Effect of steric bulk on the absolute reactivity of allene oxides†

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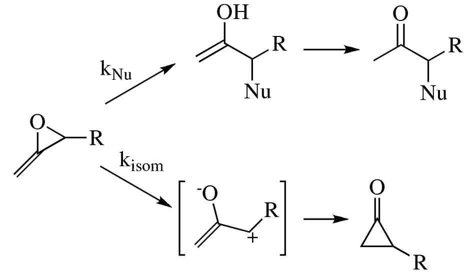
α-Alkyl substituted fluorenylidene allene oxides were generated photochemically from appropriately substituted fluorenol derivatives in 2,2,2-trifluoroethanol (TFE) in order to assess the affect of steric bulk on the absolute reactivity of the allene oxides. The absolute reactivities of the allene oxides were measured using nanosecond laser flash photolysis, and were found to change little in TFE upon going from α-methyl to α-butyl to α-*t*-butyl. However, all three α-alkyl substituted allene oxides were considerably more reactive than the α-hydrogen derivative, indicating that steric bulk did not result in a decrease in reactivity as is typically found in other allene oxides. The contrary reactivity of the fluorenylidene allene oxides is explained by examining in detail the reactions of these allene oxides, determined from product studies.

Introduction

Theoretical and experimental chemists have been interested in the chemistry of allene oxides for several decades.[1–3] Much of the original interest in these compounds came from their close relationship with cyclopropanones, which are structural isomers of allene oxides.[4–9] Allene oxides have also been implicated as intermediates in the conversion of fatty acids to cyclopentenones and α-ketols in some plants and marine organisms,[10,11] and have also been used as intermediates in synthetic organic chemistry.[11–21]

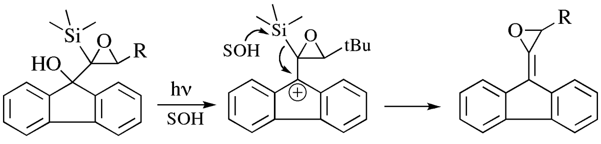
Product studies have demonstrated convincingly that allene oxides undergo two characteristic reactions.[1,2] One of these is the S_N2-like addition of a nucleophile to give an α-substituted ketone, and the other is isomerization to the cyclopropanone through an oxyallyl intermediate, Scheme 1. For most allene oxides, one or both of these reactions is rapid. As a result, allene oxides are typically too short-lived to be directly observed when generated as intermediates in solution. Notable exceptions are evident for some allene oxides with at least one bulky *t*-butyl group attached to the α-carbon (R = *t*-butyl, Scheme 1). These allene oxides can be very long-lived and in some cases are sufficiently stable to be purified by distillation and characterized by standard spectroscopic methods such as NMR spectroscopy.[2,22,23]

In those cases where the allene oxides are isolable, the function of the bulky groups must be to dramatically slow the main reaction of the allene oxides. As recognized by Chan and Ong in their seminal study of allene oxide chemistry,[1,2] the steric bulk of a large α-*t*-butyl group clearly slows the reactions and thus enhances the lifetimes of allene oxides if the main reaction is nucleophilic addition *via* an S_N2-like mechanism. However, if the main reaction is not direct attack of a nucleophile on the α-carbon, how a bulky substituent will affect the reactivity of the allene oxide is not immediately obvious.



Scheme 1 Main reactions of allene oxides.

Since most allene oxides are unstable, it is difficult to carry out comprehensive studies on the effect of structure on their absolute reactivity. In previous work,[24] we showed that absolute rate constants for the reactions of the fluorenylidene allene oxide **2a**, Scheme 2 (R = H), can be obtained by a rapid photoinduced elimination reaction of 9-(1-trimethylsilyl-1,2-epoxyethyl)-9*H*-fluoren-9-ol **1a**. Kinetic data coupled with product studies provided evidence that in TFE **2a** undergoes exclusive isomerization to the cyclopropanone by a mechanism involving rate determining oxyallyl zwitterion formation. In the present work, the same methodology was used to generate α-alkyl substituted 9-fluorenylidene allene oxides **2b–d**, Scheme 2, including the bulky *t*-butyl derivative. This has allowed us to investigate the absolute reactivity of allene oxides as a function of the steric and electronic effects of the alkyl substituents.



2a-d

1a R = H
1b R = CH_3
1c R = $(CH_2)_3CH_3$
1d R = $C(CH_3)_3$

Scheme 2 Photochemical generation of α-alkyl fluorenylidene allene oxides.

