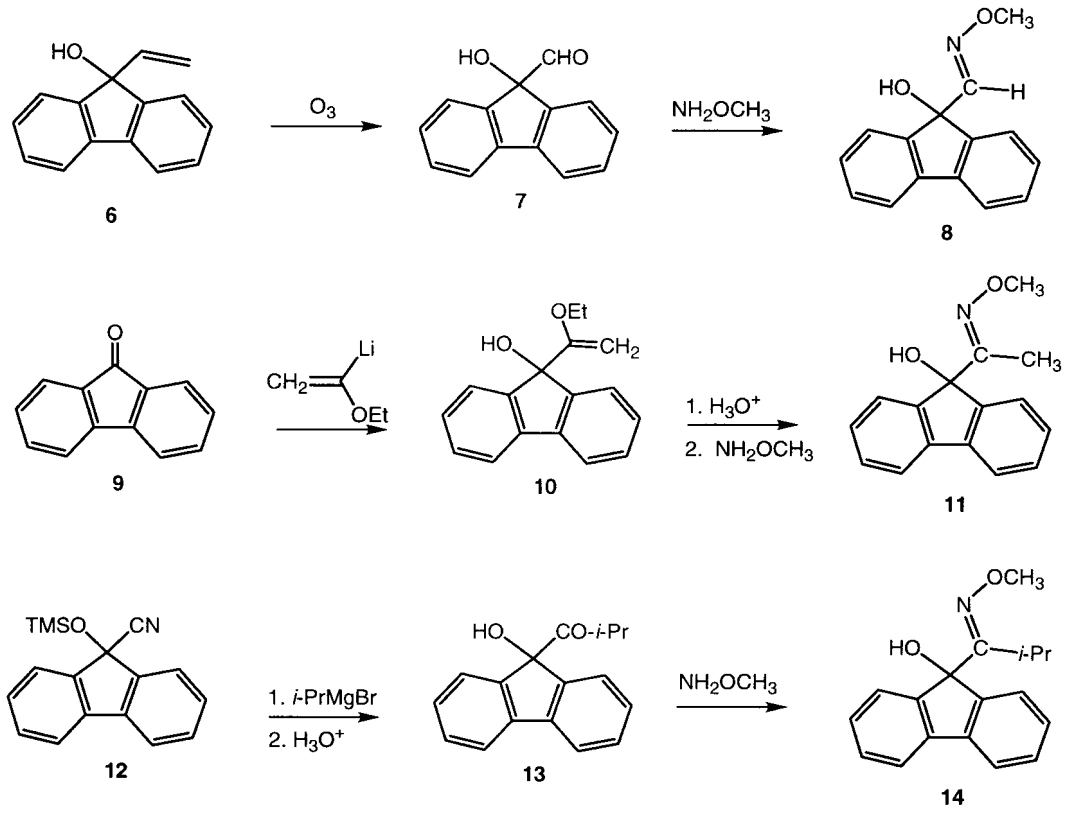




Solvolytic studies

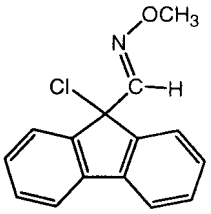
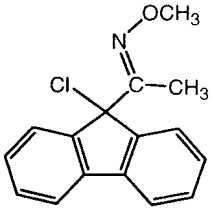
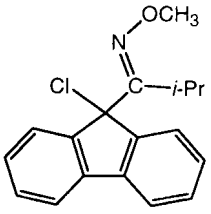
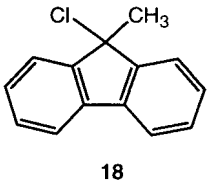
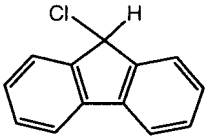
The chlorides **15, 16** and **17** were solvolyzed in methanol containing 2,6-lutinine as a buffering base. These substrates were highly reactive in methanol where the simple substitution products, the corresponding 9-methoxy derivatives, were the only products formed. Table 1 summarizes first-order rate constants for these reactions, which were determined by UV spectrophotometry. For comparison purposes, the methanolysis rates of the tertiary and secondary chlorides **18** and **19** are also given (for previous kinetic studies on dinitrobenzoate analogs of **18** and **19**, see Friedrich and Taggart[13]).

