# New Synthesis of Aryl-Substituted Sulfonium Salts and Their Applications in Photoinitiated Cationic Polymerization

S. R. Akhtar,† J. V. Crivello,*,† J. L. Lee,‡ and M. L. Schmitt†

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180, and General Electric Corporate Research and Development Center, Schenectady, New York 12301*

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This paper describes the development of a novel, general, and high-yield synthesis of aryl-substituted sulfonium salts by the direct reaction of diaryl and dialkyl sulfoxides with activated aromatic compounds in the presence of $P_2O_5$–methanesulfonic acid. In particular, the synthesis of triarylsulfonium salts bearing long alkoxy chains has led to a class of highly useful photoinitiators for cationic polymerization with high photoresponse and excellent solubility in a wide variety of monomeric and polymeric substrates. These photoinitiators are of considerable interest for use in a wide variety of UV curing and microlithographic applications.

## Introduction

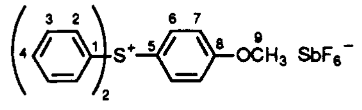
Interest in aryl-substituted sulfonium salts in this laboratory has stemmed from the observation that such compounds are highly photosensitive and can be used as efficient photochemical sources of strong Brønsted acids.[1,2] This discovery has led to extensive use of triarylsulfonium salts as photoinitiators in cationic vinyl and ring-opening polymerizations[3] and in the design of novel microelectronic photoresists.[4,5] While simple triarylsulfonium salts have found considerable use in these applications, there is considerable room for further improvement in these materials that could lead to an expansion in their range of use. Specifically, simple triphenylsulfonium salts as ionic compounds have poor solubility in nonpolar monomers and oligomers. Consequently, such monomers and oligomers are not effectively photopolymerized by using these salts. More recently, we have been exploring the relationship between the structure of various sulfonium salts and their photosensitivity and spectral response. Presently available methods for the synthesis of aryl-containing sulfonium salts are not sufficiently flexible to allow the synthesis of such salts bearing a wide variety of chromophoric groups. These considerations have prompted efforts in this laboratory to discover new methods for the synthesis of photoactive aryl-substituted sulfonium salts.[6]

## Experimental Section

**Materials.** Alkyl bromides, diphenyl sulfoxide, phenol, diphenyl sulfide, tetra-*n*-butylammonium bromide, tetramethylene sulfoxide, and $P_2O_5$ were used as purchased from Aldrich Chemical Co. Methanesulfonic anhydride (MSA), *d,l*-limonene dioxide, lauryl vinyl ether, and α-methylstyrene were purified by vacuum distillation prior to use. 1,2-Epoxydecane was obtained from ATO Chemical Co. and purified by fractional distillation prior to use. Aryl alkyl ethers used in this work were prepared by using a phase-transfer method recently described by us.[7] Epoxidized soybean (7% oxirane oxygen) and linseed (9.26% oxirane oxygen) oils were obtained from ATO Chemical Co. and were used as received. $NaSbF_6$ and $KPF_6$ were purchased from Ozark-Mahoning Co. All other chemicals were reagent grade and were used as received from their various sources. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian XL 200-MHz spectrometer. Secondary ion mass spectrometry (SIMS) was carried out in an ethylene glycol matrix using a Finnigan MAT 731 mass spectrometer.

**General Procedures for the Preparation of Aryl-Substituted Sulfonium Salts.** Two examples of the preparation of aryl-substituted sulfonium salts are given that typify the general synthetic methods used during the course of this work.

**Diphenyl(4-methoxyphenyl)sulfonium hexafluoroantimonate.** A mixture of 10.1 g (0.05 mol) of diphenyl sulfoxide and 5.4 g (0.05 mol) of anisole was placed in a 125-mL flask equipped with a thermometer and magnetic stirrer. To this mixture was added 20 mL of freshly prepared $P_2O_5$/MSA reagent,[8] and the reaction flask loosely stoppered to restrict exposure to atmospheric moisture. The color of the solution rapidly became deep purple, and the temperature rose to 55 °C. After the exotherm had subsided, the reaction mixture was stirred at 40 °C for 3 h and then poured into 200 mL of distilled water. To the slightly turbid solution there was then added 12.95 g (0.05 mol) of $NaSbF_6$, and a pale yellow oil separated that crystallized on standing. The product was isolated by filtration, washed first with water and then ether and dried at 25 °C in vacuo to give 25.4 g (96%) of nearly pure (by $^1H$ NMR) diphenyl(4-methoxyphenyl)sulfonium hexafluoroantimonate. The product was recrystallized from 2-propanol to give the pure sulfonium salt (73% yield), mp 135–136 °C. $^{13}C$ NMR ($CDCl_3$) δ $C_1$, 112.36; $C_2$, 130.28; $C_3$, 131.51; $C_4$, 133.30; $C_5$, 124.90; $C_6$, 117.32; $C_7$, 134.37; $C_8$, 164.78; $C_9$, 55.97.



**Diphenyl(4-(octyloxy)phenyl)sulfonium hexafluorophosphate.** Into a 3-L, three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and paddle stirrer were placed 224 g (3 mol) of liquified phenol (88% solution in water), 193 g (1 mol) of 1-bromooctane, 30 g of tetra-*n*-butylammonium bromide, 224 g (3 mol) of KOH pellets, 500 mL of water, and 500 mL of toluene. The reaction mixture was heated to reflux with good stirring and allowed to proceed overnight (16 h). The reaction could be conveniently monitored by using thin-layer chromatography. Silica plates were employed with *n*-heptane as the eluent. Iodine was used as the developing agent. The reaction

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† Rensselaer Polytechnic Institute.