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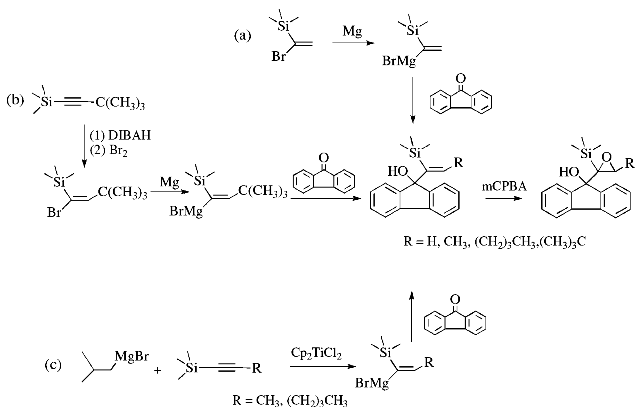
† Electronic supplementary information (ESI) available: Copies of the ^1H and ^{13}C NMR spectra of epoxides **1b–1d** and their corresponding alkenes. See DOI: 10.1039/b910887d

Results

Preparation of precursors

The precursors **1a–d** that upon irradiation led to the formation of the desired allene oxides were all prepared by addition of 1-trimethylsilyl-1-alkenylmagnesium bromides to fluorenone, followed by epoxidation with *m*-chloroperbenzoic acid, Scheme 3.



Scheme 3 Preparation of precursors **1a–1d**.

The Grignard reagent for the R = H derivative was prepared[24] by reaction of commercially available 1-bromo-1-trimethylsilylethene with Mg in ether, and added readily to fluorenone to give after epoxidation the desired allene oxide precursor **1a**, Scheme 3 (path a). The 1-bromo-1-trimethylsilyl-3,3-dimethyl-1-butene required to prepare **1d** was not commercially available, and was prepared[25] by hydroalumination of 1-trimethylsilyl-3,3-dimethyl-1-butyne with DIBAH, followed by addition of molecular bromine, Scheme 3 (path b). The Grignard reagent prepared from this material added cleanly to fluorenone to give the alkene which was readily epoxidized with *m*CPBA to give **1d**. The same synthetic procedure to give the 1-bromo-1-trimethylsilyl-1-propene required for **1b** failed, as hydroalumination of the appropriate alkyne with DIBAH followed by addition of Br_2 did not give the desired vinylbromide. Instead, the appropriate Grignard reagent was generated by a Cp_2TiCl_2 catalyzed reaction between *iso*-butylmagnesium bromide and 1-trimethylsilyl-1-propyne,[26] Scheme 3 (path c) with fluorenone being added to the reaction mixture immediately after Grignard exchange was complete. Precursor **1c** (R = $(CH_2)_3CH_3$) was prepared according to the same procedure as described for **1b**.

Kinetics: laser flash photolysis

As described previously,[24] 308 nm laser irradiation of **1a** in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) leads to formation of the 9-(1-trimethylsilyl-1,2-epoxy)-9-fluorenyl cation which then rapidly eliminates the trimethylsilyl group to give the allene oxide **2a**, Scheme 2 (R = H). This process can be detected by rapid decay of the substituted 9-fluorenyl cation at 490 nm which is matched by the growth of the allene oxide at 315 nm. Similarly, as shown in Fig. 1, laser irradiation of **1d** in HFIP led to prompt formation of a substituted 9-fluorenyl cation absorbing at 480 nm which then decayed to give a transient at 315 nm.

As shown in the inset in Fig. 1, rate constants for the decay at 480 nm, $k_{480} = 2.1 \times 10^6\ s^{-1}$ and the growth at 315 nm, $k_{315} = 1.9 \times 10^6\ s^{-1}$, matched well, indicating that the transient at 315 nm was produced by a reaction of the transient at 480 nm. These results are consistent with the photoreaction in Scheme 2, with laser irradiation causing photoheterolysis of the C–OH bond of **1d** to give the substituted 9-fluorenyl cation with absorption at 480 nm, followed by addition of solvent to the trimethylsilyl group and elimination of the trimethylsilyl ether to give the allene oxide with absorption at 315 nm. Similar results were obtained upon laser irradiation of **1b** and **1c**, indicating that they too undergo photoheterolysis to give the corresponding fluorenyl cation which then decays to give the allene oxide at 315 nm.

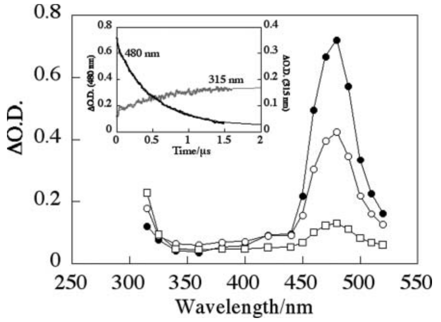


Fig. 1 Time-dependent absorption changes upon 308 nm laser irradiation of **1d** in HFIP at room temperature. Spectra were obtained (●) 20 ns, (○) 300 ns and (□) 1 μs after laser irradiation. The inset shows the decay traces at 480 and 315 nm.

