# The First Reported Halogenation of a *tert*-Butyl Group with HCl or HBr in $CHCl_3$. Unexpected Differences in the Reactions of HCl, HBr, HI, and HF with *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol

Cal Y. Meyers,* Yuqing Hou, Hisham G. Lutfi,† and Howard L. Saft‡

*Department of Chemistry and Biochemistry, Southern Illinois University, Mail Code 4409, Carbondale, Illinois 62901*

*Received June 28, 1999*

The reactions of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol (**1**) with HCl, HBr, HI, and HF, respectively, were found to follow diverse pathways. Most unexpected is the unprecedented monohalogenation of a *tert*-butyl group, *sp*-9-[*o*-(*β*-chloro-α,α-dimethylethyl)phenyl]fluorene (**2**) being formed quantitatively from **1** treated with HCl−$CHCl_3$ and *sp*-9-[*o*-(*β*-bromo-α,α-dimethylethyl)phenyl]fluorene (**3**) (>90%), along with a very small amount of *sp*-9-(*o*-*tert*-butylphenyl)fluorene (**4**), being formed from **1** treated with HBr−$CHCl_3$. The absolute structure of **2** was ascertained by X-ray crystal analysis. Likewise, the expected 9-chloro- and 9-bromofluorenes from the usual substitution of OH by halogen in reactions of alcohols with $SOCl_2$ and $SOBr_2$ were not obtained from treatment of **1** with these reagents; the only products were **2** and **3**, respectively. These products are formed by nucleophilic attack of halide ion on a *tert*-butyl methyl group of the 9-cation (**1a**) with concerted intramolecular displacement of hydride to 9-$C^+$, while **4** results from the slower electron transfer from $Br^-$ to **1a** to form free radical **1b**, which captures an H atom from HBr. The high redox potential of $I^-$ and weak HI bond ensures the rapid conversions **1a** → **1b** → **4**, making **4** the exclusive product from treatment of **1** with HI−$CHCl_3$. In contrast to the other halides, fluoride is a poor nucleophile in displacement reactions and poor electron-transfer agent. Consequently, strongly electrophilic **1a** reacts with $F^-$ to provide *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorofluorene (**5**) as the only product from the reaction of **1** with pyridine·$(HF)_x$. Dynamic NMR provided strong evidence that the reaction with HI occurs with inversion, the *ap* rotamer (**4a**) of 9-(*o*-*tert*-butylphenyl)fluorene being formed initially, followed by rotation to the isolated *sp* rotamer, **4**. The largely planar configuration of C-9 of the unsymmetrically hindered cation intermediate **1a**, responsible for this inversion and the related inversions, was supported by NMR.

## Introduction

In our studies of rotationally restricted, sterically hindered 9-substituted fluorenes,[1−8] we attempted to prepare 9-chloro- and 9-bromo-9-(*o*-*tert*-butylphenyl)-fluorene to determine the relative stabilities of their respective *ap* (**2a**, **3a**) vs *sp* (**2b**, **3b**) rotamer configurations and corresponding reactivities.[9,10] We explored the possibility of utilizing hydrogen halides to convert *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol (**1**) into the desired products. Halides differ from each other significantly in nucleophilicity, size, and redox potential. In our study of the reactions of **1** with HCl, HBr, HI, and pyridine·$(HF)_x$, respectively, these different properties came into play and led to entirely different types of products. Of special note is the unexpected and unprecedented monohalogenation of a *tert*-butyl group with a hydrogen halide. Treatment of **1** with HCl−$CHCl_3$ quantitatively provided *sp*-9-[*o*-(*β*-chloro-α,α-dimethylethyl)phenyl]fluorene (**2**), and treatment with HBr−$CHCl_3$ afforded >90% of *sp*-9-[*o*-(*β*-bromo-α,α-dimethylethyl)phenyl]fluorene (**3**). In nei-

* To whom correspondence should be addressed. E-mail: cal@chem.siu.edu. Fax: 618-453-6408.

† Present address: Department of Chemistry, University of Toronto, Toronto, ON, Canada M5S 3H6.

‡ Summer Undergraduate Chemistry Research Participant at Southern Illinois University, Carbondale, 1995; from the University of Florida, Gainesville.

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(9) The designations *sp* (synperiplanar) and *ap* (antiperiplanar) for these fluorene rotamers are in accord with Rule E-6.6, IUPAC Tentative Rules, Section E, Fundamental Stereochemistry (*J. Org. Chem.* **1970**, *35*, 2861).

(10) The *ap* and *sp* stereochemistry of a number of 9-(*o*-*tert*-butylphenyl)fluorenes in the crystalline state has been unequivocally determined by X-ray diffraction. In solution, they are effectively characterized by $^1$H NMR spectroscopy. The most striking differences emanate from the *o*-*tert*-butyl protons. In the *ap* rotomers these protons are shielded by the fluorene *π* electrons and resonate upfield in the 0.7 ppm region, while in the *sp* rotomers they are correspondingly deshielded and resonate downfield in the 1.8 ppm region. Differences are also observed in the resonances of the *ortho*-H of *ap* vs *sp* rotamers and of the H-9 of these rotamers of 9-(*o*-*tert*-butylphenyl)fluorene itself. See refs 1, 2d,e, 3, 6−8, and 11.