‡ General Electric.

[1] Knapczyk, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* **1972**, *35*, 3739. Knapczyk, J. W.; McEwen, W. E. *J. Org. Chem.* **1970**, 2539.

[2] Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.

[3] Crivello, J. V. *Adv. Polymn. Sci.* **1984**, *62*, 1.

[4] Ito, H.; Willson, C. G. Polymers in Electronics *ACS Symp. Ser. No. 242* **1984**, 11.

[5] Crivello, J. V. *Polym. Eng. Sci.* **1983**, *23*, 953.

[6] A preliminary communication describing a portion of this work has recently appeared; Akhtar, S. R.; Crivello, J. V.; Lee, J. L. *J. Org. Chem.* **1990**, *55*, 4222.

[7] Crivello, J. V.; Lee, J. L. *J. Polym. Sci.* **1989**, *27*, 3951.

[8] Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.

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mixture was cooled and transferred to a separatory funnel. The lower aqueous layer was drawn off, and the upper toluene layer was washed with 500 mL of 0.5 N NaOH to remove the excess phenol. Then, the toluene layer was washed with two 500-mL portions of water, and the toluene removed by using a rotary evaporator, leaving a pale yellow oil. Gas chromatography (Hewlett-Packard 5840A, flame ionization detector, 6 ft × $^1/_8$ in. OV-17 silicone columns) showed that the product was 98% pure with the major impurity being toluene. The yield was quantitative (207 g).

Placed in a 125-mL Erlenmeyer flask equipped with a thermometer and a magnetic stirrer were 10.1 g (0.05 mol) of diphenyl sulfoxide and 20 mL of freshly prepared $P_2O_5$/MSA reagent. To this mixture was added dropwise with stirring 10.3 g (0.05 mol) of phenyl *n*-octyl ether prepared as described above. A mild exotherm was noted with the temperature rising from 25 to 36 °C. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 1.5 h. Then the solution was poured into 200 mL of distilled water, and to the resulting turbid solution was added 9.2 g (0.05 mol) of $KPF_6$. This solution was allowed to stir for an additional 0.5 h, and the resulting semisolid product collected and washed several times with distilled water. A yield of 74% was obtained. The product was purified by recrystallization from absolute ethanol to give 13.1 g (49% yield) of the colorless crystalline diphenyl(4-(octyloxy)phenyl)sulfonium hexafluorophosphate, mp 95–97 °C.

**Photopolymerization of 1,2-Epoxydecane.** To 20 g of 1,2-epoxydecane freshly purified by fractional vacuum distillation was added 0.6 g of diphenyl(4-(dodecyloxy)phenyl)sulfonium hexafluoroantimonate. Aliquots (5 mL) of the above solution were transferred by pipet to 6-mm quartz irradiation tubes and then sealed with septa. The samples were irradiated in a Rayonette photochemical reactor equipped with 16 3600-Å lamps and a merry-go-round apparatus. At appropriate time intervals, the samples were withdrawn and immediately poured into 100 mL of methanol to which a few drops of $NH_4OH$ had been added. The polymers that precipitated were isolated by decantation and further washed with fresh methanol. The polymers were then dried to constant weight in a vacuum oven.

**Photopolymerization of Lauryl Vinyl Ether (Dodecyl Vinyl Ether).** A solution composed of freshly distilled dodecyl vinyl ether (lauryl vinyl ether) and diphenyl(4-(dodecyloxy)phenyl)sulfonium hexafluoroantimonate was prepared and warmed slightly to promote dissolution of the photoinitiator. Next, 3-mL aliquots of the above solution were transferred to quartz tubes and irradiated as described in the previous experiment. The polymers were isolated by pouring the reaction mixtures into ammoniacal methanol, collecting the precipitated polymers by filtration, washing with fresh methanol, and then drying to constant weight.

**Photopolymerization of $\alpha$-Methylstyrene.** $\alpha$-Methylstyrene was dried and distilled from calcium hydride. A master solution of $\alpha$-methylstyrene containing 1% diphenyl(4-(octadecyloxy)phenyl)sulfonium hexafluoroantimonate was prepared and divided in half. To one of the solutions was added 0.5% perylene. As described in the previous experiments, 3-mL aliquots were taken from these two master solutions and irradiated for predetermined periods of time. The polymerizations were quenched, and the yields determined as before.

**Tack-Free Cure Rate Determinations.** Tack-free cure rates were determined in air by using a Model QC 1202 UV processor obtained from RPC Equipment Co. This apparatus is equipped with two 12-in. medium-pressure mercury arc lamps mounted perpendicular to the direction of travel of the conveyor. The lamps could be operated together or independently at 380 V and 9.8 ± 0.8 A. The conveyor speed was varied between 10 and 500 ft/min. Samples were coated as 1-mil films onto glass plates by using a drawknife, passed through the irradiation chamber, and immediately tested for tack on exiting the chamber.

## Results and Discussion

**Synthesis.** A number of synthetic routes for the preparation of symmetric and unsymmetrical aryl-substituted sulfonium salts have been discovered and are described in several excellent articles and reviews.[9-15] Among the best methods for the synthesis of aryl-substituted sulfonium salts are those that rely on readily available diaryl sulfoxides as starting materials. For example, unsymmetrical aryl-substituted sulfonium salts can be prepared in moderate yields by the condensation of diaryl sulfoxides with aryl and alkyl Grignard reagents in the presence of trialkylsilyl triflates.[16] Triarylsulfonium salts can also be synthesized by the condensation of diaryl sulfoxides with aromatic hydrocarbons in the presence of aluminum chloride or sulfuric acid.[17-20] However, the low yields and restrictions placed on substrates due to the harsh reaction conditions employed in the reaction severely restrict the generality of this method.