In 2,2,2-trifluoroethanol (TFE), the 9-fluorenyl cations generated upon laser irradiation of **1a–1d** were too short-lived to be observed, and the allene oxides **2a–2d** were generated promptly within the duration of the laser pulse. Once formed, allene oxide **2a** barely decayed over the longest time-scale of 10 s available on the nanosecond laser system and was sufficiently long-lived in TFE to be observed using a conventional UV spectrometer, decaying with a rate constant of $k_{TFE} = 0.0012\ s^{-1}$.[24] On the other hand, allene oxide **2b** decayed completely within the 10 s time window, and its decay was measured using the nanosecond laser system. Allene oxide **2b** decayed in a first-order manner, Fig. 2, and fitting of the decay to a first-order rate expression gave a rate constant of $k_{TFE} = 0.54 \pm 0.5\ s^{-1}$, Table 1. Similarly, the decays of allene oxides **2c** and **2d**, Fig. 2, were also monitored using the nanosecond laser

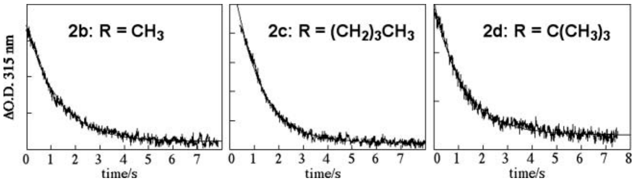


Fig. 2 Time-resolved decays of allene oxides **2b**, **2c**, and **2d** in TFE at room temperature.

Table 1 Rate constants for the decays of fluorenylidene allene oxides **2a–2d** in TFE at 23 °C

Allene Oxide	k_{TFE} (TFE)
2a, R = H[24]	$0.0012\ s^{-1}$
2b, R = CH_3	$0.54 \pm 0.5\ s^{-1}$
2c, R = $(CH_2)_3CH_3$	$0.47 \pm 0.5\ s^{-1}$
2d, R = $C(CH_3)_3$	$0.63 \pm 0.5\ s^{-1}$

system, and their rate constants were determined to be 0.47 ± 0.5 s^{-1} and 0.63 ± 0.5 s^{-1}, respectively.

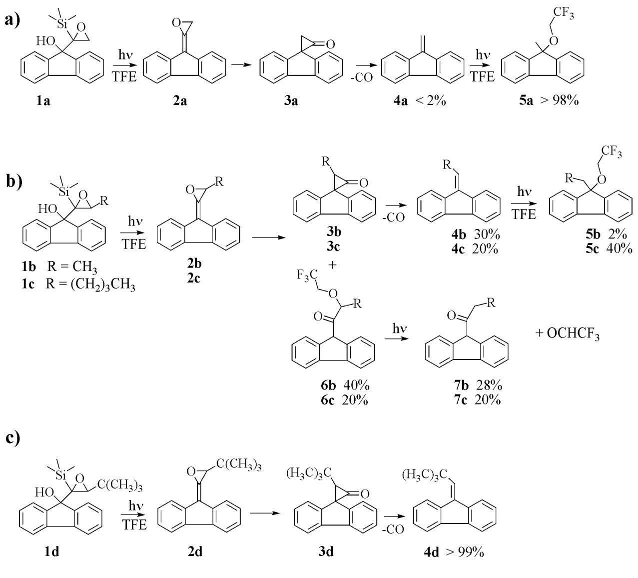
In our previous work, we showed that the observed rate constants for the decay of allene oxide **2a** in TFE increase with increasing nucleophile concentration according to eqn 1, indicating that **2a** reacts with nucleophiles *via* an S_N2-like mechanism.[24]

$$k_{obs} = k_{TFE} + k_{Nu}[Nu] \tag{1}$$

The fastest second-order rate constant for nucleophilic addition to **2a** was for iodide anion as the nucleophile, $k_{I^-} = 23\ M^{-1}\ s^{-1}$ in TFE.[24] For **2a**, only small concentrations of added iodide ion (<0.0001 M) were needed to detect an increase in k_{obs} since k_{TFE} was relatively small, $k_{TFE} = 0.0012\ s^{-1}$. For the allene oxides **2b–2d** that react with TFE with much bigger rate constants of $k_{TFE} \approx 0.5\ s^{-1}$, a clearly detectable increase in k_{obs} would require a concentration of iodide of *ca.* 0.01 M if the second-order rate constant for addition of iodide to **2b–2d** was the same as that to **2a**. No increase in k_{obs} was seen at iodide concentrations up to 0.05 M,[27] showing that the k_{I^-} values for allene oxides **2b–2d** are smaller than that for **2a**, and that the α-alkyl substituted fluorenylidene allene oxides are less reactive toward nucleophile addition *via* an S_N2 mechanism than the α-H substituted derivative.

Product studies

We showed in previous work[24] that steady-state irradiation of 9-(1-trimethylsilyl-1,2-epoxyethyl)-9*H*-fluoren-9-ol **1a** in TFE leads to the formation of two products, 9-methylene-9*H*-fluorene **4a** and 9-(2,2,2-trifluoroethoxy)-9-methyl-9*H*-fluorene **5a**, Scheme 4a. These two compounds are produced from the photogenerated allene oxide, which first isomerizes to the corresponding unstable cyclopropanone. The cyclopropanone then loses CO (either thermally or by secondary photolysis)[28] to give methylenefluorene which undergoes secondary photoinduced addition of the solvent to give the ether product.



Scheme 4 Products upon irradiation of a) **1a**, b) **1b** and **1c**, and c) **1d** in TFE.

