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Anthracene-bound sulfonium salts: highly efficient photoinitiators for cationic polymerization

A new synthesis of sulfonium salts which avoids the use of silver salts

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Abstract

The low absorptivity of triarylsulfonium salts above 320 nm limits their utilization of longer wavelength emission from light sources. Herein we report the synthesis and photoactivity of anthracene-bound sulfonium salts, in which the sulfonium salt is insulated from the anthracene chromophore by a saturated chain. The salts efficiently absorb radiation between 330 and 410 nm owing to the strong anthracene absorptivity in this spectral region. The efficiency of utilization of the absorbed radiation for generating cationic initiators is strongly dependent on the substituents attached to the sulfonium ion. Evidence is presented in support of generation of initiators for cationic polymerization by photo-induced electron transfer from the anthracene chromophore to the sulfonium group, wherein the efficiency of electron transfer is dependent on the sulfonium ion substituents. A new synthesis of sulfonium salts is also provided, which occurs by direct alkylation of diaryl dialkyl and arylalkyl sulfides by oxiranes in the presence of strong acids having non-nucleophilic anions.

Keywords: Absorption; Electron transfer; Fluorescence; Laser flash; Photoresists; Photosensitization; Redox potentials; Synthesis; Transient intermediates; UV curing

1. Introduction

Diaryliodonium and triarylsulfonium salts with non-nucleophilic anions are well-known photoinitiators for cationic polymerization [1–3]. Furthermore, although the onium salts exhibit relatively low absorptivity above 320 nm, their spectral response can be extended into the near-UV and visible spectral regions by photosensitization [4,5]. Photosensitization is known to occur both by energy and electron transfer [5,6]. However, photosensitization by energy transfer is precluded for the longer wavelength absorbing photosensitizers of interest, since their excitation energies are insufficient to populate the onium salt excited states. Accordingly, strong evidence has been provided for electron transfer-induced photosensitization of cationic polymerization by such photosensitizers, including anthracene derivatives [7,8].

As cationic polymerization proceeds, the efficiency of bimolecular photosensitization by electron transfer is expected to diminish owing to reduced mobility of the generally short-lived excited state photosensitizer donor and onium salt acceptor. This self-deceleration effect is expected to be particularly pronounced in coatings and imaging applications wherein liquid films are converted into solids or solid films are insolubilized by cross-linking. In many such applications, it is particularly important to minimize the level of unreacted functionality, so that rapid reaction rate at high extents of conversion are highly desirable.

Accordingly, we initiated a project to synthesize and evaluate the photoactivity of anthracene-bound sulfonium salts, having the general structure shown, wherein ‘An’ represents the 9-anthracenyl group, ‘R’ represents a three to four atom connecting link, ‘R^1’ and ‘R^2’ are phenyl or alkyl groups and ‘X^-’ is a non-nucleophilic anion [9].

$$\mathrm{An{-}R{-}S^{+}{-}R^1R^2X^-}$$

The anthracene-bound sulfonium salts exhibit high photoactivity both in solid photoresists and liquid coating compositions [10], which prompted further mechanistic

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studies, including quantum yield determinations, as well as stationary and time resolved spectroscopy.

2. Experimental

2.1. Synthesis

2.1.1. 3-(9-Anthracenyl)-propyl diphenylsulfonium hexafluoroantimonate (2)

To a 1 l three-neck flask with ground glass joints, fitted with a dropping funnel, condenser, nitrogen purge and mercury sealed stirrer, were added to *t*-butyl alcohol (200 ml), followed by potassium (4.88 g, 130 mmol) and anthrone (**1**) (19.4 g, 100 mmol) (Aldrich Chemical) dissolved in *t*-butyl alcohol (10 ml). Subsequently, acrylonitrile (7.3 ml, 100 mmol) in *t*-butyl alcohol (40 ml) was added dropwise over a period of 1 h, during which time a bright red precipitate separated from the solution. This mixture was refluxed for 2 h, which resulted in a bright red solution. After cooling to room temperature, concentrated hydrochloric acid (11 ml) was added in water (225 ml), followed by distillation, during which additional water (100 ml) is added. After removal of about 350 ml distillate, the contents remaining in the flask were cooled in an ice-bath, resulting in the separation of a brown oil. The solution was decanted from the oil, which was taken up in concentrated hydrochloric acid (100 ml) and refluxed for 2 h, during which time a solid precipitates. The solid precipitates was collected by filtration, washed with water and dissolved in concentrated ammonium hydroxide (360 ml), diluted by water (240 ml). Zinc dust (60 g), activated with copper sulfate, was added and the mixture was heated at 90–95 °C in an oil bath for 4 h, cooled and filtered. The filtrate was extracted with diethyl ether. Acidification of the aqueous layer with hydrochloric acid resulted in the separation of a tan oil, which solidified on standing. The solid was filtered, washed with water and dried to provide 3-(9-anthracenyl)-propionic acid (22.5 g, 90 mmol), mp 190–193 °C. Recrystallization from glacial acetic acid raised the mp to 194–195 °C.

Using the above reaction vessel, 3-(9-anthracenyl)-propionic acid (15 g, 60 mmol) in dry tetrahydrofuran (30 ml) was added to a stirred suspension of lithium aluminum hydride (5.0 g, 132 mmol) in dry tetrahydrofuran (4 ml) over a 2 h period. After stirring overnight, the mixture was place in an ice-bath, ethyl acetate (10 ml) was slowly added, followed by ice water (75 ml) and an aqueous solution of 20% hydrochloric acid (20 ml). After stirring for 2 h, the mixture was extracted with diethyl ether. The organic phase was washed with saturated sodium chloride, dried over magnesium sulfate and concentrated to provide crude 3-(9-anthracenyl)-propanol, which was recrystallized from diethyl ether-hexane to yield the purified alcohol (10.0 g, 0.042 mol).

Carbon tetrabromide (18 g, 0.054 mol) was added to a mixture of the anthracenyl propanol (12.7 g, 54 mmol) and triphenylphosphine (19 g, 73 mmol) in tetrahydrofuran (30 ml) and diethyl ether (100 ml). The resulting mixture was stirred for about 60 h, followed by evaporation of the solvent. The crude 3-(9-anthracenyl)-propyl bromide was purified by adding silica gel to a dichloromethane solution, followed by stirring for 1 h, filtration and evaporation of the solvent.