Relative rate data indicate that the oxime substituents greatly increase solvolysis rates relative to the α-H analog **19**, and two of the substrates solvolyze even faster than the α-methyl analog **18**. This indicates that the intermediate carbocations **5** are all stabilized relative to the unsubstituted 9-fluorenyl cation by the inductively electron-withdrawing oxime functional group. However, the extent of this stabilization depends on the nature of the group attached to the oxime. As the size of the group on the oxime increases from H to CH_3 to *i*-Pr, the rate constants decrease. We attribute this to steric inhibition of cation-stabilizing resonance interactions. In cation **20**, the intermediate derived from chloride **9**, it is suggested



Scheme 1

Table 1. Solvolysis rates in methanol at 25.0 °C

Substrate	k (s^{-1})	k_{rel}
 **15**	3.25×10^{-2}	19.4
 **16**	2.69×10^{-3}	1.60
 **17**	3.52×10^{-4}	0.21
 **18**	1.68×10^{-3a}	1.00
 **19**	$1.48 \times 10^{-7a,b}$	8.8×10^{-5}

[a] This work. Determined by ^{1}H NMR spectroscopy. See Experimental section.
[b] Extrapolated from data at higher temperature. k at 70.0 °C = 3.52×10^{-5} s^{-1}; k at 50.0 °C = 3.69×10^{-6} s^{-1}. $\Delta H‡ = 24.1$ kcal mol^{-1}. $\Delta S‡ = -9$ eu.

Table 2. HF/6–31G* energies of cations **20, 21** and **22**

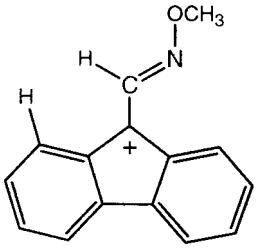
Carbocation	HF/6–31G* energy (au)	ZPE (au)
20 ($HC{=}NOCH_3$)	−704.031925	0.217659
21 ($CH_3Cx{=}NOCH_3$)	−743.068535	0.218437
22 (*i*-$PrC{=}NOCH_3$)	−821.133110	0.338677

that the resonance-stabilizing interaction of the cationic center with the oxime is maximal. However, in cation **21**, an unfavorable steric interaction of the methyl group with the hydrogen on the aromatic ring begins to twist the oxime out of conjugation with the cationic center. This unfavorable steric interaction is magnified by the larger isopropyl group of cation **22** such that conjugation is further decreased. Contributions of forms analogous to **1a** and **1b** are decreased as the oxime is twisted out of conjugation with the cationic center and this is reflected by corresponding decreases in solvolysis rates.

Computational studies

In order to gain further insight into the cationic intermediates derived from substrates **15, 16** and **17**, *ab initio* molecular orbital computational studies were carried out in the cationic intermediates **20, 21** and **22**. Table 2 gives energies of these cations and Fig. 1 shows the HF/6–31G* optimized geometries of these cations. Figure 1 shows that the fluorene ring is in complete alignment with the oxime group in cation **20**, permitting maximal conjugation. However, in cation **21** the oxime functionality is twisted out of conjugation with the fluorene ring such that the dihedral angle between the ring and the C═N is 35°. This is a result of an unfavorable interaction of the methyl group with the fluorene ring. In cation **22** the analogous dihedral angle is 42°. These rotations from planarity undoubtedly destabilize cations **21** and **22** relative to **20** and are in line with the decreasing solvolysis rates of **15, 16** and **17**. Calculated bond lengths also support the notion of steric inhibition of resonance. The N—O and C—C9 bonds of **20, 21** and **22** show progressive lengthening, whereas the C═N bond shortens. This is consistent with the oxime