10.1021/jo9910280 CCC: $18.00 
Published on Web 12/01/1999

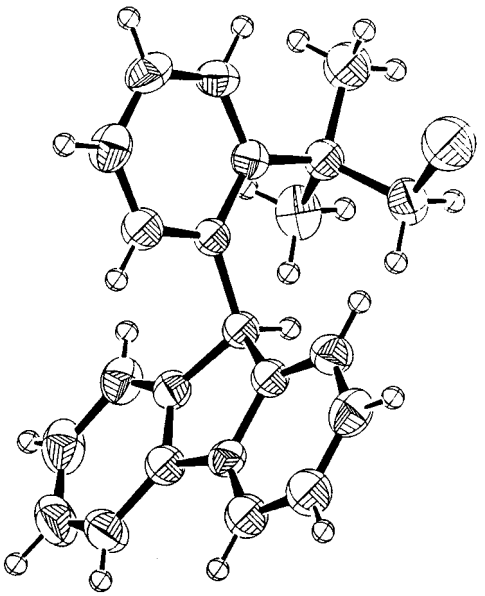
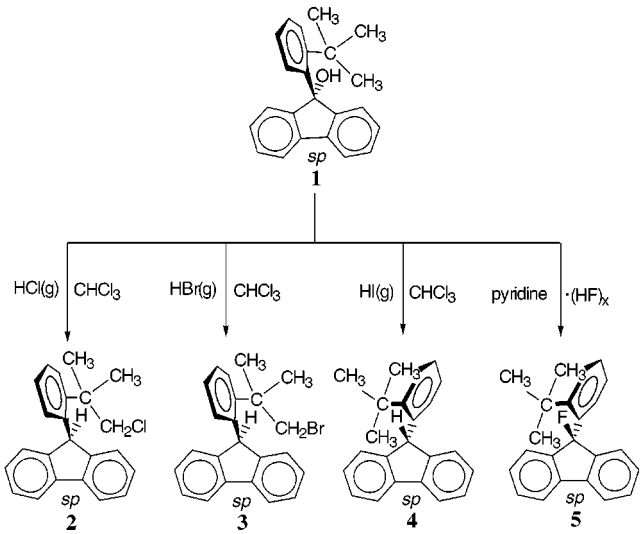


**Figure 1.** ORTEP of **2**.

**Scheme 1**

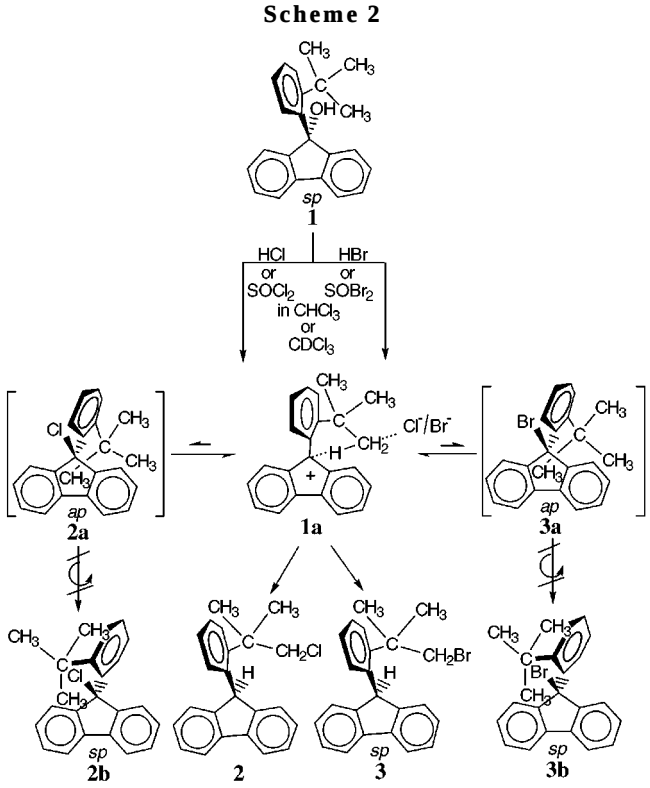



ther case was the desired 9-halo product isolated, although its fleeting presence was observable in some instances when the reaction was carried out in an NMR tube and monitored. The structure of **2** was unequivocally confirmed by X-ray crystal analysis (Figure 1).[3] Reaction of **1** with HI−$CHCl_3$ failed to produce any halogenated product; *sp*-9-(*o*-*tert*-butylphenyl)fluorene (**4**) was formed exclusively. Finally, of the hydrogen halides, only HF provided the expected 9-halo product, *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorofluorene (**5**) being the exclusive product from the reaction of **1** with pyridine·$(HF)_x$. These transformations are summarized in Scheme 1.

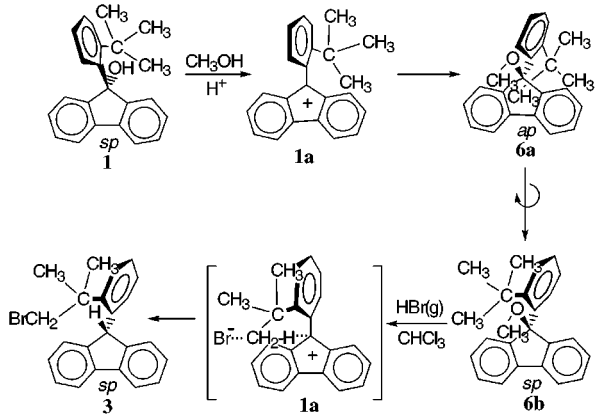
## Results and Discussion

**Halogenation of the *tert*-Butyl Group.** The desired 9-chloro- and 9-bromofluorenes from the usual substitution of OH by halogen in reactions of alcohols with $SOCl_2$ and $SOBr_2$ also were not obtained from the treatment of **1** with these reagents. Instead, only monohalogenation of the *tert*-butyl group occurred, with **2** and **3**, respectively, being formed as the major products. The mecha-