A slurry of diphenyl sulfide (0.62 g, 3.3 mmol) and silver hexafluoroantimonate dioxane complex ($AgSbF_6{\cdot}3C_4H_8O_2$; 2.2 g, 3.6 mmol) in dichloromethane (2 ml), was placed in a three-neck flask (25 ml), equipped with a dropping funnel and nitrogen purge. A solution of the anthracenyl propyl bromide (1 g, 3.3 mmol) in dichloromethane (5 ml) was added, over a 5 min period. The reaction flask was stopped and protected from light with aluminum foil. The mixture was stirred at room temperature for 10 days, after which the dark-colored mixture was transferred to an Ehrlenmeyer flask using warm dichloromethane to provide a total volume of 75 ml. Decolorizing carbon and Celite were added (0.1 g of each) and the contents were heated to boiling, followed by filtration. The filtrate was evaporated to dryness to provide a dark-colored residue (2.49 g), which was extracted three times with hexane (50 ml each time) to remove unreacted starting materials. The resulting solid (2.15 g) was recrystallized from dichloromethane–diethyl ether to provide gold crystals (1.2 g, 1.3 mmol), mp 201–203 °C, of the desired sulfonium salt **2**, as evidenced by IR, UV, NMR, and elemental analysis. Calculated for $C_{27}H_{25}F_6SSb$: C, 52.5; H, 4.1; S, 5.2. Found: C, 52.7; H, 4.0; S, 5.1.

2.1.2. 9-Anthracenyl oxiranylmethyl ether (3)

Anthrone (**1**) (9.7 g, 50 mmol) was placed in a 100 ml round bottom three-neck flask equipped with a dropping funnel, nitrogen purge, magnetic stirrer and condenser. Oxiranylmethyl chloride (23 g, 250 mmol; Eastman Kodak) and absolute ethanol (8 ml) were added to the reaction flask, which was heated to 65 °C, during which time most of the anthrone dissolved.

Sodium hydroxide (2.6 g, 65 mmol) was dissolved in water (3.0 ml) and introduced into the reaction flask dropwise over 2 h. During the addition, the reaction was allowed to cool to room temperature, followed by stirring at room temperature for 24 h.

A precipitate formed during this period, after which chloroform (50 ml) was added to the flask. Most of the precipitate dissolved in chloroform and the remaining precipitate was soluble in water. Separation of the chloroform, followed by evaporation provided an oily orange solid (12.5 g).

The crude product was crystallized from hexane. Prior to crystallization, the hot hexane was decanted from a small amount of a dark orange oil (about 2 g), which remained insoluble. The first crop of crystallized product amounted to 6.3 g (25 mmol), mp 96–100 °C; a second crop amounted to 2.1 g (8.4 mmol), mp 85–95 °C. The analytically pure ether **3**, mp 99.5–100 °C, lit mp 74–76 °C [11], could be obtained by recrystallization from dichloromethane–hexane.

The product was characterized by IR, UV, NMR, and elemental analysis. ^{1}H NMR (chloroform-d_1): δ 2.8 (m, 2H), 3.5 (m, ^{1}H), 4.3 (m, 2H), 7.3–8.7 (m, 9ArH). Calculated for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.6; H, 5.6.

2.1.3. 3-(9-Anthracenyloxy)-2-hydroxypropyl diphenylsulfonium hexafluoroantimonate (4a)

Diphenyl sulfide (6.0 g, 32 mmol) and hexafluorantimonic acid hexahydrate (6.5 g, 19 mmol) (Pennwalt) were placed in a 50 ml round bottom flask equipped with a magnetic stirrer and dropping funnel. A solution of 9-anthracenyl oxiranylmethyl ether (3.0 g, 12 mmol) and diphenyl sulfide (6.0 g, 33 mmol) in acetonitrile (6 ml) was added dropwise to the reaction flask over a period of 1 h. Water (10 ml) was added and most of the acetonitrile was removed by rotary evaporation. Subsequently, dichloromethane (50 ml) was added, which was separated from the aqueous phase, washed with aqueous sodium bicarbonate, dried over magnesium sulfate, filtered and rotary evaporated to provide a yellow oil (16.8 g). The oil was washed with hexane (3× 10 ml) to remove the excess diphenyl sulfide and the resulting viscous oil (5.2 g) was crystallized from dichloromethane–hexane to yield pale yellow crystals (2.0 g, 3.0 mmol), mp 172–175 °C, corresponding to 25% yield of the desired sulfonium salt **4a**, as evidenced by IR, UV, NMR, and elemental analysis. The analytically pure salt, mp 172–175 °C was obtained by further recrystallization from ethanol. ^{1}H NMR (acetone-d_6): δ 4.4 (d, 2H), 4.9 (m, 3H), 5.8 (s, 1H), 7.3–8.5 (m, 19ArH); ^{13}C NMR (dimethylsulfoxide-d_6): δ 47 *CH(OH), 65 ($O-^*CH_2-$), 78 ($-^*CH_2S+$), 120–145 (ArC*), 150 (ArC$^*-$O). Calculated for $C_{29}H_{25}F_6O_2SSb$: C, 51.7; H, 3.7; S, 4.8. Found: C, 51.9; H, 3.7; S, 4.7.

2.1.4. 3-(9-Anthracenyloxy)-2-hydroxypropyl methyl phenylsulfonium hexafluoroantimonate (4b)

The same procedure as above, except that methyl phenyl sulfide was used in place of diphenyl sulfide, provided pale yellow crystals of the desired sulfonium salt, mp 135–142 °C, in 55% yield, following crystallization from ethanol, as evidenced by IR, UV, NMR, and elemental analysis. The analytically pure sulfonium salt **4b**, mp 141–142 °C, was obtained by further recrystallization from ethanol. ^{1}H NMR (acetone-d_6): δ 3.5 (s, 3H), 4.4 (m, 4H), 4.9 (m, 1H), 7.3–8.7 (m, 14ArH). Calculated for $C_{24}H_{23}F_6O_2SSb$: C, 47.2; H, 3.8; S, 5.2. Found: C, 47.4; H, 3.7; S, 5.1.

2.1.5. 3-(9-Anthracenyloxy)-2-hydroxypropyl diethylsulfonium hexafluoroantimonate (4c)

The same procedure as above, except that diethyl sulfide was used in place of diphenyl sulfide, provides slightly colored crystals of the desired sulfonium salt **4c**, mp 119–123 °C, in 41% yield, following crystallization from 1,2-dichloroethane-hexane, as evidence by IR, UV, and NMR analysis. ^{1}H NMR (acetone-d_6): δ 1.7 (t, 3H), 3.7 (m, 4H), 4.05 (d, 2H), 4.45 (d, 2H), 5.0 (m, 1H), 5.8 (d, 1H), 7.3–8.7 (m, 9ArH).

2.1.6. 3-(9-Anthracenyloxy)-2-hydroxypropyl dimethylsulfonium hexafluoroantimonate (4d)

The same procedure as above, except that dimethyl sulfide was used in place of diphenyl sulfide, provides slightly colored crystals of the desired sulfonium salt **4d**, mp 109–119 °C, in 34% yield, following crystallization from dichloromethane, as evidence by IR, UV, and NMR analysis. Recrystallization raised the mp to 115–122 °C. ^{1}H NMR (acetone-d_6): δ 3.2 (s, 6H), 4.1 (d, 2H), 4.4 (d, 2H), 4.95 (m, 1H), 5.6 (s, 1H), 7.5–8.5 (m, 9ArH).

