Ken Smith is acknowledged for his wonderful efforts in setting up the NMR. Dr. Elizabeth Williams and Ms. Joanne Smith ran the ^{29}Si NMRs, Ralph May, Steve Dorn, and Hans Grade carried out the mass spectrometry analyses, and Dr. Pete Codella carried out the Raman measurements. Professor Sam Danishefsky, Yale University, is thanked for suggesting the allyltrimethylsilane experiments. Cindy Herderich is thanked for help in preparing this manuscript.

Supplementary Material Available: Figure showing relative rate of addition of $(EtO)_3SiH$ to Me_3Si(vinyl) and styrene (1 page). Ordering information is given on any current masthead page.

Photochemistry of Triarylsulfonium Salts

John L. Dektar and Nigel P. Hacker*

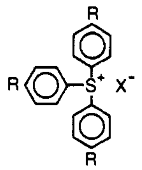
Contribution from the IBM Research Division, Almaden Research Center, San Jose, California 95120-6099. *Received August 11, 1989*

Abstract: The photolysis of triphenylsulfonium, tris(4-methylphenyl)sulfonium, tris(4-chlorophenyl)sulfonium, several monosubstituted (4-F, 4-Cl, 4-Me, 4-MeO, 4-PhS, and 4-PhCO), and disubstituted (4,4′-Me_2 and 4,4′-$(MeO)_2$) triphenylsulfonium salts was examined in solution. It was found that direct irradiation of triphenylsulfonium salts produced new rearrangement products, phenylthiobiphenyls, along with diphenyl sulfide, which had been previously reported. Similarly, the triarylsulfonium salts, with the exception of the [4-(phenylthio)phenyl]diphenylsulfonium salts, gave the new rearrangement products. The mechanism for direct photolysis is proposed to occur from the singlet excited state to give a predominant heterolytic cleavage along with some homolytic cleavage. The heterolytic cleavage gives phenyl cation and diphenyl sulfide, whereas homolytic cleavage gives the singlet phenyl radical and diphenylsulfinyl radical cation pair. These pairs of intermediates then produce the observed photoproducts by an in-cage recombination mechanism and also by reactions with the solvent. The effect of solvent viscosity, solvent polarity, anion, and aryl substituent was examined. The triplet sensitization of the sulfonium salts was also investigated. In contrast to previous reports, the triplet state of the sulfonium salt is labile, leading to a triplet geminate radical pair of phenyl radical and diphenylsulfinyl radical cation. These species ultimately form benzene and diphenyl sulfide as products. Direct photolysis of the [4-(phenylthio)phenyl]diphenylsulfonium salt, gave exclusively diphenyl sulfide, benzene, and acid and decomposes via the triplet excited state.

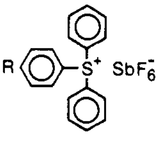
Introduction

Triarylsulfonium salts have found importance in industry as photoinitiators for cationic polymerization and as "photoacid" generators.[1,2] Sulfonium salt photochemistry is also of basic interest due to the variety of intermediates formed, and this has resulted in several studies of the photochemistry of these salts.[3-13]

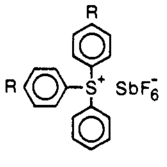
Chart I



1. R = H; X = Br, CF_3SO_3, BF_4, PF_6, SbF_6
2. R = CH_3; X = Br, CF_3SO_3, SbF_6
3. R = Cl; X = Br, SbF_6



4. R = CH_3
6. R = Cl
8. R = CH_3O
10. R = PhS
11. R = F
12. R = Br
13. R = PhCO



5. R = CH_3
7. R = Cl
9. R = CH_3O

These studies suggest that the reaction originates from the excited singlet state of the triarylsulfonium salt and that a phenyl moiety fragments from the triarylsulfonium salt by either a homolytic pathway, to give either a phenyl radical and a diphenylsulfinyl

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radical cation pair[3,5,11] or a heterolytic pathway to give phenyl cation and diphenyl sulfide.[3,4] Subsequent reactions of the phenyl radical and the phenyl cation pairs were then proposed to account for the other photoproducts. A proton acid was also reported to be generated, arising from the reaction of diphenylsulfinyl radical cation or the phenyl cation with solvent. It was reported, however, that the amount of acid generated exceeded the formation of diphenyl sulfide by up to three times, and an additional mechanism explaining this phenomenon was postulated.[7-13]

These previous investigations have shown that the photolysis of triarylsulfonium salts occurs by cleavage of a carbon-sulfur bond in a fairly efficient process. The details of the reactions occurring subsequent to this cleavage were unclear. To resolve the apparent differences in observations and interpretations of the above studies, it seemed necessary to perform a systematic investigation into the photochemistry of triarylsulfonium salts. Parameters to be examined would be the variation of anion, solvent, and aryl substituent and their effect on product formation and sulfonium salt disappearance. Of particular interest was the observation of an excess of acid relative to diphenyl sulfide, which cannot be reasonably accounted for by the previously proposed mechanisms. The current study sought to provide a firm mechanistic explanation for this phenomenon. Another interesting feature was the report of the occurrence of both homolytic and heterolytic cleavages from the excited state of arylsulfonium salts. Most investigations have only been concerned with the homolytic pathway, and information about the relative importance of the alternative heterolytic reaction was desired.

We recently discovered that triphenylsulfonium salts produce (phenylthio)biphenyls in significant amounts, upon direct irradiation[14] and examined how the relative amounts of these products varied upon irradiation in solvents of different viscosity.[15] We have also reported the observation of triplet-sensitized photolysis of triphenylsulfonium salts,[16] which had not previously been observed, and new products from naphthalene-sensitized photolysis of triphenylsulfonium salts.[17] We report herein the comprehensive investigation of the photochemistry of the triarylsulfonium salts.

Results

Spectroscopy. The triarylsulfonium salts were synthesized by modification of the Grignard procedure[18] followed by metathesis of the anion or by phenylation of diarylsulfides with diphenyliodonium hexafluoroantimonate[19] (see Experimental Section). In addition to varying the anion of the triphenylsulfonium salts **1**, several series of substituted triphenylsulfonium salts were prepared. The mono-, bis-, and tris(4-methylphenyl)- (**4**, **5**, and **2**) and mono-, bis-, and tris(4-chlorophenyl)- (**6**, **7**, and **3**, Chart I) sulfonium salts were prepared. The mono- and bis-4-methoxyphenyl salts **8** and **9** and the 4-(phenylthio)phenyl salt **10** were prepared to study electron-donating substituents. The 4-fluorophenyl and the 4-bromophenyl salts **11** and **12**, in combination with 4-chlorophenyl salt **6**, were prepared to examine the possible effect of "heavy atoms". 4-Benzoyl salt **13** was prepared to investigate both the possible internal triplet sensitization and the effect of an electron-withdrawing substituent.

The substituents on the phenyl rings influence the ultraviolet spectra of the triarylsulfonium salts. The parent, triphenylsulfonium **1**, shows the principle absorption maximum at 235 nm with an extinction coefficient of 18 600 cm^{-1} M^{-1}. In mono-4-methyl salt **4**, the maximum is red-shifted to 240 nm (14 500 cm^{-1} M^{-1}), in bis-4-methyl salt **5** the maximum is at 242 nm (22 200 cm^{-1} M^{-1}), and the tris-methyl salt **2** shows a maximum at 244 nm (26 000 cm^{-1} M^{-1}). Thus, the trend for increasing 4-methyl substitution is to red shift the absorption with an increase in the intensity, although the effect becomes weaker with each additional substitution. An analogous trend is seen with increasing 4-chloro substitution, with a red shift and an increase in intensity in the maximum with increasing substitution. However, the *onset* of strong absorption is not influenced by the 4-chloro and 4-methyl substituents, which occurs about 290 nm in the triphenyl, 4-methyl salts, and 4-chloro salts. In contrast, with 4-methoxy substitution in the salts mono-4-methoxy **8** and bis-4-methoxy **9**, the onset of strong absorption occurs at about 300 nm. The maximum is shifted to 262 nm, with the extinction coefficient of **8** being 17 700 cm^{-1} M^{-1} and of **9** being 25 300 cm^{-1} M^{-1}. The 4-benzoyl salt **13** has a maximum at 258 nm (27 700 cm^{-1} M^{-1}), with onset occurring at 305 nm. The benzoyl group is electron-withdrawing, as is the diphenylsulfonio group, and thus no charge-transfer stabilization of the ground state is possible. In contrast, the 4-phenylthio salt **10**, which has the electron-donating phenylthio group in resonance with the electron-withdrawing sulfonium sulfur, shows the most red-shifted maximum at 300 nm (20 300 cm^{-1} M^{-1}), with onset of absorption occurring at 360 nm. As judged by the σ^+ Hammett constants, the methoxy group is considered to be more electron donating than the phenylthio group, which is not consistent with the position of the maximum of the substituted sulfonium salts. An explanation for the red shift of salt **10** relative to the methoxy salt **8** is that sulfur accomodates a positive charge better than oxygen. Thus, a charge-transfer transition to an excited state where electron density decreases on the phenylthio sulfur and increases on the sulfonium sulfur might be responsible for the observed transition. Such transitions are observed in the ultraviolet spectra of "push-pull" substituted aromatic compounds, such as 4-(dimethylamino)-1-cyanobenzene.[20] This would mean that the lowest energy singlet excited state would change from a $\sigma - \sigma^*$ for the triphenylsulfonium salt[21] to the charge-transfer transition for phenylthio salt **10**. The shift of the absorption maximum to lower energy, relative to triphenylsulfonium, is 11 kcal mol^{-1} for methoxy salt **8** and 25 kcal mol^{-1} for phenylthio salt **10**, based on the shift in the absorption maximum.

Exploratory Photochemistry. To verify the previously described photochemistry of triphenylsulfonium salts, an investigation of the volatile photoproducts was undertaken. An aliquot of a 0.01 M solution of triphenylsulfonium triflate (**1**-Tf) in acetonitrile was irradiated in a quartz tube for several minutes by using a Rayonet reactor equipped with RPR-2540 lamps. Capillary GLC analysis of the solution revealed, by comparison with authentic materials, the formation of diphenyl sulfide and small amounts of biphenyl, as previously reported.[3,4,5,7-13] When a solution of **1**-BF_4 and **1**-PF_6 was irradiated in methanol at low conversion, similar products were obtained. No trace of fluorobenzene was observed, in contrast to the earlier report of significant amounts of fluorobenzene formation.[4] Surprisingly, in all of these irradiations at long GLC retention times, three more products were formed, one of which was formed in substantial amounts. GC/MS of these photoproducts revealed a parent molecular ion of mass 262, which represents formal loss of trifluoromethanesulfonic acid from the salt **1**-Tf. The three isomeric (phenylthio)biphenyls, which could be these photoproducts, were prepared by reaction of potassium thiophenoxide with the appropriate isomeric bromobiphenyl.[22] The synthetic (phenylthio)biphenyls had the same retention times as the new photoproducts, and had similar GC/mass spectra. These products were present at very low photochemical conversion of the sulfonium salt, and their formation was linear with irradiation time at short exposures. *o*- (**14**) *m*- (**15**), and *p*-(phenylthio)biphenyl (**16**) are primary photoproducts in the photochemistry of **1**-Tf. Exploratory studies

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Scheme I. Photoproducts from Direct Irradiation of Triphenylsulfonium Salts

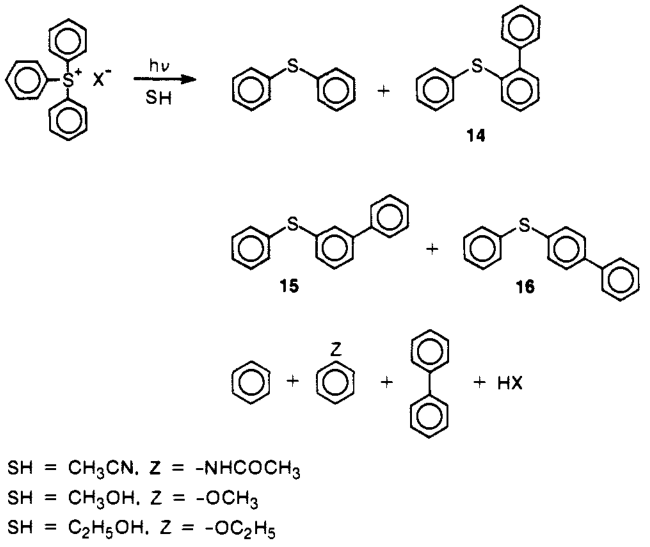


Table I. Products (Concentration × 10^{-4} M) from Photolysis of 0.01 M Acetonitrile Solutions of Triphenylsulfonium Triflate at λ = 254 nm

	biphenyl	Ph_2S	Ph_2S_2	14	15	16	H^+
air[a]	nd[b]	2.99	0.12	3.53	0.35	0.70	8.89
N_2[c]	0.25	3.12	0.12	3.41	0.36	0.69	8.24