**Scheme 2**



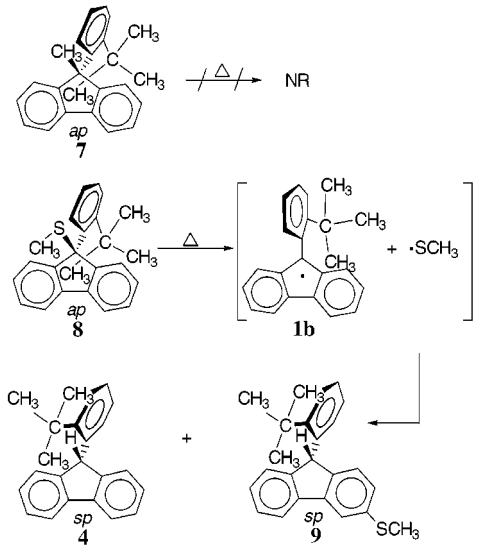

**Scheme 3**




nism leading to the halogenation of the *tert*-butyl group of **1** treated with HCl, HBr, $SOCl_2$, or $SOBr_2$, respectively, is illustrated in Scheme 2. Small yields of **2** were observed in reactions of **1** with $[ClC(O)]_2$, $CH_3C(O)Cl$, and $(CF_3SO_2)_2O$/*n*-$Bu_4N^+Cl^-$, respectively, and **3** was a product obtained in the reaction **1** or its lithiated salt with $(CF_3SO_2)_2O$/*n*-$Bu_4N^+Br^-$. Treatment of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenyl methyl ether (**6b**) with HBr−$CHCl_3$ also provided **3** almost exclusively (Scheme 3). A related study showed that 9-deuterated **4**, neutral or acidified with triflic acid, was passed through a silica gel column without undergoing any D/H exchange. These results and the fact that products **2** and **3** possessed 9-H regardless of whether the substrate was **1** or **1**-OD, the reagent was the corresponding hydrogen halide or the other reactive halogen compounds, or the solvent was $CHCl_3$, $CDCl_3$, or $CH_2Cl_2$, prove that the 9-H atom in these products emanated from the (*tert*-butylphenyl)fluorene moiety itself and most probably from the *tert*-butyl group.

Chlorination and bromination of a *tert*-butyl group with the respective hydrogen halide or thionyl halide appar-

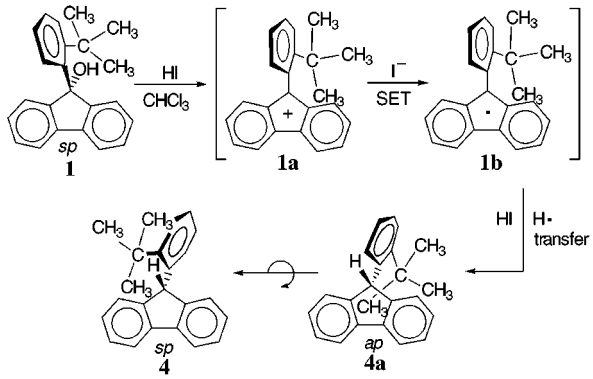
**Scheme 4**




ently have not previously been reported. In the case of these halogenations occurring with **1**, special circumstances prevail. As illustrated in Scheme 2, initial formation of the expected relatively stable fluorenyl cation **1a** is followed by halide attack on C-9$^+$, directly producing *ap*-9-(*o*-*tert*-butylphenyl)-9-chlorofluorene (**2a**) and *ap*-9-(*o*-*tert*-butylphenyl)-9-bromofluorene (**3a**), respectively. Because of the strain imposed on the *ap* rotamers of 9-(*o*-*tert*-butylphenyl)fluorenes by the *tert*-butyl group impinging on the fluorene ring's $\pi$ electrons, rotation to the thermodynamically preferred *sp* rotamers generally occurs.[2d,e,4−7,11,12] However, like the corresponding *ap* rotamers of 9-(*o*-*tert*-butylphenyl)-9-methylfluorene (**7**) and 9-(*o*-*tert*-butylphenyl)-9-methylthiofluorene (**8**),[6,7] the *ap* rotamers **2a** and **3a** are the preferred configurations because the steric interaction between the large 9-substituent and the *tert*-butyl group in the *sp* rotamers (**2b**, **3b**) effects an even greater strain. While **7** is strained, it is stable, but **8** undergoes homolysis of the *S*-fluorenyl bond on standing to provide $CH_3S\cdot$ and fluorenyl radical **1b**, which leads to the formation of *sp*-**4** and *sp*-9-(*o*-*tert*-butylphenyl)-3-methylthiofluorene (**9**) (Scheme 4).[7] Likewise, **2a** and **3a** undergo halogen C-9 cleavage, but heterolytically and more rapidly than **8**, and cannot be isolated. The equilibria **2a** ⇌ **1a** and **3a** ⇌ **1a** allow the halide ions to attack a *tert*-butyl methyl group whose hydride simultaneously is transferred to the cationic C-9. This is, in essence, an $S_N2$ reaction in which the leaving group is a hydride attracted to a cation by their intramolecular proximity, leading to thermodynamically favored bond formation. In support of this mechanism is our observation that cation **1a**, in the *absence* of halide ions, has a longevity of at least several days, and its NMR spectra were recorded (vide infra). This type of $S_N2$ displacement of hydride is unusual and should not be deemed similar to the common intramolecular hydride shift leading to a more stable carbocation.

As illustrated in Scheme 2, the conversion of **1** to **2** and **3**, respectively, via this mechanism would afford configurational retention.[1] Likewise, as shown in Scheme 3, similar treatment of the 9-methoxy derivative **6b** with $HBr-CHCl_3$ also provided **3** and, presumably, with retention of configuration. However, this scheme also illustrates that the sequential conversion **1** → **6a** → **6b** → **3** (or **2**) involves *inversion*, which occurs in the initial

**Scheme 5**




step, 9-OH → 9-$OCH_3$, via cation **1a**, which is attacked on its less hindered face by $CH_3OH$.[1] A parallel inversion via free radical **1b** was indicated by a dynamic NMR study (vide infra). The stereochemical consequences of the reactions described here were confirmed in our studies employing chiral substrates[1] and will be reported subsequently.