C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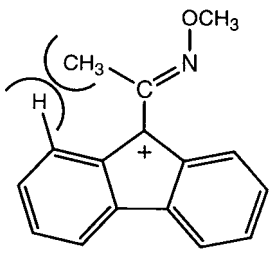
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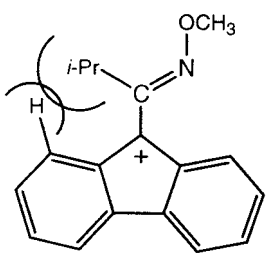
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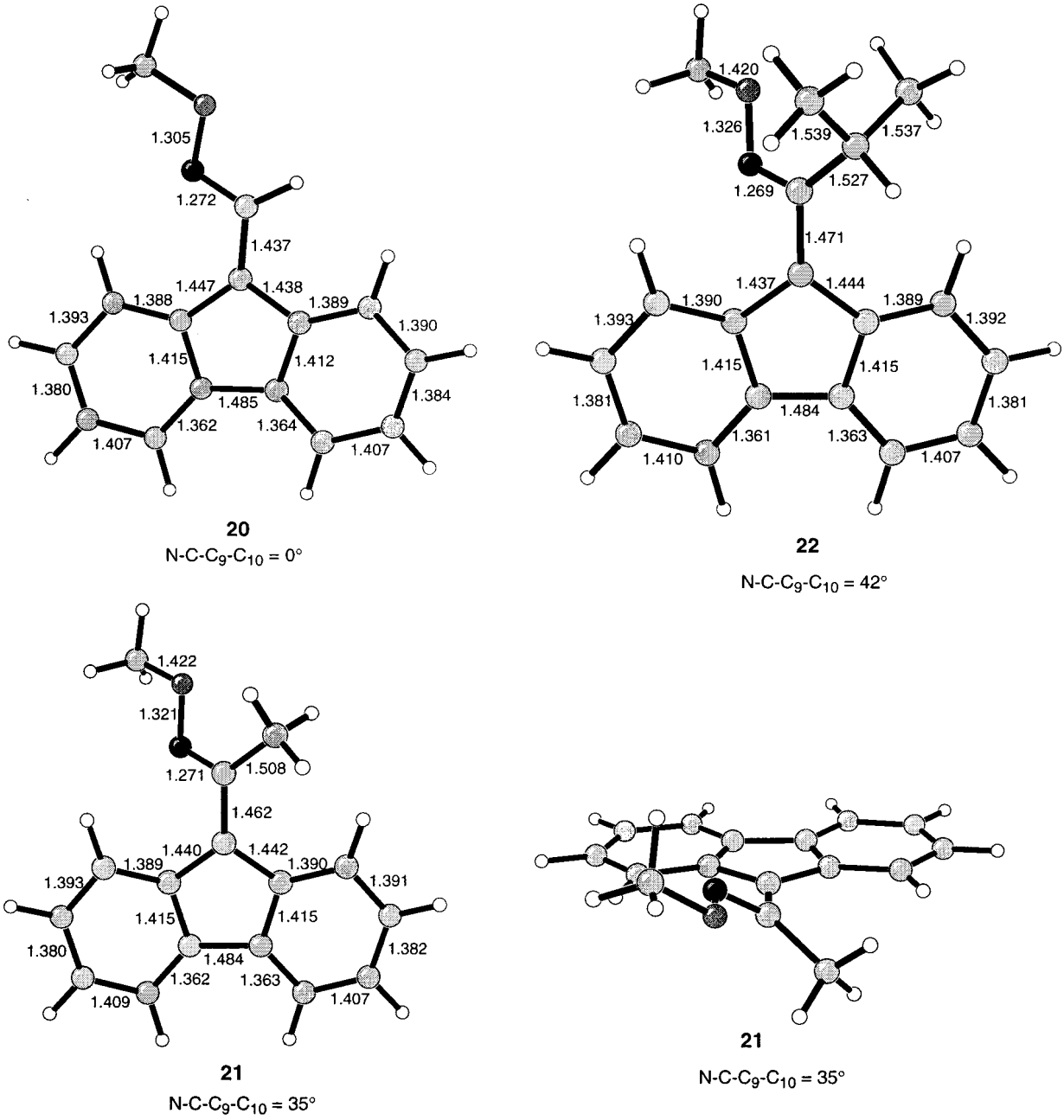
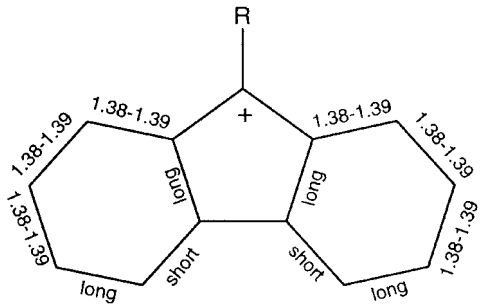