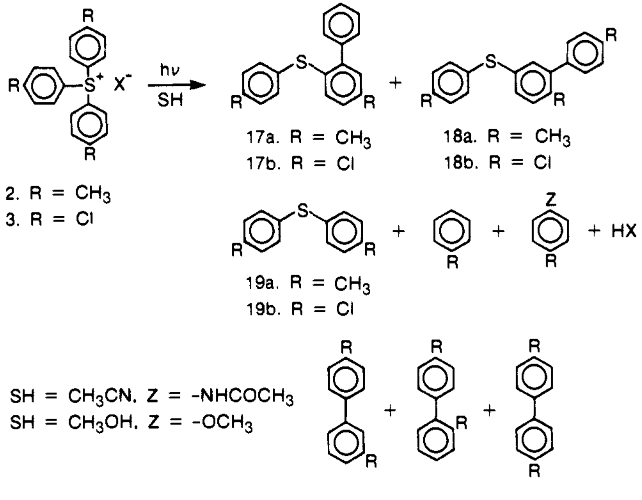
[a] Sample open to air. [b] Not detected. [c] Purged with solvent saturated nitrogen.

showed these compounds were also formed in methanol and dichloromethane solvents and were formed when the anion was Br^-, PF_6^-, BF_4^-, and SbF_6^- (Scheme I).

Product formation was measured against acid formation and sulfonium disappearance in the photolysis of triphenylsulfonium triflate (**1**-Tf) in acetonitrile, in air-saturated and nitrogen-purged solution. Acid was measured spectrophotometrically by using 4-nitrophenoxide as an indicator. The amount of sulfonium salt was measured by using the cobalt thiocyanate complex as previously described.[23] The products formed in parallel irradiations of air- and nitrogen-purged solutions are acid, biphenyl, diphenyl sulfide, diphenyl disulfide, sulfides **14**, **15**, and **16** (Table I). The formation of biphenyl and some of the diphenyl sulfide is suppressed in the air-saturated solutions; however, the major photoproduct is always the *o*-(phenylthio)biphenyl (**14**) regardless of whether air is present. If the sulfur-containing products are summed with twice the diphenyl disulfide concentration, the concentration is 7.82 × 10^{-4} M in air and 7.81 × 10^{-4} M in nitrogen-purged solutions. The sulfur-containing products account for 95% of the acid formed in the nitrogen-purged photolysis of **1**-Tf in acetonitrile, while the presence of oxygen lowers this fraction to 88%. The decrease in the amount of the sulfonium salt measured by a spectrochemical technique[23] is in good agreement (within 5%) with the nitrogen-purged value of the total of volatile photoproducts. Thus by inclusion of the previously unreported rearrangement products **14**, **15**, and **16**, the amount of acid correlates well with total product formation, and sulfonium salt disappearance. Also, the presence of air in the irradiation sample leads to an increase in the amount of acid detected by our method. We also found that irradiation of a solution of diphenyl sulfide in the presence of air produced small amounts of acid.

Tris(4-methylphenyl)sulfonium triflate (**2**-Tf) was chosen for a detailed examination of the photoproducts, as toluene, a probable photoproduct, was easier to quantify than benzene. Irradiation of a 0.01 M solution in acetonitrile using four Rayonet photochemical reactor 254-nm lamps, under nitrogen, for 120 s in a quartz tube, gave ~6.5% conversion of the salt **2**-Tf to products, as judged by the total of the sulfur containing products. HPLC of the irradiation solution gave the same decrease in concentration of **2**-Tf, within the rather large error (20%) of the technique. At long retention time, two major products were observed by GLC. 4′,5-Dimethyl-2-[(4-methylphenyl)thio]biphenyl (**17a**) and 4′,6-dimethyl-3-[(4-methylphenyl)thio]biphenyl (**18a**) were independently prepared by Gomberg–Bachmann reaction of 4-methylbenzenediazonium hexafluorophosphate with bis(4-methylphenyl) sulfide (**19a**).[24] These compounds had the same retention time as the long retention time photoproducts and had similar mass spectra. The sulfur-containing products comprised of sulfide **17a** (59%), sulfide **18a** (9%), and sulfide **19a** (32%). Toluene was found to be present in 52% of the amount of ditolyl sulfide **19a**, and 4-methylacetanilide was found to be present in 72% of **19a** (Scheme II). There is a fairly large error in the quantification of the 4-methylacetanilide, which may explain the observation that the tolyl fragments are present in 124% relative to ditolyl sulfide. Three bitolyls were also present as minor products, the 3,4′ isomer being the major isomer, followed by the 2,4′, with a small quantity of the 4,4′ isomer. The salt **2**-Tf was also irradiated in methanol under similar conditions and the sulfides **17a** (64%), **18a** (3.6%), and **19a** (32%) were formed. Toluene was present at 40% of the concentration of ditolyl sulfide **19a** and 4-methylanisole was formed in 45% of the concentration of **19a**. Only 3,4′-bitolyl and 4,4′-bitolyl were present, with the 3,4′ isomer predominant.

Scheme II. Photoproducts from Direct Irradiation of Tris(4-methylphenyl)- and Tris(4-chlorophenyl)sulfonium Salts



The photolysis of tris(4-methylphenyl)sulfonium triflate (**2**-Tf) was also examined briefly by ^{1}H NMR. After irradiation of a 0.05 M solution of **2**-Tf in methanol-d_4 (λ = 254 nm), several new resonances appeared in the methyl region of the spectrum, upfield of the methyl resonance of the starting salt **2**-Tf. The three different methyl resonances of 4′,5-dimethyl-2-[(4-methylphenyl)thio]biphenyl (**17a**), which was found to be the major recombination product by GLC, were apparent, by comparison with an authentic sample, along with peaks due to toluene, 4-methoxytoluene, and ditolyl sulfide. Thus the results of our ^{1}H NMR study fully support our data obtained from the capillary GLC analysis of the products of photolysis of the triarylsulfonium salts.

Photolysis of the tris(4-chlorophenyl)sulfonium triflate (**3**-Tf) was studied qualitatively by GC/MS. GC peaks with the correct molecular ions for the sulfides **17b** (*m/e* 364), **18b** (*m/e* 364), and **19b** (*m/e* 254), were recorded, along with two dichlorobiphenyls (*m/e* 222), presumably formed from secondary photolysis of sulfides **17b** and **18b**. In addition, some minor peaks with molecular ions (*m/e* 330) corresponding to loss of chlorine from **17b** or **18b** and two peaks with molecular ions (*m/e* 364) corre-

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sponding to isomers of the sulfides **17b** and **18b** were detected. The former GC peaks are probably secondary photoproducts from photodechlorination of the sulfides **17b** and **18b**, whereas the latter isomers are likely to be the result of chlorine scrambling from secondary photolysis of **17b** and **18b** by a dechlorination–chlorination mechanism. Thus, with the exception of the lability of the chlorine substituent, the major photodecomposition pathway for **3**-Tf is identical with **2**-Tf.

To determine the mechanism of origin of the (phenylthio)biphenyl-type products, a crossover experiment was performed. A solution of triphenylsulfonium hexafluoroantimonate (0.017 M) and tris(4-methylphenyl)sulfonium hexafluoroantimonate (0.0071 M) in acetonitrile was irradiated for 20 min in a Rayonet reactor (λ = 254 nm). The concentrations were selected to provide equal absorption of light by the two salts at 254 nm. The acetonitrile solution was extracted with hexane, and the hexane was analyzed by GC/MS and with a GC/FID. Fifty-nine peaks were observed, with 93% of the FID area in 12 peaks that corresponded to the photoproducts of **1**-SbF_6 and **2**-SbF_6 when each salt was irradiated separately. No peak corresponding to methylbiphenyl, the recombination crossover product of a phenyl radical and a tolyl radical, was present. Two peaks with a mass of 290, corresponding to dimethyl(phenylthio)biphenyl, were present in trace amounts. Thus, we conclude that the overwhelming majority of recombination products (the (phenylthio)biphenyls) and the biaryls are formed via an intramolecular rearrangement or an in-cage fragmentation–recombination reaction and not by diffusion of the reactive intermediates through the solvent.

An important factor in the progress of the photolysis of the sulfonium salts **1**–**3** is the absorbance of the photoproducts. Significant absorption of the incident radiation by photoproducts can slow the reaction, an "inner-filter effect", and, if the primary photoproducts are photochemically reactive, secondary photolysis occurs and the result is an altered product distribution. The extinction coefficients of triphenylsulfonium salt **1** and the photoproducts at 254 nm in acetonitrile are as follows (cm^{-1} M^{-1}): **1**, 9600; benzene, 100; biphenyl, 16 600; anisole, 360; acetanilide, 8700; diphenyl sulfide, 10 600; sulfide **14**, 13 900; sulfide **15**, 30 100; and sulfide **16**, 16 700. With use of a photoproduct distribution obtained at 7.2% conversion of starting sulfonium salt, the relative absorbance by the photoproducts is 11.5% of the incident light in acetonitrile at 254 nm. The absorbance of light by the photoproducts is even more pronounced at 300 nm, where salt **1** has an extinction coefficient of only 50, and the sulfides have extinction coefficients of the order of 2000. The situation is only slightly better for the substituted salts. The tris-tolyl salt **2** has a stronger absorption, and the rearranged photoproduct sulfides have relatively weaker absorption than the corresponding compounds resulting from the irradiation of the parent salt, because of steric hindrance to planarity of the conjugated π system **1**. These results show that secondary photolysis and internal filtering in the sulfonium salt system are likely to occur. Thus initial product ratios and quantum yields need to be determined at the lowest conversion possible and must be adjusted for secondary photolysis and photoproduct absorption. In a concentration against time of irradiation study, the rate of formation of photoproducts against time was found to be linear up to about 3.5% conversion of the starting salt **1**-Tf. At 11% conversion, the amounts of the photoproducts formed was found to be about 10% less than the amounts calculated by extrapolation from 3.5% conversion. In this investigation, all quantum yields and relative quantum yields were determined at about 1–2% conversion, with stirring of the photolysis solution.

Biphenyl was found to be a significant product in the direct photolysis of triphenylsulfonium triflate. A concentration vs time study of the formation of the photoproducts of **1**-Tf showed that biphenyl was not a significant *primary* photoproduct at 0.01 M concentration, since there was an induction time before its appearance in the nitrogen-purged photolysis. At the onset of biphenyl formation with increasing time of irradiation, the onset of diphenyl disulfide formation was also found to occur. Upon prolonged irradiation, the relative amounts of the (phenylthio)biphenyls decrease. This would imply that biphenyl observed in the irradiation of salt **1** is a product of the photolysis of the (phenylthio)biphenyls and is thus a secondary photoproduct of the photolysis of salt **1**. In fact, when an acetonitrile solution of 2-(phenylthio)biphenyl (**14**) is irradiated, biphenyl is formed, along with diphenyl disulfide. Additional evidence for the origin of the major amount of the biphenyl in the irradiation of arylsulfonium salts at these concentrations and light intensities is that the irradiation of tris(4-methylphenyl)sulfonium triflate (**2**-Tf) yields 2,4′-dimethylbiphenyl and 3,4′-dimethylbiphenyl and only a small amount of 4,4′-dimethylbiphenyl. If the biaryls resulted from coupling of aryl radicals, then the 4,4′-dimethylbiphenyl should be the only biaryl product observed. Scheme II shows that the 2,4′- and the 3,4′-dimethylbiphenyl should be the products from the photolysis of the (phenylthio)biphenyl-type products formed in the irradiation of **2**-Tf. Interestingly, previous work on the photolysis of tris(4-methoxyphenyl)sulfonium hexafluoroarsenate detected the presence of three isomeric dimethoxybiphenyls, although their formation was thought to occur by the combination of two 4-methoxyphenyl radicals.[5]

Table II. Quantum Yields of Triphenylsulfonium Salts, λ = 248 nm

1 salt	concn	solvent	Φ_{PhBr}[a]	$\Phi_{\mathrm{Ph_2S}}$[b]	Φ_{14}[c]	Φ_{PTBP}[d]
triflate	0.010 M	MeCN	–	0.21	0.24	0.31
bromide	0.010 M	MeCN	0.022	0.24	0.22	0.28
triflate	0.051 M	MeCN	–	0.21	0.25	0.32
bromide	0.053 M	MeCN	0.074	0.34	0.20	0.25
triflate	0.011 M	MeOH	–	0.19	0.25	0.31
bromide	0.011 M	MeOH	0.0074	0.20	0.24	0.31
bromide + 0.1 M TBAB[e]	0.011 M	MeOH	0.029	0.23	0.22	0.27

[a] Bromobenzene appearance. [b] Diphenylsulfide appearance. [c] Sulfide **14** appearance. [d] Total of sulfides **14**, **15**, and **16** appearance. [e] TBAB = Tetrabutylammonium bromide.

