2.00–1.70 (m, 4 H), 1.20–1.60 (m, 18 H). MS: m/z 245 (M^+), 162, 132, 106, 93. HRMS for $C_{17}H_{27}N$ (M^+) calcd 245.2144, found 245.2145.

(4-Pyridyl)cyclododecane (16b). This was a yellow oil (10%). IR ($CHCl_3$): 2920, 2860, 1595, 1520, 1445 cm^{-1}. ^1H NMR: δ 8.45 (br s, 2 H), 7.09 (br d, 2 H), 2.75 (qnt, 1 H), 1.1–1.90 (m, 22 H). MS: m/z 245 (M^+), 146, 106, 93. HRMS for $C_{17}H_{27}N$ (M^+) calcd 245.2144, found 245.2143.

Cyclododecyl 2-Pyridyl Sulfide (8d). Compound **8d** isolated here (5.6%) was compared with the authentic sample.

General Procedure for Gif^{IV} Oxidation. A mixture of pyridine (28 mL), acetic acid (2.3 mL, 40 mequiv) containing $FeCl_2 \cdot 4H_2O$ (14.8 mg, 7×10^{-3} mmol), and hydrocarbon was placed in a 150-mL Erlenmeyer flask. Zinc powder (1.3 g; 20 mg) was added and kept suspended in solution by stirring. The mixture was stirred open to air at room temperature until the zinc powder disappeared (8–10 h). The resulting dark-brown solution was subjected to the work-up procedure described in Table VIII.

Stability of *sec*-Alkylpyridine-Coupled Products under Gif^{IV} Conditions. (a) For 2-(2-Pyridyl)adamantane (4). Compound **4** (213 mg, 1.0 mmol) was subjected to Gif^{IV} conditions. The chilled reaction mixture was acidified with 25% H_2SO_4 (v/v) and extracted with ether (4 × 25 mL). The combined ether layers were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to dryness. The ^1H NMR spectrum of the residue was compared with the spectra of 2-adamantanone and 2-adamantanol. Neither of these compounds was present. The IR spectrum did not show any carbonyl absorption.

The acidic aqueous layer was basified (20% NaOH) and extracted with ether (4 × 50 mL). The combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated to dryness at room temperature using a dry ice cooled rotary evaporator. The recovery of **4** (82%) was determined by comparing the intensity of the ^1H NMR peak representing the α-2-adamantyl proton with the protons of CH_2I_2 (δ = 3.8 ppm) added as an internal standard.

(b) For 2-(4-Pyridyl)adamantane (5). A Gif^{IV} reaction was performed in the presence of **5** (158 mg, 0.75 mmol), and the reaction mixture was worked up as described for compound **4**. The neutral extracts did not contain any oxidation products (^1H NMR and IR). A major proportion of **5** (73%) was found in the basic fraction as determined by ^1H NMR using CH_2I_2 as internal standard.

(c) For (2-Pyridyl)cyclohexane (15a).[3] Compound **15a** (161 mg, 1.0 mmol) was incubated under Gif^{IV} conditions. The resulting solution was worked up as described for compound **4**. The neutral fraction was treated with 2,4-dinitrophenylhydrazine reagent. There was no detectable amount of cyclohexanone dinitrophenylhydrazone. The basic fraction was purified by column chromatography on silica gel using petroleum ether as eluent. ^1H NMR of the fraction containing **15a** was recorded using CH_2I_2 as internal standard. The yield of **15a** was 50%.

Oxidation of Adamantane with and without *sec*-Adamantylpyridine-Coupled Products. (a) Without *sec*-Adamantylpyridine-Coupled Products 4 and 5. Adamantane (272 mg, 2.0 mmol) was oxidized by a Gif^{IV} oxidation reaction. The resulting residue was treated with 5% NaOH (50 mL) and extracted with ether (4 × 100 mL). The combined ether extracts were washed once with water, dried ($MgSO_4$), and concentrated to 20 mL. The analysis of this concentrate (GC) for the coupled products showed compounds **2** (5.66%), **3** (7.65%), **4** (<0.5%), and **5** (<0.5%).