**Replacement of the 9-OH by H.** The ability of halide ions to donate an electron increases in the order $F^- < Cl^- < Br^- < I^-$, the respective standard reduction potentials of the corresponding halogens being 2.87, 1.3583, 1.065, and 0.5338 V.[13] The reduction potential of fluorenyl cation has been reported to be 0.76,[14] 0.68,[15] and 0.85[16] V. In light of the sterically imposed instability of the 9-Cl and 9-Br *ap* compounds **2a** and **3a**, the further enhanced steric strain enforced by the even larger iodine atom would almost certainly preclude the formation of the corresponding 9-I compound, if not the transition state required for the attack by $I^-$ on cation **1a**. The combination of redox potentials of $I^-$ and fluorenyl cation apparently favors exclusive electron transfer in the reaction of **1** with $HI-CHCl_3$ over nucleophilic hydride displacement of the type followed by $Cl^-$ and $Br^-$. As illustrated in Scheme 5, single electron transfer from HI to initially formed cation **1a** provides free radical **1b**, which, in turn, abstracts a hydrogen atom from HI to form *ap*-(*o*-*tert*-butylphenyl)fluorene (**4a**). Rapid rotation of **4a** provides the thermodynamically preferred *sp* rotamer, **4**, the quantitatively isolated product.

The stereochemistry of this transformation was suggested when the reaction was carried out at −50 °C and continuously monitored by dynamic NMR. At −40 °C, the exclusive formation of *ap* rotamer **4a** was observed, as reflected by the sharp singlet at $\delta$ 0.69 representing the highly shielded *tert*-butyl group. Rotation to *sp* **4** occurred as the temperature was allowed to rise; the singlet at $\delta$ 1.72 of its deshielded *tert*-butyl group appeared and grew in intensity as that at $\delta$ 0.69 was correspondingly reduced. Rotomerization was essentially complete at 20

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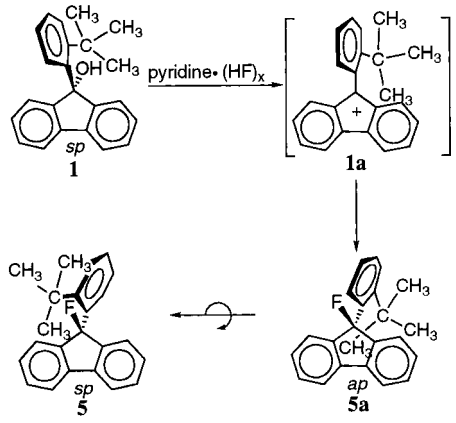
**Scheme 6**

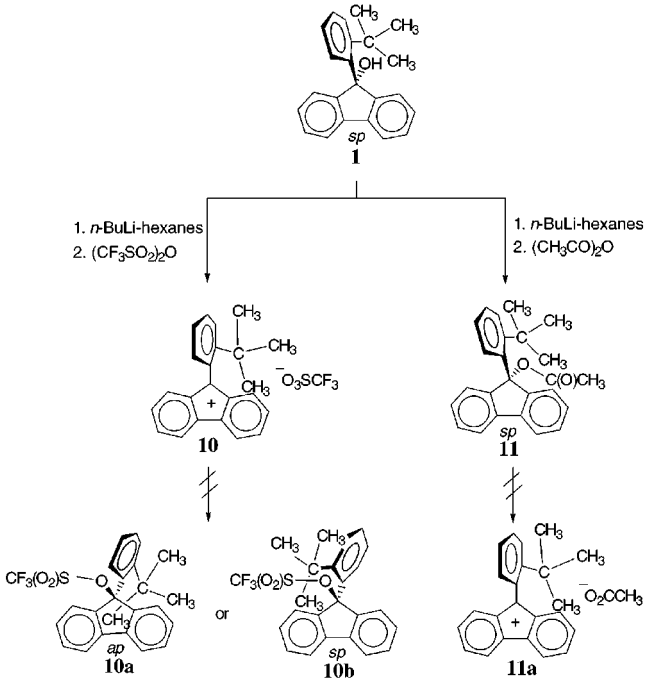



°C. These results suggested that the conversion of **1** to **4a** proceeds via initial inversion followed by rotation, a mechanism that was strongly supported by related reactions carried out with chiral substrates.[1] This SET mechanism and the fact that the redox potential of $Br^-$ is between that of $I^-$ and $Cl^-$ account for our observations that the reactions of **1** or **6b** with HBr always provided a small amount of **4** along with **3**, while the reactions of **1** with HCl, $SOCl_2$, oxalyl chloride, or acetyl chloride produced **2** but no **4**. It should be pointed out that reactions of **1** with triflic anhydride/*n*-$Bu_4N^+Cl^-$ or $Br^-$ always provided substantial amounts of **4** along with small amounts of **2** or **3**, but the formation of **4** resulted from a mechanism entirely different from that described above.[1,7b]

**Replacement of 9-OH by F.** Of the four halide ions, $F^-$ is the smallest, least nucleophilic in displacement reactions and has the poorest electron-transfer ability. Ironically, because of these characteristics, the required intermediacy of cation **1a**, and the specific steric requirements imposed by the hindered 9-(*o-tert*-butylphenyl)-fluorenyl system, only $F^-$ provides the "expected" 9-halo product. Scheme 6 illustrates the conversion of **1** with pyridine•$(HF)_x$ to cation **1a**, which provides *ap*-9-(*o-tert*-butylphenyl)-9-fluorofluorene (**5a**) by attack of $F^-$ at C-9. As described for the other reactions, attack on cation **1a** most reasonably occurs on the less hindered face, giving rise to inversion at C-9. Rapid rotation leads to the almost quantitative isolation of the thermodynamically preferred *sp* rotamer **5**.