Salt Effects. Quantum yields were determined for the photolysis of triphenylsulfonium bromide and triflate in acetonitrile (Table II). It can be seen from the table that the presence of bromide ion affects both the absolute and relative efficiency of product formation. The presence of the nucleophilic bromide ion serves to increase the amount of escape product, diphenyl sulfide, and decrease the amount of recombination product, (phenylthio)biphenyl. As seen from the table, in both methanol and acetonitrile, bromide decreases the quantum yield of recombination product formation and increases the escape quantum yield by the same amount, except in the 0.05 M acetonitrile experiment, where the recombination quantum yield decreases by 0.07 and the diphenyl sulfide quantum yield increases by 0.13 on change of anion from triflate to bromide. This effect is stronger in the less nucleophilic solvent acetonitrile. The amount of bromobenzene formed is of the order of magnitude as the change in quantum yields of the sulfur containing products. This experiment suggests that bromide is able to intercept the caged intermediates to some extent, and divert the intermediates away from recombination. The most likely intermediate for bromide to intercept would be phenyl cation. Thus, this experiment provides evidence for the intermediacy of phenyl cation in the mechanism of recombination product formation. Phenyl cation as an intermediate in the formation of the escape product was indicated by the formation of anisole and acetanilide, formed respectively by reaction of phenyl cation with methanol and acetonitrile.

Bromide is able to increase the quantum yield for photodecomposition, as shown by the increase in quantum yield in the 0.05 M solutions in acetonitrile. This would come about if a mechanism of internal conversion was attack at sulfur by phenyl cation. Bromide partially diverts phenyl cation from this reaction and increases the sulfonium consumption quantum yield.

Additional evidence for phenyl cation intermediacy is provided by the efficiencies of bromobenzene and anisole formation. The quantum yield for anisole formation is 0.143 for irradiation of 0.011 M **1**-triflate and bromide solutions and is 0.122 for irradiation of 0.011 M **1**-Br and 0.1 M tetrabutylammonium bromide. In methanol, the selectivity of bromide relative to methanol for

Table III. Solvent Effects on Product Formation from Irradiation of Triphenylsulfonium Triflate, λ = 254 nm

solvent	η	Rel Φ	(**14** + **15** + **16**):Ph_2S
CH_2Cl_2	0.41	1.00	1.68
CH_3CN	0.35	0.94	1.05
$CH_3CO_2CH_3$	0.36	0.93	1.72
CH_3OH	0.55	0.93	1.28
$C_2H_5CO_2CH_3$		0.91	1.77
$CH_3CO_2C_2H_5$	0.44	0.80	1.91
C_2H_5OH	1.12	0.74	1.74
$(CH_3)_2CHOH$	2.20	0.57	2.56
$HOCH_2CH_2OH$	18.0	0.33	2.07
Glycerol	1500	0.11	5.63

Table IV. Effect of Solvent Viscosity on Triphenylsulfonium Triflate (**1**-Tf) Photolysis

solvent	viscosity (cP)	Φ_{total}[a]	Φ_{Ph_2S}	Φ_{14}	Φ_{15}	Φ_{16}
methanol	0.545	0.50	0.189	0.247	0.022	0.042
15% glycerol	1.20	0.47	0.165	0.254	0.018	0.031
30% glycerol	3.05	0.38	0.130	0.224	0.012	0.019

[a] Quantum yield of total sulfur-containing products. Solutions are in methanol, and viscosities were measured at 23 °C.

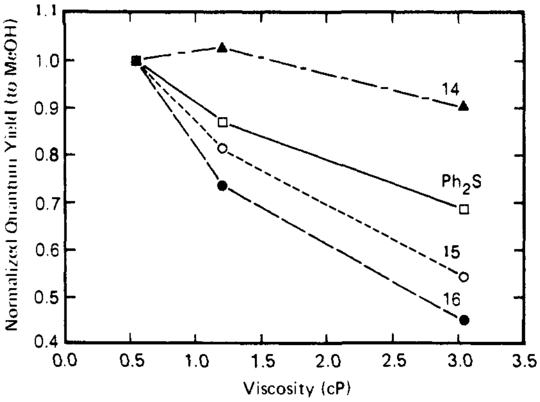

Figure 1. Viscosity dependence of triphenylsulfonium triflate photolysis at λ = 248 nm.

the phenyl fragment is about 50–100:1. The selectivity of methyl iodide for bromide over methanol is about 600000:1.[26] If ion pairing effects are important for the sulfonium salt in methanol, then they should enhance the selectivity of bromide over methanol. Thus, the species that reacts with bromide or methanol is not very selective. Phenyl cation should be a nonselective electrophile.

Solvent Effects. The relative quantum yields for formation of the organic photoproducts in a variety of solvents are shown in Table III. A general trend of decreasing relative quantum yield, and increasing ratio of (phenylthio)biphenyls to diphenyl sulfide, is observed as the solvent viscosity increases. The solvent mixtures shown in Table IV were selected for similar polarity as measured by E_T 30, although glycerol is a better hydrogen atom donor towards radicals than methanol. The effect of increase in viscosity is to decrease the disappearance quantum yield, and to increase the relative amounts of recombination to escape products. Figure 1 shows the change in product distribution, normalized to a quantum yield of one for each product in methanol. The effect of increasing viscosity causes initially an increase in the relative yield of 2-(phenylthio)biphenyl and a decrease in the yield of the 3 and 4 isomers. As viscosity is further increased, the relative yields of all three (phenylthio)biphenyls decreases, due to more recombination of the sulfide and phenyl fragments, without rearrangement, to give starting material. The largest relative decrease in quantum yield is for the 4-substituted (phenylthio)biphenyl, followed by the 3 isomer.

Table V. Polarity Effects on Triphenylsulfonium Triflate Photolysis

solvent	viscosity (cP)[a]	polarity (E_T 30)	$\Phi_{Total\ S}$[b]	**14**:Ph_2S	ratio **14**:**15**:**16**
EtOAc	0.426	38.1	0.46	2.07	87:5:8
CH_2Cl_2	0.449[c]	41.1	0.49	1.73	84:5:11
MeOH	0.545	55.5	0.50	1.32	79:7:14
MeCN	0.375[c]	46.0	0.53	1.16	78:7:15

[a] From ref 51. [b] Sum of product quantum yields for sulfur containing products. [c] At 15 °C.

The change in reaction efficiency and product distribution with change in solvent polarity at similar viscosity is shown in Table V. There is a small decrease in quantum yield with decrease in solvent polarity. More recombination occurs relative to escape in the less polar solvents, along with a change in the distribution of the rearrangement products.

Viscosity effects were also investigated in ethanol/glycerol mixtures, the aim being to minimize the variation in solvent polarity and to systematically vary the viscosity. Tris(4-methylphenyl)sulfonium triflate was irradiated in ethanol and 30% glycerol in ethanol. The relative quantum yield for reaction was taken to be the relative rate of formation of the sum of the sulfur containing products. The relative quantum yield in 30% glycerol in ethanol solution is 74% of that occurring in ethanol, which is consistent with the viscosity effects obtained on photolysis of triphenylsulfonium salts in various alcohols. In addition, the ratio of the ortho sulfide **17a** to the meta sulfide **18a** increases from 23 in ethanol to 36 in 30% glycerol. The ratio of the ortho sulfide **17a** to ditolyl sulfide **19a**, which is a measure of the amount of recombination relative to fragmentation, is 3.36 in ethanol and 4.17 in 30% ethylene glycol. Finally, the ratio of the sum of the toluene concentration plus twice the 4,4′-bitolyl concentration to ditolyl sulfide **19a**, which should be a measure of the radical-derived escape products to the total escape products, is 0.62 in ethanol and 0.69 in 30% ethylene glycol. Presumably, the remainder of the phenyl moieties are found in phenyl cation derived products, such as phenetole.

Substituent Effects. The relative photoreactivity of some of the substituted sulfonium salts was determined by measuring the rate of acid formation. Product analysis could not be used, as it was not possible to obtain authentic samples of all of the photoproducts, particularly for the unsymmetrically substituted salts. HPLC analysis of the amount of conversion of the sulfonium salt was also used and showed a correlation with the acid values. The errors in the HPLC analysis for amount of sulfonium salt photolyzed were fairly large, being about 20%, as compared with the error in the acid measurement technique which is about 5%. It was found that the monosubstituted SbF_6 salts bromo **12**, fluoro **11**, chloro **6**, and tris-tolyl **2** formed acid at about the same rate as triphenyl **1**. Bis-chlorophenyl salt **7** formed acid at 95% of the triphenylsulfonium efficiency, tris-chloro **3** reacted at 92%, mono-methoxy **8** formed acid at 64%, and bis-methoxy **9** produced acid at only 59% of the salt **1** efficiency. The 4-phenylthio salt **10**, however, produced acid at 112% of the triphenylsulfonium rate. Finally, the 4-benzoyl salt **13** produced acid at only 20% of the triphenyl salt **1** rate. From these results, both the 4-benzoyl and methoxy groups depress the acid production rate. The 4-phenylthio group appears exceptional, in that it produces significantly more acid than triphenylsulfonium, as opposed to the stronger electron-donating methoxy group, which produces less acid than the salt **1**.

The types of products and the regioselectivity of product formation were qualitatively examined for some of the salts. 4-Benzoylphenyldiphenylsulfonium hexafluoroantimonate (**13**) on irradiation produces (phenylthio)benzophenone and diphenyl sulfide, in a 15:1 ratio. When this ratio is corrected for the symmetry of the salt because there are two ways to make (phenylthio)benzophenone and only one way to make diphenyl sulfide, the ratio is 7.5:1. Also, there are two long retention time peaks in the GC trace, which were found in GC/mass spectra to have molecular formulae consistent with the recombination products. 4-Methoxyphenyl salt **8** and the bis-methoxyphenyl salt **9** were

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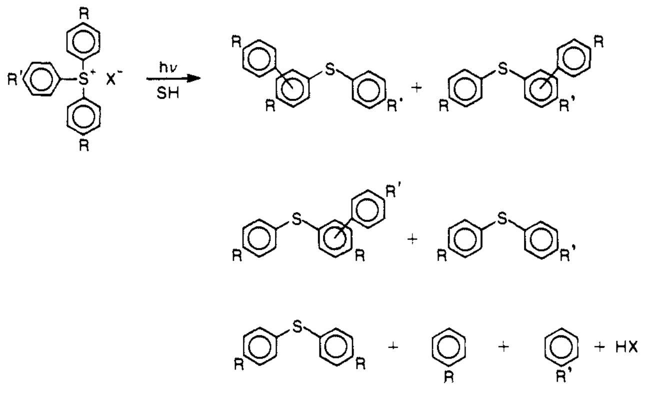
(25) Kalmus, C. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 449.
(26) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.