(b) With *sec*-Adamantylpyridine-Coupled Products 4 and 5. A mixture of adamantane (272 mg, 0.17 mmol), (2-pyridyl)-2-adamantane (38.6 mg, 0.17 mmol), and (4-pyridyl)-2-adamantane (18.1 mg, 0.085 mmol) was subjected to Gif^{IV} oxidation conditions. The chilled (ice bath) mixture was acidified with 25% (v/v) H_2SO_4 and extracted with ether (4 × 50 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated to dryness. The ^1H NMR of the residue with CH_2I_2 as internal standard showed 10.5% of 2-adamantanone (**12**) and 3.5% of 2-adamantanol (**10**).

The acidic aqueous solution was basified (20% NaOH) and extracted with ether (4 × 50 mL). The combined ether extracts were washed with water, dried ($MgSO_4$), and concentrated to 20 mL. The concentrate contained **2** (5.55%), **3** (12.7%), **4** (97.7% recovery), and **5** (94.8% recovery) as determined by GC analysis.

Photolysis of Acyl Derivatives 7 under 4% Oxygen in Nitrogen. A steady stream of nitrogen (30 mL/min) and air (7.5 mL/min) was maintained with needle valves. Each gas, after being mixed in a flask, was blown over the surface of the stirred pyridine (28-mL)–acetic acid (2.3-mL) solution containing compound **7**. The photolysis was carried out with two W lamps situated 25 cm from the reaction flask for 2 h, at 12 °C. The reaction mixture was analyzed as described in Table VIII. The products and their quantities are given in Table V.

Gif^{IV} Oxidations of Hydrocarbons Adamantane (1), Cyclohexane, and Cyclododecane under a Flow of 4% Oxygen in Nitrogen. A stable stream of nitrogen (30 mL/min) and air (7.5 mL/min) was maintained with the aid of needle valves. Each gas was connected to inlets of a flask that served as a premixing chamber. The gas mixture was then blown over the surface of the stirred reaction mixture which was composed of hydrocarbon, $FeCl_2 \cdot 4H_2O$ (8 mg, 4×20^{-2} mmol), and zinc powder (1.3 g, 20 mg) in pyridine (28 mL)–acetic acid (2.3 mL, 40 mmol). The solution was stirred at a rate to keep the zinc in suspension for 24 h at room temperature. The resulting dark solution was worked up after combining with the contents of the cold trap (dry ice–acetone) attached to the outlet of the reaction vessel. The workup and method of analysis are described in Table VIII. The amount of hydrocarbon used and quantities of products found are listed in Table VI.

Acknowledgment. We thank the N.S.F. and the N.I.H. for partial support of this work and Prof. D. T. Sawyer for helpful discussions.

Ylidions: A New Reactive Intermediate Prepared by Photosensitized One-Electron Oxidation of Phenacyl Sulfonium Ylides

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Abstract: The chemistry of a series of phenacyl sulfonium ylides was studied. Their photosensitized one-electron oxidation by 9,10-dicyanoanthrcene generates ylidions, a new class of radical cation intermediates. In some cases, the ylidions cleave to form a free alkyl radical and a cation; in others, they are attacked by nucleophiles or by an alkene. The chemical properties displayed by the phenacyl sulfonium ylidions appear to be controlled primarily by the nature of the sulfur-bound alkyl groups. The direct photolysis and thermolysis of the phenacyl sulfonium ylides was examined for comparison with their one-electron oxidation. Some of the ylides undergo the Stevens rearrangement either when heated or photolyzed. Contrary to an earlier report, there is no evidence that direct photolysis of a phenacyl sulfonium ylide leads to formation of benzoylcarbene.

Ylides play important roles in both practical and theoretical organic chemistry.[1] Numerous studies of their chemical and physical properties have related their unique bonding pattern to their characteristic reactivity.[2] Surprisingly, an aspect of the

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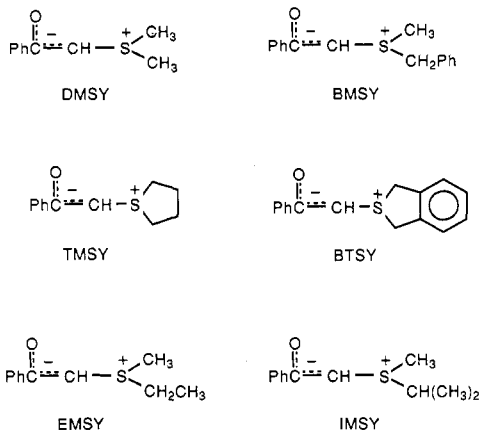
Chart I