Figure 1. HF/6–31G* calculated structures of cations **20–22**

twisting progressively out of conjugation with the cationic center. These studies also shed light on the nature of 9-fluorenyl cations. Calculated bond length data suggest that whereas charge is delocalized into the fluorene ring, it is not uniformly delocalized throughout the fluorene portion of these cations. The six-membered rings of cations **20–22**, and also the parent 9-fluorenyl cation,[10,11] all show three C—C bonds of intermediate length (1.38–1.39 Å), followed by alternating long (1.41 Å), short (1.36 Å) and long (1.42 Å) bonds. Using a valence bond description, these cations are best represented by the incompletely delocalized form **23a**. Contributions of 'antiaromatic' forms **23b** and **23c** are of less importance. In other words, these 9-fluorenyl cations have charge delocalized to the '*para*-positions' (carbons 3 and 6) but delocalization occurs to only two of the four possible '*ortho*-positions' (carbons 1 and 8). They are 'nonatetraenyl cations.' Hence these cations are less stable than benzhydryl cation analogs, where charge delocalization is more extensive. These suggestions are in line with the classification of the 9-fluorenyl cation as non-aromatic by Jiao *et al.* based on calculated magnetic susceptibility exaltation.[10] The older stability criterion also supports the non-aromatic nature of fluorenyl cations, since these cations can be easily generated under solvolytic conditions.

D



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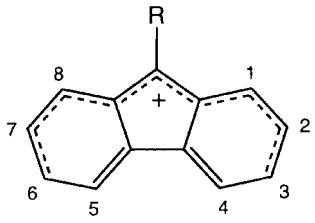
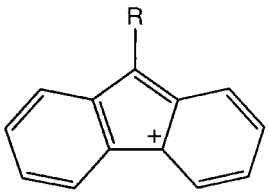
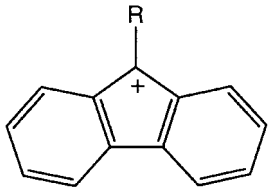


23a



23b



23c

CONCLUSIONS

Fluorenyl carbocations substituted at the 9-position with the formally electron-withdrawing oxime functional groups $CH{=}NOCH_3$, $CH_3C{=}NOCH_3$ and *i*-$PrC{=}NOCH_3$ are easily generated under solvolytic conditions. These cations are stabilized relative to α-H analogs by a conjugative interaction with the oxime group. Rate data and computational studies suggest that stabilization of 9-fluorenyl cations by $CH{=}NOCH_3$ is greater than stabilization by $CH_3C{=}NOCH_3$, which is in turn greater than that by *i*-$PrC{=}NOCH_3$. This is due to increasing steric factors which cause the oxime to rotate progressively out of conjugation with the cationic center. Computational studies also suggest that 9-fluorenyl cations are not antiaromatic. They are essentially delocalized 'nonatetraenyl' cations, where formally antiaromatic resonance forms contribute little to the overall structure.

EXPERIMENTAL

Preparation of oxime 8. A solution containing 671 mg of 9-hydroxy-9-vinylfluorene[14] (3.23 mmole) in 15 ml of methanol was cooled to −78 °C and ozonized exhaustively. The mixture was then warmed to room temperature and a solution of 380 mg of dimethyl sulfide in 2 ml of diethyl ether was added. The solvent was removed using a rotary evaporator and the residue was taken up in diethyl ether. The ether solution was washed with water and saturated sodium chloride solution and then dried with a mixture of Na_2SO_4 and $MgSO_4$. After filtration, about 90% of the solvent was removed using a rotary evaporator to give crude 9-formyl-9-hydroxyfluorene, which was converted directly to the α-hydroxyoxime **8**.