**NMR Identification of 9-(*o-tert*-Butylphenyl)-9-fluorenyl Cation (1a).** As a means to support the suggested $sp^2$ hybridization of C-9 of cation **1a** and, therefore, the stereochemistry of its *o-tert*-butylphenyl moiety as being between that of the *ap* and *sp* rotamers, 9-(*o-tert*-butylphenyl)-9-fluorenyl triflate (**10**) was prepared. The blood-red solution in $CDCl_3$ indicated that **10** in this medium exists as its dissociated salt, so that an NMR spectrum would be that of cation **1a**. The observed singlet at $\delta$ 1.51 was ascertained to be associated with the *tert*-butyl hydrogens on the basis of its integration relative to that of the aromatic protons. The correct ratio, 9:12, was observed, indicating the exclusivity of salt **10** relative to the *ap* and *sp* esters, **10a** and **10b**. The resonance in the $^{13}C$ spectrum at $\delta$ 215.66 correctly identified the 9-$C^+$. The *tert*-butyl singlet at $\delta$ 1.51 of cation **1a** is indeed between that of the shielded *tert*-butyl ($\delta$ 0.69) of *ap* **4a** and deshielded *tert*-butyl ($\delta$ 1.72) of **4**. In contrast to the triflate, the acetate was shown to exist

**Scheme 7**




exclusively as the colorless ester, **11**, which showed no indication of dissociating into the corresponding salt. The formation and comparison of these structures are illustrated in Scheme 7.

## Experimental Section

**General Methods.** Melting points are corrected unless stated otherwise. $^1H$ and $^{13}C$ NMR spectra were taken at 300 and 75 MHz, respectively, in $CDCl_3$ solution, and IR spectra were taken on Nujol mulls. **Note:** Trifluoromethanesulfonic acid (triflic acid) and its anhydride are very corrosive and hygroscopic and should be handled with extreme care.

***sp*-9-(*o-tert*-Butylphenyl)-9-fluorenol (1)** was prepared as reported with its X-ray structure.[8] The synthesis was essentially the same as that reported earlier by the Ōki group.[12]

**Formation of *sp*-9-[*o*-(β-Chloro-α,α-dimethylethyl)phenyl]fluorene (2). Method A. Reaction of 1 with HCl in $CDCl_3$.** HCl gas, generated by the dropwise addition of concd $H_2SO_4$ onto solid NaCl, was bubbled into $CDCl_3$ for 30 min to provide a saturated solution. This solution (0.5 mL) was added to an NMR tube containing **1** (8.4 mg, 0.027 mmol). Shaking the tube provided a colorless solution that slowly became pale yellow within 10 min. After 45 min, NMR indicated that some starting material ($\delta$ 1.8, singlet) was still present. Most of the *tert*-butyl resonance was at $\delta$ 0.8 (broad singlet) and there was a broad singlet at $\delta$ 1.34, a singlet at $\delta$ 8.20 and a very broad hump at $\delta$ 8.68. After 5 h formation of **2** was detected by NMR, although the spectrum was largely similar to the earlier ones. After 72 h, the solution contained 26% of **2** and 41% of **1**. While the peaks at $\delta$ 1.34 and 8.20 had disappeared, the others observed earlier were present. After 5 days the solvent was evaporated. NMR of the residue showed it to be essentially pure **2** (>95% yield), whose structure was verified by X-ray diffraction[3] (colorless crystals from hexanes, mp 176.5−178 °C). $^1H$ NMR: $\delta$ 1.81 (s, 6 H), 4.16 (s, 2 H), 5.65 (s, 1 H), 6.25 (dd, $J$ = 7.8, 1.5 Hz, 1 H), 6.93 (ddd, $J$ = 7.8, 7.2, 1.2 Hz, 1 H), 7.15 (ddd, $J$ = 8.1, 7.2, 1.5 Hz, 1 H), 7.25 (m, $J$ = 7.8, 1.2, 0.9 Hz, 4 H); 7.39 (m, $J$ = 7.8 Hz, 2 H); 7.45 (dd, $J$ = 8.1, 1.2 Hz, 1 H); 7.83 (d, $J$ = 7.8 Hz, 2 H). The resonance at $\delta$ 5.65 for 1 H showed that no deuterium had been incorporated at C-9. $^{13}C$ NMR: $\delta$ 26.67, 40.98, 51.08, 55.76, 119.93, 125.09, 126.47, 127.26, 127.30, 127.44, 127,57, 131.18, 139.88, 141.02, 143.20, 149.48. IR: 3061 (w), 2953 (s), 1486 (m), 764 (m), 743 (s), 724 (m) $cm^{-1}$.

**Method B. Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)fluorene-9-OD (1-OD) with Thionyl Chloride.** To an NMR tube containing a colorless solution of **1** (15.3 mg, 0.049 mmol) in $CDCl_3$ (0.6 mL) was added four drops of $D_2O$, and the tube was shaken and then left standing for 30 min. The $D_2O$ (top phase) was removed via syringe, leaving a colorless solution whose NMR spectrum exhibited no OH signal and identified the product as **1**-(9-OD). The molar ratio of residual HOD ($\delta$ 4.79) to **1**-(9-OD) was 1:14.6. Thionyl chloride (14 drops) was added, and the tube was shaken vigorously. Within 10 min the mixture became blood red. After a few more minutes an NMR spectrum detected the formation of **2** and also exhibited large humps at $\delta$ 0.85 and 7.3. The deep red coloration changed to yellow after 90 min; NMR indicated the almost-exclusive presence of **2**. No deuterium was indicated on C-9 or any other position, and the ratio 1:2:6:1 of 9-H/$ClCH_2$/$CH_3$/H6′ was identical to that of **2** obtained from the same treatment of **1** with $SOCl_2$, which indicates that the 9-H is not derived from the 9-OH. Purification by column chromatography and recrystallization from hexanes provided white crystals having the same mp and NMR spectra noted above for **2**.

**Method C. Reaction of 1 with Oxalyl Chloride.** Oxalyl chloride (six drops) was added to an NMR tube containing a colorless solution of **1** (17.1 mg, 0.054 mmol) in ca. 0.7 mL of $CDCl_3$. The solution became yellow on being shaken. After 30 min, its NMR spectrum indicated the presence mainly of starting material, which was entirely consumed after 150 min. NMR indicated that 16% of **1** was converted into **2**.