chemistry of ylides that has been largely ignored is their one-electron oxidation. Removal of an electron from an ylide generates an odd-electron cation that has been designated an "ylidion" by Radom and co-workers, who recently reported examination of these species by means of ab initio theoretical methods.[3] We are aware of only two instances in which ylidions have been considered to participate in chemical processes. Twenty years ago, Lepley invoked and then discounted participation of an ylidion in the Stevens rearrangement of an ammonium ylide.[4] More recently, we searched without success for evidence of this path in the oxidation of 9-dimethylsulfonium fluorenylide.[5] We report herein the first experimental examination of reactive ylidions. Photochemical one-electron oxidation of phenacyl sulfonium ylides, Chart I, gives ylidions, which in some instances cleave to give free radicals, in others are attacked by nucleophiles, and in some cases react with alkenes to give addition products.

Results

(A) Preparation and Physical Properties of Phenacyl Sulfonium Ylides. The ylides shown in Chart I were prepared by treatment of their corresponding phenacyl sulfonium salts with base[6] and were purified by recrystallization. They are air-sensitive, very pale yellow solid materials. The infrared absorption spectra of the ylides show a characteristic band at ca. 1519 cm^{-1}, indicative of a delocalized "phenacyl anion" structure.[7] Their UV–vis absorption spectra are essentially independent of the nature of the sulfur-bound alkyl groups. In each of the cases examined, the ylide exhibits a strong band at ca. 315 nm (CH_3CN solution, ϵ_{max} = 18 000 M^{-1} cm^{-1}) that tails to ca. 370 nm. Estimation of the O–O band position for the ylide absorptions indicates that their lowest singlet excited states have energies of ca. 77 kcal/mol. No fluorescence or phosphorescence could be detected from the ylides either at room temperature or at 77 K. The phenacyl sulfonium ylides are relatively easily oxidized compounds: cyclic voltammetry measurements reveal an irreversible one-electron wave with a peak at ca. 0.5 V versus SCE in CH_3CN solution for each of the ylides of Chart I.

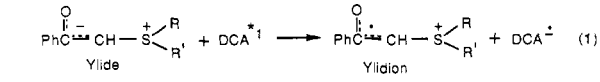
(B) Phenacyl Sulfonium Ylides: Electron-Transfer-Sensitized Photolysis, Thermolysis, and Direct Photolysis. The chemical reactions of the phenacyl sulfonium ylides were examined under three sets of conditions: photosensitization ($\lambda > 400$ nm) with 9,10-dicyanoanthracene (DCA); thermolysis in refluxing CH_3CN; and direct irradiation at ca. 350 nm (Rayonet Photoreactor). The products of these reactions were identified by comparison with authentic materials. We found that the outcome of the reactions of these ylides depends remarkably on the activating conditions and upon the details of their structures.

Table I. Yields of Products from the Reaction of Phenacyl Sulfonium Ylides

	thermolysis[a]		direct[b]	DCA[c] sensitization	
	Stevens[d]	α-(methylthio)-acetophenone	Stevens[d]	(4)	1
DMSY	0	0	0	0	90
EMSY	0	100	0	0	82
IMSY	0	100	60	38	10
BMSY	77	0	78	52	26
TMSY	0	0	64	0	85
BTSY	90	0	88	0	65

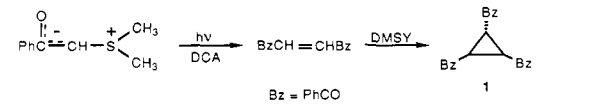
[a] The ylide was heated in refluxing CH_3CN (or toluene) for several hours. [b] Irradiated in a Rayonet photoreactor at 350 nm in CH_3CN solution. [c] Irradiated at $\lambda > 400$ nm in CH_3CN solution. DCA absorbs all the light. [d] Stevens rearrangement product; The 1,2-shift from sulfur to the methine group of the ylide.