A mixture of the crude 9-formyl-9-hydroxyfluorene obtained above, 512 mg of pyridine (6.46 mmol) and 5 ml of diethyl ether was stirred while adding 270 mg of methoxylamine hydrochloride. The mixture was stirred for 12 h at room temperature and then diluted with 20 ml of diethyl ether. The ether solution was then washed with water, dilute HCl solution and saturated sodium chloride solution. The ether phase was dried using a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator and the residue was chromatographed on 19 g of silica gel and eluted with increasing amounts of diethyl ether in hexanes. The α-hydroxyoxime **8** (331 mg; 43% yield from 9-hydroxy-9-vinylfluorene) eluted with 15% diethyl ether in hexanes, m.p. 132–133 °C. ^{1}H NMR ($CDCl_3$), δ 7.646 (d of d of d, J = 7.5, 1.2, 0.6 Hz, 2 H), 7.475 (d of d of d, J = 7.2, 1.2, 0.6 Hz, 2 H), 7.404 (t of d, J = 7.5, 1.2 Hz, 2 H), 7.317 (t of d, J = 7.5, 1.2 Hz, 2 H), 7.202 (s, 1 H), 3.945 (s, 3 H), 3.920 (br, 1H). ^{13}C NMR ($CDCl_3$), δ 149.4, 145.1, 140.1, 129.7, 128.2, 124.9, 120.2, 80.7, 62.3. Analysis: calculated for $C_{15}H_{13}NO_2$, C 75.30, H 5.48; found, C 75.16, H 5.36%.

Preparation of chloride 15. A mixture of 23 mg of α-hydroxyoxime **8** (0.097 mmol), 50 mg of sodium carbonate and 1.5 ml of diethyl ether was stirred under nitrogen while adding 25 mg of thionyl chloride (0.21 mmol) in 0.5 ml of diethyl ether. The mixture was stirred for 3 days at room temperature. Filtration and removal of solvent using a rotary evaporator gave 20 mg of chloride **15** (82% yield) as an oil. The pure chloride **15** decomposed on standing at room temperature for prolonged periods. ^{1}H NMR ($CDCl_3$), δ 7.790 (s, 1 H), 7.673 (d of m, J = 7.2 Hz,

2 H), 7.649 (d of m, $J = 7.2$ Hz, 2 H), 7.433 (t of d, $J = 7.5$, 1.5 Hz, 2 H), 7.365 (t of d, $J = 7.2$, 1.2 Hz), 3.819 (s, 3H). ^{13}C NMR ($CDCl_3$), δ 147.7, 144.0, 139.1, 129.9, 128.3, 126.1, 120.4, 68.5, 62.2. Exact mass (EI) calculated for $C_{15}H_{12}ClNO$, 257.0607; found, 257.0619.

Preparation of oxime 11. A solution of 403 mg of ethyl vinyl ether (4.22 mmol) in 5 ml of dry tetrahydrofuran was cooled to −78 °C and 1.7 ml of 1.7 M *tert*-butyllithium (2.89 mmol) in pentane was added dropwise. This mixture was warmed to −10 °C for a few minutes before cooling back to −78 °C. A solution of 403 mg of fluorenone (2.22 mmol) in 5 ml of tetrahydrofuran was added dropwise. The solution was stirred for 10 min at −78 °C, warmed to 0 °C and then quenched with 15 ml of water. The mixture was extracted with diethyl ether and the ether extract was washed with water and saturated sodium chloride solution and then dried over a mixture of Na_2SO_4 and $MgSO_4$. Filtration and removal of the solvent using a rotary evaporator gave 516 mg of yellow oil, which contained a 1:1 mixture of fluorenone and enol ether **10**.

The oil obtained above was dissolved in 8 ml of tetrahydrofuran as 2 ml of water and two drops of concentrated H_2SO_4 were added. This mixture was stirred for 12 h at room temperature and then extracted into 15 ml of diethyl ether. The ether extract was washed with water and saturated sodium chloride solution and then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator and the residue was chromatographed on a 10 g of silica gel. 9-Acetyl-9-hydroxyfluorene (136 mg; 27% yield from fluorenone) eluted with 10% diethyl ether in hexanes. ^{1}H NMR ($CDCl_3$), δ 7.717 (d of t, $J = 7.8$, 1.2 Hz, 2 H), 7.49–7.41 (m, 2 H), 7.327 (d of d, $J = 1.8$, 1.2 Hz, 2 H), 7.313 (d, $J = 1.2$ Hz, 2 H), 5.119 (br, 1 H), 1.646 (s, 3 H). ^{13}C NMR ($CDCl_3$), δ 206.9, 144.3, 141.4, 129.8, 128.4, 123.8, 120.5, 88.2, 22.4.