In a recent patent, Smith and Olofson[21] describe the condensation of diphenyl sulfoxide with aromatic compounds in the presence of phosphorus pentoxide to give triarylsulfonium salts in low yields. When this reaction was repeated in this laboratory it became obvious that the major source of the poor yields was the heterogeneity of the reaction medium due to the insolubility of the phosphorus pentoxide in the reaction mixture. Similar conclusions were reached when attempts in this laboratory were made to replace $P_2O_5$ with polyphosphoric acid (PPA) as a dehydrating agent. Other workers[22] have described the use of mixtures of methanesulfonic acid and trifluoroacetic anhydride for the preparation of triarylsulfonium salts in good yields.

While the above work was in progress, we encountered a paper by Eaton and co-workers,[8] who reported that a 1:10 solution of phosphorus pentoxide in methanesulfonic acid ($P_2O_5$/MSA) functions as a convenient strong acid and dehydrating reagent and can be used in place of PPA in many reactions. For example, recently, $P_2O_5$/MSA has been used as a dehydrating agent in several types of condensation polymerization reactions, including the synthesis of poly(benzoxazinone)s and poly(benzimidazole)s.[23] Eaton and co-workers have pointed out that one very great advantage of the $P_2O_5$/MSA reagent is that many organic compounds dissolve in the reagent to form homogeneous solutions. Further, they noted that sulfonation of electron-rich aromatic compounds that can occur with methanesulfonic acid in the presence of $P_2O_5$[24] can be avoided

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(9) Lowe, P. A. In *The Chemistry of the Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Vol. 1, p 13.

(10) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides, Emerging Synthetic Intermediates*, Academic Press: London, 1975.

(11) Marino, J. P. *In Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thieme Verlag: Stuttgart, 1976; Vol. 1.

(12) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 9.

(13) Badet, B.; Julia, M. *Tetrahedron Lett.* **1979**, *13*, 1101. Badet, B.; Julia M.; Lefebvre, C. *Bull. Soc. Chem. Fr.* **1984**, 11–431.

(14) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055.

(15) Crivello, J. V.; Lam, J. H. W. *Synth. Commun.* **1979**, *9*(3), 151.

(16) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571.

(17) Courtot, C.; Tung, T. Y. C. R. *Hebd. Seances Acad. Sci., Ser. C*, **1933**, *197*, 1227.

(18) Smiles, S.; Le Rossignol, R. *J. Chem. Soc.* **1906**, *89*, 696.

(19) Kehrmann, F.; Lievermann, S.; Frumkine, P. *Chem. Ber.* **1918**, *51*, 474.

(20) Luttringhaus, A.; Hauschild, K. *Chem. Ber.* **1939**, *72*, 890.

(21) Smith, G. H.; Olofson, P. M. U.S. Patent 4,231,951 (Nov 4, 1980) to 3M Company; *Chem. Abstr.* **1979**, *91*, 142166m.

(22) Endo, Y.; Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1981**, *29*, 3753.

(23) Ueda, M.; Komatsu, S. *J. Polymn. Sci. Polym. Chem. Ed.* **1989**, *27*, 1017; *Ibid. J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2815.

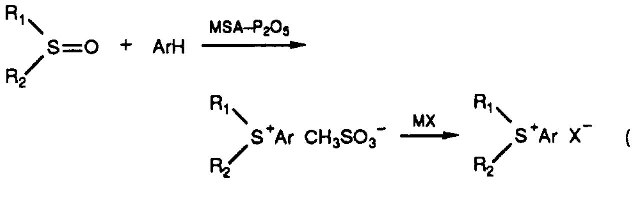
(24) Field, L.; Settlage, P. H. *J. Am. Chem. Soc.* **1954**, *76*, 1222.