Table 2 Relative yields of isomerization and solvent addition products after steady-state irradiation of precursors **1a–1d** in TFE at room temperature

	Isomerization	Solvent addition
Precursor	**4 + 5**	**6 + 7**
1a, R = H[24]	>99%	—
1b, R = CH_3	32%	68%
1c, R = $(CH_2)_3CH_3$	60%	40%
1d, R = $C(CH_3)_3$	>99%	—

In the present work, irradiation of methyl **1b** (R = CH_3) and *n*-butyl **1c** (R = $(CH_2)_3CH_3$) substituted precursors in neat TFE gave product mixtures substantially more complicated than that observed after irradiation of **1a**. In both cases, GC analysis showed the formation of four products, which were separated by column chromatography and characterized by GC/MS and ^{1}H-NMR spectroscopy. Two of the four products from **1b** were identified as the alkene **4b** (30% by GC) and the trifluoroethyl ether **5b** (2%), Scheme 4b, generated from the cyclopropanone in the same manner as described above. The other two products were identified as the α-keto ether **6b** (40%) and the ketone **7b** (28%), with **6b** arising from nucleophilic addition of solvent, and **7b** presumably being generated by secondary Norrish Type II photofragmentation of **6b**. Analogous products were obtained upon irradiation of precursor **1c**, with the relative yields of the four products given in Scheme 4b.

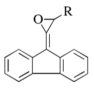
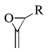
Irradiation of **1d** in TFE led to the formation of only 9-(2,2-dimethylpropylidene)-9*H*-fluorene **4d**, Scheme 4c. This product is formed upon decarbonylation of the cyclopropanone, as described above for **1a**. A summary of the products arising from isomerization and solvent addition is given in Table 2.

Discussion

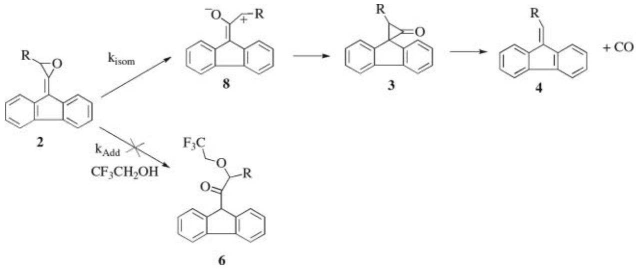
As mentioned in the introduction, a common strategy used to stabilize allene oxides sufficiently so that they can be isolated, involves adding bulky groups like the *t*-butyl group to various positions of the allene oxide, including to the epoxide ring, and several examples demonstrating the effectiveness of this strategy are available in the early allene oxide literature.[2,22,23] More recently, the effect of steric bulk on the reactivity of simple α-alkyl substituted allene oxides has been quantified, with the *t*-butylallene oxide in acetonitrile being at least 100 times less reactive than the parent unsubstituted allene oxide,[29] Table 3. As well, a steady decrease in reactivity is observed as the bulk of the α-alkyl group is increased from H to methyl to *iso*propyl to *t*-butyl.[29] In contrast, the steric bulk of the alkyl group does not decrease the reactivity of the fluorenylidene allene oxides. Instead, *t*-butyl derivative **2d** is 500 times more reactive than the parent H derivative **2a**, while increasing the steric bulk from methyl to *n*-butyl to *t*-butyl has little influence on the observed reactivity, Table 3.

To rationalize the contrasting behavior between the fluorenylidene and the simple α-alkyl allene oxides, the main reactions of the allene oxides must be identified. Of particular importance is to determine if the solvent addition products observed after generation of allene oxides **2b** and **2c** are derived from direct S_N2 addition to the allene oxides or *via* addition to oxyallyl intermediates produced upon ring opening of the allene oxides.

Table 3 Relative rate constants for the decays of substituted fluorenylidene allene oxides in TFE, and substituted alkyl allene oxides[29] in acetonitrile at 23 °C

	 k_{rel}	 k_{rel}
R = H	0.0019[24]	>100
R = CH_3	0.86	16
R = $(CH_2)_3CH_3$	0.75	—
R = $CH(CH_3)_2$	—	2.1
R = $C(CH_3)_3$	1.0	1.0

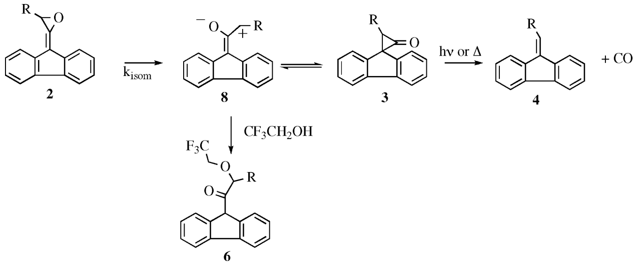
We previously established[24] that the sole reaction of allene oxide **2a** in TFE is the rate-determining formation of an oxyallyl zwitterion **8a** (R = H, Scheme 5) which then collapses to the cyclopropanone, and that no products from nucleophilic addition of the solvent to the allene oxide are detected by GC. Thus, the pseudo first-order rate constant k_{Add} for direct S_N2-like nucleophilic addition of the solvent to allene oxide **2a** must be at least 50 times smaller than the rate constant for isomerization ($k_{isom} = 0.0012\ s^{-1}$ [24]), which means that the pseudo-first-order rate constant k_{Add} for **2a** must be $<2.4 \times 10^{-5}\ s^{-1}$ ($= 0.0012\ s^{-1} \times 1/50$).