Scheme III. Photoproducts from Direct Irradiation of Mono- and Disubstituted Triphenylsulfonium Salts



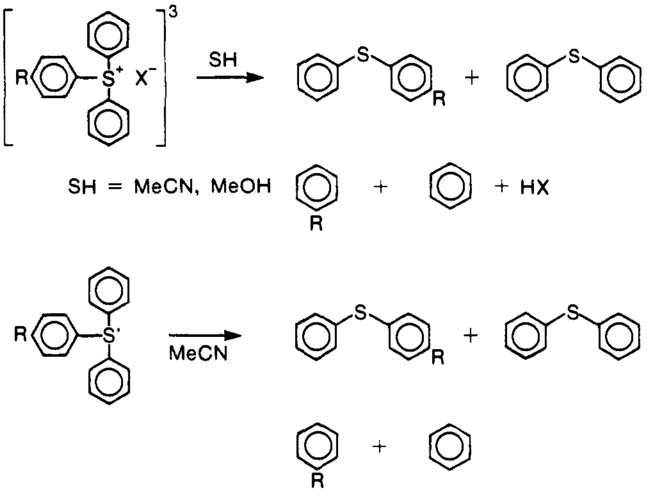
R = H; R' = CH$_3$, CH$_3$O, PhCO, F, Br, Cl
R' = H; R = CH$_3$, CH$_3$O, Cl

also irradiated, and the products were examined by GC (Scheme III). Salt **8** produced both methoxyphenyl phenyl sulfide and diphenyl sulfide, in a 0.76:1 ratio, or a 0.38:1 corrected ratio. A significant quantity of at least seven long retention time products was formed, which by GC/MS had the correct parent ion (*m/e* 292) for the rearrangement products. Salt **8** has the possibility of forming eight isomeric rearrangement products. Bis-methoxy salt **9** gave bis(methoxyphenyl) sulfide and methoxyphenyl phenyl sulfide in a 0.24:1 ratio, which when corrected is 0.48:1. Seven long retention time products were observed by GC, with the correct molecular ion (*m/e* 322) for the rearrangement products. Seven possible isomers can occur for this rearrangement in the photolysis of salt **9**. Similar results were obtained from photolysis of the 4-methyl **4**, 4-chloro **6**, and 4-fluoro **11** salts. In the all cases examined, for the sulfide fragmentation products, the major sulfide formed had the electron-withdrawing group, and the aryl fragment preferentially lost had the electron-donating group. Selectivity in the direct photolysis to form these products was moderate. Without knowing the absolute quantities of the rearrangement products, no conclusions can be drawn about relative importance of substituents on the regioselectivity of the initial cleavage of the sulfonium salt, but clearly both types of carbon–sulfur bonds in the mono- and disubstituted sulfonium salts can undergo photochemical cleavage. This cleavage then leads to the formation of both cage-escape products (the diaryl sulfides) and cage-recombination products (the (arylthio)biaryls).

Table VI. Ratio of Substituted Aryl Phenyl Sulfide to Diphenyl Sulfide on Irradiation of Monosubstituted Aryl Sulfonium Salts

	Photolysis Method		
salt	direct (λ = 254 nm)	acetone-sensitized	anthracene-sensitized
(p-FPh)Ph$_2$S$^+$ SbF$_6^-$	10.79	3.61	1.46
(p-ClPh)Ph$_2$S$^+$ SbF$_6^-$	4.91	0.46	1.23
(p-MePh)Ph$_2$S$^+$ SbF$_6^-$	1.34	0.50	3.46
(p-MeOPh)Ph$_2$S$^+$ SbF$_6^-$	0.76	0.020	3.17

Scheme IV. Products from Photodecomposition by Triplet Energy Transfer and Electron-Transfer Sensitization of Sulfonium Salts



R = F, Cl, Me, MeO

Triplet Photoreactivity. As a preliminary experiment in the study of solvent effects on triphenylsulfonium salt photoreactivity, 1.0×10^{-2} M solutions of **1**-SbF$_6$ were irradiated in acetone, acetonitrile, ethyl acetate, methanol, and ethanol. The ratios of the total of the (phenylthio)biphenyls to diphenyl sulfide obtained on 254-nm irradiation were, correspondingly, 0.60, 1.73, 2.81, 1.70, and 2.37. Under these conditions, the acetone solution absorbed about 55% of the incident radiation. To determine if triplet sensitization of the triphenylsulfonium salt was responsible for the anomalous ratio of products in acetone, the same solution was irradiated by using 300-nm Rayonet lamps through Pyrex. Under these conditions acetone absorbed greater than 98% of the light. No (phenylthio)biphenyls were observed, and only diphenyl sulfide and benzene were formed at a fairly rapid rate. Thus, it appears that the triplet state of triphenylsulfonium can be formed via acetone sensitization and reacts to form diphenyl sulfide, presumably through a triplet diphenylsulfinyl radical cation–phenyl radical pair. The relative rates of formation of diphenyl sulfide were determined with use of sensitizer solutions in acetonitrile, where the sensitizer concentration was adjusted so the sensitizer absorbed more than 98% of the light at 300 nm. Irradiation in pure acetone had a rate of 81 relative to occurring upon xanthone sensitization, while irradiation of an acetonitrile solution of 1-indanone sensitizer gave a relative rate of 10.1 and acetophenone had a relative rate of 7.5. Irradiation of **1**-Tf in the absence of sensitizer under the same conditions produced a relative rate of 0.95, with some traces of sulfide **14**. When a nitrogen-purged solution of acetophenone and **1**-Tf was irradiated against an air-saturated sample the relative rate was 7.5 vs 0.80. The triplet-state energies for the sensitizers are as follows: acetone, ca. 80 kcal mol^{-1}; 1-indanone, 75.8; acetophenone, 74.1; and xanthone, 74.0.[27] The limiting quantum yield and the Stern–Volmer quenching constant were determined for quenching of acetone and 1-indanone by triphenylsulfonium triflate by product analysis. The limiting quantum yield in acetone is 0.76, and the $k_q\tau$ is 620. For 1-indanone, the quantum yield is 0.37 and the quenching constant is 17. These results indicate that the triplet excited state of triphenylsulfonium is highly labile. The reason for the decrease in the limiting quantum yield with sensitizer may be that one of the products of the photolysis, diphenyl sulfide, has a triplet energy of 70 kcal mol^{-1},[28] and can act as a competitive quencher of the excited state of the sensitizer. The efficiency of production of diphenyl sulfide is correlated with the triplet energy of the sensitizer, and oxygen strongly quenches the formation of product. These results are best explained by triplet energy transfer to **1**, followed by homolytic dissociation of the sulfonium triplet to a phenyl radical–diphenylsulfinyl radical cation *triplet* radical pair. In contrast to the singlet radical pair which results from direct irradiation of triphenylsulfonium salts, the triplet pair reacts only via cage-escape reactions, with no formation of the (phenylthio)biphenyl recombination products. The triplet state of **1** would appear to be about 75 kcal mol^{-1} above the ground state, which is consistent with the phosphoresence quenching results.[7]

The sensitized irradiation of triphenylsulfonium triflate by 1-indanone in methanol was carried out. Even at 10% conversion, no trace of anisole was formed. This is in contrast to the direct irradiation of **1**-Tf in methanol, where anisole is a significant product. The failure to observe the formation of anisole in the triplet sensitized irradiation argues against the involvement of phenyl cations in this process.

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(27) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(28) Becker, R. S.; Jordan, A. D.; Kolc, J. *J. Chem. Phys.* **1973**, *59*, 4024.

Substituent effects were also examined in the triplet-sensitized irradiation of some sulfonium salts (Table VI). Solutions (0.005 M) of the hexafluoroantimonate salts **1**, mono-methyl **4**, mono-chloro **6**, mono-fluoro **11**, and mono-methoxy **8** were irradiated at 300 nm in nitrogen-purged acetone solution. All salts formed only a mixture of aryl phenyl and diphenyl sulfides, at the same rate, within 5%. Also, the respective arenes and benzene were formed (Scheme IV). The ratios of the sulfides formed are corrected, because diphenyl sulfide formation is only half as probable as aryl phenyl sulfide formation. The ratios for aryl phenyl sulfide relative to diphenyl sulfide are as follows: for fluoro **11**, 1.80; methyl **4**, 0.248; chloro **6**, 0.230; and for methoxy **8**, 0.010. These results contrast with the direct irradiation of methoxy salt **8**, in which a mixture of methoxyphenyl phenyl sulfide and phenyl sulfide were obtained, along with significant quantities of the rearrangement products. The trends observed in the ratios of products with change in substituent is roughly in the same direction as the direct irradiation. Compared with only the escape products from the direct irradiation of these salts, triplet cleavage is more selective toward loss of the aryl fragment with the electron-donating group.

These results can also explain the anomalous behavior of the phenylthio salt **10**. This salt, on direct irradiation, produced acid at 112% of the triphenyl salt **1** rate, in comparison with methoxy salt **8**, which produced acid at only 64% of the **1** rate. Also, no long retention time peaks in the GC trace, which might correspond to the rearrangement products of salt **10**, were observed. It has previously been observed that salt **10** regioselectivity cleaves to form diphenyl sulfide, and not 1,4-bis(phenylthio)benzene,[29] and this finding is confirmed in our investigations. These results taken together argue strongly for the direct photolysis of phenylthio salt **10** proceeding through the triplet state. The regioselectivity observed in the irradiation of **10** is the same as for the triplet cleavage of methoxy salt **8** and differs from that in the direct irradiation of methoxy salt **8**. The absence of rearrangement products is consistent with all of the triplet reactions of the sulfonium salts studies so far but not with the direct irradiation results. Finally, the acid formation rate on direct photolysis appears to be lowered by increasing numbers of electron-donating substituents except for phenylthio, which increased the rate over all other substituents. There has been mention that the cleavage of salt **10** occurs via a triplet state as deduced from a flash photolysis experiment.[11] The most likely explanation for the triplet cleavage of salt **10** is that the singlet cleavage reaction becomes slower with respect to the intersystem crossing reaction. Methoxy salt **8** shows a lower quantum yield on direct photolysis, which may either result from enhanced back-reaction of the initially formed cleavage products or from increased stability of the initially formed sulfonium excited state. To form the observed products, back-reaction would have to occur regioselectivity at sulfur, with no ring attack that would form (phenylthio)biphenyl-type products. The observations for salt **10** render the first possibility unlikely. If phenylthio increases the stability of the singlet excited state in a similar way as the methoxy substituent, then this stability might give intersystem crossing a chance to compete with the photochemistry of the singlet state of salt **10**. The rate of intersystem crossing is known to depend on the relative energetics of the excited singlet and triplet state, in that a relatively small but exothermic relationship of the singlet and triplet states results in a maximum ISC rate.[30] The triplet state of sulfonium salts seems to be around 75 kcal mol^{-1}, and the ultraviolet spectrum of phenylthio salt **10** is the most red-shifted of any of the simply substituted sulfonium salts. The onset of absorption is about 350 nm, which corresponds to an energy of 82 kcal/mol^{-1}. Also, UV spectroscopy indicates that the lowest singlet excited state is a charge-transfer excited state for the phenylthio derivative **10** which would enhance ISC, whereas the lowest singlet excited state for the triphenylsulfonium salt is $\sigma - \sigma^*$.[21] Thus, it appears that both a stabilization of the singlet state and an increase in ISC is feasible for the salt **10** and may serve to explain its unusual photochemistry.

Discussion

The photochemical reactivity of triarylsulfonium salts has been known since 1970, when a study of the photolysis of these salts in alcohol solvents was reported.[3] On irradiation of triphenylsulfonium salts for 61 h in a 16-bulb Rayonet reactor, a complex distribution of products was obtained. Several mechanisms were proposed, with the excited-state homolysis of the sulfonium salt to phenyl radical and diphenylsulfinyl radical cation being the mechanism most consistent with the evidence. It should be noted, however, that under these conditions, the assignment of products as directly arising from the sulfonium salt is tenuous, as the products may actually be formed from stable intermediate photoproducts. Another study using a similar irradiation time and solvent found significant quantities of anisole and fluorobenzene among the photoproducts.[4] This study concluded that a heterolysis of the sulfonium salt excited state was an operative mechanism.