Table I.[a] Synthesis of Triarylsulfonium Salts $(R_1)_2S^+R_2X^-$

| $R_1$ | $R_2$ | $X^-$ | yield, (%) | mp, °C (lit.) | $\lambda_{max}$ ($\epsilon$) | | elem anal. % C | H | S |
|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $4\text{-}C_6H_4OCH_3$ | $SbF_6^-$ | 87 | 135–136 | 260 (16 700) | calc | 43.10 | 3.21 | 6.05 |
| | | | | | | fnd | 43.02 | 3.41 | 6.02 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_2H_5$ | $PF_6^-$ | 76 | 102–103 | 261 (17 100) | calc | 53.10 | 4.20 | 7.08 |
| | | | | | | fnd | 53.40 | 4.31 | 7.56 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_8H_{17}$ | $PF_6^-$ | 74 | 95–97 | 262 (18 600) | calc | 58.21 | 5.78 | 5.97 |
| | | | | | | fnd | 58.21 | 5.80 | 6.10 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_{10}H_{21}$ | $SbF_6^-$ | 50 | 70–72 | 262 (17 600) | calc | 51.30 | 5.34 | 4.89 |
| | | | | | | fnd | 51.27 | 5.44 | 4.66 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_{12}H_{25}$ | $SbF_6^-$ | 76 | 79–82 | 262 (18 100) | calc | 52.71 | 5.71 | 4.69 |
| | | | | | | fnd | 52.70 | 5.89 | 4.92 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_{18}H_{37}$ | $SbF_6^-$ | 98 | 92–95 | 262 (17 400) | calc | 56.32 | 6.65 | 4.17 |
| | | | | | | fnd | 56.02 | 6.79 | 4.55 |
| $C_6H_5$ | $4\text{-}C_6H_4SC_6H_5$ | $SbF_6^-$ | 90 | 118–119 (118–119)[21] | 246, 305 (25 500, 17 700) | calc | 47.59 | 3.14 | 10.58 |
| | | | | | | fnd | 47.58 | 2.95 | 10.69 |
| $C_6H_5$ | $2\text{-}C_6H_3SC_6H_4$ (2-dibenzothienyl) | $SbF_6^-$ | 19 | 184–185 | 235, 267, 330 (45 800, 30 400, 3500) | calc | 47.60 | 2.81 | 10.58 |
| | | | | | | fnd | 47.90 | 2.81 | 10.53 |
| $C_6H_5$ | $4\text{-}C_6H_4OC_6H_5$ | $PF_6^-$ | 76 | 110–111 | 267 (18 700) | calc | 57.60 | 3.80 | 6.40 |
| | | | | | | fnd | 57.31 | 3.86 | 6.77 |
| $C_6H_5$ | $4\text{-}C_6H_4C(CH_3)_3$ | $PF_6^-$ | 37 | 136–140 (133–136)[15] | 237 (15 900) | calc | 56.90 | 4.96 | 6.90 |
| | | | | | | fnd | 56.80 | 4.86 | 7.04 |
| $C_6H_5$ | $3,5\text{-}(CH_3)_2\text{-}4\text{-}HOC_6H_2$ | $PF_6^-$ | 37 | 155–165 | 268 (11 600) | calc | 53.10 | 4.20 | 7.08 |
| | | | | | | fnd | 53.13 | 4.17 | 6.99 |
| $C_6H_5$ | $2\text{-}C_4H_3S$ | $PF_6^-$ | 51 | 177–183 | 268 (10 300) | calc | 46.30 | 3.14 | 15.46 |
| | | | | | | fnd | 46.80 | 3.12 | 15.75 |
| $CH_3$ | $4\text{-}C_6H_4OCH_3$ | $PF_6^-$ | 47 | 74–90 | 244 (10 200) | calc | 34.39 | 4.14 | 10.19 |
| | | | | | | fnd | 34.42 | 4.19 | 10.14 |
| $c\text{-}C_4H_8$ | $4\text{-}C_6H_4OCH_3$ | $PF_6^-$ | 59 | 104–106 | 246 (11 000) | calc | 38.82 | 4.41 | 9.41 |
| | | | | | | fnd | 38.90 | 4.49 | 9.35 |

[a] Reactions carried out by using 0.05 mol of sulfoxide and aromatic compound in 20 mL of 1:10 $P_2O_5$/MSA at 20–40 °C for 1–3 h.

by carrying out reactions at temperatures from 25 to 60 °C. It has now been discovered that the condensation of sulfoxides with aromatic compounds proceeds smoothly in the presence of 1:10 mixtures of $P_2O_5$/MSA (eq 1) to give good-to-excellent yields of the desired aryl-substituted sulfonium salts.



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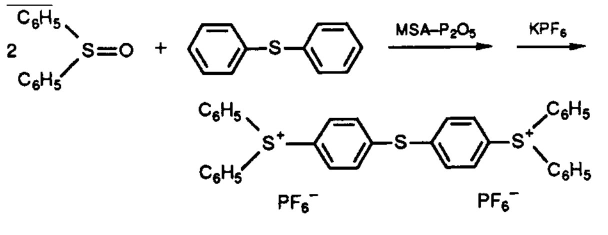
The reaction shown in eq 1 is a new general synthetic method that can be applied to the preparation of a wide range of photoactive sulfonium salts. Table I gives the structures and properties of a number of sulfonium salts that were prepared by using this new method, many of which are novel. The sulfonium salts shown in Table I were isolated by pouring the reaction mixtures containing the sulfonium mesylate salts into water followed by an in situ metathesis with an equivalent of an alkali- or alkaline-earth metal salt of the desired anion, $X^-$, to precipitate the water-insoluble sulfonium salt. As has been shown in the past, those sulfonium salts bearing the most weakly nucleophilic anions such as $PF_6^-$, $AsF_6^-$, or $SbF_6^-$ are the most active in photoinitiated cationic polymerizations.[11] Further purification of the metathesized salts can then be achieved using such standard techniques as recrystallization, trituration, and silica gel column chromatography.

Typically, reaction between the sulfoxide and the aromatic compound proceeds rapidly and homogeneously under very mild conditions. Presumably, $P_2O_5$ reacts on dissolution in MSA to generate mixed anhydrides, which are responsible for the excellent dehydrating characteristics of this reagent. Simply, stirring the dialkyl or diaryl sulfoxide with the aromatic compound at 25 °C in the presence of $P_2O_5$/MSA is accompanied by the liberation of heat and in many cases the immediate formation of red and purple solutions which are presumed to be due either to Meisenheimer or charge-transfer complexes.

The reaction shown in eq 1 can be characterized as a typical electrophilic substitution reaction. As a consequence, the reaction proceeds most satisfactorily when the aromatic substrate bears electron-donating substituents. Thus, while nitrobenzene and benzonitrile react very sluggishly, alkyl- and alkoxy-substituted benzenes undergo facile conversions to the corresponding sulfonium salt products. In these cases, only the 4-isomers are isolated as the sole products of the reaction. This is, presumably, due to the large steric requirements of the reactive electrophile, i.e., the protonated sulfoxide. As a result of the regioselectivity, such sulfonium salts are usually highly crystalline, and the isolated yields are typically high.