Scheme 5 Isomerization and S_N2-like addition reactions of allene oxides in TFE.

In the present work, product studies show that addition of TFE is a major reaction for the methyl substituted allene oxide **2b** and the *n*-butyl substituted allene oxide **2c**, with TFE addition products comprising 68% and 40% of the total products generated from **2b** and **2c**, respectively. If the addition products arise from direct S_N2-like addition of the solvent to the allene oxide, the rate constant for the direct S_N2 addition of TFE to **2b**, calculated using the overall rate constant of $0.54\ s^{-1}$ for the decay of **2b**, would be $k_{Add} = 0.38\ s^{-1}$ ($= 0.54\ s^{-1} \times 68\%$). Similarly, the direct S_N2-like addition of TFE to **2c** would take place with a rate constant of $k_{Add} = 0.19\ s^{-1}$ ($= 0.47\ s^{-1} \times 40\%$). These rate constants are about four orders of magnitude greater than the upper limit for the rate constant for addition of TFE to allene oxide **2a**, calculated above to be $<2.4 \times 10^{-5}\ s^{-1}$. Such a large increase in S_N2 reactivity is unreasonable since the increased steric bulk of the alkyl groups at the reactive center would decrease the rate constant for such a reaction. We can therefore conclude that the TFE addition products are not generated by the direct S_N2 reaction, a conclusion that is supported by the kinetics experiments showing that allene oxides **2b–2d** were less reactive towards S_N2 addition of I^- than **2a**.

The results instead lead to the conclusion that the solvent-addition products from **2b** and **2c** are generated after rate-determining formation of the corresponding oxyallyl intermediates **8b** and **8c**. Presumably, the oxyallyl intermediates are trapped by solvent, Scheme 6, in competition with ring-closure to the cyclopropanones, or solvent adds to the oxyallyl intermediates *via* a cyclopropanone-oxyallyl equilibrium[30–32] in competition with thermal or photochemical decarbonylation of the cyclopropanone.



Scheme 6 Isomerization and S_N1-like addition reactions of allene oxides in TFE.

The presence of the α-alkyl groups is likely to be responsible for allowing oxyallyls **8b** and **8c** to be trapped by solvent while **8a** exclusively cyclizes to the cyclopropanone. The electron-donating abilities of these groups would stabilize **8b** and **8c** compared to **8a**, so that direct addition of solvent to the oxyallyl intermediates becomes competitive with collapse to the cyclopropanone, Scheme 6. Furthermore, the presence of the alkyl groups might shift the cyclopropanone–oxyallyl equilibrium in the oxyallyl direction, allowing for more solvent addition products to be formed instead of products derived from decarbonylation.

The *t*-butyl derivative **2d** only gave products formed from the cyclopropanone, indicating that its main reaction is also rate-determining oxyallyl **8d** formation. In this case, the oxyallyl intermediate only cyclizes to give products from cyclopropanone **3d**, since nucleophilic addition would require addition to a highly hindered neopentyl cation.

Even though mechanistic details for formation of the solvent adducts from **2b** and **2c** are not clear, the data lead to the conclusion that the rate-determining step in the reactions of the allene oxides **2a–2d** is ring opening to the oxyallyl intermediates **8a–8d**, with direct S_N2 addition to the allene oxides not contributing to the overall rate constant for the decay of the allene oxides. In this reaction, the electron-donating alkyl groups stabilize the oxyallyl intermediate, and the reactivities of the allene oxides increase markedly even in the presence of a bulky *t*-butyl group. In contrast, the simple α-alkyl allene oxides studied earlier do not isomerize.[2,29] Their reactivity is therefore dictated by the rate constant for their S_N2-like reaction, which is clearly slowed by the presence of bulky groups. Thus, the lifetimes of allene oxides that are prone to isomerization *via* an oxyallyl zwitterion will decrease in the presence of a bulky alkyl group simply by virtue of the stabilizing effect of the substituent, while allene oxides whose main reaction is nucleophilic addition are the ones whose lifetimes increase upon addition of a bulky substituent.

Conclusions

Photoelimination is an effective method for the rapid generation of substituted fluorenylidene allene oxides and allows for the use of fast reaction methods to study the absolute kinetics of the reactions of the allene oxides. The rate constants for the reactions of the α-alkyl substituted fluorenylidene allene oxides, together with results from product studies, show that increasing steric bulk decreases the lifetime of these allene oxides, due to their main reaction being ring-opening to oxyallyl intermediates. The results from this work therefore show that adding bulky groups will only be an effective strategy for stabilizing allene oxides if their main reaction is direct nucleophilic addition.

Experimental

General

Melting points were determined using Fisher-Jones melting apparatus. NMR identification was performed using a Bruker Tecmag AC-250 (250 MHz) or a Bruker Avance (500 MHz) spectrometer. Chemical shifts are given in δ (ppm) units relative to a TMS standard. ^{13}C NMR spectra were obtained at 125 MHz. Coupling constants are given with units of Hz. GC/MS analysis was carried out using a Perkin Elmer Turbomass GC-MS system. High resolution mass spectra were obtained using a Bruker microTOF Focus ESI-TOF MS.