The photoactivity of triarylsulfonium salts gained additional interest when these compounds were found to be photoinitiators of cationic polymerization.[5] In connection with the polymerization studies, some investigation of the solution photochemistry was also performed. Additional evidence was provided for the excited-state homolysis mechanism by irradiation of tris(4-methoxyphenyl)sulfonium hexafluoroarsenate monitored by ^1H NMR in acetone-d_6. It should be noted that we have found acetone to be a triplet sensitizer (vide supra) and promotes homolysis from the triplet excited state to a triplet radical pair which gives 100% escape products. However we have shown in the direct photolysis, more than half of the sulfur containing products derived from the sulfonium salt are present as the (phenylthio)biphenyl rearrangement products. These authors also reported quantum yields for the formation of bis(4-methoxyphenyl) sulfide from tris(4-methoxyphenyl)sulfonium hexafluoroarsenate of 0.17 at 313 nm and 0.19 at 366 nm in acetonitrile.[31]

Another set of investigators studied both the flash photolysis and products of irradiation of triarylsulfonium salts.[7-13] The photolysis of triphenylsulfonium hexafluoroarsenate was found to have a quantum yield of 0.26 for diphenyl sulfide formation and 0.74 for acid formation, at less than 20% conversion with ±20% error. The value of 0.26 is close to our value of 0.19 for diphenyl sulfide formation in the photolysis of triphenylsulfonium triflate in acetonitrile, but the value of 0.74 for acid formation is higher than our quantum yield of triphenylsulfonium consumption of 0.53. We have found that a conversion of 20% is too high to obtain an accurate quantum yield in the triphenylsulfonium system, due to absorption of light by the photoproducts and have used a conversion of 1–2% to circumvent this problem. In addition, we estimate the error in our quantum yield measurement techniques to be at most 5%. We found that the presence of oxygen tends to increase the amount of acid observed relative to argon- or nitrogen-purged solutions. Interestingly, these investigators speculated on the homolytic recombination mechanism to form (phenylthio)biphenyl product **16**,[13] but despite a number of investigations on the photochemistry of arylsulfonium salts, this product or its isomers **14** or **15** were not observed. The formation of "excess acid" was proposed to occur via a bimolecular reaction of diphenyl sulfide with diphenylsulfinyl radical cation.[7-13] Under our conditions, at low conversion, this mechanism cannot be operating, as the initial concentration of diphenyl sulfide is zero, leading to a zero rate of this reaction. By this mechanism, the amount of acid formed relative to diphenyl sulfide formation should also show a dependence on time of irradiation, which was not demonstrated. Flash photolysis of 4-(phenylthiophenyl)diphenylsulfonium hexafluoroarsenate found that the diphenyl-

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(29) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2697.

(30) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978.

(31) The text in ref 5 reports the substrate as tris(4-methylphenyl)sulfonium salt but the figure shows tris(4-methoxyphenyl)sulfonium salt. The correct compound is tris(4-methoxyphenyl)sulfonium. The authors thank Professor J. V. Crivello for this information. One reviewer has incorrectly cited the quantum yield as being for the tris(4-methylphenylsulfonium).[12,18]

Scheme V. Mechanism for Direct Photolysis of Triphenylsulfonium Salts

$$\mathrm{Ph_3S^+\ X^-} \xrightarrow{h\nu} \overline{[\mathrm{Ph_3S^+\ X^-}]^*} \qquad (1)$$

$$\overline{[\mathrm{Ph_3S^+\ X^-}]^*} \longrightarrow \overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \qquad (2)$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow \overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \qquad (3)$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow 14 + 15 + 16 + \mathrm{H^+} \qquad (4)$$

$$\overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \longrightarrow 14 + 16 + \mathrm{H^+} \qquad (5)$$

$$\overline{\mathrm{Ph_2S\quad Ph^+\quad X^-}} \longrightarrow \mathrm{Ph_2S + Ph^+ + X^-} \qquad (6)$$

$$\overline{\mathrm{Ph_2S^{+\cdot}\quad Ph^\cdot\quad X^-}} \longrightarrow \mathrm{Ph_2S^{+\cdot} + Ph^\cdot + X^-} \qquad (7)$$

$$\mathrm{Ph^+ + RH} \longrightarrow \mathrm{PhR + H^+} \qquad (8)$$

$$\mathrm{Ph_2S^{+\cdot} + RH} \longrightarrow \mathrm{Ph_2S^+{-}H + R^\cdot} \qquad (9)$$

$$\mathrm{Ph_2S^+{-}H} \longrightarrow \mathrm{Ph_2S + H^+} \qquad (10)$$

$$\mathrm{Ph^\cdot + RH} \longrightarrow \mathrm{PhH + R^\cdot} \qquad (11)$$

$$\mathrm{Ph^\cdot + R^\cdot} \longrightarrow \mathrm{Ph{-}R} \qquad (12)$$

$$\mathrm{Ph^\cdot + Ph^\cdot} \longrightarrow \mathrm{Ph{-}Ph} \qquad (13)$$

$$\mathrm{R^\cdot + R^\cdot} \longrightarrow \mathrm{R{-}R} \qquad (14)$$

sulfinyl radical cation was produced as a transient species. We have found that the photolysis of this salt proceeds through homolysis of the triplet state, in contrast to the photolysis of the parent triphenylsulfonium salts, which occurs by a predominantly heterolytic mechanism. The products from the heterolysis, phenyl cation and diphenyl sulfide, would be expected to absorb near the absorption of triphenylsulfonium in the ultraviolet, so that these species would be difficult to observe by flash photolysis. It is also apparent that the extrapolation of similar reactivity from the 4-(phenylthio)phenyl salt to the triphenyl salt is not justified.

Our investigations of the photochemistry lead us to propose a somewhat different mechanism for photolysis than that put forth earlier. We find that our results are best explained by proposing the products arise from a major path involving heterolytic cleavage and a minor path involving homolytic cleavage (Scheme V). The details of these mechanisms account for all of the observations made in this study.

The rearrangement products observed in the direct irradiation of triarylsulfonium salts are similar to those obtained in the photo-Fries reaction[25] and can be formally derived from the sulfonium salt by migration of an aryl moiety from sulfur to one of the other aryl sulfide rings, followed by loss of H^+. In (arylmethyl)benzylsulfonium salts, however, such recombination products have been observed.[21] The formation of these products was proposed to occur either in-cage from a geminate radical pair or via a concerted mechanism. However, there are important differences between the traditional photo-Fries reaction and the photorearrangement of sulfonium salts. The photo-Fries reaction usually proceeds through the excited singlet state to form a radical pair, by homolysis of a carbon–heteroatom bond. In this reaction, fragmentation and recombination products are formed. In the initial report of the photo-Fries reaction, the ratios of 2- to 3- to 4-hydroxyacetophenone recombination product obtained on irradiation of phenyl acetate were 60:1:50.[32] There are only two other reports of a photo-Fries reaction forming a meta recombination product, in nonstructurally constrained systems.[33,34] In the present study, significant quantities of meta recombination product were found. The reason for this difference between triarylsulfonium salt photolysis and the photo-Fries reaction is that the sulfonium salt photolysis apparently proceeds through dissociation of the carbon–sulfur bond to form both a phenyl cation–diphenyl sulfide pair by a heterolytic cleavage, and a phenyl radical–diphenylsulfinyl radical cation singlet pair by a homolytic cleavage. The regioselectivity of the photo-Fries reaction of phenyl acetate is governed by the delocalization of the odd-electron density of the intermediate phenoxyl radical onto the ortho and para positions of the phenoxyl radical. This leads to the almost exclusive formation of *o*- and *p*-hydroxyacetophenone products. A similar situation would occur in the homolysis of the triphenylsulfonium salt, and we have obtained evidence for this regioselectivity (vide infra). Heterolysis of triphenylsulfonium would result in a phenyl cation–diphenyl sulfide geminate pair. The phenyl cation in this pair could react with the diphenyl sulfide in an electrophilic aromatic substitution reaction, which could result in a larger relative amount of the *m*-(phenylthio)biphenyl product.

Evidence for phenyl cation involvement in escape product formation is the observation of acetanilide in acetonitrile solution and anisole in methanol solution. The increase in the relative amount of the escape product, diphenyl sulfide, to the recombination products, the (phenylthio)biphenyls, on increasing bromide anion concentration points towards phenyl cation being an intermediate in the formation of the (phenylthio)biphenyls. The bromide reacts with the phenyl cation in cage, which serves to decrease the amount of recombination product, and as a consequence of the phenyl cation trapping, increases the quantum yield of diphenyl sulfide. In addition, the formation of the *m*-(phenylthio)biphenyl (**15**), in comparison with thermal and other reactions which form (phenylthio)biphenyls, argues for the intermediacy, in part, of phenyl cation. The thermolysis of benzenediazonium tetrafluoroborate in acetonitrile in the presence of diphenyl sulfide yields a 2:1 ratio of sulfide **16** to **15**, in addition to sulfide **14**. These conditions (acetonitrile solvent) have been reported to lead to the formation of aryl cations or aryl cation like species.[35] The regioselectivity of the reaction of phenyl radical with diphenylsulfinyl radical cation can be judged from another reaction. The photoreaction of naphthalene with triphenylsulfonium initially yields a geminate tetrad of naphthalene radical cation, phenyl radical, diphenyl sulfide, and anion.[17] Naphthalene radical cation subsequently oxidizes the diphenyl sulfide to form diphenylsulfinyl radical cation, which then can react with the phenyl radical to form (phenylthio)biphenyls. In this reaction, almost no meta product **15** is formed, the ratio of **16** to **15** being at least 10:1. Phenyl radical has previously been reported to react with diphenylsulfinyl radical cation to yield triphenylsulfonium cation, although the possibility of formation of the (phenylthio)biphenyls was not further examined.[36] The isomer distribution actually obtained on direct irradiation of salt **1** resembles the reaction of benzenediazonium (producing phenyl cation) with diphenyl sulfide and not the cage reaction of phenyl radical with diphenylsulfinyl cation. These observations are best explained by invoking the intermediacy of phenyl cation in the direct photolysis of triphenylsulfonium salts. We did not observe fluoroarenes in the photolysis of sulfonium hexafluorophosphate and tetrafluoroborate salts, in contrast to a previous investigation which reported fluorobenzene formation.[4] Since this previous investigation used an extremely long irradiation time with an intense source of ultraviolet light, it is likely that the fluoroarenes observed were secondary photoproducts. The photolysis and thermolysis of *p*-methylbenzenediazonium tetrafluoroborate in various solvents has been studied.[37] This investigation found, for methanol solvent, the ratio of the solvent substitution product 4-methylanisole to the Schiemann product 4-fluorotoluene was 15:1 for photolysis, and 25:1 for thermolysis. It can be concluded that the formation of the fluoroarene Schiemann product is a minor reaction for the decomposition of diazonium salts in polar solvents. Thus, the failure in our investigation to find fluoroarene does not contradict the involvement of phenyl cations in sulfonium photolysis.

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Direct cleavage to form a phenyl radical–diphenylsulfinyl radical cation pair is also a possibility. The diphenylsulfinyl radical cation has been observed from the flash photolysis of the (phenylthio)phenyl sulfonium salt **10**[9,11] and has also been observed in the triplet-sensitized photolysis of the triphenyl salt **1**.[38] Formation of this pair is necessary to explain the formation of the reduction product benzene. It is possible that the excited state of the sulfonium salt undergoes nonspecific cleavage to form both the heterolytic and homolytic products. Another possible explanation for the formation of the phenyl radical–diphenylsulfinyl pair would be that phenyl cation is a sufficiently strong oxidizing agent to oxidizing diphenyl sulfide. Although no direct determination of the oxidation potential of phenyl radical has been made, an estimate can be made by use of the gas-phase phenyl radical vertical ionization potential (9.20 V),[39] and a correlation between vertical ionization potential and the oxidation potential in acetonitrile vs SCE.[40,41] More recently, a study has reported that this value of the ionization potential represents ionization to the first triplet excited state of phenyl cation and that a better value for the ionization to the ground state would be 8.79 eV.[42] Use of this value in the correlation leads to an estimate of the oxidation potential of the phenyl radical of 2.10 V. This value, combined with the oxidation potential of diphenyl sulfide (1.41 V, MeCN, SCE, Pt electrode)[43] yields a ΔE of -16 kcal mol^{-1}, with the phenyl radical–diphenylsulfinyl radical cation pair more stable. The photochemistry of triarylsulfonium salts, through this model, would involve heterolytic cleavage to form phenyl cation, followed by a competition between rapid electron transfer to form the phenyl radical–diphenylsulfinyl radical cation pair and recombination to produce the (phenylthio)biphenyls, although the direct formation of both pairs of intermediates from the sulfonium salt excited state is not ruled out by the experimental evidence. Formation of the phenyl cation–diphenyl sulfide pair from the phenyl radical–diphenyl sulfinyl cation pair would be prohibited on energetic grounds.

