

Photo-Stevens Rearrangement of 9-Dimethylsulfonium Fluorenylide

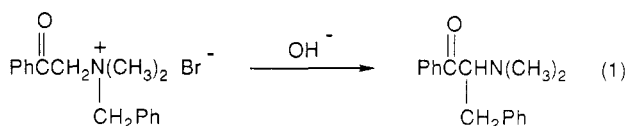
Jian-Jian Zhang and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

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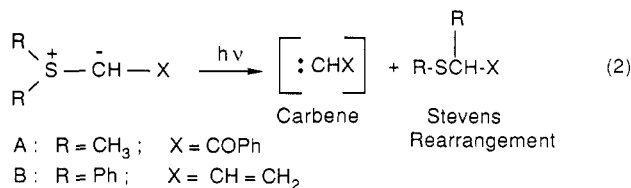
The direct irradiation of 9-dimethylsulfonium fluorenylide (DMSF) in acetonitrile or THF gives primarily the Stevens rearrangement product 9-methyl-9-(methylthio)fluorene and the dimeric bis[9-(methylthio)fluorenyl]. The mechanism of this reaction was investigated by kinetic, product, and isotope tracer techniques. The results indicate that the primary photochemical step is bond homolysis from an σ^* singlet state of the ylide. Oxidation of the ylide does not lead to chemical reaction.

In 1928 Stevens and co-workers reported that treatment of phenacyldimethylammonium bromide with base results in its rearrangement to 2-(dimethylamino)-3-phenylpropionophenone (eq 1).¹ This transformation has come to be generally known as the Stevens rearrangement.



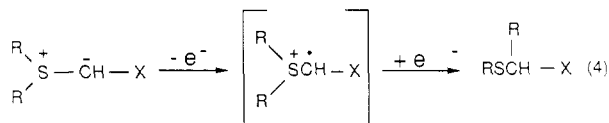
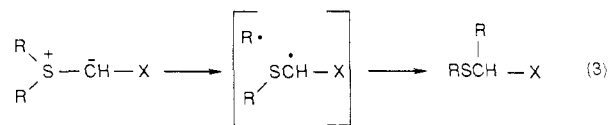
Subsequent research has shown that the Stevens rearrangement proceeds through an intermediate ylide, and that it also occurs in sulfonium and phosphonium compounds.² Special attention was drawn to the mechanism of the Stevens rearrangement when it appeared that it might be an exception to the principles of conservation of orbital symmetry. The [1,2]-sigmatropic shift in the ylide proceeds with (partial) retention of the configuration of the migrating group in defiance of the allowed (but sterically impossible) inversion for a concerted process and the expectation of racemization for the simplest stepwise pathways. This dilemma was resolved by experiments that supported formation of intermediate short-lived radicals that coupled to form products in competition with their rotation and diffusion apart.³ It is well-known that the topological requirements for rearrangement of electronically excited species are in general precisely opposite those of the corresponding ground states. Thus, an electronically excited ylide undergoing the Stevens rearrangement might follow an uninhibited, concerted path to the product of the retained configuration.

The photochemistry of sulfonium ylides has not been studied in detail. Trost reported that irradiation of dimethylsulfonium phenacylide gives products primarily from carbene formation and a low yield of propiophenone from presumed secondary photolysis of the Stevens rearrangement product (eq 2).⁴ It was also found that irra-



diation of diphenylsulfonium allylide gives both carbene-derived and Stevens rearrangement products.⁵ Caserio and co-workers studied the photochemistry of some cyclic, carbonyl-stabilized sulfonium ylides and reported products characteristic of the Stevens rearrangement.⁶ Maki and Hiramitsu observed that irradiation of some heterocyclic ylides gives products derived from Stevens rearrangement.⁷ More recently, Griller and co-workers reported that irradiation of diazofluorene in the presence of sulfides gives Stevens rearrangement products presumably by secondary photolysis of the first-formed ylide.⁸ Since some ylides that do not rearrange thermally do undergo facile photo-Stevens reaction, this route could prove to be a useful, general, synthetic transformation.