When the dialkyl sulfoxides, dimethyl sulfoxide, and tetramethylene sulfoxide were substituted for diaryl sulfoxides in the above reaction, the corresponding aryldialkylsulfonium salts were obtained in good-to-excellent yields. These reactions proceeded smoothly and exothermically at temperatures from 50 to 60 °C. Thus, this novel condensation reaction provides a very convenient route to the synthesis of aryldialkylsulfonium salts, which are difficult to prepare by using alternate techniques.

Condensation of a 2:1 stoichiometric ratio of diphenyl sulfoxide and diphenyl sulfide resulted in the isolation in 30% yield of the bissulfonium salt bis[4-(diphenylsulfonio)phenyl] sulfide bishexafluorophosphate[25] (eq 2).



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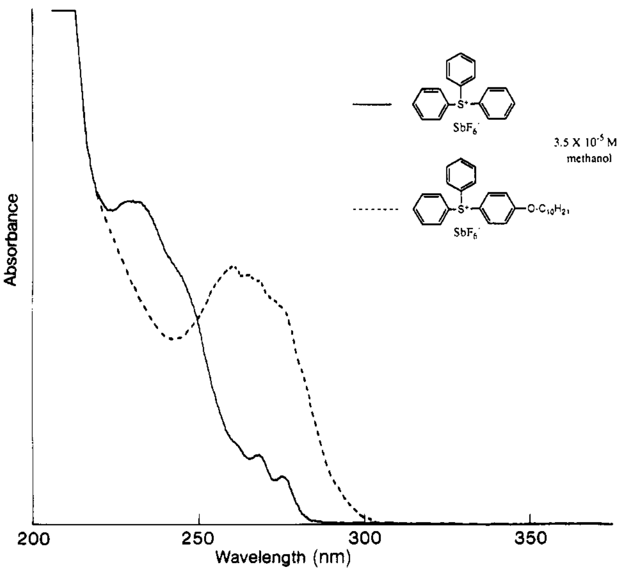

**Figure 1.** Comparison between the UV spectra of (triphenylsulfonium)$^+$SbF$_6^-$ and (diphenyl(4-octyloxy)phenyl)sulfonium$^+$-SbF$_6^-$. Both salts are $3.8 \times 10^{-5}$ M in methanol.

**Characterization.** All the sulfonium salts appearing in Table I were thoroughly characterized by means of their $^1$H and $^{13}$C NMR and UV spectra and in some cases by secondary ion mass spectroscopy (SIMS). Their melting points were compared with those of the authentic compounds prepared by alternate methods, and in nearly all cases, satisfactory elemental analyses were obtained.

Of particular interest in this work was the preparation of triarylsulfonium salts bearing linear alkyl and alkoxy substituents. Variations in the number and length of the alkyl and alkoxy groups allow one to vary both the UV absorption and the solubility characteristics. As the alkoxy chain is lengthened from 1 to 18 carbon atoms, there is a marked increase in the solubility of the salts in nonpolar solvents and monomers. Thus, while unsubstituted sulfonium salts and those with alkoxy chains of 1–6 carbon atoms are insoluble in all hydrocarbon solvents, those with 8–18 carbon atoms are soluble in toluene.

As noted in Table I, all of the alkoxy-substituted triarylsulfonium salts have similar UV absorption characteristics. For example, (4-(octadecyloxy)phenyl)diphenylsulfonium salts have their $\lambda_{max}$ at 260–263 nm in the UV, while the corresponding triphenylsulfonium salts absorb at 237 nm. The photosensitivity of this class of photoinitiators, therefore, lies in the short-wavelength region of the UV spectrum. A comparison of the UV spectra between (triphenylsulfonium)$^+$SbF$_6^-$ and a typical alkoxy-substituted triarylsulfonium salt, (4-(octyloxy)-phenyl)diphenylsulfonium)$^+$SbF$_6^-$ is shown in Figure 1. It should be pointed out that the UV absorption characteristics of triarylsulfonium salts are dependent only on the character of the organic cation and independent of the anion for those salts bearing inorganic anions such as PF$_6^-$, SbF$_6^-$, AsF$_6^-$, and BF$_4^-$. The longer wavelength absorption of the alkoxy-substituted triarylsulfonium salts are advantageous since these bands overlap better with the major mercury emission band in the region at 254 nm than those of the corresponding triphenylsulfonium salt. Consequently, alkoxy-substituted triarylsulfonium salts are more efficient photoinitiators of cationic polymerization when the most common sources of UV irradiation, mercury arc lamps, are used.

In Figure 2 is shown the $^{13}$C NMR spectrum of (diphenyl(4-octyloxy)phenyl)sulfonium)$^+$PF$_6^-$. The peak assignments are clear and unambiguous, and the absorption of every carbon atom can be assigned with certainty. For comparison, the chemical shifts for the related simple (diphenyl(4-methoxyphenyl)sulfonium)$^+$PF$_6^-$ salt have been included in the experimental portion of this paper. The $^{13}$C NMR spectrum of the novel compound (diphenyl(2-thienyl)sulfonium)$^+$PF$_6^-$ is given in Figure 3. This compound is readily prepared by this method and is an excellent photoinitiator for cationic polymerization.