A solution containing 136 mg of 9-acetyl-9-hydroxyketone (0.606 mmol), 3 ml of pyridine and 61.9 mg of methoxylamine hydrochloride (0.728 mmol) was heated at 60 °C for 12 h. The mixture was taken up in 15 ml of diethyl ether and the ether solution was washed with water, dilute hydrochloric acid and saturated sodium chloride solution. The ether phase was dried over a mixture of Na_2SO_4 and $MgSO_4$. Filtration and removal of solvent by rotary evaporation gave 109 mg (71% yield) of the α-hydroxyoxime **11**, m.p. 93–97 °C. ^{1}H NMR ($CDCl_3$), δ 7.659 (d of m, $J = 8.1$ Hz, 2 H), 7.42–7.35 (m, 4 H), 7.291 (t of d, $J = 8.1$, 1.2 Hz, 2 H), 5.037, (br, 1 H), 4.023 (s, 3 H), 1.252 (s, 3 H). ^{13}C NMR ($CDCl_3$), δ 156.0, 149.5, 146.2, 140.7, 135.8, 129.3, 128.1, 124.1, 123.5, 119.9, 83.3, 62.1, 10.8. Analysis: calculated for $C_{16}H_{15}NO_2$, C 75.87, H 5.97; found, C 75.69, H 5.73%.

Preparation of chloride 16. A solution containing 103 mg of the α-hydroxyoxime **11** (0.407 mmol), 100 mg of sodium carbonate and 3 ml of diethyl ether was stirred under nitrogen and 145 mg of thionyl chloride in 0.5 ml of diethyl ether was added dropwise. The mixture was stirred for 12 h at room temperature. The mixture was then filtered and the solvent was removed using a rotary evaporator to give 124 mg (99% yield) of chloride **16**, m.p. 110–112 °C. ^{1}H NMR ($CDCl_3$), δ 7.647 (d of m, $J = 7.2$ Hz, 2 H), 7.564 (d of m, $J = 7.3$, 2 H), 7.387 (t of d, $J = 7.5$, 1.2 Hz), 7.311 (t of d, $J = 7.2$, 1.2 Hz, 2 H), 3.916 (s, 3H), 1.684 (s, 3 H). ^{13}C NMR ($CDCl_3$), δ 154.1, 145.3, 139.4, 129.6, 128.3, 125.6, 120.3, 72.7, 62.0, 12.2. Exact mass (EI) calculated for $C_{16}H_{14}ClNO$, 271.0764; found, 271.0772.

Preparation of oxime 14. A solution of 0.550 g of silylated cyanohydrin **12**[15] (1.97 mmol) in 5 ml of dry diethyl ether was stirred under nitrogen and 3.0 ml of 1.0 M isopropylmagnesium bromide in diethyl ether was added dropwise. The mixture was stirred for 12 h at room temperature and then quenched with 5 ml of saturated NH_4Cl solution. The mixture was taken up in diethyl ether and the ether extract was washed with water and saturated sodium chloride solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. The mixture was filtered and the solvent was removed using a rotary evaporator. The residue was dissolved in 8 ml of tetrahydrofuran and 2 ml of water was added followed by 0.204 g of concentrated H_2SO_4. The mixture was stirred for 12 h at room temperature and then taken up in diethyl ether. The ether phase was washed with saturated sodium hydrogencarbonate solution, water and saturated sodium chloride solution. The ether phase was then dried over Na_2SO_4 and $MgSO_4$, filtered and the solvent was removed using a rotary evaporator. The residue was chromatographed on 20 g of silica gel and eluted with 5% diethyl ether in hexanes to give 0.232 g (55% yield) of the α-hydroxyketone **13**. ^{1}H NMR ($CDCl_3$), δ 7.736 (d of m, $J = 7.8$ Hz, 2 H), 7.48–7.41 (m, 2 H), 7.35–7.28 (m, 4 H), 2.096 (heptet, $J = 7.2$ Hz, 1 H), 0.726 (d, $J = 6.9$ Hz, 6 H). ^{13}C NMR ($CDCl_3$), δ 213.8, 143.9, 141.8, 129.8, 128.1, 124.4, 120.5, 88.2, 33.6, 20.4.