The mechanism of the thermal Stevens rearrangement has been carefully investigated. Homolysis of a carbon-heteroatom bond to form a neutral radical pair is believed to be the critical initial step in most examples⁹ of this process (eq 3). This conclusion is supported by isotope tracer results, CIDNP evidence, stereochemical probes, and solvent viscosity studies.³ An alternative path considered first by Lepley has single-electron oxidation of the ylide as the key initial step.¹⁰ This process yields a radical cation, which could rearrange to give characteristic Stevens products (eq 4). This possibility was considered again



more recently by Radom and co-workers who calculated theoretical reaction paths for some ionized ylides, which they call "ylidions".¹¹ Their findings suggest that the prototype sulfonium ylidion ($\text{H}_2\text{SCH}_2^{+\cdot}$) exists in a potential minimum and will not spontaneously rearrange.

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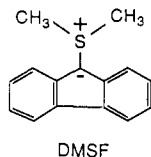
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We report herein the examination of the photochemistry of 9-dimethylsulfonium fluorenylide (DMSF); its irradiation gives the Stevens rearrangement product by a dissociative mechanism, but its one-electron oxidation to the ylidion does not initiate this reaction.



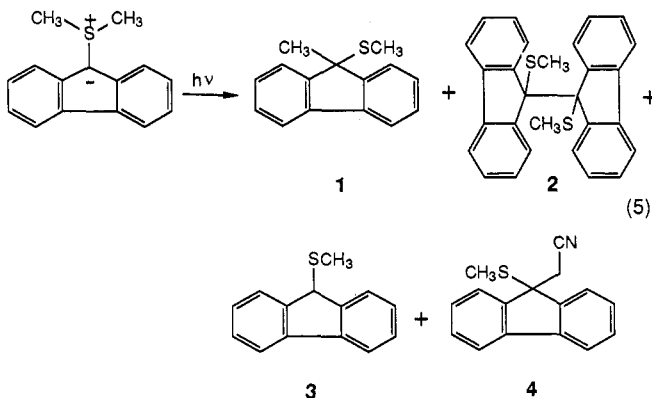
Results

(1) Absorption Spectroscopy. The ylide DMSF was prepared according to the literature procedure by deprotonation of the sulfonium salt.¹² It is a stable, air-sensitive, pale yellow solid. The UV-visible spectrum of DMSF in acetonitrile shows two absorption features, a strong band ($\epsilon = 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) at 255 nm and a weaker band ($\epsilon = 4.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) with a maximum at 362 nm. In some samples there is an additional very weak absorption band with a maximum in the visible region (ca. 450 nm) due to contamination by a trace (<0.7%) of bisfluorenylidene; its presence does not affect the photochemistry of the ylide.

DMSF fluoresces weakly in fluid solution at room temperature and more strongly at 77 K in a frozen 2-methyltetrahydrofuran glass. The fluorescence emission spectrum has a maximum at ca. 455 nm (excitation at 360 nm), and the emission intensity decreases appropriately as the ylide is consumed by irradiation. The lifetime of the emitting state is less than 2 ns at room temperature and is 40 ns at 77 K. Observation of fluorescence shows that the singlet excited state of this ylide does not dissociate immediately on excitation.

(2) Electrochemistry. The electrochemical behavior of DMSF was investigated by cyclic voltammetry in acetonitrile solution. The ylide shows an irreversible, one-electron oxidation wave with peak position at ca. 1.3 V vs SCE.

(3) Photolysis in Solution. Direct irradiation of a nitrogen-purged acetonitrile solution of DMSF at room temperature (350 nm, Rayonet photoreactor) gives two major and two minor products. Thermolysis of the ylide in refluxing acetonitrile for 24 h does not give any reaction. The products of the photolysis were identified spectroscopically and by comparison with authentic samples independently prepared to be 9-methyl-9-(methylthio)fluorene (1, 52%), bis[9-(methylthio)fluorenyl] (2, 35%) formed from the dimerization of 9-(methylthio)fluorenyl radicals, 9-(methylthio)fluorene (3, <5%), and 9-(cyano-methyl)-9-(methylthio)fluorene (4, <5%) (eq 5). The



relative composition of the product mixture stays constant throughout the irradiation since all products are stable and essentially transparent at the irradiating wavelength. Similar results are obtained from photolyses carried out at 254 nm except that dimer 2 is converted by secondary irradiation to bisfluorenylidene. The quantum efficiency for consumption of DMSF at room temperature in acetonitrile was measured by comparison with ferrioxalate actinometry to be 0.077. The reaction products and efficiency are unaffected by addition of tetramethyldiazetidine dioxide (TMDD, a triplet quencher, $4.4 \times 10^{-3} \text{ M}$, $E_T = 42 \text{ kcal/mol}$) to the mixture. The singlet energy of DMSF is greater than that of the analogous fluorenone; therefore, we expect that its triplet energy also will be greater than that of the ketone (53 kcal/mol). Thus, this finding indicates that long lived triplet excited states are not intermediates in the photo-Stevens rearrangement of this ylide.