2.1.7. Reaction of 9-anthracenyl oxiranylmethyl ether with α-(ethylthio)-acetophenone

α-(Ethylthio)-acetophenone (8.0 g, 44 mmol; Fairfield Chemical) and hexafluoroantimonic acid hexahydrate (1.6 g, 4.6 mmol) were place in a 25 ml round bottom flask, equipped with magnetic stirrer and dropping funnel. The reaction flask was cooled to 0 °C in an ice-bath and a solution of 9-anthracenyl oxiranylmethyl ether (1.0 g, 4.0 mmol) in acetonitrile (7 ml) was added dropwise over a 45 min period. After stirring overnight, the volatiles were removed by rotoevaporation and the resulting oil was washed with hexane:benzene mixture (1:1) (3× 10 ml) to provide a yellow paste (2.8 g). Attempts to crystallize the paste dichloromethane-benzene resulted in a purified oil, which did crystallized from ethanol.

Recrystallization from ethanol provides white crystals (0.7 g), mp 151–152 °C. On the basis of IR, UV, and NMR analysis, the product was not the expected 3-(9-anthracenyloxy)-2-hydroxypropyl ethyl phenacylsulfonium hexafluoroantimonate (**4e**), but is assigned as ethyl oxiranylmethyl phenacylsulfonium hexafluoroantimonate (**5**). ^{1}H NMR (acetone d_6): δ 1.5 (t, 3H), 3.7 (m, 5H), 4.15 (m, 2H), 4.5 (d, 1H), 5.45 (m, 1H). Calculated for $C_{13}H_{17}O_2S$: C, 33.0; H, 3.6; S, 6.7. Found: C, 33.3; H, 3.6; S, 6.9.

2.1.8. 2-Hydroxy-3-phenoxypropyl diphenylsulfonium hexafluoroantimonate (6a)

Diphenyl sulfide (2.0 g, 11 mmol) and hexafluoroantimonic acid hexahydrate (0.9 g, 2.6 mmol) were placed in a 25 ml round bottom flask, equipped with a magnetic stirrer and dropping funnel. The flask was then cooled to 0 °C in an ice-bath and a solution of oxiranylmethyl phenyl ether (0.33 g, 2.2 mmol; Aldrich Chemical) in acetonitrile (1 ml) was slowly added dropwise, followed by stirring for 6 h at 0 °C. After stirring overnight, the volatiles were removed by rotoevaporation to provide an oily mixture to which water (5 ml) was added. The liquids were decanted from the resulting oil, which was dissolved in dichloromethane. The dichloromethane solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, filtered and evaporated. The resulting oil could not be crystallized, but was purified by dissolving in dichloromethane, followed by addition of diethyl ether to cause reprecipitation. The purified oil (0.35 g, 0.61 mmol, 28% yield) was identified as the desired salt **6a** by IR, UV, and NMR analysis. ^{1}H NMR (acetone-d_6): δ 4.3 (d, 2H), 4.8 (m, 3H), 5.8 (s, 1H), 6.7–7.5 (m, 18ArH).

*2.1.9. 2-Hydroxy-3-phenoxypropyl diethylsulfonium hexafluorantimonate (**6b**)*

The same procedure as above, except that diethyl sulfide was used in place of diphenyl sulfide, provided the desired salt **6b** as a purified oil in 25% yield. ^{1}H NMR (acetone-d_6): δ 1.5 (t, 6H), 3.6 (m, 4H), 4.2 (d, 2H), 4.7 (m, 1H), 5.2 (s, 1H), 6.7–7.5 (m, 6ArH).

*2.1.10. 2-Hydroxy-3-phenoxypropyl dimethylsulfonium hexafluoroantimonate (**6c**)*

The same procedure as above, except that dimethyl sulfide was used in place of diphenyl sulfide, provided the desired salt **6c** as a purified oil in 26% yield. ^{1}H NMR (acetone-d_6): δ 3.2 (s, 6H), 3.8 (m, 2H), 4.2 (d, 2H), 4.7 (m, 1H), 5.4 (d, 1H), 6.7–7.5 (m, 6ArH).

*2.1.11. 2-Hydroxycyclohexyl dimethylsulfonium hexafluoroantimonate (**7**)*

Dimethyl sulfide (1.5 g, 24 mmol) and hexafluoroantimonic acid hexahydrate (1.8 g, 5.2 mmol) were placed in a 50 ml round bottom flask equipped with a magnetic stirrer and dropping funnel. A solution of cyclohexene oxide (1.5 g, 15 mmol) and dimethyl sulfide (1.7 g, 27 mmol) was added dropwise. After stirring for 15 min, water (5 ml) was added and excess dimethyl sulfide was removed by rotoevaporation. The remaining liquid was decanted from the resulting oil, which was washed with hexane (3× 10 ml) and dissolved in dichloromethane. Crystallization from dichloromethane–hexane provided the desired salt **7** (0.5 g, 1.3 mmol) in 9% yield as white crystals, mp 82–91 °C. The analytically pure salt, mp 89–92 °C, was obtained by a second recrystallization. ^{1}H NMR (acetone-d_6): δ 1.25–2.7 (m, 8H), 3.1 (d, 6H), 3.6 (m, 1H), 3.9 (m, 1H), 5.0 (d, 1H), 7.5–8.5 (m, 9ArH). Calculated for $C_8H_{17}F_6OSSb$: C, 24.2; H, 4.3; S, 8.0. Found: C, 24.3; H, 4.2; S, 7.6.

2.1.12. 2-Hydroxycyclohexyl diphenylsulfonium hexafluoroantimonate

An attempt to prepare this compound by the above procedure, with the exception that diphenyl sulfide was used in place of dimethyl sulfide, was unsuccessful.

2.2. Photopolymerization studies

The anthracene-bound sulfonium salts were evaluated and compared as photoinitiators for cationic polymerization in a photoresist formulation of epoxy resins [10].[1] The photoinitiator (2.5 wt.% of epoxy resins) was dissolved in a mixture of a bisphenol A epoxy-formaldehyde condensate (SU-8, Celanese Corp; 78 wt.%), a bisphenol A epoxy (XD7342, Dow Chemical; 5 wt.%) and a bis-cycloaliphatic epoxy (CY-179, Ciba Geigy; 17 wt.%). Films (25 μm thick) were applied to a photoresist substrate by spin coating and exposed with a medium pressure, mercury arc lamp. Exposure was directed through a Stouffer 21-step transmission wedge, wherein absorbance of the wedge increases by a factor $2^{1/2}$ for each step from 1 to 21, thereby decreasing exposure intensity with increasing step number. Following exposure, the photoresist was heated at 100 °C for 10 min and developed with an appropriate solvent. Photoactivity of the anthracene-bound sulfonium salts was also compared with a commercial photoinitiator for cationic polymerization (MASH), consisting of a mixture of arylsulfonium hexafluoroantimonate salts. This material was provided as GE UVE 1014 (General Electric) and is currently available as UVI 6974 (Union Carbide).