**Method D. Reaction of 1 with Acetyl Chloride.** Acetyl chloride (1 drop, freshly distilled, bp: 51−52 °C) was added to an NMR tube containing a solution of **1** (19.9 mg, 0.063 mmol) in ca. 0.5 mL of $CDCl_3$. The colorless solution was unchanged on vigorous shaking. After 10 min, NMR exhibited the presence of **1** and acetyl chloride in a ratio of 1:0.86. A small additional amount of acetyl chloride was then added, and after 90 min NMR indicated the ratio was 1:1.84. After several days, the presence of **1** (22%), **2** (19%), and *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenyl acetate (ester) (**11**) (vide infra) was indicated by NMR.

**Method E. Reaction of 1 with $(CF_3SO_2)_2O$ Followed by *n*-$Bu_4N^+Cl^-$.** A 10-mL single-necked, round-bottomed flask equipped with a stir bar and containing a colorless solution of **1** (0.171 g, 0.51 mmol) in 3 mL of $CH_2Cl_2$ was sealed with a rubber septum and flushed with argon. The flask was immersed in a liquid nitrogen−acetone bath and kept at −30 °C, and 0.10 mL of triflic anhydride (0.59 mmol) was injected. The mixture turned deep red immediately, indicating the formation of cation **1a** (triflate salt **10**, vide infra), and was stirred at −30 °C for 30 min, at the end of which time a solution of (*n*-Bu)$_4N^+Cl^-$ in 3 mL of $CH_2Cl_2$ was added. The bath was removed, and the reaction mixture was stirred at room temperature for 2 h, during which time the mixture gradually became reddish-brown. TLC indicated that only a small amount of **1** remained. The reaction mixture was diluted with 40 mL of ether and filtered; the filtrate was washed with aqueous $NaHCO_3$ and then water. The organic layer was dried over anhyd $MgSO_4$, filtered through a thin layer of silica gel, and concentrated in vacuo to a solid, shown by $^1$H NMR to contain a small amount of **2** along with other major products.

**Formation of *sp*-9-[*o*-(*β*-Bromo-α,α-dimethylethyl)phenyl]fluorene (3). Method A. Reaction of 1 with HBr**. A colorless solution of **1** (42.5 mg, 0.135 mmol) in chloroform (5 mL) was prepared in a 10-mL round-bottomed flask equipped with a stir bar and septum. Stirring was begun, and HBr gas was bubbled in, at which time the solution became yellow and then deep red over a period of 1 h. The flask was then sealed with a glass stopper and Parafilm, and stirring was continued for an additional 2 h, after which time the red color faded. The solvent was removed by rotary evaporation, leaving a pale red solid that was filtered through silica gel with hexanes as eluting agent. Evaporation of the filtrate left a light yellow solid (50.8 mg) shown by $^1$H NMR to be composed of **3** (92.0% yield) and *sp*-(9-*o*-*tert*-butylphenyl)fluorene (**4**) (7.6% yield). Dry-column chromatography with hexanes as eluting agent provided white crystalline **3**, mp 186.5−187.5 °C. $^1$H NMR: $\delta$ 1.84 (s, 6 H), 4.09 (s, 2 H), 5.64 (s, 1 H), 6.25 (dd, $J$ = 1.5, 7.8 Hz, 1 H), 6.93 (ddd, $J$ = 1.5, 7.2 Hz, 1 H), 7.15 (ddd, $J$ = 1.5, 7.2, 8.1 Hz, 1 H), 7. 25 (m, $J$ = 1.2, 1.8, 7.5, 7.8 Hz, 4 H), 7.39 (ddd, $J$ = 2.1, 7.5, 7.8 Hz, 2 H), 7.47 (dd, $J$ = 1.2, 8.1 Hz, 1 H), 7.83 (dd, $J$ = 0.9, 7.5 Hz, 2 H). $^{13}$C NMR: $\delta$ 29.53, 40.30, 46.26, 51.11, 119.94, 125.17, 126.46, 127.28, 127.37, 127.57, 131.23, 139.90, 141.03, 143.26, 149.46. IR: 3061 (w), 2953 (s), 1486 (m), 764 (m), 743 (s), 724 (m) cm$^{-1}$. Anal. Calcd for $C_{23}H_{21}Br$: C, 73.21; H, 5.61. Found: C, 72.92; H, 5.74.

**Method B. Reaction of 1 with Thionyl Bromide**. Thionyl bromide (0.02 mL, 0.26 mmol) was added to a colorless solution of **1** (28.4 mg, 0.09 mmol) in $CDCl_3$ (ca. 0.5 mL) in an NMR tube. After the red thionyl bromide was added, the mixture turned yellow very rapidly. An NMR spectrum obtained after 13 min exhibited, among other resonances, three singlets at $\delta$ 1.84, 4.09, and 5.64 with an integration ratio of 6:2:1, indicating the initial formation of **3**. The mixture was allowed to stand for 6 days. The solvent was removed in vacuo, and the solid residue was washed with cold hexanes. Recrystallization from hexanes provided white crystalline **3**, mp 186−187.5 °C.

**Method C. Reaction of 1 with $(CF_3SO_2)_2O$ Followed by *n*-$Bu_4N^+Br^-$.** A 10-mL one-necked, round-bottomed flask containing a stirred colorless solution of **1** (51.9 mg, 0.17 mmol) in 2 mL of dry $CH_2Cl_2$ was cooled in a liquid nitrogen−acetone bath (−30 °C). Triflic anhydride (0.10 mL, 0.59 mmol) was injected, and the solution turned deep-red immediately, indicating the formation of cation **1a** (triflate salt **10**, vide infra). Stirring was continued at −30 °C for 15 min; a red solid precipitated. The liquid was removed with a pipet and a solution of *n*-$Bu_4N^+Br^-$ (246 mg, 0.76 mmol) in 3 mL of dry $CH_2Cl_2$ was added to the residual red solid. The cold bath was removed, and the mixture was stirred at room temperature for 15 min, during which time the mixture gradually became reddish-brown. The solvent was removed in vacuo and the residue extracted with hexanes. Evaporation of the extract in vacuo left a brown solid that was shown by $^1$H NMR to contain **3** and **4** in a ratio of 3.4:1.