The possibility that irradiation of DMSF leads to reversible cleavage of the fluorene-sulfur bond and formation of fluorenylidene was examined by including sufficient (2.0 M) methyl alcohol or styrene in the reaction solution to trap the carbene.¹³ These reagents are known to react rapidly and irreversibly to give products uniquely characteristic of fluorenylidene. No carbene-derived products could be detected under these conditions from photolysis of DMSF either at 254 or at 350 nm.

A classical crossover experiment was used to decide if formation of the Stevens product occurred by an inter- or intramolecular process. Irradiation of a 1:1 mixture of hexadeuterio-DMSF [$(\text{CD}_3)_2$] and DMSF in acetonitrile at room temperature gives the results displayed in Table I. The Stevens product is formed completely (within the 5% experimental error) by an intramolecular reaction, but dimer 2 is revealed by this experiment to result from the combination of two free 9-(methylthio)fluorenyl radicals, which of course must be so.

The temperature and solvent dependence of DMSF photolyses were examined to help define the reaction mechanism. As the viscosity of the solvent is increased by cooling the reaction mixture to -15°C or by changing the solvent from acetonitrile to benzonitrile, the yield of the Stevens rearrangement product increases at the expense of dimer 2; the data are summarized in Table II. This behavior is characteristic of the formation of free radicals in the primary photochemical step and their subsequent partitioning between product formation by "in-cage" recombination and escape to bulk solution.

Laser transient absorption spectroscopic experiments support the formation of free-radical intermediates in the photolysis of this ylide. Irradiation of DMSF with a nitrogen laser (337 nm, 13 ns, 7 mJ) in acetonitrile solution generates a transient species within the rise time of the laser pulse. The transient intermediate decays over a period of several hundred microseconds. The absorption spectrum of the transient product shows an apparent maximum at 485 nm; a position consistent with other fluorenyl radicals that have been observed.¹³ The same transient spectrum can be generated by laser irradiation of a solution of 9-(methylthio)fluorene in di-*tert*-butyl peroxide. Neither the yield or the lifetime of the transient product formed from irradiation of the ylide are affected by TMDD. These experiments support assignment of the transient species to the 9-(methylthio)fluorenyl radical and

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Table I. Crossover Experiment with Deuterium-Labeled Ylide in Acetonitrile

DMSF- <i>d</i> ₀ ^a	DMSF- <i>d</i> ₆	1- <i>d</i> ₀ ^c	1- <i>d</i> ₆	1- <i>d</i> ₃	2- <i>d</i> ₆ ^d	2- <i>d</i> ₆	2- <i>d</i> ₃
48 ^b	52	50	42	5	28	22	46
48	53	49	45	3	28	21	47

^aDMSF-*d*₀ = FLS(CH₃)₂; DMSF-*d*₆ = FLS(CD₃)₂. ^bProportions of ylide in starting mixture determined by ¹H NMR spectroscopy. ^c1-*d*₀ = FL(CH₃)(SCH₃); 1-*d*₆ = FL(CD₃)(SCD₃); 1-*d*₃ = FL(CD₃)(SCH₃) + FL(CH₃)(SCD₃). ^dThe deuteriated dimers as for 1 above.

Table II. Solvent and Temperature Dependence of the Photoproducts from DMSF

solvent	temp, °C	product yields, %			
		1	2	3	4
CH ₃ CN	35	52	35	~5	~5
CH ₃ CN	-15	62	24	~5	~5
PhCN	35 ^a	80	18		
PhCN	-15	86	12		

^aThese results are unaffected by addition of 9,10-dihydroanthracene to scavenge cage-escaped radicals.

exclude the possibility that its precursor is a long-lived (τ greater than 15 ns) species (the triplet ylide, for example).