Preliminary investigation of the sensitization by DCA revealed that each of the ylides examined quenches the fluorescence of DCA at approximately the diffusion-limited rate (2×10^{10} M^{-1} s^{-1}). The quenching reaction cannot be energy transfer, since the singlet energy of DCA (68 kcal/mol) is well below that of the ylide. However, quenching of singlet DCA by electron transfer from the ylide to form DCA radical anion ($DCA^{\bullet-}$) and the ylidion, eq 1, is predicted to occur at the diffusion-limited rate by application of the Weller equation[8] (ΔG_{ET} = ca. −30 kcal/mol). This prediction was confirmed for the case of DMSY. Irradiation of an acetonitrile solution containing DCA and the ylide (0.025 M) at 388 nm with a pulsed dye laser (20 ns, 10 mJ) shows essentially instantaneous formation of $DCA^{\bullet-}$ detected by observation of its characteristic absorption spectrum.[9] No transient absorption signals that might be assigned to the product of ylide oxidation were detected in the region probed (400–650 nm).



(1)

(1) Dimethylsulfonium Phenacylide (DMSY). The reactions of DMSY illustrate one extreme in the range of behavior observed for the phenacyl sulfonium ylides. The DCA-sensitized photolysis of DMSY results in efficient consumption of the ylide and formation of *trans*-1,2,3-benzoylcyclopropane (**1**) in 90% yield (30% conversion). The formation of benzoylcyclopropane from DMSY requires combination of three ylide molecules. However, it is well-known that DMSY reacts rapidly with 1,2-dibenzoylethylene to give cyclopropane **1** in high yield.[7,11] On this basis, we reason that the DCA-initiated photoreaction of DMSY gives dibenzoylethylene and that this compound undergoes a subsequent Michael reaction with unconsumed ylide to give **1** as the ultimate product, eq 2. In contrast to the DCA-sensitized photoreaction, direct irradiation of DMSY in CH_3CN solution for 20 h does not cause any chemical reaction of the ylide.[10] Similarly, thermolysis of DMSY in refluxing CH_3CN for 20 h does not result in a



(2)

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(9) The laser spectrometer will be described in detail in a forthcoming report.
(10) Trost[7,11] reported that the direct irradiation of DMSY in ethyl alcohol solution (0.5 M) ($\lambda > 319$, Pyrex) leads to cyclopropane **1** and several minor products indicating the intermediacy of benzoylcarbene.
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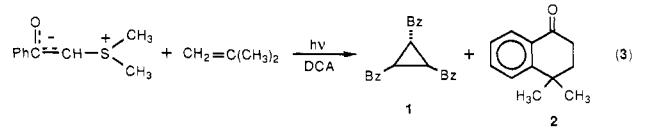
reaction; the ylide is recovered unchanged.

An electron-transfer sensitization route for the DCA-initiated reaction of DMSY is supported by our finding that the reaction of DMSY in the presence of DCA is quenched completely by diazabicyclo[2.2.2]octane (DABCO) itself an efficient electron-donating quencher of DCA excited singlet state.[12] In contrast to the effect of DABCO, the formation of cyclopropane **1** is not inhibited at all when tetra-*n*-butylammonium acetate is added to the reaction mixture. This observation is of special significance when compared with related reactions of BMSY reported below. The DCA-sensitized reaction of DMSY is similarly unaffected when the reaction solution contains isopropyl alcohol (2.5 M). This finding rules out participation of benzoylcarbene in the DCA-sensitized reaction of the ylide since the carbene will react rapidly and irreversibly with the alcohol.[13] These experiments and results from similar studies of the other ylides examined are summarized in Table I.

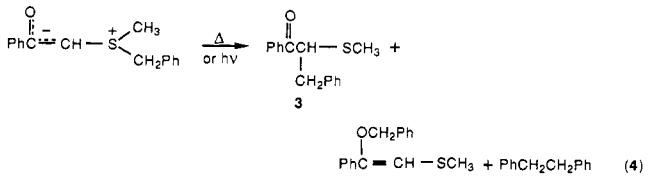
The DCA-sensitized reaction of DMSY in acetonitrile solution containing isobutene (0.7 M) gives cyclopropane **1** (24%) and an additional product shown to be 4,4-dimethyl-1-tetralone (**2**, 52%), eq 3. Irradiation of a DMSY solution containing isobutene in



(3)

the absence of DCA either with light >400 nm or at ca. 350 nm, where the ylide absorbs strongly, does not result in the formation of tetralone **2**. Similarly, tetralone **2** is not formed when an acetonitrile solution of DMSY, DCA, and isobutene is kept in the dark. Significantly, isobutene does not quench the fluorescence of DCA in acetonitrile solution, nor does it prevent formation of $DCA^{\bullet-}$ from photosensitization of DMSY.