Synthesis of allene oxide precursors 1b–1d

9-(1-Trimethylsilyl-1,2-epoxyprop-1-yl)-9*H*-fluoren-9-ol 1b. Following the method described by Sato *et al.*,[26] *iso*-butylmagnesium bromide (1.0 M in Et_2O, 6.00 mmol, 6 mL) was added drop-wise over 10 min to a suspension of Cp_2TiCl_2 (0.30 mmol, 0.08 g) in ether (5 mL) contained in an argon-flushed three-necked round bottom flask fitted with a septum, stopcock and condenser. The dark brown mixture was heated to reflux for 15 min, after which it was cooled to room temperature and 1-trimethylsilyl-1-propyne (3.00 mmol, 0.34 g) was added. The solution was brought to reflux for a further 4 h. The reaction was then cooled to room temperature and an ethereal solution of fluoren-9-one (3.00 mmol, 0.54 g) was gently added. The mixture was vigorously stirred for an additional 30 min, after which time it was quenched with a sat. NH_4Cl solution (15 mL). The organic layer was dried (anhydrous Na_2SO_4), and the solvent was removed under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.38$, 15% ethyl acetate/hexanes) to yield 9-(1-trimethylsilyl-1-propenyl)-9*H*-fluoren-9-ol (0.48 g, 54%) as a pale yellow oil; δ_H (500 MHz; $CDCl_3$) 7.66 (2H, d), 7.39–7.42 (2H, m), 7.31–7.36 (4H, m), 7.25 (1H, q, *J*7), 2.03 (1H, s), 2.0 (3H, d, *J*7), –0.37 (9H, s); δ_C (125 MHz; $CDCl_3$) 151.0, 147.3, 139.7, 136.8, 128.7, 128.3, 124.7, 120, 85.8, 14.5, 1.0; EI-MS: 294 (M+).

9-(1-Trimethylsilyl-1-propenyl)-9*H*-fluoren-9-ol (1.37 mmol, 0.41 g) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C in an ice bath. Dry *meta*-chloroperbenzoic acid (1.93 mmol, 0.33 g) was added in six portions and the reaction was left to stir for 2 h. The mixture was then washed with sat. $NaHCO_3$ (10 mL), sat. $NaHSO_3$ (10 mL), and finally once more with sat. $NaHCO_3$ (10 mL). The combined aqueous layers were extracted three times with ethyl acetate. The mixed organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.23$, CH_2Cl_2) followed by recrystallization from ethanol to give 9-(1-trimethylsilyl-1,2-epoxyprop-1-yl)-9*H*-fluoren-9-ol **1b** (0.28 g, 54%) as colorless needles; mp = 173–175 °C; δ_H (500 MHz; $CDCl_3$) 7.66 (1H, d), 7.62 (1H, d), 7.56 (1H, d), 7.28–7.35 (5H, m), 4.00 (1H, q, *J*6.0), 2.83 (1H, s), 1.53 (3H, d, *J*6), –0.46 (9H, s); δ_C (125 MHz; $CDCl_3$) 149.5, 144.9, 141.7, 140.5, 130.1, 129.2, 128.5, 128, 125.4, 123.9, 120.4, 120.3, 81.0, 59.7, 53.4, 16.2, –0.5; HRMS (ESI) calc'd for $C_{19}H_{22}O_2SiNa$ $(M + Na)^+$ 333.1287, found $(M + Na)^+$ 333.1281.

9-(1-Trimethylsilyl-1,2-epoxyhex-1-yl)-9*H*-fluoren-9-ol 1c. In a Schlenk flask fitted with a septum, an ethereal (5 mL) suspension of Cp_2TiCl_2 (0.65 mmol, 0.16 g) was cooled to 0 °C in an ice bath. To this was added *iso*butylmagnesium bromide (1.05M in diethylether, 19.00 mmol, 20 mL) dropwise over a 10 min period. The resulting dark purple mixture remained at 0 °C for 20 min, after which 1-trimethylsilyl-1-hexyne (12.90 mmol, 2.00 g) was added. The solution was then brought to room temperature where it remained for an additional 6 h. An ethereal solution (15 mL) of 9-fluorenone (12.00 mmol, 2.16 g) was then added dropwise and the mixture was vigorously stirred for 12 h; after which time it was quenched with 15% aqueous HCl (20 mL). The aqueous layer was separated and extracted with diethylether (3 × 10 mL). All organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.6$, $CHCl_3$) to yield 1.51 g (37% yield) of 9-(1-trimethylsilyl-1-hexenyl)-9*H*-fluoren-9-ol as a pale yellow oil; δ_H (500 MHz; $CDCl_3$) 7.64 (2H, d, *J*7.3), 7.38–7.42 (2H, m), 7.28–7.33 (4H, m), 7.14 (1H, t, *J*8.0), 2.43 (2H, q, *J*7.5), 2.09 (1H, s), 1.60 (2H, p, *J*7.5), 1.52 (2H, p, *J*7.5), 1.04 (3H, t, *J*7.5), –0.39 (9H, s); δ_C (125 MHz; $CDCl_3$) 149.6, 143.4, 141.9, 137.8, 129.9, 128.2, 124.3, 121.1, 84.4, 33.7, 32.2, 24.5, 14.9, 0.6.