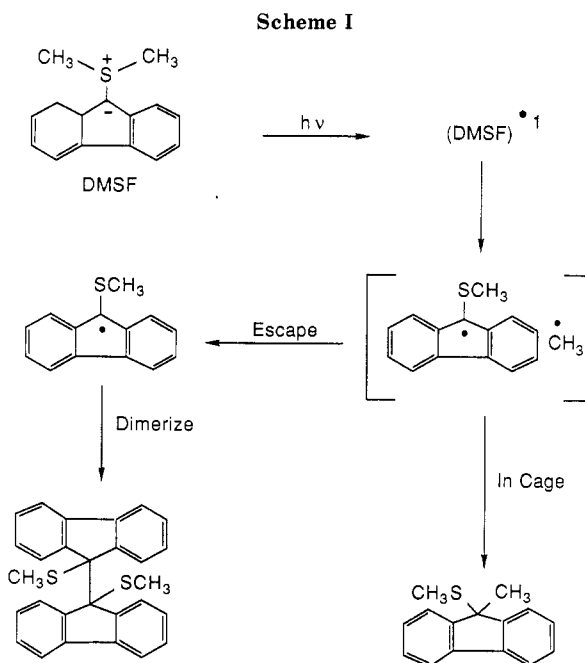
(4) **One-Electron Oxidation of DMSF.** We examined the possibility that the Stevens rearrangement of DMSF could be initiated by oxidation of the ylide. Electronically excited states were used as the oxidants in the first set of experiments.

The usual Stern-Volmer experiments show that the fluorescence of *N,N'*-diacetylindigo (DAIN) in acetonitrile is quenched at a diffusion limited rate ($1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) by DMSF. The mechanism for quenching cannot be energy transfer because the singlet energy of DAIN (48.8 kcal/mol)¹⁴ is well below that of the ylide (67.7 kcal/mol). However, calculations from the Weller equation show that the free energy for electron transfer from the ylide to singlet excited DAIN is exothermic by ca. 5 kcal/mol and, therefore, quenching by this route is expected to occur at the diffusion limited rate.¹⁵ Irradiation of an acetonitrile solution of DMSF and DAIN with a filtered sodium vapor lamp (510 nm, only DAIN absorbs the light) for 24 h does not give any reaction. Similarly, irradiation of electron-transfer sensitizers thioindigo or (dicarboxybi-pyridyl)ruthenium(II)¹⁶ in acetonitrile solutions of DMSF does not lead to reaction of the ylide.

Conventional, thermal, one-electron oxidants are similarly incapable of initiating the Stevens rearrangement of DMSF. No rearrangement product could be detected when acetonitrile solutions of DMSF were treated with cupric perchlorate, tris(4-bromophenyl)ammonium hexachloroantimonate, or dioxygenyl hexafluoroantimonate.¹⁷

Discussion

The results show that photolysis of DMSF leads to cleavage of a carbon-sulfur bond in the excited singlet state and formation of the 9-(methylthio)fluorenyl and methyl radicals (Scheme I). The alternative bond cleavage to form fluorenylidene and dimethyl sulfide does not occur. The radical pair formed in the initial bond cleavage step may recombine within the solvent cage to reform the starting ylide or to form the Stevens rearrangement product. These radical recombination reactions apparently



compete with escape of the radicals from the cage. The cage-escaped radicals do not give Stevens rearrangement product; instead, the free methyl radical reacts with the solvent to give (presumably) methane and the cyanomethyl product 4. The free 9-(methylthio)fluorenyl radical is consumed predominantly by its dimerization to give 2.

There is no evidence that the hoped for concerted Stevens rearrangement from the ylide excited singlet state competes with the simple bond homolysis reaction. This outcome may be a consequence of the electronic nature of the excited state. Gassman and co-workers¹⁸ concluded from calculations that the optimum conformation for simple sulfur ylides has the lone-pair electrons of the sulfur and of the carbanion in perpendicular planes. This prediction is supported by an X-ray study of dimethylsulfonium cyclopentadienylylide.¹⁹ A qualitative PMO assessment of the states of sulfonium ylides for this geometry reveals that the lowest singlet state has a predominantly $n\sigma^*$ (nonbonding of the carbanion, antibonding for the methyl-sulfur bond) configuration.²⁰ With this in mind, it is clear that the carbon-sulfur bond order decreases (crudely to zero) in the excited state, and rapid homolysis to radicals is the expected result.

Oxidation of DMSF to the ylidion does not initiate the Stevens rearrangement. This may simply be a consequence of an unfavorable enthalpy for conversion of this ylidion to the radical cation of 1. The substituted 9-fluorenyl radical is specially stabilized by resonance, and its conversion to a sulfide radical cation may impose an insur-

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mountable activation barrier.