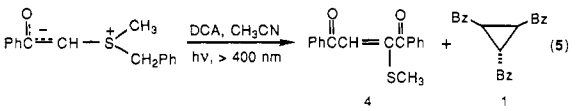
(2) Benzylmethylsulfonium Phenacylide (BMSY). The chemistry of BMSY has been investigated previously. Baldwin and co-workers conclude that its thermolysis in toluene causes homolytic cleavage of a carbon–sulfur bond to form a benzyl radical and a thiomethyl-substituted benzoyl radical.[14] Recombination of this radical pair within the initial solvent cage is thought to give the Stevens rearrangement product (**3**), while escape from the solvent cage forms free radicals which, eventually, are consumed in diffusive reencounter reactions. In contrast to the behavior of DMSY, we find that both the thermolysis of BMSY in refluxing CH_3CN and its direct irradiation at 350 nm give the same products in essentially the same ratio as is reported by Baldwin for its thermolysis in toluene, eq 4. On this basis, it seems



(4)

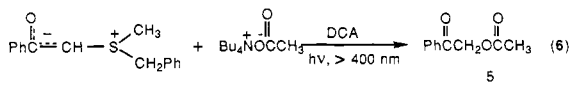
that the direct irradiation of BMSY leads to carbon–sulfur bond homolysis and radical pair formation just as in the thermolysis.[15] This behavior is similar to that observed for photolysis of dimethylsulfonium fluorenylide.[5]

The DCA-sensitized photolysis of BMSY initiates a new set of reactions whose products are not observed in its thermolysis or its direct irradiation. The Stevens rearrangement product **3** is not formed under DCA-sensitized conditions. The major products of this reaction are 1,2-(dibenzoyl)vinyl methyl sulfide (**4**, obtained as a mixture of *E* and *Z* isomers, 52%), cyclopropane **1** (26%), and benzylmethyl sulfide (18%), eq 5. These results



(5)

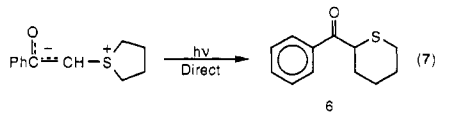
show that the reaction of BMSY proceeds along a different path when it is sensitized by DCA than when it is initiated by thermolysis or by its direct irradiation. The DCA-sensitized photoreaction of BMSY is quenched by DABCO, just as the reaction of DMSY. But, for this ylide, the addition of tetra-*n*-butylammonium acetate (1×10^{-2} M) alters the reaction course. In the presence of the acetate, the major product is ester **5**, eq 6. Evidently, an intermediate formed in the DCA sensitization of BMSY can be intercepted by the acetate anion.



(6)

The DCA-sensitized irradiation of BMSY in acetonitrile solution containing isobutene gives the sulfide **4** (63%) and the tetralone **2** (26%); no cyclopropane **1** was detected by GC/MS analysis. This finding indicates that isobutene captures a "common" intermediate in the DCA-sensitized reaction of DMSY and BMSY. In the absence of the alkene, the intermediate goes on to form cyclopropane **1**.

(3) Tetramethylenesulfonium Phenacylide (TMSY). Thermolysis, direct irradiation, and DCA-sensitized photolysis of TMSY each give a unique outcome. Heating a solution of TMSY at reflux in toluene or CH_3CN does not initiate a reaction; the ylide is recovered unchanged. However, irradiation of an CH_3CN solution of TMSY at 350 nm converts it to 2-benzoyltetrahydrothiopyran (**6**, 64% at 22% conversion), the Stevens rearrangement product, eq 7. Thus, TMSY is an additional example



(7)

of an ylide that undergoes a photochemical Stevens rearrangement even though the thermally initiated process is thwarted.[5,16] The DCA-sensitized reaction of TMSY resembles that of DMSY: the exclusive product under these conditions is cyclopropane **1**, which is formed in 85% yield at 30% conversion.

(4) EMSY, IMSY, and BPSY. The pattern of reactivity observed for DMSY, BMSY, and TMSY is repeated in the chemical behavior of the other phenacyl sulfonium ylides we investigated. BPSY, which contains a benzylic group bound to sulfur, undergoes both efficient thermal and direct photochemical Stevens rearrangement to give 2-benzoyl-3,6-dihydro-4,5-benzothiophene in high yield. In contrast, the DCA-sensitized reaction of this ylide gives **1** in 65% yield at 35% conversion.