*m*CPBA (0.87 mmol, 0.15 g), 9-(1-trimethylsilyl-1-hexenyl)-9*H*-fluoren-9-ol (0.59 mmol, 0.23 g) and CH_2Cl_2 (10 mL) were placed in a single neck flask fitted with a septum; the reaction remained at 0 °C for 2 h. The mixture was then transferred to a separatory funnel were it was washed with sat. $NaHCO_3$ (10 mL), sat. $NaHSO_3$ (10 mL), and finally once more with sat. $NaHCO_3$ (10 mL). The combined aqueous layers were extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.48$, 25% ethyl acetate/hexanes) and gave 0.16 g (78%) of 9-(1-trimethylsilyl-1,2-epoxyhex-1-yl)-9*H*-fluoren-9-ol **1c** as a thick yellow oil; δ_H (500 MHz; $CDCl_3$) 7.56–7.68 (3H, m), 7.26–7.45 (5H, m), 3.90 (1H, t, *J*7.0), 1.82 (2H, m), 1.65 (2H, m), 1.51 (2H, m), 0.97 (3H, t, *J*7.5), –0.47 (9H, s); δ_C (125 MHz; $CDCl_3$) 149.2, 144.6, 141.4, 140.2, 129.8, 128.3, 127.7, 120.2, 80.6, 57.8, 29.6, 22.6, 14.0, –0.6; HRMS calc'd for $C_{22}H_{28}O_2SiNa$ $(M + Na)^+$ 375.1756, found $(M + Na)^+$ 375.1747.

9-(3,3-Dimethyl-1-trimethylsilyl-1,2-epoxybut-1-yl)-9*H*-fluoren-9-ol 1d. In a three necked round bottom flask fitted with a septum, stopcock and thermometer was placed *E*-1-bromo-3,3-dimethyl-1-trimethylsilylbut-1-ene[25] (2.10 mmol, 0.50 g) in THF (5 mL) and the mixture was cooled to –96 °C in a hexanes/N_2 (*l*) bath. Butyl lithium (1.60 M solution in hexanes, 2.31 mmol, 1.44 mL) was added slowly (30 min) so as no increase above –85 °C could occur; the mixture remained cold for an additional hour. In a separate flask fluoren-9-one (2.00 mmol, 0.36 g), THF (5 mL) and $BF_3 \cdot Et_2O$ (2.00 mmol, 0.25 mL) were cooled to −96 °C. The latter was added to the former so no increase above −85 °C could occur. The reaction was allowed to stir cold for one hour followed by a slow rise to room temperature over a period of 2 h. The resulting orange mixture was poured into 15% aqueous HCl, shaken and then extracted three times with ether. The organic layers were combined, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.11$, 5% ethyl acetate/hexanes) and gave 0.30 g (45% yield) of 9-(3,3-dimethyl-1-trimethylsilyl-1-butenyl)-9*H*-fluoren-9-ol as a faint yellow oil; δ_H (500 MHz; $CDCl_3$) 7.62 (2H, d, *J*7.5), 7.34–7.38 (3H, m), 7.26–7.29 (4H, m), 1.31 (9H, s), −0.32 (9H, s); δ_C (125 MHz; $CDCl_3$) 154.3, 150.2, 140.7, 132.8, 129, 128.1, 123.7, 120.3, 84.7, 34.4, 31.9, 3.2.

m-Chloroperbenzoic acid (0.53 mmol, 0.09 g) and 9-(3,3-dimethyl-1-trimethylsilyl-1-butenyl)-9*H*-fluoren-9-ol (0.38 mmol, 0.13 g) were dissolved in CH_2Cl_2 (5 mL) and stirred for 2 h at 0 °C. The mixture was then washed with sat. $NaHCO_3$ (10 mL), sat. $NaHSO_3$ (10 mL), and finally once more with sat. $NaHCO_3$ (10 mL). The combined aqueous layers were extracted three times with ethyl acetate. The mixed organic layers were dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel ($R_f = 0.53$, 25% ethyl acetate/hexanes) and gave 0.11 g (79% yield) of 9-(3,3-dimethyl-1-trimethylsilyl-1,2-epoxybut-1-yl)-9*H*-fluoren-9-ol **1d** as a pale yellow powder; mp = 112 °C; δ_H (500 MHz; $CDCl_3$) 7.60–7.68 (3H, m), 7.28–7.35 (5H, m), 3.86 (1H, s), 2.77 (1H, s), 1.20 (9H, s), −0.36 (9H, s); δ_C (125 MHz; $CDCl_3$) 150, 144.7, 142.1, 140.7, 129.9, 129, 128.5, 127.9, 124.8, 123.1, 120.5, 120.4, 67.4, 59.6, 32.0, 28.1, 1.3; HRMS (ESI-MS) calc'd for $C_{22}H_{28}O_2SiNa$ $(M + Na)^+ = 375.1756$, found $(M + Na)^+$ 375.1727.