It is interesting to note that SIMS provides a convenient method for the confirmation of structures of aryl-substituted sulfonium salts, including even the higher molecular weight members of the series of alkoxy-substituted triarylsulfonium salts. For example, the 4-(octyloxy) and 4-(octadecyloxy)-substituted triphenylsulfonium hexafluorophosphate salts show molecular ions at 391 and 531 amu, respectively, corresponding to the mass of their sulfonium cations. It is also notable that both of these compounds undergo a regular degradation of their alkoxy groups in the spectrometer with the loss of fragments that correspond to a reduction in mass by one methylene unit at a time.

**Photosensitivity and Utility in Photoinitiated Cationic Polymerization.** All the aryl-substituted sulfonium salts shown in Table I are photoactive and when irradiated in the presence of typical cationically polymerizable monomers such as epoxides, α-methylstyrene, and vinyl ethers initiate rapid and exothermic polymerization. Because of their attractive solubility characteristics, initial interest was focused on evaluating those triarylsulfonium salts bearing long alkoxy chains.

In Figures 4 and 5 are given plots of the percent conversion to polymer as a function of time for the photoinitiated cationic polymerizations, respectively, of 1,2-epoxydecane and dodecyl vinyl ether. In both cases, photopolymerizations were not successful using triphenylsulfonium hexafluoroantimonate due to the insolubility of this photoinitiator in the monomers. However, when dodecyloxy and octadecyloxy-substituted triphenylsulfonium salts were used, polymerization of the epoxide and vinyl ether monomers proceeded smoothly and to high conversion.

Figure 6 depicts plots for the photoinduced polymerization of α-methylstyrene in the presence and absence of perylene as a photosensitizer. A wide variety of long-chain alkoxy-substituted triarylsulfonium salts are readily soluble in α-methylstyrene monomer whereas triphenylsulfonium salts are not. In this case, (diphenyl(4-(octadecyloxy)-phenyl)sulfonium)$^+$SbF$_6^-$ was used at a 1% by weight basis with respect to the monomer. The unsensitized photolysis shows the presence of a considerable inhibition period, perhaps due to the presence of residual impurities in the monomer. In contrast, the perylene-photosensitized photopolymerization proceeds virtually without an inhibition period. Perylene is an excellent photosensitizer at wavelengths from 390 to 439 nm for the photolysis of triarylsulfonium salts in general and alkoxy-substituted triarylsulfonium salts in particular.[26] Increased acid production resulting from the combined unsensitized as well as the perylene-photosensitized photolysis of the triarylsulfonium salt may overwhelm the impurity level and result in the observed enhanced photopolymerization

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(25) Chang, K.-T. U.S. Patent 4,197,174, Apr 8 1980 to the American Can Co.; *Chem. Abstr.* **1980**, *93*, 73973z.

(26) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1059.

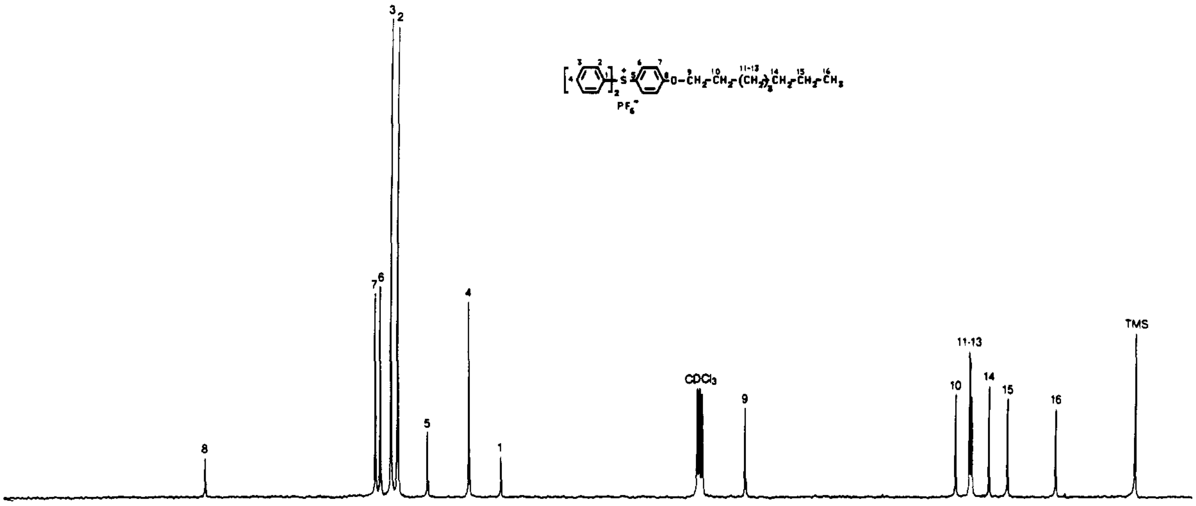

**Figure 2.** $^{13}$C NMR spectrum of (diphenyl(4-octyloxy)phenyl)sulfonium)$^+$PF$_6^-$ in CDCl$_3$: $\delta$ C$_1$, 112.18; C$_2$, 130.45; C$_3$, 131.61; C$_4$, 117.80; C$_5$, 125.20; C$_6$, 133.56; C$_7$, 134.45; C$_8$, 164.54; C$_9$, 69.11; C$_{10}$, 31.75; C$_{11}$, 29.25; C$_{12}$, 29.16; C$_{13}$, 28.85; C$_{14}$, 25.88; C$_{15}$, 22.63; C$_{16}$, 14.10.