Thermolysis of EMSY, which has an ethyl group bound to sulfur, gives only α-(thiomethyl)acetophenone by a presumed base (ylide) initiated β-elimination reaction.[17] A related reaction occurs when IMSY, which has an isopropyl group bound to sulfur, is thermolyzed. Direct irradiation of EMSY does not result in detectable reaction of the ylide, and irradiation of IMSY results in its very slow consumption with the formation of the Stevens rearrangement product and several secondary photolysis products.

The contrasting behavior in the DCA-sensitized reactions of EMSY and IMSY is quite informative. The former gives only cyclopropane **1** in 82% yield (31% conversion), but the latter gives predominantly the vinyl methyl sulfide **4** (38%) and only a 10% yield of cyclopropane **1**. Evidently, the change in the sulfur-bound alkyl group from ethyl to isopropyl affects significantly the path followed in the DCA-sensitized reactions of these ylides.

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Discussion

Ylidions were first considered seriously as reactive intermediates by Radom and co-workers from a computational point of view.[3] Their analysis led to the conclusion that the prototype sulfonium ylidion ($H_2SCH_2^{\bullet+}$) exists in a potential energy minimum and that it will not spontaneously rearrange or fragment. The investigation of the ylides reported herein was designed to explore experimentally the chemical properties of phenacyl sulfonium ylidions.

(A) Thermolysis of Phenacyl Sulfonium Ylides. The thermolytic behavior of the ylides that we examined follows the pattern previously observed for related compounds.[15] Cleavage of a carbon–sulfur bond occurs readily for those cases that can generate a stabilized alkyl radical (i.e., benzyl). Subsequent in-cage coupling to give the Stevens rearrangement product competes with escape of the radicals from the solvent cage. Ylides that cannot generate a stabilized radical do not react in this way.

(B) Direct Irradiation of Phenacyl Sulfonium Ylides. The results of direct irradiation of the ylides are enigmatic. It was previously reported that photolysis of a concentrated solution of DMSY causes its fragmentation to form dimethyl sulfide and benzoylcarbene.[7,11] Formation of the carbene was deduced from the isolation of cyclopropane **1** and from capture of the putative carbene by cyclohexene and alcohols. We are unable to reproduce these experiments. In our hands, the direct irradiation of DMSY causes no observable reaction. There is an explanation for this seeming contradiction. The primary products of the DCA-sensitized reaction of DMSY are those that were previously though to arise from its direct irradiation. The presence of a small, unnoticed amount of a similarly acting sensitizer in the earlier experiments would resolve the discrepancy.

The products formed from those ylides that do react when directly irradiated are the same as are found from their thermolyses. As noted previously,[5] a PMO assessment of the excited states of sulfonium ylides reveals a predominant $n\sigma^*$ excited singlet state having a reduced carbon–sulfur bond order.[18] Rupture of this weakened bond leads to the same pair of radical intermediates that is believed to be formed from thermolysis of the ylide. Importantly, some thermally inert ylides do undergo this reaction from their excited state.

(C) Generation and Reactions of Phenacyl Sulfonium Ylidions. It is clear from consideration of the results described above that the DCA-sensitized irradiation of the sulfonium ylides creates an intermediate that is not formed in either the thermal reaction or in the unsensitized photochemical reaction of the ylides. On energetic grounds, the mechanism for sensitization by DCA cannot be singlet energy transfer to the ylide. Based on the thermodynamic feasibility for one-electron oxidation of the ylide by excited DCA, the confirmation of rapid reaction of the ylides with excited DCA from consideration of the kinetics of the fluorescence quenching, and the results of the time-resolved absorption experiments, it seems certain that the operative sensitization mechanism with DCA is single-electron transfer. This reaction will convert the sulfonium ylide to its corresponding sulfonium ylidion.

Scheme I is an outline of a proposed mechanism that account for the experimental facts uncovered about the properties of phenacyl sulfonium ylidions. It seems that the chemical properties of these intermediates are controlled primarily by the nature of the alkyl groups bound to the sulfur atom.