Photolysis. General procedure

In a quartz tube sealed with a septum, an allene oxide precursor **1b–1d** (0.05 g) was dissolved in 15 mL of TFE. The solution was degassed with nitrogen for 20 min. Steady state irradiation of the sample was conducted in a Rayonet photoreactor using low pressure mercury lamps (300 nm emission) for 20 min. The post-irradiation solution was analyzed by GC, GC-MS and, following chromatographic separation, ^{1}H-NMR. Characterization data after irradiation of each of the allene oxide precursors are given below. Yield refers to relative yield of products by GC.

9-(1-Trimethylsilyl-1,2-epoxyprop-1-yl)-9*H*-fluoren-9-ol 1b. (i) 9-Ethylidenefluorene[33] (**4b**) (30% of products by GC) δ_H (500 MHz; $CDCl_3$) 7.64–7.98 (4H, m), 7.26–7.46 (4H, m), 6.90 (1H, q, *J*7.5), 2.44 (3H, d, *J*7.5); GC-MS (*m*/*z*): 192 (100), 191 (85), 165 (55), 95 (20), 83 (15).

(ii) 9-Ethyl-9-(2,2,2-trifluoroethoxy)fluorene (**5b**) (2%) δ_H (500 MHz; $CDCl_3$) 7.30–7.82 (m, 8H), 3.60 (2H, q, *J*9.0), 2.37 (3H, q, *J*7.5), 0.92 (3H, t, *J*7.5); GC-MS (*m*/*z*): 263 (100), 193 (5), 180 (55), 152 (30), 57 (30).

(iii) 1-(9-Fluorenyl)-2-(2,2,2-trifluoroethoxy)-1-propanone (**6b**) (40%) δ_H (500 MHz; $CDCl_3$) 7.28–7.79 (8H, m,), 5.07 (1H, s,), 3.81 (1H, q, *J*7.0, 3.32 (2H, q, *J*8.5), 1.08 (3H, d, *J*7.0); GC-MS (*m*/*z*): 320 (3), 292 (7), 165 (100), 139 (8), 127 (80), 83 (21).

(iv) 1-(9-Fluorenyl)-1-propanone[34] (**7b**) (28%) δ_H (500 MHz; $CDCl_3$) 7.30–7.84 (8H, m), 5.05 (1H, s), 3.56 (2H, q, *J*7.5), 0.96 (3H, t, *J*7.5); GC-MS (*m*/*z*): 222 (15), 207 (3), 165 (65), 139 (10), 57 (100).

9-(1-Trimethylsilyl-1,2-epoxyhex-1-yl)-9*H*-fluoren-9-ol 1c. (i) 9-Pentylidenefluorene[35] (**4c**) (20% of products by GC) δ_H (500 MHz; $CDCl_3$) 7.32–7.84 (8H, m), 6.85 (1H, t, *J*9.0), 2.30 (6H, m), 0.90 (3H, t, *J*7.0); GC-MS (*m*/*z*): 234 (25), 202 (9), 191 (55), 178 (100), 165 (25).

(ii) 9-Pentyl-9-(2,2,2-trifluoroethoxy)fluorene (**5c**) (40%) GC-MS (*m*/*z*): 334 (5), 263 (100), 180 (30), 178 (25) 152 (15).

(iii) 1-(9-Fluorenyl)-2-(2,2,2-trifluoroethoxy)-1-hexanone (**6c**) (20%) δ_H (500 MHz; $CDCl_3$) 7.29–7.78 (8H, m), 5.07 (1H, s), 3.88 (2H, q, *J*8.0), 3.25 (1H, m), 2.50 (6H, m), 1.10 (3H, t, *J*7.0); GC-MS (*m*/*z*): 362 (2), 334 (5), 169 (30), 165 (35), 139 (10), 113 (20), 69 (100).

(iv) 1-(9-Fluorenyl)-1-hexanone (**7c**) (20%) δ_H (500 MHz; $CDCl_3$) 7.32–7.88 (8H, m), 4.60 (1H, s), 3.35 (2H, m), 2.30 (8H, m), 0.90 (3H, t, *J*7.0); GC-MS (*m*/*z*): 264 (15), 165 (70), 139 (8), 99 (100), 71 (70), 43 (73).

9-(3,3-Dimethyl-1-trimethylsilyl-1,2-epoxybut-1-yl)-9*H*-fluoren-9-ol 1d. 9-(2,2-Dimethylpropylidene)fluorene[36] **4d** (100% of products by GC) δ_H (500 MHz; $CDCl_3$) 7.60–7.98 (4H, m), 7.24–7.40 (4H, m), 6.93 (1H, s), 1.52 (9H, s); GC-MS (*m*/*z*): 234 (56), 219 (100), 204 (28), 191 (30), 178 (38), 165 (65).

Laser flash photolysis

The laser system has been previously described.[37] The allene oxide precursors were dissolved in TFE to give a solution with an absorbance of *ca.* 0.4 at 308 nm, and the solutions were then irradiated with 308 nm laser pulses from an excimer laser (37 mJ/pulse, 6 ns pulse width). Due to the high photosensitivity of the precursors to laser irradiation, each sample was subjected to a single laser pulse. A flow system was used in the generation of the absorption spectra.

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