Related studies were carried out on liquid UV curable epoxy coatings.[2] These studies included photosensitization of the MASH composition with 9-methylanthracene (**8**).

2.3. Acid quantum yields

Acid quantum yields were determined using a merocyanine dye indicator **9**, which exhibits a strong absorption maximum at about 600 nm. This absorption is absent in the protonated form **10**, which exhibits an absorption maximum at about 400 nm. The shift in absorption allows acid concentration to be determined sensitively by a photometric method [12].

A solution of the sulfonium salt (8×10^{-3} M) in acetonitrile (1 ml) was exposed using a OAI 30/5 exposure tool (xenon/mercury lamp) through 365 nm band pass filters. Photolysis was carried out to about 1% conversion and the number of photons absorbed was determined to be 4.8×10^{16} by chemical actinometry (Aberchrome 540). Following exposure, a solution of the dye (2×10^{-4} M) in acetonitrile (1 ml) was added to the photolyzed sulfonium salt solution for acid determination. The dye was also added to the sulfonium salt solution, prior to exposure, to determine the presence of acid impurity in the samples.

2.4. Stationary-state absorption and fluorescence measurements

Absorption spectra were recorded on a Hewlett-Packard 8451A Diode Array or IBM 9430 UV/Vis Spectrophotometer. Fluorescence spectra were recorded on a Spex DM3000f or Perkin Elmer MPF-44B Spectrofluorometer.

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[1] The solid photoresist studies were carried out at IBM Corp.

[2] The studies on liquid UV curable coatings were carried out at Ciba Geigy Corp.

Room temperature measurements were made using 1 cm^2 quartz cuvettes. Measurements at 77 K were made in a quartz Dewar cooled with liquid nitrogen. Sulfonium salt solutions exhibited an absorbance of about 0.1 at the exciting wavelength of 366 nm.

2.5. Laser flash studies

Laser flash experiments were carried out on solutions having absorbances between 0.1 and 0.6 at 337 nm. Solutions were bubbled with N_2 prior to the experiments.

Transient emission experiments were carried out using a Nitromite laser (PRA-100) that generated a 120 ps pulse at 337 nm as the exciting beam. The emission was passed through a monochromator (Bausch and Lomb 33-86-07). The output from the photomultiplier (Hamamatsu 928) was captured by a programmable digitizer (Tektronix 7912AO) interfaced with a computer (Tektronix 4052). Singlet lifetimes were calculated automatically by the computer using a home-written program. An average rate constant of 4 was taken for each measurement, which was repeated at least four times. Accordingly, singlet lifetimes were derived from an average rate constant of 16.

Room temperature singlet lifetimes were determined in 1 cm^2 square quartz cuvettes. Singlet lifetimes at 77 K in a methanol glass (80% methanol, 10% water, 10% acetonitrile) were determined in a quartz Dewar with a path length of about 0.2 cm.

Transient absorption measurements were conducted in 0.2 cm × 0.8 cm quartz cells. An excimer laser (Lambda-Physik EMG 100, N_2/He) was used to generate a 6 ns pulse of 337 nm radiation with a pulse energy of 7 mJ per pulse. Transient absorption spectra were obtained with a pulsed xenon lamp (Osram, XBO 450W) and monochromator (Bausch and Lomb 33-86-02). The signal from the photomultiplier (Hamamatsu 928) was captured by the storage oscilloscope (Tektronix A10), interfaced either with a Tektronix 4052A computer or a Zenith ZCM-1390 computer via a Tektronix C10001 video camera.

3. Results and discussion

3.1. Synthesis

Our interest was to prepare sensitizer-bound sulfonium salts in which the sensitizer and sulfonium salt groups are separated by three to four atoms, in order to facilitate through–space interaction. Previous studies on through–space, intramolecular interactions, including excimer formation [13], have provided support for favorable interaction with three atom spacer groups. The anthracene chromophore was chosen as the sensitizer group, since it was know that photoinitiated cationic polymerization by aryl sulphonium salts is sensitized by anthracene. Furthermore, anthracenes absorb is strongly in the 350–400 nm spectral region, where there is strong emission from commonly utilized medium pressure, mercury arc lamps.

Our synthetic goal was accomplished by two approaches, first in a straight-forward, multi-step procedure and secondly, by a more direct, novel method. Both procedures started from alkylation of anthrone (**1**).

Alkylation of anthrone with acrylonitrile, in the presence of potassium *t*-butoxide, resulted in Michael addition to acrylonitrile at the C-10 position of anthrone, corresponding to the carbon site of anthrone ambident anion. The nitrile adduct was hydrolyzed to the corresponding carboxylic acid, followed by conversion of the anthrone group into the anthracene group by reduction with zinc dust. The resulting 3-(9-anthracenyl)-propionic acid was reduced to the corresponding alcohol, which was converted into the bromide. Reaction of the bromide with diphenyl sulfide and the dioxane complex of silver hexafluoroantimonate provided the desired 3-(9-anthracenyl)-propyl diphenylsulfonium salt **2**, as shown in path (a) of Scheme 1. The salt was characterized by IR, UV, NMR, and elemental analysis.

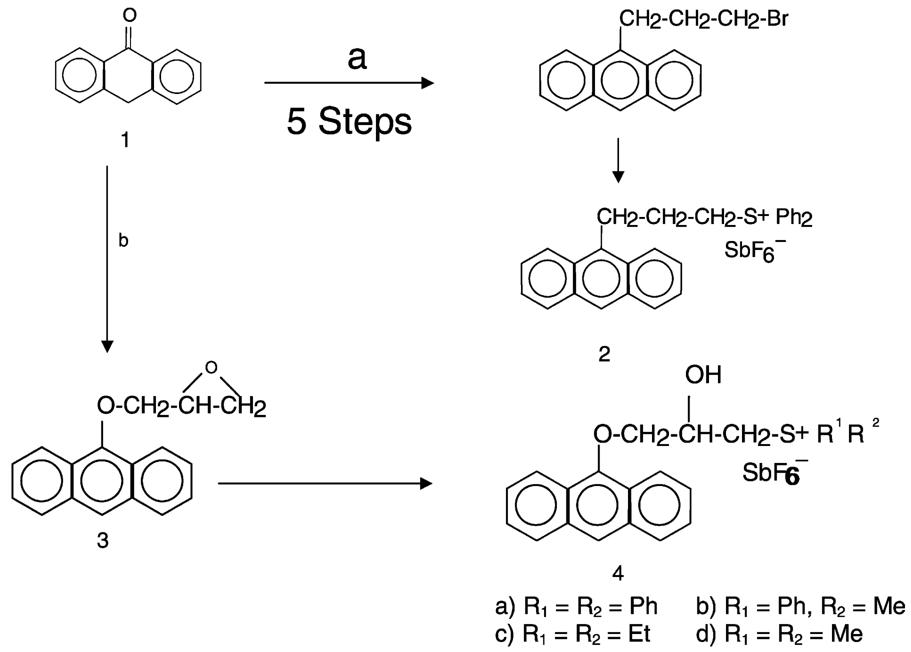
In contrast, alkylation of anthrone (**1**) with oxiranylmethyl chloride, in the presence of sodium ethoxide, occurred predominately at the oxygen site of the anthrone ambident anion to provide 9-anthracenyl oxiranylmethyl ether (**3**). Ring opening of the oxiranyl group with diphenyl sulfide and hexafluoroantimonic acid hexahydrate directly afforded the desired 3-(9-anthracenyloxy)-2-hydroxypropyl diphenylsulfonium salt (**4a**), as shown in path (b) of Scheme 1.