Experimental Section

General Procedures. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a Varian XL-200 (200 MHz, FT) spectrometer. Mass spectral data were obtained on a Varian MAT CH-5 or 731 mass spectrometer. Fluorescence spectra were recorded on a Farrand Mark I spectrofluorometer. Direct photolyses were carried out in a Rayonet photochemical reactor equipped with 350-nm or 254-nm lamps. The sensitization experiments were performed by irradiation with a sodium vapor lamp equipped with a glass filter that cuts off light below 510 nm. Elemental analyses were performed by the Analysis Laboratory, University of Illinois. All melting points are uncorrected. The laser spectrometer has been described previously.²¹ TMDD was prepared by the procedure of Ullman.²²

Preparation of 9-Dimethylsulfonium Fluorenylide (DMSF). A 10% aqueous sodium hydroxide solution was added to a stirred solution of 2.2 g (72 mmol) of dimethyl-9-fluorenylsulfonium bromide^{12b} in 50 mL of water until the precipitation of a solid product ceased. The product was collected by filtration and washed successively with water, 95% ethanol, absolute ethanol, and ether to give 0.91 g (56%) of a pale yellow solid: mp 121–122 °C (lit. mp 120–122 °C,^{12b} mp 70–75 °C,^{12a} mp 126–127 °C²³); ^1H NMR (CD_3CN) δ 8.01 (d, 2 H), 7.65 (d, 2 H), 7.24 (dt, 2 H), 6.79 (dt, 2 H), 3.03 (s, 6 H); ^{13}C NMR (CDCl_3) showed eight different carbons at δ 138, 134, 129, 122, 120, 166, 114, 28. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.87; H, 6.18, S, 13.96.

Preparation of 9-Methyl-9-(methylthio)fluorene (1). A solution of 0.64 g (6.0 mmol) of lithium diisopropylamide (LDA) in 30 mL of THF at -78 °C and 1.08 g (6.0 mmol) of 9-methylfluorene under N_2 was stirred for 30 min, and then, 0.564 g (6.0 mmol) of dimethyl disulfide in 5 mL of THF was added dropwise. The mixture was warmed to room temperature and 10 mL of water was added. The usual extractive workup with diethyl ether gave a yellow solid, which was recrystallized from methanol to give 0.57 g (42%) of 1 as flesh-colored crystals: mp 66–67 °C (lit.²⁴ 63–65 °C); ^1H NMR (CD_3CN) δ 7.77 (m, 2 H), 7.58 (M, 2 H), 7.40 (m, 4 H), 1.74 (s, 3 H), 1.31 (s, 3 H); MS (EI), m/e 226 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.60; H, 6.09; S, 14.45.

Preparation of 9-(Methylthio)fluorene (3). A solution of sodium methyl thiolate (0.70 g, 10 mmol) was added dropwise to 2.44 g (10 mmol) of 9-bromofluorene in 60 mL of DMSO at 0 °C under N_2 . The reaction mixture was stirred at room temperature for 2 h, and then, 100 mL of ice-water was added. The usual extractive workup with diethyl ether gave a brown oil, which was recrystallized from methanol to give 0.72 g (34%) pale yellow crystals: mp 48–49 °C (lit.²² 47–48 °C); ^1H NMR (CDCl_3) δ 7.69 (m, 4 H), 7.38 (m, 4 H), 4.87 (s, 1 H), 1.38 (s, 3 H); MS (EI), m/e 212 (M^+).

Preparation of 9-(Cyanomethyl)-9-(methylthio)fluorene (4). Methylolithium (0.682 mL, 1.5 mmol) was added dropwise to a solution of 0.318 g (1.5 mmol) of 3 in 30 mL of THF at -78 °C under N_2 . Then 0.10 mL (1 equiv) of chloroacetonitrile in 10 mL of THF was added all at once. The reaction was warmed to room temperature, stirred for 2 h, and quenched with 40 mL of water. The usual extractive workup with diethyl ether gave a yellow solid, which was purified on a Chromatron with 20% ethyl acetate in hexane as eluant to give 0.182 g (48.3%) of 4 as a pale yellow solid: mp 106–109 °C; ^1H NMR (CDCl_3) δ 7.69 (m, 4 H), 7.42 (m, 4 H), 3.05 (s, 2 H), 1.39 (s, 3 H); MS (EI), m/e 251 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{SN}$: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.42; H, 5.36; N, 5.45; S, 12.77.