**Method D. Reaction of 1-OLi with $(CF_3SO_2)_2O$ Followed by *n*-$Bu_4N^+Br^-$.** A 10-mL single-necked, round-bottomed flask equipped with a stir bar and containing **1** (51.9 mg, 0.17 mmol) was sealed with a rubber septum and flushed with argon, and 2 mL of dry ether was added. The stirred colorless solution was cooled to −30 °C in a liquid nitrogen−acetone bath, and an *n*-BuLi-hexanes solution (0.15 mL, 1.2 M, 0.18 mmol) was injected. After this colorless reaction mixture was stirred for 10 min, triflic anhydride (0.10 mL, 0.59 mmol) was added by injection. The reaction mixture turned deep-red immediately, indicating the formation of cation **1a** (triflate salt **10**, vide infra). Stirring at −30 °C was continued for 30 min, and the reaction setup was transferred to a drybox. The liquid portion of the reaction mixture was removed via a syringe and a solution of *n*-$Bu_4N^+Br^-$ (150 mg, 0.46 mmol) in dry $CH_2Cl_2$ (3 mL) was added to the residue by injection. The mixture became brownish yellow immediately and, after being swirled at room temperature for 15 min, was transferred to a separatory funnel. The reaction flask was washed with 40 mL of ether, and the washings were transferred to the funnel. This solution was washed with aqueous $NaHCO_3$ and then water, and the organic layer was dried over anhyd $MgSO_4$, filtered, and passed through silica gel. The solution was concentrated in vacuo leaving a light brown solid, 55 mg, whose $^1$H NMR spectrum exhibited **3** and **4** as major products in a ratio of 23:77.

**Method E. Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenyl Methyl Ether (6b) with HBr.** Compound **6b** was prepared as reported.[7b] The reaction of **6b** (50 mg, 0.15 mmol) with HBr was carried out following the procedure described above for the reaction of **1** with HBr. The observations were essentially identical. The light yellow solid (57.3 mg) obtained after evaporating the hexanes was shown by $^1$H NMR to be composed of **3** (89.0% yield) and **4** (8.5% yield). Dry-column chromatography with hexanes as eluting agent provided white crystals of **3**, mp 186.5−187.5 °C.

**Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol (1) with HI. Quantitative Formation of *sp*-9-(*o*-*tert*-Butylphenyl)fluorene (4).** A 25-mL round-bottomed flask containing **1** (250 mg, 0.80 mmol) and $CHCl_3$ (3 mL) and fitted with a rubber septum was swirled to provide a colorless solution. HI gas was bubbled in, which immediately turned the solution dark brown. Oily brown droplets appeared at the bottom of the flask. After the mixture was swirled occasionally over a 15-min period, TLC (9:1 hexanes/ether) exhibited two spots, neither of which was from **1**. The reaction mixture was transferred to a separatory funnel, the residue being washed into the funnel with 15 mL of $CHCl_3$, and the solution was washed sequentially with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$ and water. The now-colorless $CHCl_3$ layer was separated, dried over anhyd $MgSO_4$, and rotary evaporated, leaving a pale yellow solid, **4**, (230 mg; 97% yield) identified by $^1$H NMR and mp (179−180 °C, white crystals from hexanes−isooctane).[8,12]

**Dynamic NMR Stereochemical Study of the Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol (1) with HI.** Initial Formation of *ap*-9-(*o*-*tert*-Butylphenyl)fluorene (4a). An NMR tube containing **1** (8.0 mg) and a trace of TMS was capped and cooled to −50 °C in a liquid nitrogen−acetone bath. HI was bubbled into $CDCl_3$ to saturation, and the solution was then cooled to −50 °C and transferred to the NMR tube. After 20 min, a $^1$H NMR spectrum obtained at −40 °C exhibited sharp singlets at $\delta$ 0.69 (*t*-Bu) and 5.17 (H-9) associated with the *ap* rotamer (**4a**) of 9-(*o*-*tert*-butylphenyl)fluorene. Only a very small singlet at $\delta$ 1.72 (*t*-Bu) suggested the presence of a slight amount of the *sp* rotamer (**4**), which could have been formed from traces of 1 stuck to the upper wall of the NMR tube and not kept at low temperature. The ratio **4a/4** was 100:2. No starting material was observed. An NMR spectrum obtained when the solution warmed to −20 °C exhibited only slightly more **4**, the ratio **4a/4** being 100:5. The ratio at −10 °C was 100:14; at 0 °C, 100:36. After 25 min at room temperature, the resonances of **4a** were barely visible, the spectrum clearly exhibiting the presence of **4** almost exclusively. The conversion was quantitative.

**Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol (1) with Pyridine·$(HF)_x$. Exclusive Formation of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorofluorene (5).** To a plastic bottle containing finely powdered **1** (157 mg, 0.5 mmol) and equipped with a stir bar was added pyridine·$(HF)_x$ (Acros Organics; 5 mL). The reaction mixture turned red immediately. The bottle was sealed with a rubber septum and flushed with argon, and the mixture was stirred magnetically. The deep red color gradually turned to light brown in 1 h. TLC (silica gel, hexanes/ether 9:1) showed a new spot and indicated only a small amount of **1**. The mixture was extracted with hexanes (10 mL × 3). The combined hexanes solution was evaporated in vacuo, leaving a light brown solid, 154 mg, mp 149.5−152.5 °C (dec, melt turned dark brown with gas evolution) shown by $^1$H NMR to be composed of **5** (96%) and **1** (4%). The product is sensitive to moisture and was hydrolyzed back to **1** on silica gel. Several recrystallizations from hexanes provided colorless crystals, mp 154.0−155.5 °C dec. $^1$H NMR $\delta$: 1.70 (d, $J$ = 1.5 Hz, 9 H), 6.46 (ddd, $J$ = 7.8, 1.8 Hz, 1 H), 6.83 (dddd, $J$ = 7.8, 7.2, 2.1 Hz, 1 H), 7.11 (ddd, $J$ = 8.1, 7.2, 1.8 Hz, 1 H), 7.21 (t, $J$ = 7.8 Hz, 2 H), 7.28 (m, $J$ = 7.5 Hz, 2 H), 7.37 (dddd, $J$ = 7.5, 1.5 Hz, 2 H), 7.60 (dd, $J$ = 8.1, 1.2, 1 H), 7.66 (d, $J$ = 6.9 Hz, 2 H). $^{13}$C NMR $\delta$: 33.21 (d, $J$ = 12.8 Hz), 36.64, 103.95 (d, $J$ = 186.08 Hz), 120.17, 125.29 (d, $J$ = 1.8 Hz), 125.55, 127.00, 127.48, 128.73 (d, $J$ = 2.1 Hz), 129.82 (d, $J$ = 2.3 Hz), 130.46 (d, $J$ = 4.3 Hz), 137.01 (d, $J$ = 26.6 Hz), 140.02 (d, $J$ = 2.9 Hz), 148.83 (d, $J$ = 3.2 Hz), 149.21 (d, $J$ = 19.5 Hz). IR: 3048 (m), 2962(vs), 2868 (s), 1610 (w), 1490 (m), 1400 (w), 1368 (m), 1176 (s), 1012 (vs), 765 (vs), 729 (vs) cm$^{-1}$. Anal. Calcd for $C_{23}H_{21}F$: C, 87.31; H, 6.69; F, 6.00. Found: C, 87.67; H, 6.68; F, 5.97.

**Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol (1) with Triflic Acid in $CDCl_3$. Formation of 9-(*o*-*tert*-Butylphenyl)-9-fluorenyl Triflate (Salt) (10) and NMR Identification of 9-(*o*-*tert*-Butylphenyl)-9-fluorenyl Cation (1a).** Triflic acid (0.02 mL, 0.23 mmol) was added to a colorless solution of **1** (15.9 mg, 0.05 mmol) in $CDCl_3$ (0.7 mL). The solution turned blood red instantly. After 15 min, NMR showed that all of **1** was consumed, sharp singlets at $\delta$ 1.51 and 0.51 appeared, and resolution of the aromatic region was poor. In the spectra obtained after 18.5 and 49 h, the aromatic-proton resolution was good, the intensity of the singlet at $\delta$ 0.51 increased, and the ratio of *tert*-butyl hydrogens ($\delta$ 1.51) to aromatic hydrogens remained 9:12. The major component of this deep red solution was the 9-cation **1a**. The peak at $\delta$ 0.51 was believed to be from the erosion of the cap of the NMR tube by triflic acid. $^1$H NMR: $\delta$ 1.51 (s, 9 H), 6.88 (ddd, $J$ = 7.8, 7.5, 0.6 Hz, 2 H), 6.96 (dd, $J$ = 0.6, 7.2 Hz, 4 H), 7.23 (dd, $J$ = 1.5, 7.8 Hz, 1 H), 7.39 (ddd, $J$ = 1.2, 7.5, 7.2 Hz, 2 H), 7.48 (ddd, $J$ = 0.9, 7.2, 7.8, 8.1 Hz, 1 H), 7.78 (ddd, $J$ = 1.5, 7.5, 7.2 Hz, 1 H), 7.88 (d, $J$ = 8.1 Hz, 1 H). $^{13}$C NMR: $\delta$ 33.91, 38.36; 116.21, 120.41, 125.96, 126.34, 127.90, 131.34, 133.00, 136.21, 141.60, 143.48, 149.48, 149.83, 153.45, 215.66.

**Reaction of 1-OLi with $(CH_3CO)_2O$. Preparation of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenyl Acetate (Ester) (11).** Into a 25-mL one-necked flask equipped with a magnetic stir bar and a septum and containing **1** (110 mg, 0.35 mmol) and hexanes (8 mL) was bubbled argon to replace air. The mixture was stirred, providing a colorless solution. The flask was cooled in an ice bath, and an *n*-BuLi-hexanes solution (0.30 mL, 1.2 M, 0.36 mmol) was injected; the reaction mixture became light yellow. The ice bath was removed, freshly distilled acetic anhydride (0.15 mL, 1.59 mmol) was injected, and the mixture was stirred for 3 h during which time white solid gradually formed. The solid was removed by filtration, and the filtrate was evaporated under reduced pressure to give 107 mg of a semisolid that contained 85.6% (73.3% yield) of **11**, determined by NMR. Compound **11** was easily hydrolyzed into **1** on a TLC plate. Recrystallization from hexanes gave white crystals of **11**, mp 159−161.5 °C. $^1$H NMR: $\delta$ 1.82 (s, 9 H), 2.07 (s, 3 H), 6.43 (d, $J$ = 8.1 Hz, 1 H), 6.76 (ddd, $J$ = 7.2, 7.8, 0.6 Hz, 1 H); 7.04 (ddd, $J$ = 7.8, 1.2 Hz, 1 H); 7.19 (m, $J$ = 0.9, 7.5 Hz, 4 H); 7.35 (ddd, $J$ = 7.5, 1.8 Hz, 2 H); 7.57 (dd, $J$ = 8.4, 1.2 Hz, 1 H); 7.72 (d, $J$ = 7.5 Hz, 2 H). $^{13}$C NMR: $\delta$ 22.53, 34.04, 37.39, 91.70, 120.03, 123.72, 125.62, 126.55, 127.88, 128.43, 128.72, 131.52, 138.71, 141.09, 147.09, 150.59, 166.83. IR: 3072 (w), 1765 (vs), 1616 (w), 1372 (s), 735 (s). Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.58; H, 6.28.

**Acknowledgment.** Partial support of this research from Southern Illinois University through doctoral fellowship (Y.H.) and Distinguished Professorship (C.Y.M.) funding, from the Department of Chemistry and Biochemistry Summer Undergraduate Research Program (H.L.S.), and the University Research Foundation, La Jolla, is gratefully acknowledged.

JO9910280