The corresponding methyl phenyl sulfonium salt (**4b**), diethyl sulfonium salt (**4c**) and dimethyl sulfonium salt **4d** were prepared, accordingly, from the corresponding sulfides. The salts were characterized by IR, UV, NMR, and elemental analysis. Yields for their direct formation by ring opening of the oxirane at the terminal carbon ranged from 25 to 55%. No efforts were made to optimize yields. However, some insight regarding yields was provided in our attempt to prepare the 3-(9-anthracenyloxy)-2-hydroxypropyl ethyl phenacylsulfonium salt (**4e**).

Rather than the expected product **4e**, reaction of **3** with α-(ethylthio)-acetophenone and hexafluoroantimonic acid hexahydrate provided ethyl oxiranylmethyl phenacylsulfonium salt **5**, which was characterized by IR, UV, NMR, and elemental analysis.

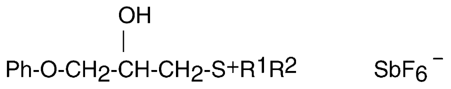
The formation of **5**, which was obtained in 28% yield, is attributed to further reaction of the desired product **4e** by protonation at C-10 of the anthracene ring, in the strongly acidic medium, followed by oxirane formation with displacement of anthrone, as depicted in Scheme 2. In the event that **5** is, in fact, produced in this manner from **4e**, it appears probable that salts **4a–d** also react in the same manner, thereby reducing their yields. In this event, carrying out the reactions under milder conditions is expected to enhance the yields.

The direct formation of sulfonium salts by alkylation of sulfides with oxiranes was also carried out on oxiranylmethyl



Scheme 1. Synthesis of anthracenyl bound sulfonium salts.

phenyl ether and cyclohexene oxide. The reaction of diphenyl, diethyl and dimethyl sulfide with oxiranylmethyl phenyl ether, together with hexafluoroantimonic acid hexahydrate, provides the desired salts **6a–c**, respectively, in 25–28% yield, as evidenced by IR, UV, and NMR analysis.



$$\mathrm{Ph\text{-}O\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}S^{+}R^1R^2}\qquad \mathrm{SbF_6^-}$$

6

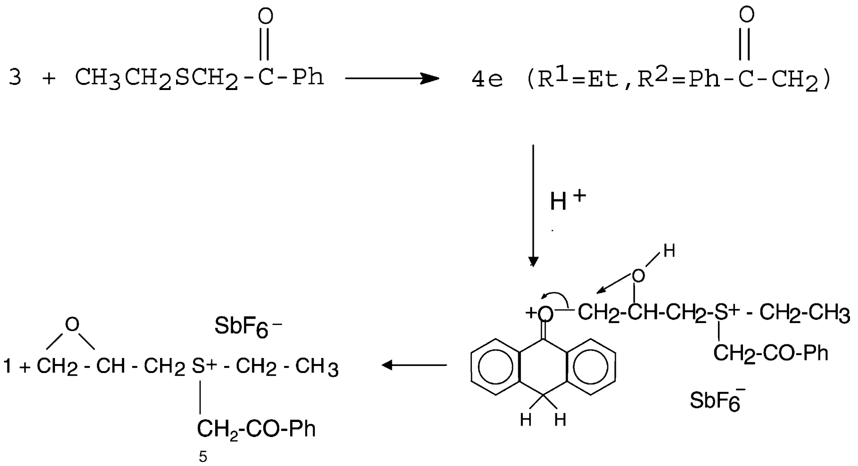
a) $R^1 = R^2 = Ph$
b) $R^1 = R^2 = Et$
c) $R^1 = R^2 = Me$

Reaction of cyclohexene oxide with dimethyl sulfide and hexafluoroantimonic acid hexahydrate provides the desired salt **7**, as evidenced by IR, UV, NMR, and elemental analysis, but the yield was only 9%. Furthermore, the corresponding reaction with diphenyl sulfide was unsuccessful. These results suggest that the ring-strained cyclohexene oxide follows an alternative reaction course, predominately, which may be acid-catalyzed oligomerization.

High resolution NMR of **7** supported the e-configuration, which is shown, owing to the H_1H_2 coupling constant of 10.4 Hz, which is expected for diaxial coupling.

3.2. Photopolymerization studies

The anthracene-bound sulfonium salts were evaluated and compared as photoinitiators for cationic polymerization



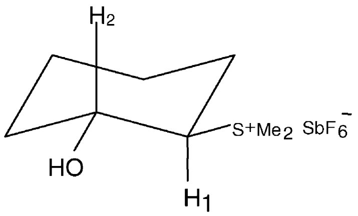
Scheme 2. Proposed pathway for reaction of 9-anthracenyl oxiranylmethyl ether (**3**) with α-(ethylthio)-acetophenone.

Table 1
Photosensitivity of sulfonium salts in epoxy photoresist[a]

Sulfonium salt	Exposure dose (mJ/cm^2)	Steps held
2	500	14
4a	500	13
4a	50	6
4b	500	8
4c	2000	Wash-off
4d	2000	Wash-off
MASH	500	4

[a] See Section 2.2 for experimental details.

in a photoresist formulation, comprised of epoxy resins. The anthracene-bound sulfonium salts were also compared with a commercial photoinitiator for cationic polymerization (MASH), consisting of a **m**ixture of **a**ryl **s**ulfonium **h**exafluoroantimonate salts.



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As described in Section 2.2, photoresist films (25 μm thick) were applied to a photoresist substrate by spin coating and exposed through a Stouffer 21-step transmission wedge. Absorptivity of the wedge increases by a factor of $2^{1/2}$ for each step, thereby resulting in decreased exposure intensity with increasing step number.

The results are provided in Table 1 in terms of the number of steps held following development.

The anthracenyl-propyl diphenylsulfonium salt **2**, photoresist composition exhibited 14 steps held (i.e. steps 15–21 were washed off by the developer) for an exposure dose of 500 mJ/cm^2. In the anthracenyloxy-hydroxypropyl series **4**, the diphenylsulfonium salt **4a** composition exhibited 13 steps held for a dose of 500 mJ/cm^2, similar to **2**. Exposure of the **4a** composition to 50 mJ/cm^2 resulted in 6 steps held. The decrease of 7 steps for the 10-fold decrease in exposure dose corresponds to the decrease in absorbance of about 11-fold for the 7 steps, i.e. $2^{7/2}$. These results indicate that each additional step held corresponds to an increase in photosensitivity by a factor of about $2^{1/2}$, corresponding to an increase of about 2-fold for each additional 2 steps held.