A solution containing 48 mg of α-hydroxyketone **13** (0.19 mmol), 2 ml of pyridine and 29 mg of methoxylamine hydrochloride (0.25 mmol) was sealed in a Pyrex tube under nitrogen. This tube was heated for 3 days at 100 °C, cooled and then opened. The mixture was taken up in diethyl ether and extracted with water, dilute hydrochloric acid and saturated sodium chloride. The ether phase was dried over Na_2SO_4 and $MgSO_4$. Filtration and removal of solvent by rotary evaporation gave 38 mg of the α-hydroxyoxime **14** (72% yield), m.p. 125–128 °C. ^{1}H NMR ($CDCl_3$), δ 7.637 (d of m, $J = 7.5$, 2 H), 7.43–7.35 (m, 4 H), 7.32–7.25 (m, 2 H), 5.259 (br, 1 H), 3.986 (s, 3H), 1.448 (heptet, $J = 7.2$ Hz, 1 H), 0.829 (d, $J = 7.2$, 6 H). ^{13}C NMR ($CDCl_3$), δ 161.2, 145.8, 141.2, 129.4, 128.0, 124.5, 120.1, 83.4, 62.5, 29.8, 18.1.

Analysis: calculated for $C_{18}H_{19}NO_2$, C 76.84, H 6.81; found, C 76.68, H 6.63%.

*Preparation of chloride **17**.* A solution containing 48 mg of α-hydroxyoxime **14** (0.173 mmol), 50 mg of sodium carbonate and 3 ml of diethyl ether was stirred under nitrogen and 66 mg of thionyl chloride in 0.25 ml of diethyl ether (0.518 mmol) was added dropwise. The mixture was stirred for 12 h at room temperature, the sodium carbonate was removed by filtration and the solvent was removed using a rotary evaporator to give 50 mg (97% yield) of chloride **17**. ^{1}H NMR ($CDCl_3$), δ 7.681 (d of m, J = 7.5 Hz, 2 H), 7.573 (d of m, J = 7.8 Hz, 2 H), 7.417 (t of d, J = 7.5, 1.2 Hz, 2 H), 7.336 (t of d, J = 7.5, 1.2 Hz, 2 H), 3.949 (s, 3 H), 1.793 (heptet, J = 7.2 Hz, 1 H), 0.967 (d, J = 7.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$), δ 159.1, 145.4, 139.7, 129.7, 128.2, 125.5, 120.4, 72.9, 62.2, 31.1, 18.4. Exact mass (EI) calculated for $C_{18}H_{18}C1NO$ 299.1077; found, 299.1069.

Kinetic studies. Rates of solvolyses of chlorides **15–18** in methanol (2.5×10^{-4} M in 2,6-lutidine) were monitored by UV spectrophotometry at 245 nm using the previously described method.[16] A solution of about 10 mg of the appropriate chloride in 1 ml of anhydrous diethyl ether was prepared and a 5 µl aliquot of this solution was injected into a cuvette containing 3 ml of 2.5×10^{-4} M 2,6-lutidine in methanol at 25.0 °C. This initiated the kinetic run. Absorbance changes were monitored for two half-lives and infinity readings were taken after 10 half-lives. Solvolysis of chloride **18** in methanol was monitored by ^{1}H NMR spectroscopy using our previously described kinetic method.[17] The chloride **18** was dissolved in a 0.05 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. First-order rate constants were determined by standard least-squares methods. All kinetic runs were performed in duplicate (maximum error ±1%) and the rate constants given in Table 1 represent average values.

Computational studies. Ab initio molecular orbital calculations were performed using the Gaussian 94 series of programs.[18] Structures were characterized as minima via frequency calculations, which showed no negative frequencies.

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