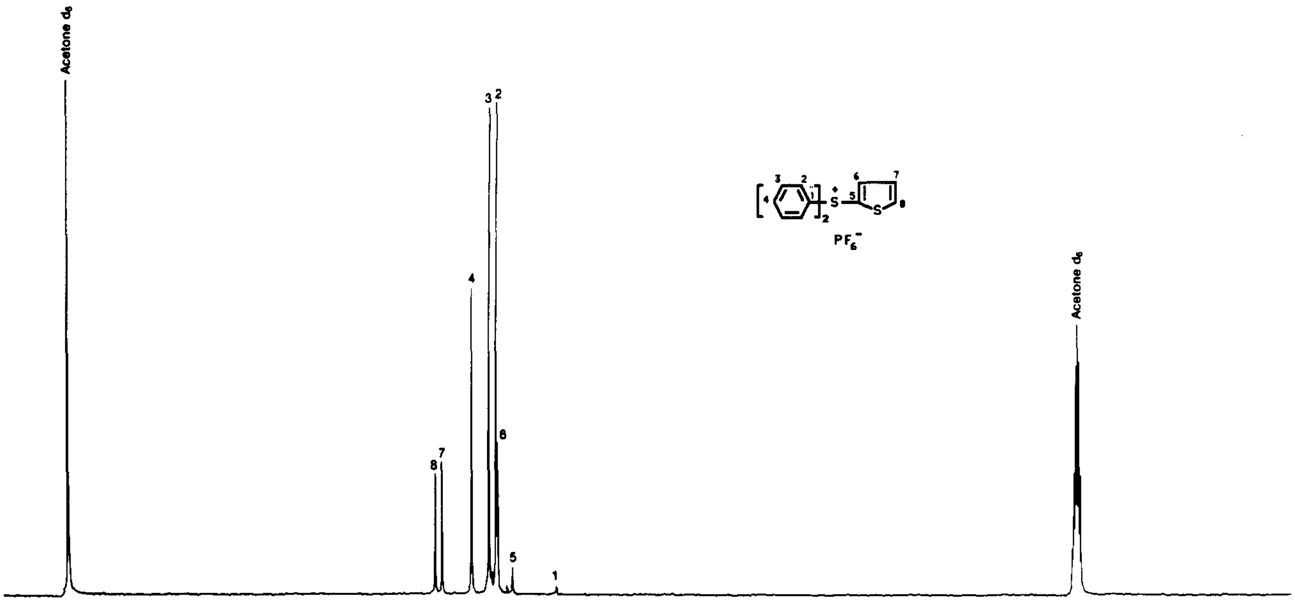

**Figure 3.** $^{13}$C NMR spectrum of (diphenyl(2-thiophenyl)sulfonium)$^+$PF$_6^-$ in acetone-$d_6$; $\delta$ C$_1$, 119.9; C$_2$, 131.13; C$_3$, 131.44; C$_4$, 135.51; C$_5$, 128.35; C$_6$, 132.39; C$_7$, 140.72; C$_8$, 141.90.

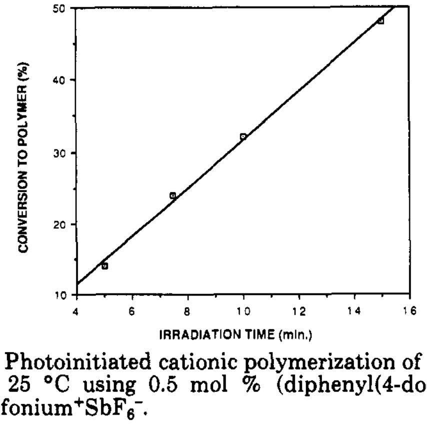

**Figure 4.** Photoinitiated cationic polymerization of 1,2-epoxydecane at 25 °C using 0.5 mol % (diphenyl(4-dodecyloxy)phenyl)sulfonium$^+$SbF$_6^-$.

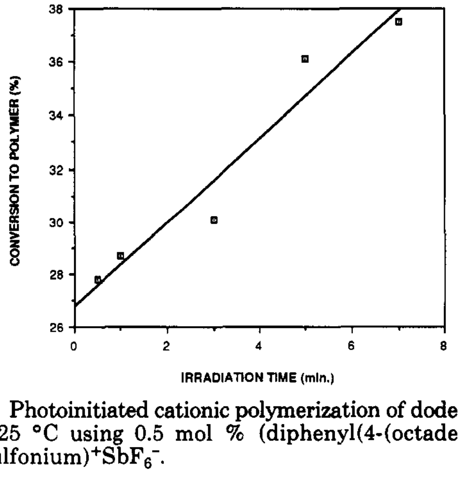

**Figure 5.** Photoinitiated cationic polymerization of dodecyl vinyl ether at 25 °C using 0.5 mol % (diphenyl(4-(octadecyloxy)phenyl)sulfonium)$^+$SbF$_6^-$.

rate. The reason for the acceleration observed after the induction period in the direct photopolymerization is not understood at this time. It does appear that both sensitized and unsensitized polymerizations reach high conversions upon long irradiation times and that the differences between these two reactions at long irradiation times may not be significant.

A study of the effects of UV light intensity and concentration of (diphenyl(4-(decyloxy)phenyl)sulfonium)$^+$-

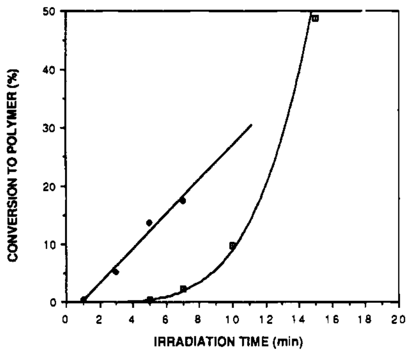

**Figure 6.** Direct (□) and photosensitized (♦) photopolymerization of $\alpha$-methylstyrene at 25 °C with 1% (diphenyl(4-octadecyloxy)phenyl)sulfonium)$^+SbF_6^-$ and 0.1% perylene.