The corresponding methyl phenylsulfonium salt **4b** composition exhibited 8 steps held for 500 mJ/cm^2, corresponding to a decrease in photosensitivity of about 5–6-fold relative to **4a**.

In contrast, no photoinitiator activity was exhibited by the diethylsulfonium and dimethylsulfonium salt compositions, **4c** and **4d**, respectively, even for an exposure dose of 2000 mJ/cm^2, as evidenced by total wash-off of the photoresist.

Photopolymerization activity of the commercial photoinitiator, MASH, was of four steps held at 500 mJ/cm^2. The mixture has recently been reported to consist predominately of diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate and bis[4-(diphenylsulfonio) phenyl] sulfide bishexafluoroantimonate [3]. The presence of the bis-salt was not recognized in an earlier report [14].

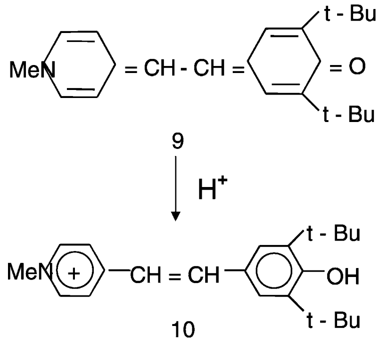
These results demonstrate that the anthracene-bound diphenylsulfonium salts (**2** and **4a**) and methyl phenylsulfonium salt (**4b**) exhibit substantially higher photoactivity, compared to the commercial photoinitiator. However, absorptivity of the anthracene-bound sulfonium salts is also substantially higher, particularly in the 350–400 nm range, where there is strong emission from the medium pressure, mercury arc lamp.

Studies on cationic polymerization of epoxy-functional liquid coatings were also carried out, using the anthracene-bound sulfonium salts (see Footnote 2). *Intramolecular* sensitization by the anthracene-bound sulfonium salts was compared with a corresponding *intermolecularly* sensitized MASH composition, using 9-methylanthracene (**8**), as the sensitizer. In contrast to the photoresist studies, absorptivities of the sensitized MASH composition, **s**ensitized **m**ixed **a**ryl **s**ulfonium **h**exafluoroantimonate (SMASH), and the anthracene-bound sulfonium salt compositions are similar.

The order of photoactivity of the anthracene-bound sulfonium salts in the UV cure studies was found to parallel the photoresist results, i.e. **2** > **4a** ≫ **4b**. Photoactivity of the SMASH was significantly less than **4b**, which confirmed substantially enhanced reactivity by intramolecular sensitization, wherein the anthracene-bound sulfonium group has at least one phenyl substituent. As in the photoresist studies, alkyl-substituted anthracene-bound sulfonium salts **4c** and **4d** showed essentially no activity.

3.3. Acid quantum yields—support for concerted electron-transfer-induced, bond cleavage

Acid quantum yields were determined photometrically using the merocyanine indicator dye **9**, as described in Section 2.3. Protonation of **9** to **10** (Scheme 3) is accompanied by a



Scheme 3. Merocyanine acid indicator dye.

large hypsochromic shift in the absorption maximum from 600 to 400 nm.

By this method, acid quantum yields from photolysis of anthracene-bound diphenylsulfonium salts **2** and methyl phenylsulfonium salt **4b** were found to be 0.32 and 0.21, respectively, in acetonitrile. This order of acid generation is consistent with the order of photoactivity of **2** and **4b** from the photoimaging and photocuring studies. The limiting quantum yield for acid formation by *intermolecular* sensitized photolysis of triphenylsulfonium hexafluoroantimonate by the same method, using anthracene as the sensitizer, was found to be 0.08 [15]. This result is in accord with limiting yields of 0.08–0.09 for diphenyl sulfide formation from anthracene-sensitized photolysis of triphenylsulfonium salts, reported by DeVoe et al. [8] and Timpe Bah [16]. The higher acid quantum yields for the anthracene-bound sulfonium salts **2** and **4b**, relative to intermolecular anthracene sensitization, are also consistent with the photocuring results.

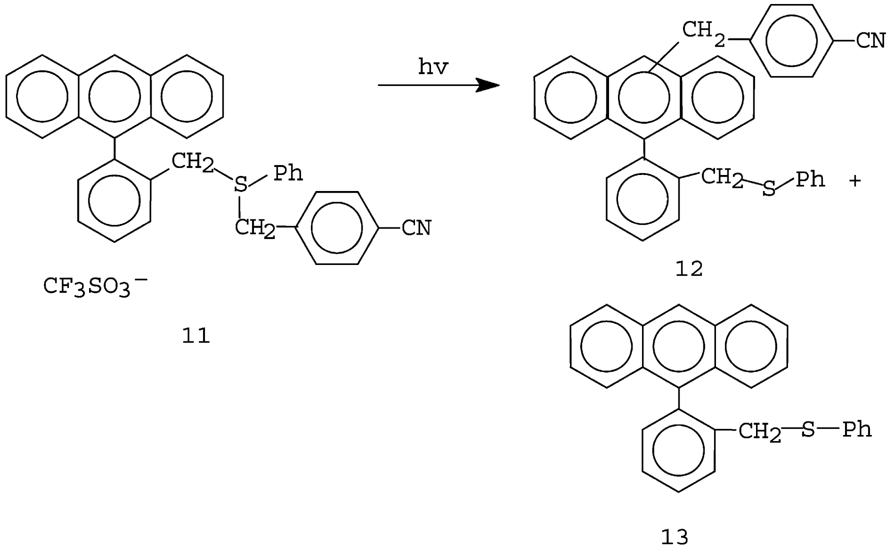
DeVoe et al. [8] also determined that the quantum yield for diphenyl sulfide formation was equivalent to the quantum yield for disappearance of anthracene. The major photoproducts derived from anthracene were phenylated anthracenes (55%) of which 73% was 9-phenylanthracene. The authors proposed that excited singlet state anthracene forms an encounter complex with the triphenylsulfonium cation from which electron transfer occurs, followed by dissociation of the reduced triphenylsulfonium radical into diphenyl sulfide and phenyl radical. Phenylated anthracenes were reported to arise by in-cage combination of phenyl radical with the oxidized anthracene radical cation, followed by elimination of a proton. Evidence for anthracene-sensitized photolysis of triphenylsulfonium salts by an electron transfer mechanism from anthracene excited singlet state had been provided earlier in photoinitiated cationic polymerization studies [5,7]. Sensitization by energy transfer from anthracene excited singlet or triplet state or by electron transfer from anthracene triplet was shown to be energetically unfavorable.