A possible mechanism for the formation of anisole (in methanol) and acetanilide (in acetonitrile) might be the solvolysis of the excited state of the sulfonium salt. The evidence of the solvent dependence of the quantum yields renders this hypothesis unlikely, however. If solvent assistance were necessary, then the overall quantum yield should show a dependence on solvent nucleophilicity. However, there is not much change in the quantum yield of sulfonium salt disappearance with change in solvent. Methanol is more nucleophilic than acetonitrile, yet the quantum yield is 5% lower. Thus, the solvent does not appear to play a major role in determining the overall efficiency of the initial photoreaction. The solvent is important in the subsequent reactions of the initially formed reactive intermediates, through viscosity and polarity effects.

The products obtained are consistent with the proposed mechanism. Benzene is formed from the reaction of phenyl radical with hydrogen atom donors, presumably the solvent. Diphenyl sulfide is formed when the phenyl cation reacts with a solvent molecule instead of diphenyl sulfide in cage. Diphenyl sulfide might also be formed by cage escape of diphenylsulfinyl radical cation and reduction by abstraction of hydrogen from the solvent as proposed earlier.[3] However, there is no direct evidence to support or rule out this proposal. The (phenylthio)biphenyls result from in-cage combination of phenyl cation and diphenyl sulfide, or phenyl radical–diphenylsulfinyl radical cation singlet pair, through a cyclohexadienyl cation intermediate, which can lose H^+. Diphenyl disulfide results from the secondary photolysis of diphenyl sulfide or the (phenylthio)biphenyls, which produce phenylthio radical and an aryl radical. The stability of phenylthio radical prevents hydrogen-abstraction reactions, and the only alternative available is dimerization. Biphenyl results from the secondary photolysis of the (phenylthio)biphenyls, through the intermediacy of biphenyl radicals. Acid is produced from the reaction of phenyl cation with solvent, phenyl cation with diphenyl sulfide, phenyl radical with diphenylsulfinyl radical cation, and diphenylsulfinyl radical cation with solvent. The amount of acid found correlates well with the amount of products obtained on photolysis of triphenylsulfonium salts.

Evidence for this mechanism is also provided by the solvent effects observed. The major effect of an increase in solvent viscosity is to decrease the rate of formation of products. It is most likely that this occurs through an increase in the rate of re-formation of starting sulfonium salt, instead of an inhibition of the initial photo cleavage. Evidence for the re-formation of triphenylsulfonium cation from the photolytic intermediates is also provided by the increase in sulfonium disappearance quantum yield in acetonitrile with increasing bromide concentration. This increase would occur by diversion of phenyl cation from attack on diphenyl sulfide by bromide. In addition, phenyl radical has been reported to react with diphenylsulfinyl radical cation to yield triphenylsulfonium cation,[36] and so the photochemical internal conversion pathway of re-formation of the sulfonium salt is possible from both sets of the postulated intermediates. Viscosity also increases the ratio of rearrangement products, (phenylthio)biphenyls, to escape product, diphenyl sulfide, which should result if the intermediate species could not diffuse apart as rapidly. An additional effect with increase in viscosity is to increase the relative amount of the 2-(phenylthio)biphenyl recombination product to the 3-(phenylthio)biphenyl and the relative amount of the 3 isomer to the 4 isomer. Thus, increase in solvent viscosity inhibits the formation of the more distant rearranged products.

The effect of solvent polarity, which is to increase the relative amount of rearrangement to escape in less polar solvents, is more difficult to explain. A possible explanation is that the less polar solvents, ethyl acetate and dichloromethane, are much less nucleophilic than methanol and acetonitrile, and this would slow the rate of reaction of the aryl cage species with the solvent cage. If the rate of recombination reactions are less affected by change in solvent than the cage-escape reactions, then more recombination product would be obtained in less polar solvents.

The tris(4-methylphenyl)sulfonium photolysis results obtained in the mixed alcohol solvents also support some other aspects of this proposed mechanism. The fraction of escape products appearing as radical-derived products increases with solvent viscosity. This would be the case if phenyl radical was a secondary product of the initial photoproduct, probably from the phenyl cation–diphenyl sulfide–counter ion geminate triad. The phenyl cation trapping efficiency would be lower in the more viscous solvent, which means that the rate of electron transfer relative to trapping should increase, which would then lead to more radical derived products. An unlikely alternate explanation would be that the viscous solvent favors more homolytic cleavage from the sulfonium excited state than heterolytic cleavage. It is unclear how viscosity would have this effect. The increase in the ratio of the ortho sulfide to the meta sulfide with viscosity shows that, at least, the meta sulfide formation is viscosity dependent. This can be explained by a process where the phenyl moiety in the initially formed triad must reorient in-cage to the meta position of the diphenyl sulfide moiety for this reaction to occur. This can be rationalized by invoking a viscosity dependent solvent cage "loosening" which is necessary for this in-cage reorientation to occur. The influence of viscosity on this ratio renders unlikely a concerted rearrangement, not involving caged fragment species, as a much smaller viscosity effect would result. The decrease in the relative quantum yield with increasing viscosity is also consistent with this in-cage reorientation process. Here, a recombination of the product triad to form starting sulfonium salt would account for the lowering of quantum yield, as the more viscous solvent should slow down the in-cage reorientation to form recombination products, relative to the proposed re-formation of sulfonium salt, which would require

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no reorientation. The ratio of rearrangement products to ditolyl sulfide increases with viscosity, as the increase in solvent viscosity should favor the in-cage recombination reactions over the diffusion and solvent reaction of the triad fragments. Finally, the solvent viscosity results show that the formation of rearrangement products must be a cage type reaction, as opposed to the formation of these products by diffusion of the initial photolysis products through solution.

A cage reaction is indicated in the mechanism of formation of the (phenylthio)biphenyl products on direct irradiation of the triphenylsulfonium salts. These products are not formed by diffusion of the reactive intermediates through the solvent as indicated by the viscosity and crossover experiments. However, the solvent cage is reactive with the proposed intermediates, which are the phenyl cation–diphenyl sulfide pair and the phenyl radical–diphenylsulfinyl radical cation pair. Thus, the reactions which we have called "escape" reactions result not only from the diffusive escape of the reactive intermediates from the solvent cage, but also from in-cage reaction of these intermediates with the solvent. Thus, these solvent reactions serve to decrease the cage lifetime from that which might be expected from these species in an inert solvent cage.

Product formation from direct photolysis of triphenylsulfonium salts can be described by three types of processes. In Scheme V, steps 1–5 represent the in-cage reactions from decomposition of the singlet excited state to give the (phenylthio)biphenyls and acid. Reactions of the cationic species with the solvent cage, steps 6–10, also give acid, along with diphenyl sulfide. Finally, the radical species react with solvent and terminate by radical–radical reactions in steps 11–14.

Triplet Reactivity. Previous workers have reported of a lack of triplet state reactivity of arylsulfonium salts and proposed that sensitization can only occur by an electron transfer mechanism.[7-13] Our results show that the triplet excited state is highly labile, that the relative rate of formation of aryl sulfide photoproducts is correlated with sensitizer energy, and that the rate is retarded by oxygen. The electron transfer mechanism can be ruled out for acetone sensitization by a consideration of the regioselectivity of cleavage for a monosubstituted sulfonium salt. Direct irradiation of mono-*p*-methoxy salt **9** produced a ratio of methoxyphenyl phenyl sulfide to diphenyl sulfide of 0.76:1, along with recombination products (Table VI). Acetone sensitization of salt **9** gave a ratio of 0.02:1, with no recombination products. Anthracene sensitization, which proceeds by a electron-transfer mechanism,[7-13,17,44] produced a ratio of sulfides of 3.17:1, again with no formation of recombination products. It is clear from these results that each method of photolysis proceeds by a different mechanism. The reason for the selectivity in cleavage of the triplet state of salt **9** is unclear, but is probably related to the strength of the two types of aryl–sulfur bonds in the triplet state.

No recombination products, (phenylthio)biphenyls, are observed in the triplet-sensitized photolysis, which apparently proceeds through a triplet phenyl radical–diphenylsulfinyl radical cation geminate pair. Evidence for this homolysis is the absence of phenyl cation derived products and the observation of the diphenylsulfinyl radical cation by flash photolysis under acetone-sensitized conditions.[38] This triplet radical pair would diffuse apart and react with the solvent before intersystem crossing to form the singlet geminate radical pair occurs. If the singlet radical pair were formed, the (phenylthio)biphenyl recombination products would be expected to form. However, it was observed in the photolysis of 2-(*tert*-butylthio)acetophenone, which proceeds through a triplet state, that 40% of the phenacyl radicals escaped the solvent cage, and the remaining 60% of the radical pairs underwent in-cage reactions to re-form the starting ketone.[45] The initially formed triplet radical pair would have to undergo intersystem crossing to the singlet radical pair to re-form starting material, and apparently, the cage lifetime permitted this process to occur. The radical pair in this reaction is less reactive than the sulfonium derived radical pair; the phenacyl sulfide yields a phenacyl radical and a *tert*-butylthio radical, whereas the sulfonium salt yields phenyl radical and diphenylsulfinyl radical cation. The higher reactivity of the sulfonium-derived radical pair with the solvent would decrease the cage lifetime. Since no recombination products are observed, the cage lifetime appears to be less than the intersystem crossing lifetime for the sulfonium-derived radical pair.

It is interesting to compare the triplet-sensitized reaction of the triarylsulfonium salts with that of the diaryliodonium salts.[44,46] Triplet-sensitized photoreaction of diaryliodonium salts leads to the formation of products similar to those found in the direct irradiation, in a similar distribution, although the sensitizer absorbs most of the incident light in the sensitized process.[44,46] The implication of these results for iodonium salts is that intersystem crossing in the initial photochemical triad (either phenyl radical–iodobenzene radical cation-anion or phenyl cation–iodobenzene anion) is rapid compared with the rate of reaction to form products or diffusion. Iodine is known to have an enhancing effect on the rate of intersystem crossing. The sulfonium results presented here argue for slow intersystem crossing relative to in-cage reaction and diffusion. Thus, no recombination products are obtained.

Conclusions

This investigation has resolved the incongruities between the previous studies of the photochemistry of triarylsulfonium salts. We have found that the direct photolysis proceeds by both heterolytic and homolytic cleavage of the singlet excited sulfonium salt, with the heterolytic cleavage predominating. The reactive intermediates formed from this bond cleavage undergo cage reactions to generate (phenylthio)biphenyls, previously undetected photoproducts, and escape reactions with the solvent. It is possible that the phenyl cation is able to oxidize the diphenyl sulfide in cage, leading to formation of singlet phenyl radical–diphenylsulfinyl radical cation pair. We also found that the triplet state of the triarylsulfonium states is reactive. Triplet sensitization of these salts leads only to escape products, diaryl sulfide and arene.

Various perturbations upon the basic triphenylsulfonium system were examined. Solvent viscosity affected the distribution of products in a way consistent with the proposed mechanism. Solvent polarity had a strong effect whose origins are not clear. Nucleophilic anions could intercept some of the reactive intermediates, and thus alter the observed product distribution. Substituents, in most cases, lowered the quantum yield of the salt photodissociation process. For the important case of *p*-phenylthio, however, the quantum yield increased. By comparison with other data, we conclude that the direct photolysis of the [*p*-(phenylthio)phenyl]diphenylsulfonium salt proceeds through the triplet state, unlike the parent triphenylsulfonium salt.

Experimental Section

General. ^{1}H NMR spectra were determined on a Varian EM-390 (90 MHz) or on an IBM-250 (250 MHz) spectrometer. ^{13}C NMR spectra were determined on the IBM-250 at 63 MHz. Ultraviolet spectra were measured on a Hewlett-Packard 8451 spectrometer. Infrared spectra were measured on an IBM instruments IR-44 spectrophotometer. Melting points were determined in open capillaries, on a "Mel-temp" apparatus (Laboratory Devices). Capillary GLC analysis was performed on a Hewlett-Packard 5890 with flame ionization detector, equipped with a Shimadzu Chromtopac C-R1B integrator/recorder or a Hewlett-Packard 3396A integrator/recorder. The column was a J&W Scientific DB-1 (cross-linked methyl silicone) 0.4 μm by 0.18 mm by 20 m. GC/MS were determined on a Hewlett-Packard 5995 spectrometer, equipped with a J&W Scientific DB-1 column similar to that used on the capillary GLC/FID instrument.