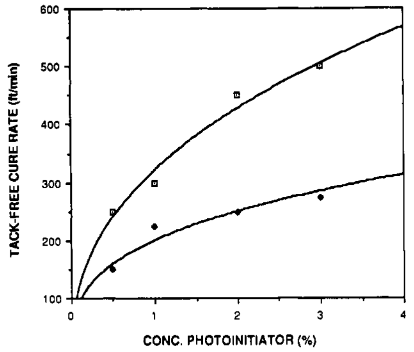

**Figure 7.** Study of the effect of light intensity and concentration of (diphenyl(4-(decyloxy)phenyl)sulfonium)$^+SbF_6^-$ on the photoinitiated polymerization of *d,l*-limonene dioxide (two 300-W lamps; one 300-W lamp).

$SbF_6^-$ on the rates of the cross-linking photoinduced polymerization of *d,l*-limonene dioxide is shown in Figure 7. Similar curves were obtained for this monomer at the two different levels of radiation intensity, however, with higher rates being observed as expected at the higher intensity level.

In Figure 8 is shown a study of the polymerizations of two epoxidized unsaturated triglycerides; epoxidized linseed oil and epoxidized soybean oil. Both of these materials are very hydrocarbon-like with respect to their solvent characteristics. Simple triarylsulfonium salts are ineffective as photoinitiators for these multifunctional monomers due to their insolubility. In contrast, long-chain alkoxy-substituted sulfonium salts, for example, the diphenyl(4-(decyloxy)phenyl)sulfonium hexafluoroantimonate salt used in these studies, are very soluble in these monomers and can be used to carry out their facile photoinitiated cationic polymerization. It is interesting to note that the curves indicating rates of polymerization as measured by the tack-free cure times for both of these related materials are parallel to one another. Because of its higher epoxy content, epoxidized linseed oil (9% oxirane oxygen) is more reactive than epoxidized soybean oil (7% oxirane oxygen).

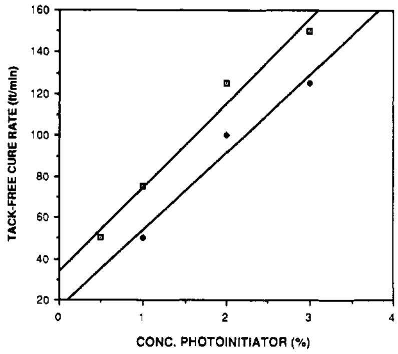

**Figure 8.** The photoinitiated polymerization of epoxidized linseed oil (□) and epoxidized soybean oil (♦) with various concentrations of (diphenyl(4-(decyloxy)phenyl)sulfonium)$^+SbF_6^-$.

## Conclusions

The condensation of dialkyl and diaryl sulfoxides with aromatic compounds substituted with electron-donating substituents in the presence of $P_2O_5$/MSA provides a simple, one-pot synthesis of aryl-substituted sulfonium salts in good-to-excellent yields. Several novel sulfonium salts have been prepared and have been fully characterized during the course of this work. Those sulfonium salts containing long alkoxy substituents are especially attractive as photoinitiators because of their excellent UV spectral absorption characteristics, their solubility in nonpolar monomers and polymers, and their high efficiency in photoinitiated cationic polymerization.

**Acknowledgment.** We acknowledge the financial support of General Electric Co. during the course of this work.

**Registry No.** $(Ph)_2S^+C_6H_4$-*p*-OMe·$SbF_6^-$, 127279-74-7; $(Ph)_2S^+C_6H_4$-*p*-OEt·$PF_6^-$, 106875-86-9; $(Ph)_2S^+C_6H_4$-*p*-O$(CH_2)_8$H·$PF_6^-$, 127331-45-7; $(Ph)_2S^+C_6H_4$-*p*-O$(CH_2)_{10}$H·$SbF_6^-$, 127279-76-9; $(Ph)_2S^+C_6H_4$-*p*-O$(CH_2)_{12}$H·$SbF_6^-$, 127279-79-2; $(Ph)_2S^+C_6H_4$-*p*-O$(CH_2)_{18}$H·$SbF_6^-$, 127279-81-6; $(Ph)_2S^+C_6H_4$-*p*-SPh·$SbF_6^-$, 71449-78-0; $(Ph)_2S^+$2-$C_6H_3SC_6H_4$·$SbF_6^-$, 127279-83-8; $(Ph)_2S^+C_6H_4$-*p*-OPh·$PF_6^-$, 127279-84-9; $(Ph)_2S^+C_6H_4$-*p*-Bu-*t*·$PF_6^-$, 66482-56-2; $(Ph)_2S^+$3,5-$(CH_3)_2$-4-$HOC_6H_2$·$PF_6^-$, 127279-86-1; $(Ph)_2S^+$2-$C_4H_3S$·$PF_6^-$, 127279-88-3; $(CH_3)_2S^+C_6H_4$-*p*-OMe·$PF_6^-$, 127279-89-4; (*c*-$C_4H_7$)$S^+C_6H_4$-*p*-OMe·$PF_6^-$, 129570-30-5; H(C$H_2)_{12}$OCH=$CH_2$ (homopolymer), 29160-06-3; 1,2-epoxydecane (homopolymer), 71332-29-1; $\alpha$-methylstyrene (homopolymer), 25014-31-7; *d,l*-limonene dioxide (homopolymer), 29616-43-1.