DeVoe et al. proposed that the major inefficiency in the process is back-electron transfer, which occurs at close to the theoretically limiting rate. Accordingly, one possible explanation for the 2–3-fold higher quantum yields with the anthracene-bound sulfonium salts **2** and **4b** is a reduced efficiency of back electron transfer. However, it appears unlikely that the rate for back transfer is reduced in the anthracene-bound salts. Alternatively, the higher quantum yields may reflect a more competitive bond cleavage, cationic radical/radical coupling process.

Saeva et al. [17] have proposed concerted, intramolecular electron-transfer-induced bond cleavage to account for the relatively high quantum yield of photocleavage ($\Phi = 0.32$) of *p*-cyanobenyl radical from anthracene-bound *p*-cyanobenzyl-sulfonium salt **11** (Scheme 4). Subsequent coupling of the *p*-cyanobenzyl radical with the anthracenyl cation radical provides photorearranged *p*-cyanobenzylated anthracenes **12** in 44% yield with $\Phi = 0.15$. Escape products, including debenzylated sulfide **13**, were formed in 56% yield with $\Phi = 0.17$, which accounted for the remaining mass balance. The corresponding napthacene-bound sulfonium salt afforded photorearranged products in quantitative yield with $\Phi = 0.25$.

Benzyl-substituted sulfonium salts are reported as latent thermal initiators for cationic polymerization, owing to thermal lability of the benzyl-sulfonium bond [18]. Such thermal lability reduces the utility of benzyl-sulfonium salts as photoinitiators for cationic polymerization, owing to shortened shelf life.

The X-ray crystal structure of **11** shows that the 9-phenyl group is oriented orthogonal to the plane of the anthracene ring, which places the sulfonium group directly over the anthracene ring in the lowest energy conformation. Accordingly, it appears reasonable that the three



Scheme 4. Photorearrangement of sulfonium salt **11**.

Table 2
Absorbance changes, relative fluorescence intensity (I_f), and singlet lifetimes (τ_f) for anthracene-bound sulfonium salts and model anthracene compounds[a]

Anthracene compound	Decrease in absorption (%)	Relative I_f	τ_f (ns) (CH_3CN-ambient)	τ_f (ns) (CH_3OH glass; 77 K)
2	25	0.20	<1	14.2
4a	55	0.20	1.2	13.3
4b	50	0.48	3.1	13.5
4d	10	0.95	7.6	13.5
8	0	1.0	5.2	14.3
3	0	1.0	6.4	15.1

[a] See text for details.

and four atom spacing in anthracene-bound salt **2** and appropriately-substituted salts **4**, respectively, also allows for favorable intramolecular electron-induced, concerted bond cleavage. Furthermore, proximity of the cleavage products is expected to promote efficient cation radical–radical coupling, which accounts for the high quantum yields of acid formation.

3.4. Absorption and fluorescence—correlation of results with photoactivity

UV-Vis absorption spectra of the anthracene-bound sulfonium salts are similar to that of anthracene, but are red-shifted by about 10 nm. The major λ_{max} at 366 nm exhibits molar absorptivity of about $10^4\,cm^{-1}\,M^{-1}$, similarly to 9-methylanthracene (**8**). However, in contrast to anthracene, 9-methylanthracene (**8**) and 9-anthracenyl oxiranylmethyl ether (**3**), absorptivity at 366 nm decreases on continued exposure in the UV-Vis spectrophotometer. Within a half an hour, the decrease in absorptivity was most pronounced for **4a** and **4b** (50–55%), compared to **2** (25%) and **4d** (10%), as shown in Table 2.

Fluorescence emission of the salts is also similar to that of anthracene, but red-shifted by 10–15 nm, so that the major λ_{max} appears to 415 nm. However, normalized room temperature fluorescence intensity was substantially reduced (by 80%) for both anthracene-bound diphenylsulfonium salts **2** and **4a** and by 50% for methyl phenylsulfonium salt **4b**.

Furthermore, normalized fluorescence intensity at 415 nm increased with continued excitation of **2**, **4a** and **4b** in the spectrofluorometer at 366 nm. On the other hand, the fluorescence intensity of anthracene-bound dimethylsulfonium salt **4d** was essentially equivalent to that of anthracene and did not change with continued excitation.

These results provide further support for facile acid generation by photoinduced electron transfer/cleavage and rearrangement of the anthracene-bound sulfonium salts **2**, **4a** and **4b**. The low fluorescence yields indicate that the excited singlet state anthracene chromophore is quenched intramolecularly by electron transfer to the sulfonium group. The accompanying increase in fluorescence intensity is indicative of electron-induced cleavage of the quenching group, thereby enhancing anthracene fluorescence. Furthermore, the accompanying decrease in anthracene absorbance at 366 nm is consistent with a photorearrangement process, which shifts the absorption to longer wavelengths. The facility of the process is evidenced by its occurrence on exposure to the relatively weak spectrophotometer radiation sources.

Fluorescence lifetimes of the anthracene-bound sulfonium salts and model compounds in acetonitrile at room temperature and methanol glass at 77 K are also provided in Table 2.

Non-participation of **4d** (and presumably **4c**) in these processes is supported by the absence of quenching of anthracene fluorescence by trimethylsulfonium tetrafluoroborate. In contrast, anthracene fluorescence is readily quenched by triphenylsulfonium salts [7,8]. Room temperature fluorescence lifetimes of the anthracene-bound diphenylsulfonium salts **2** and **4a** were substantially reduced relative to 9-methylanthracene (**8**) and anthracenyl oxiranylmethyl ether (**3**). And the corresponding lifetime of methyl phenylsulfonium salt **4b** was intermediate. The same trend was also observed in glycerol. However, all the lifetimes in the methanol glass at 77 K were essentially equivalent, signifying the absence of intramolecular electron-transfer-induced cleavage under these conditions.

The time resolved fluorescent lifetimes nicely complement the stationary-state fluorescence intensity results, both of which are in agreement with the order of acid quantum yields and photopolymerization activity of the anthracene-bound sulfonium salts.

The results can be explained in terms of the Rehm–Weller relationship, wherein photoinduced electron transfer approaches the rate of diffusion as the free energy change ΔG approaches -40 kJ/mol [19]. ΔG may be estimated from Eq. (1), where E^{ox} and E^{red} are half-wave redox potentials for one-electron oxidation of the electron donor (anthracene) and reduction of the acceptor (sulfonium salt), respectively, in volts; E^* is the excitation energy of the reactive state (excited singlet anthracene) in kJ/mol and the 96.5 factor converts redox potentials in volts into kJ/mol:

$$\Delta G = 96.5(E^{ox} - E^{red}) - E^* \tag{1}$$

Accordingly, ΔG values were calculated from redox potentials, in volts relative to SCE, for reduction of triphenylsulfonium (−1.1) [20] dimethyl phenylsulfonium (−1.7), [21] and trimethylsulfonium (−2.0) [22] ions by anthracene (1.1) [23], in the excited singlet state (319 kJ/mol). The resulting

ΔG values of −107, −49, and −20 kJ/mol for triphenylsulfonium, dimethyl phenylsulfonium, and trimethylsulfonium ion, respectively, indicate that the thermodynamics are unfavorable for diffusion controlled reduction of the trialkylsulfonium ion (corresponding to **4c** and **4d**) and increase in favorability with increasing phenyl-substitution. A redox potential for diphenyl methyl sulfonium ion (corresponding to **4a**) was not found, but is expected to lie between those of triphenylsulfonium and dimethyl phenylsulfonium ions. Furthermore, a concerted electron transfer-cleavage process is expected to be favored for diphenyl-substituted **4a** relative to monophenyl-substituted **4b** owing to the weaker S-alkyl bond in **4a** [21].