Direct Irradiation of DMSF at 350 nm. Typical Procedure. A solution of DMSF was placed in a Pyrex round-bottomed flask equipped with a stir bar and rubber septum. The solution was purged with N_2 for 30 min, and a balloon filled with N_2 was fitted to the flask via a syringe needle. The sample was irradiated in a Rayonet photochemical reactor with 350-nm lamps while being stirred. The reaction was examined periodically by UV-vis spectroscopy. The UV absorption band of DMSF at 362 nm disappeared as the reaction proceeds. The solvent was removed under reduced pressure, and the products were characterized by ^1H NMR spectroscopy.

A. Irradiation in Acetonitrile at 350 nm. A 3.84×10^{-3} M solution of DMSF in acetonitrile was irradiated at 350 nm until the UV spectrum showed complete reaction. Evaporation of the solvent under reduced pressure gave an orange solid. The crude product was analyzed by ^1H NMR spectroscopy, which showed that the two major products were 1 (52.5%) and 2 (35.0%); the yields of two minor products 3 and 4 were both less than 5%. Dimer 2 was isolated by MPLC using 10% ethyl acetate in hexane as eluant to give white-yellowish crystals: mp 230–232 °C; ^1H NMR (CDCl_3) δ 7.20 (m, 16 H), 1.21 (s, 6 H); MS (EI), m/e 422 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{S}_2$: C, 79.58; H, 5.25; S, 15.17. Found: C, 79.30; H, 5.53; S, 15.17.

B. Irradiation of DMSF at 254 nm. A 7.10×10^{-3} M solution of DMSF in acetonitrile was irradiated in a Rayonet photochemical reactor equipped with 254-nm lamps. The UV spectrum of the reaction solution shows that a new absorption band at 450 nm appears at the same rate as starting material (362 nm) is consumed. When the irradiation was complete, the solvent was evaporated; a red-orange solid remained. The products were isolated by chromatography. In addition to those products isolated from irradiation at 350 nm, a red solid, mp 188–189 °C, was also obtained. Its spectral properties are identical with those of authentic bisfluorenylidene. Irradiation of dimer 2 under these conditions converts it cleanly to bisfluorenylidene.

Crossover of DMSF- d_6 and DMSF- d_0 . Dimethylsulfonium fluorenylide DMSF- d_6 (0.119 g, 0.51 mmol) and DMSF- d_0 (0.11 g, 0.49 mmol) were dissolved in 180 mL of freshly distilled acetonitrile. The solution was irradiated at 350 nm until the UV absorption band of DMSF at 362 nm had completely disappeared. The solvent was removed under vacuum. Compounds 1 and 2 were isolated by MPLC with hexane as eluant. The isotope incorporation data are listed in Table II. 1: MS (FI, 731) m/e (area) 226 (172 411), 227 (31 855), 228 (11 388), 229 (12 748), 230 (31 70), 231 (79 56), 232 (162 139); MS (FI, 731), m/e (area) for unlabeled 226 (M^+ , 113 096), 227 (19 941), 228 (66 32), 229 (970). 2: MS (FI, 731), m/e (area) 422 (195 49), 423 (61 97), 424 (37 74), 425 (33 567), 426 (10 795), 428 (16 142), 429 (86 91), 430 (31 98); MS (FI, 731), m/e (area) for unlabeled 422 (M^+ , 79 226), 423 (24 559), 424 (10 028), 425 (23 29).

Irradiation of DMSF in Acetonitrile Solution Containing Styrene or Methanol. A 3.50×10^{-3} M solution of DMSF in acetonitrile containing freshly distilled styrene (2 M) was placed in a Pyrex round-bottomed flask and purged with N_2 for 30 min. The sample was irradiated at 350 nm until the UV absorption band of DMSF at 362 nm had completely disappeared. The solvent was removed under vacuum. The ^1H NMR spectrum of the residue showed that 1 and 2 were the major products. The cyclopropane formed by addition of fluorenylidene to styrene could not be detected. Similarly, irradiation in the presence of methanol gives no 9-methoxyfluorene. However, care must be taken to avoid the thermal Sommelet rearrangement for the ylide under these conditions.

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Registry No. 1, 84811-78-9; 2, 84811-81-4; 3, 59431-17-3; 4, 112270-23-2; DMSF, 72393-25-0.

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