Synthesis. The preparation of the parent triphenylsulfonium salts **1** was achieved either by reaction of phenylmagnesium bromide with diphenyl sulfoxide[18] or by the copper-catalyzed reaction of a diphenyliodonium salt with diphenyl sulfide.[19] The Lewis acid catalyzed reaction of benzene with chlorine and sulfur compounds does not produce pure triphenylsulfonium salts, but rather a mixture of oligomeric condensation products.[47] The Grignard route was chosen because it yielded relatively

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large quantities of salt with good purity. This method was used to prepare **1-Br** and -BF_4, tris(4-methylphenyl)sulfonium (**2**) bromide, and tris(4-chlorophenyl)sulfonium (**3**) bromide. Conversion of the bromides into the hexafluoroantimonate and hexafluorophosphate salts was accomplished simply by stirring the bromide with $NaSbF_6$ or KPF_6 in anhydrous acetone. The use of anhydrous acetone eliminates the possibility of hydrolysis of the hexafluoroantimonate anion, which occurs rapidly in aqueous solution.[48] The bromides were also converted to the trifluoromethanesulfonate (triflate) salts by reaction of triflic acid with the bromide in dichloromethane. The unsymmetrically substituted sulfonium salts were prepared by the second procedure,[19] reaction of diphenyliodonium hexafluoroantimonate with the appropriately substituted aryl sulfide.

Triphenylsulfonium Bromide (1-Br). The preparation of **1**-Br was a modification of the literature synthesis.[18] Bromobenzene (47 g, 0.30 mol) and Mg (7.0 g, 0.29 mol) were used to form phenylmagnesium bromide in 140 mL of anhydrous ether. The ether was removed with stirring under aspirator vacuum with slow heating to 80 °C. Benzene (50 mL) was added, followed by *n*-heptane (100 mL). Diphenyl sulfoxide (12.1 g, 0.060 mol) was dissolved in benzene (75 mL). This solution was added to the Grignard solution slowly over 1 h at 80 °C. Stirring was continued for 3 h, followed by cooling to ambient temperature. A 25% solution of hydrobromic acid in water (200 mL) was added slowly to the reaction mixture (exothermic). The layers were separated, and the organic layer was extracted twice with 30-mL portions of 5% aqueous hydrobromic acid. The combined aqueous layers were extracted three times with 250-mL portions of dichloromethane. The dichloromethane extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The yellow residue was dissolved in the minimum amount of dichloromethane, and four volumes of ether was added to precipitate **1**-Br: 10.80 g, 52% based on sulfoxide; mp 285–7 °C (lit.[18] 285–6 °C); ^{1}H NMR ($CDCl_3$) δ 7.8 (m); IR (KBr pellet) 1473, 1442, 1063, 994, 770, 754, 684, 502 cm^{-1}.

In a similar fashion, **2**-Br and **3**-Br were prepared.

Tris(4-methylphenyl)sulfonium bromide (2-Br): mp 238–41 °C; ^{1}H NMR (acetone-d_6) δ 7.5–7.8 (m, 4 H), 2.45 (s, 3 H); IR (KBr pellet) 1586, 1486, 1400, 1186, 1182, 1069, 826, 818, 808, 520, 502 cm^{-1}. Anal. Calcd for $C_{21}H_{21}SBr$: C, 65.45; H, 5.49; S, 8.32. Found: C, 64.86; H, 5.40; S, 8.63.

Tris(4-chlorophenyl)sulfonium bromide (3-Br): ^{1}H NMR (chloroform-*d*) δ 8.0 (d, 2 H), 7.6 (d, 2 H). This salt was highly hygroscopic and was converted to either the hexafluoroantimonate or triflate immediately.

Triphenylsulfonium Hexafluoroantimonate (1-SbF_6). Triphenylsulfonium bromide (15.0 g, 0.044 mol) and sodium hexafluoroantimonate (11.3 g, 0.044 mol) were suspended in 250 mL of acetone, with stirring, for 1 h. The remaining solid was filtered, the acetone was removed from the filtrate under reduced pressure, and the resulting solid was recrystallized from 250 mL of 95% ethanol/5% 2-propanol. White crystals were obtained: 18.67 g, 85% yield; mp 177–8 °C; ^{1}H NMR (acetone-d_6) δ 7.8 (m); IR (KBr pellet) 1478, 1449, 1066, 997, 753, 749, 659 cm^{-1}; UV (CH_3CN) λ_{max} 235 nm (18 600), 268 (3700), 277 (2600). Anal. Calcd for $C_{18}H_{15}SF_6Sb$: C, 43.31; H, 3.03; S, 6.42. Found: C, 43.38; H, 3.01; S, 6.48.

In a similar fashion, the SbF_6 salts of **2** and **3** were prepared.

Tris(4-methylphenyl)sulfonium hexafluoroantimonate (2-Sb_6): mp 145–7 °C; ^{1}H NMR (acetone-d_6) δ 7.5–7.8 (m, 4 H), 2.45 (s, 3 H); IR (KBr pellet) 1588, 1487, 1401, 1185, 814, 657, 504 cm^{-1}; UV (CH_3CN) λ_{max} 244 nm (26 000). Anal. Calcd for $C_{21}H_{21}SF_6Sb$: C, 46.60; H, 3.91; S, 5.92. Found: C, 46.65; H, 3.86; S, 6.08.

Tris(4-chlorophenyl)sulfonium hexafluoroantimonate (3-SbF_6): mp 197–8 °C; ^{1}H NMR (acetone-d_6) δ 7.95 (d, 2 H), 7.80 (d, 2 H); IR (KBr pellet) 1565, 1474, 1397, 1089, 1007, 827, 746, 654, 505, 487 cm^{-1}; UV (CH_3CN) λ_{max} 248 nm (30 500).

Triphenylsulfonium Trifluoromethanesulfonate (2-Tf). A 25.6-g portion of triphenylsulfonium bromide was dissolved in 200 mL of dichloromethane. Trifluoromethanesulfonic acid (6.8 mL) was added in one portion. The solution was heated to reflux for 2 h and evolved HBr fumes. The solution was cooled and washed with two 50-mL portions of water and with one 50-mL portion of aqueous saturated sodium bicarbonate solution. The dichloromethane layer was dried with $MgSO_4$, and the solvent was removed with use of a rotary evaporator. The white solid was dissolved in 1 L of boiling ethyl acetate, filtered, and cooled slowly to give white crystals, which were collected to give 25.6 g (83%): mp 132–4 °C (lit.[49] mp 135–7 °C); ^{1}H NMR (acetone-d_6) δ 7.8 (m); ^{13}C NMR (acetone-d_6) δ 135.53, 132.44, 132.20, 125.86, 122.35 (q); IR (KBr pellet) 1477, 1449, 1263, 1153, 1033, 755, 745, 689, 639, 516 cm^{-1}.

In a similar fashion, 2-Tf and 3-Tf were prepared.

Tris(4-methylphenyl)sulfonium trifluoromethanesulfonate (2-Tf): mp 105–6 °C; ^{1}H NMR (acetone-d_6) δ 7.5–7.8 (m, 4 H), 2.45 (s, 3 H); IR (KBr pellet) 1591, 1262, 1224, 1154, 1032, 811, 639, 634, 518 cm^{-1}. Anal. Calcd for $C_{22}H_{21}S_2O_3F_3$: C, 58.13; H, 4.66; S, 14.11. Found: C, 58.26; H, 4.71; S, 14.29.

Tris(4-chlorophenyl)sulfonium trifluoromethanesulfonate (3-Tf): mp 114–6 °C; ^{1}H NMR (acetone-d_6) δ 8.00 (d, 2 H), 7.80 (d, 2 H); IR (KBr pellet) 1476, 1281, 1275, 1257, 1227, 1167, 1092, 1033, 1009, 748, 697, 642 cm^{-1}. Anal. Calcd for $C_{19}H_{12}S_2O_3Cl_3F_3$: C, 44.24; H, 2.35; S, 12.43. Found: C, 43.50; H, 2.50; S, 12.08.

General Procedure for Arylation of Aryl Sulfides.[19] An equimolar mixture of the sulfide and diphenyliodonium hexafluoroantimonate and 3 mol % of cupric acetylacetonate was suspended in chlorobenzene and heated to reflux for 3 h. The mixture was cooled, washed with three portions of ether, and dissolved in a minimum amount of dichloromethane. The dichloromethane solution was filtered through silca gel, and the solvent was removed under reduced pressure. The residue was recrystallized from 95% ethanol/5% 2-propanol to give white to off-white crystals. The following salts were prepared in this way.

(4-Methylphenyl)diphenylsulfonium hexafluoroantimonate (4-SbF_6): mp 101–2 °C; ^{1}H NMR (acetone-d_6) δ 7.9 (m, 12 H), 7.65 (d, 2 H), 2.50 (s, 3 H); ^{13}C NMR (acetone-d_6) 147.0, 135.4, 133.1, 132.4, 132.1, 131.8, 125.8, 122.0, 21.5 ppm; IR (KBr pellet) 1633, 1602, 1493, 1452, 1189, 1158, 1071, 1028, 752, 697, 686, 659 cm^{-1}; UV (CH_3CN) λ_{max} 240 nm (19 500). Anal. Calcd for $C_{19}H_{17}SF_6Sb$: C, 44.47; H, 3.34; S, 6.25. Found: C, 44.48; H, 3.33; S, 6.57.

Bis(4-methylphenyl)phenylsulfonium hexafluoroantimonate (5-SbF_6): mp 119–20 °C; ^{1}H NMR (acetone-d_6) δ 7.94–7.81 (m, 5 H), 7.78 (d+, 4 H), 7.65 (d+, 4 H), 2.49 (s, 6 H); ^{13}C NMR (acetone-d_6) 147.1, 135.3, 133.0, 132.3, 131.9, 131.6, 126.4, 122.3, 21.5 ppm; IR (KBr pellet) 1591, 1492, 1478, 1448, 1187, 1073, 812, 752, 698, 687, 659, 510 cm^{-1}; UV (CH_3CN) λ_{max} 242 nm (22 200). Anal. Calcd for $C_{20}H_{19}SF_6Sb$: C, 45.56; H, 3.63; S, 6.08. Found: C, 45.56; H, 3.66; S, 6.39.

(4-Chlorophenyl)diphenylsulfonium hexafluoroantimonate (6-SbF_6): mp 133–6 °C; ^{1}H NMR (acetone-d_6) δ 8.0–7.7 (m); ^{13}C NMR (acetone-d_6) δ 141.65, 135.70, 133.76, 132.51, 132.10, 125.48, 124.49; IR (KBr pellet) 1478, 1450, 1396, 1092, 1069, 1009, 828, 750, 744, 682, 656, 508 cm^{-1}; UV (CH_3CN) λ_{max} 240 nm (21 900). Anal. Calcd for $C_{18}H_{14}SClF_6Sb$: C, 40.52; H, 2.64; S, 6.01. Found: C, 40.51; H, 2.64; S, 6.43.

Bis(4-chlorophenyl)phenylsulfonium hexafluoroantimonate (7-SbF_6): mp 186–8 °C; ^{1}H NMR (acetone-d_6) δ 8.00–7.81 (m); ^{13}C NMR (acetone-d_6) δ 141.8, 135.8, 133.8, 132.6 (two carbons) 132.2, 125.3, 124.3; IR (KBr pellet) 1478, 1450, 1397, 1092, 1009, 829, 820, 744, 681, 658, 644, 510 cm^{-1}; UV (CH_3CN) λ_{max} 244 nm (27 300). Anal. Calcd for $C_{18}H_{13}SCl_2F_6Sb$: C, 38.06; H, 2.31; S, 5.65. Found: C, 38.02; H, 2.27; S, 6.22.

(4-Methoxyphenyl)diphenylsulfonium hexafluoroantimonate (8-SbF_6): mp 136–7 °C; ^{1}H NMR (acetone-d_6) δ 7.8 (m, 12 H), 7.30 (d, 2 H), 3.90 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 165.70, 135.23, 134.67, 132.32, 131.54, 126.74, 118.02, 114.42, 56.61; IR (KBr pellet) 1589, 1495, 1451, 1447, 1267, 1177, 1024, 747, 697, 684, 665, 656 cm^{-1}; UV (CH_3CN) λ_{max} 262 nm (17 700). Anal. Calcd for $C_{19}H_{17}SOF_6Sb$: C, 43.12; H, 3.24; S, 6.06. Found: C, 43.08; H, 3.20; S, 6.35.