Accordingly, photoactivity of the anthracene-bound sulfonium salts as well as their absorption and fluorescence behavior are readily explicable in terms of photoinduced, intramolecular electron transfer from excited singlet anthracene to the sulfonium ion group.

3.5. Transient absorption—possible detection of anthracenyl cation from cation radical–radical coupling

Time resolved absorption spectra were obtained by ns laser flash studies at 337 nm. The results with anthracene-bound diphenylsulfonium salt **2** and 9-methylanthracene (**8**) with and without triphenylsulfonium tetrafluoroborate (**14**) are summarized in Table 3. In each case, a transient absorption band is observed at 428 nm, which is quenched by oxygen, and can be assigned to the triplet anthracene chromophore [24].

Anthracene-bound diphenylsulfonium salt **2** and the 9-methylanthracene (**8**)–triphenylsulfonium tetrafluoroborate (**14**) mixture also exhibit an absorption band at about 480 nm. The transient decay at 480 nm is first (or pseudo first) order with a lifetime of about 0.6 μs. This transient is unaffected by oxygen. Substantially longer-lived, broad, weak absorption is also observed underlying the 480 nm transient as well as at about 700 nm. Anthracene-bound diphenylsulfonium salt **4a** exhibit similar transients; however, the 480 nm transient was too weak to analyze.

DeVoe et al. [8] also reported transient absorption bands at 430 and 480 nm from ps laser flash studies on mixtures of anthracene and triphenylsulfonium hexafluorophosphate. The transients were assigned to triplet anthracene (430 nm) and anthracene radical cation ($Ar^{+\bullet}$) (480 nm). Anodically generated $Ar^{+\bullet}$ absorbs at 480 nm, although the major absorption is at 725 nm. Kochi coworkers [25] have reported that $Ar^{+\bullet}$, generated by ps laser flash photolysis, absorbs primarily at 725 nm.

Table 3
Initial lifetime (τ_i) of transients at 428 and 480 nm[a]

Anthracene compound	τ_i (428 nm)	τ_I (480 nm)
2	8	0.6 (0.8[b])
8 + **14**	10	0.6 (0.6[b])
8	17	Not observed

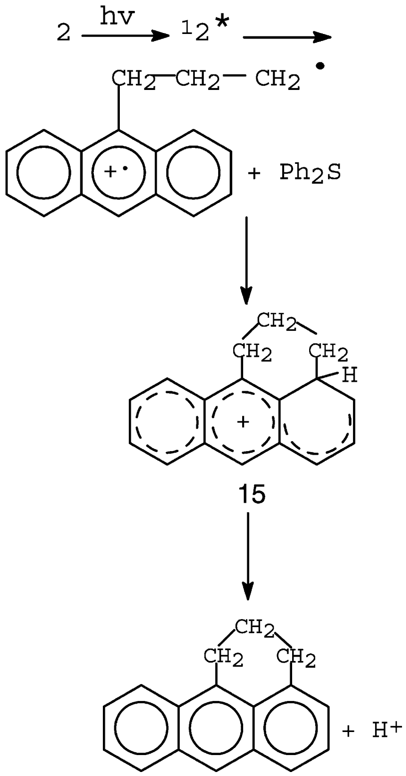
[a] See text for details.

[b] Saturated O_2 solution.

The transient absorption spectrum of 9-methylanthracene (**8**) with triphenylsulfonium tetrafluoroborate (**3**) exhibits a distinct absorption band at 480 nm with a lifetime of 0.6 μs (see Table 3), but only weak, ill-defined absorption at 725 nm. The absence of a strong band at 725 nm and the lifetime of 0.6 μs do not appear to be consistent with the anthracene cation radical ($An^{+\bullet}$) assignment for the 480 nm transient. Cage-escaped $An^{+\bullet}$ is expected to live at least tens of microseconds since decay of $An^{+\bullet}$ can be measured by electrochemical methods [26]. Furthermore, methylanthracene cation radical, generated by photoionization in sodium dodecyl sulfate micelles, was found to survive for at least microseconds [27].

Alternatively, the 480 nm transient may be assigned to the anthracenyl cation group, generated by in-cage coupling of the oxidized anthracenyl cation radical with the free radical species from reductive cleavage of the sulfonium ion group, as shown in Scheme 5 for the anthracene-bound diphenylsulfonium salt **2**.

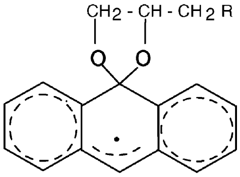
Photoexcitation to the excited singlet state $^{1}\mathbf{2}^{*}$ results in favorable, intramolecular electron transfer from the anthracene chromophore to the sulfur group concurrently with C–S bond cleavage. Bond cleavage may occur as shown in Scheme 5, followed by cation radical–radical coupling to generate the anthracene cation intermediate **15**, which may give rise to the 480 nm transient absorption, shown in



Scheme 5. Photorearrangement of sulfonium salt **2**.

Table 2. The anthracene chromophore is regenerated with formation of a proton.

Alternatively, although thermodynamically less favorable, electron transfer from the anthracene chromophore to the sulfonium salt group may occur concurrently with cleavage of a phenyl sulfur bond. In-cage coupling of the phenyl radical with the anthracene cation radical chromophore generates a phenylated anthracene cation intermediate from which the corresponding phenyl anthracene is generated together with a proton, in accordance with DeVoe et al. [8].



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The relatively weak 480 nm absorbance for anthracene-bound diphenylsulfonium salt **4a**, as compared with **2**, may be attributed to reaction of the hydroxyl group of **4a** with the corresponding anthracene cation radical intermediate, thereby reducing its lifetime. For example, following photoinduced electron transfer from the anthracene chromophore to the sulfonium salt group, the hydroxy group of **4a** may intercept the oxidized anthracenyl cation radical to produce intermediate **16**, wherein R represents the reduced and possibly, cleaved sulfonium group. The greater decrease in steady state absorptivity of hydroxy-functional **4a** and **4b** relative to **2**, as shown in Table 2, is also consistent with this hypothesis, since the anthracene chromophore is thereby diminished.

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