Bis(4-methoxyphenyl)phenylsulfonium hexafluoroantimonate (9-SbF_6): mp 112–4 °C; ^{1}H NMR (acetone-d_6) δ 7.80 (m, 9 H), 7.34 (d, 4 H), 3.95 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 165.5, 134.9, 134.2, 132.2, 131.0, 117.9, 115.6, 56.6; IR (KBr pellet) 1591, 1576, 1497, 1311, 1271, 1179, 1075, 1022, 833, 756, 659, 527 cm^{-1}; UV (CH_3CN) λ_{max} 262 nm (25 300). Anal. Calcd for $C_{20}H_{19}SO_2F_6Sb$: C, 42.96; H, 3.43; S, 5.73. Found: C, 42.84; H, 3.42; S, 6.03.

[4-(Phenylthio)phenyl]diphenylsulfonium hexafluoroantimonate (10-SbF_6): mp 121–3 °C; ^{1}H NMR (acetone-d_6) δ 7.90–7.78 (m, 12 H), 7.58–7.53 (m, 5 H), 7.43 (d, 2 H); ^{13}C NMR (acetone-d_6) δ 149.30, 135.64, 135.44, 132.74, 132.41, 131.82, 131.15, 130.87, 130.33, 129.36, 125.93, 121.11; IR (KBr pellet) 1562, 1472, 1447, 1064, 998, 757, 683, 655, 494 cm^{-1}; UV (CH_3CN) λ_{max} 300 nm (20 300). Anal. Calcd for $C_{24}H_{19}S_2F_6Sb$: C, 47.46; H, 3.15; S, 10.56. Found: C, 47.48; H, 3.14; S, 10.80.

(4-Fluorophenyl)diphenylsulfonium hexafluoroantimonate (11-SbF_6): mp 151–2 °C; ^{1}H NMR (acetone-d_6) δ 8.04 (m, 2 H), 7.93 (m, 10 H), 7.82 (t+, 2 H); ^{13}C NMR (acetone-d_6) δ 166.9 (d, *J* = 264 Hz), 135.6, 135.36 (d, *J* = 10 Hz), 132.48, 131.96, 125.84, 121.15 (d, *J* = 5 Hz), 119.85 (d, *J* = 24 Hz); IR (KBr pellet) 1590, 1494, 1477, 1450, 1446,

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1245, 1162, 843, 752, 683, 658, 525 cm^{-1}; UV (CH_3CN) λ_{max} 236 nm (17800). Anal. Calcd for $C_{18}H_{14}SF_7Sb$: C, 41.81; H, 2.73; S, 6.20. Found: C, 41.82; H, 2.69; S, 6.53.

(4-Bromophenyl)diphenylsulfonium hexafluoroantimonate (12-SbF$_6$): mp 169–71 °C; ^{1}H NMR (acetone-d_6) δ 8.02 (dt, 2 H), 7.96–7.75 (m, 12 H); ^{13}C NMR (acetone-d_6) δ 135.7, 135.5, 133.7, 132.5, 132.1, 130.2, 125.4, 125.2. IR (KBr pellet) 1482, 1476, 1450, 1068, 1007, 826, 748, 728, 682, 664, 656, 504 cm^{-1}; UV (CH_3CN) λ_{max} 244 nm (22700). Anal. Calcd for $C_{18}H_{14}SBrF_6Sb$: C, 37.40; H, 2.44; S, 5.55. Found: C, 37.44; H, 2.38; S, 5.80.

(4-Benzoylphenyl)diphenylsulfonium hexafluoroantimonate (13-SbF$_6$): mp 125–7 °C; ^{1}H NMR (acetone-d_6) δ 7.4–8.3 (m); ^{13}C NMR (acetone-d_6) δ 195.2, 143.60, 136.96, 135.87, 134.38, 132.76, 132.62, 132.42, 132.15, 130.83, 129.60, 129.32, 125.33; IR (KBr pellet) 1661, 1448, 1400, 1283, 1252, 915, 802, 782, 750, 696, 684, 659 cm^{-1}; UV (CH_3CN) λ_{max} 326 nm (5200). Anal. Calcd for $C_{25}H_{19}SOF_6Sb$: C, 49.77; H, 3.17; S, 5.32. Found: C, 49.79; H, 3.14; S, 5.39.

2-(Phenylthio)biphenyl (14).[24] Under nitrogen, thiophenol (5.85 g, 0.053 mol) and potassium hydroxide (3.8 g) in 50 mL of dimethylformamide was heated to reflux, and 10 mL of water and solvent was distilled off. The solution was cooled, and 2-bromobiphenyl (10.0 g, 0.043 mmol) was added in 20 mL of dimethylformamide. The reaction mixture was heated at reflux for 5 h, and 20 mL of solvent was distilled. The remaining solution was cooled, and 150 mL of water and 40 mL of hexanes were added. The layers were separated, the hexanes layer was washed twice with 50-mL portions of water, and the hexanes layer was dried ($MgSO_4$). The solvent was removed with use of a rotary evaporator, and the residue distilled under vacuum to give 5.1 g: bp 170–3 °C (1.5 Torr), 46%; ^{1}H NMR (chloroform-d) δ 7.0–7.3 (m); ^{13}C NMR (chloroform-d) δ 142.97, 140.56, 135.57, 134.94, 131.77, 131.17, 130.50, 129.31, 129.07, 127.97, 127.89, 127.37, 127.05, 126.73; IR (NaCl plates, thin film) 1583, 1476, 1462, 1439, 1426, 1039, 1024, 1009, 773, 747, 700, 692 cm^{-1}; UV (CH_3CN) no maximum above 200 nm, 254 nm (13900), 300 nm (2800), 313 nm (800). Anal. Calcd for $C_{18}H_{14}S$: C, 82.40; H, 5.38; S, 12.22. Found: C, 82.43; H, 5.29; S, 12.51.

The other two isomers were prepared similarly.

3-(Phenylthio)biphenyl (15): bp 184–90 °C (2 Torr); ^{1}H NMR (chloroform-d) δ 7.0–7.7 (m); ^{13}C NMR (chloroform-d) δ 142.16, 140.24, 136.32, 135.56, 131.03, 129.64, 129.53, 129.48, 129.16, 128.73, 127.52, 127.05, 127.01, 125.82; IR (NaCl plates, thin film) 1588, 1583, 1478, 1467, 1439, 755, 742, 698, 614, 596, 583, 532 cm^{-1}; UV (CH_3CN) λ_{max} 250 nm (31100). Anal. Calcd for $C_{18}H_{14}S$: C, 82.40; H, 5.38; S, 12.22. Found: C, 82.48; H, 5.33; S, 12.33.

4-(Phenylthio)biphenyl (16): mp 60–61 °C; ^{1}H NMR (chloroform-d) δ 7.1–7.7 (m); ^{13}C NMR (chloroform-d) δ 140.19, 139.87, 135.65, 134.85, 131.25, 131.08, 129.19, 128.78, 127.78, 127.42, 127.07, 126.88; IR (KBr pellet) 1480, 1453, 1440, 1086, 1080, 1023, 829, 763, 749, 742, 697, 690 cm^{-1}; UV (CH_3CN) λ_{max} 262 nm (18800) 282 (18400). Anal. Calcd for $C_{18}H_{14}S$: C, 82.40; H, 5.38; S, 12.22. Found: C, 84.94; H, 5.30; S, 12.45.

Photoproducts 17 and 18.[26] Bis(4-methylphenyl) sulfide (10 g) was heated to melting. Potassium acetate (0.82 g) and acetonitrile (50 μL) was added, followed by 4-methylbenzenediazonium hexafluorophosphate (1.1 g). The mixture was stirred for 3 h at 50 °C. The mixture was cooled, dissolved in 50 mL of hexane, and extracted twice with 25-mL portions of water. The hexanes were dried ($MgSO_4$) and were removed under reduced pressure. The residue was distilled under vacuum to remove most of the unreacted ditolyl sulfide. The pot residue was chromatographed on silica gel, with hexane elutant. The fractions containing the desired products (by GLC) were then further purified by preparative GLC (Shimadzu GC-8A, 0.25 in. by 10 ft, 5% SP-2100 (methyl silicone) on Chromosorb G, AW-DMCS, 60–80 mesh).

4′,5-Dimethyl-2-[(4-methylphenyl)thio]biphenyl (17a): ^{1}H NMR (chloroform-d) δ 7.36–7.08 (m, 11 H), 2.44 (s, 3 H), 2.39 (s, 3 H), 2.37 (s, 3 H); UV (CH_3CN) no maximum above 200 nm, 254 nm (17900), 300 (7760), 313 (3000); GC/MS m/e = 304.

4′,6-Dimethyl-3-[(4-methylphenyl)thio]biphenyl (18a): ^{1}H NMR (chloroform-d) δ 7.29–7.08 (m, 11 H), 2.39 (s, 3 H), 2.32 (s, 3 H), 2.23 (s, 3 H); UV (CH_3CN) λ_{max} 248 nm (23700); GC/MS m/e = 304.

Photochemistry. Irradiations were carried out on solutions purged with solvent-saturated argon or nitrogen. Sulfonium solution (3–5 mL) was placed in tubes, and sealed with a rubber septum. Irradiation was performed with a Rayonet photochemical reactor, RPR-100. Two or four bulbs were used; RPR-2537A which produce 90% of their light at 254 nm, bulbs were used for 254-nm irradiation, and RPR-3000A which produce maximum light at 300 nm and have a bandwidth of about 40 nm, bulbs, were used for the 300-nm irradiations. Quartz tubes were used for the 254-nm irradiations, and Pyrex tubes for the 300-nm irradiations. A carousel was used to obtain uniform irradiation; the variation in product formation from tube to tube irradiated in parallel was about 4%. The photolyzed solutions were analyzed by GLC by direct injection or by treatment of the photolysate with water and hexane, followed by analysis of the hexane phase. Authentic samples of the photoproducts were used to obtain response ratios, which were used in quantification of the samples against an internal standard (diphenylmethane for the direct injections, and n-tetradecane for the hexane-extracted irradiations). Acid was determined by titrating with sodium p-nitrophenoxide. Freshly prepared trifluoromthanesulfonic acid solutions were used to prepare a standard curve of p-nitrophenoxide absorbance at 440 nm. Irradiated samples were then added to nitrophenoxide solution, and their concentration was determined. Sulfonium salt concentrations were determined by HPLC and by the spectrochemical determination previously reported.[23]

Quantum Yields. Quantum yields were determined with a modified PTI Quantacount, which was calibrated with use of ferrioxalate actinometry.[50] The excitation wavelength was 248 nm with a 8-nm bandpass. The fluence incident on the sample was about 2 × 10^{15} photons s^{-1}. Samples were irradiated in 1 cm^2 fused-silica cuvettes, which were purged prior to irradiation with solvent-saturated argon. The irradiation solution was magnetically stirred, which was found to be necessary to obtain reproducible quantum yields. The irradiated solutions were then analyzed by hexane extraction and gas chromatography as described above.

Registry No. 1-Br, 3353-89-7; **1-SbF$_6$**, 57840-38-7; **1-Tf**, 66003-78-9; **2-Br**, 3744-11-4; **2-SbF$_6$**, 62770-64-3; **2-Tf**, 127820-38-6; **3-Br**, 125428-43-5; **3-SbF$_6$**, 125853-08-9; **3-Tf**, 127820-39-7; **4-SbF$_6$**, 127855-15-6; **5-SbF$_6$**, 127855-16-7; **6-SbF$_6$**, 77785-82-1; **7-SbF$_6$**, 127855-18-9; **8-SbF$_6$**, 127279-74-7; **9-SbF$_6$**, 127855-20-3; **10-SbF$_6$**, 71449-78-0; **11-SbF$_6$**, 127855-21-4; **12-SbF$_6$**, 127855-22-5; **13-SbF$_6$**, 127855-24-7; **14**, 39950-36-2; **15**, 113792-74-8; **16**, 59090-57-2; **17a**, 127820-40-0; **18a**, 127820-41-1; bromobenzene, 108-86-1; diphenylcadium·SbF_6^-, 52754-92-4; thiophenol, 108-98-5; 2-bromobiphenyl, 2052-07-5; bis(4-methylphenyl) sulfide, 620-94-0; 4-methylbenzenediazonium·PF_6^-, 673-44-9; diphenyl sulfoxide, 945-51-7.

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