In the absence of a trapping reagent, there are three reactions paths that phenacyl sulfonium ylidions follow when they are formed from an ylide in a photochemical electron-transfer reaction. The first is simply energy-wasting back-electron transfer to regenerate the ylide and the ground-state sensitizer. This process controls the overall efficiency of the photosensitization reaction but does not affect its outcome. The second route followed by phenacyl sulfonium ylidions is homolytic cleavage of a carbon–sulfur bond to generate a free alkyl radical and a cation, path A

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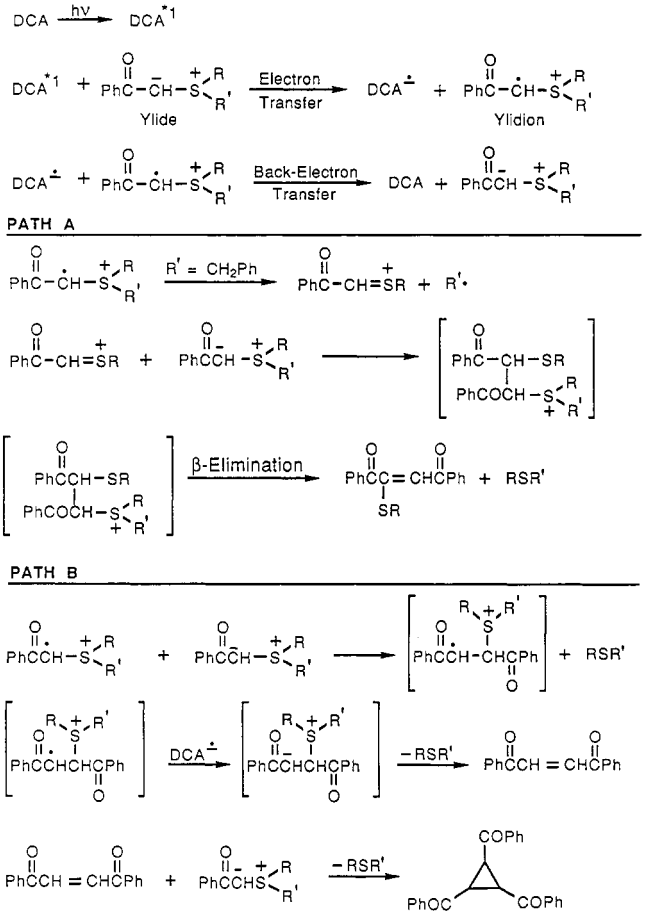
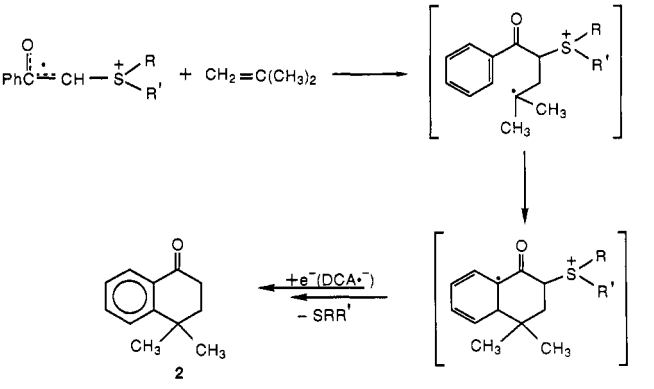
Scheme I



Scheme II



of Scheme I. The third route, path B of Scheme I, is attack of the ylidion by nucleophiles.

Path A is dominant when the free radical formed is benzylic, as it is for BMSY, but it is apparently too slow to compete when bond cleavage would form a methyl or ethyl radical as is required for DMSY and EMSY. However, the fragmentation to form a secondary radical (2-propyl from IMSY) apparently occurs with a competitive rate. In the next step along path A, the cation formed from the bond cleavage of the ylidion combines with nucleophiles present in the reaction solution. Normally the ylide itself is the attacking nucleophilic species, and this reaction leads to dibenzoylvinyl methyl sulfide (**4**) after loss of RSR'. When sufficient acetate ion is present in the reaction mixture, the ylidion-derived cation is trapped by this nucleophile, and the ylide is converted to ester **5** by this sequence.

The ylidions that have not fragmented to form an alkyl radical are consumed by a bimolecular reaction with the ylide, path B of Scheme I, or by reaction with an added alkene, Scheme II. These reactions underscore the dual nature of ylidions as both

an electron-deficient and an odd-electron intermediate.

Ylidions are electrophiles in their reaction with the ylide. In Scheme I, a displacement of RSR′ by the ylide is postulated to convert the ylidion to a 1,3-radical cation intermediate. Electron-transfer annihilation of this radical cation with $DCA^{\bullet-}$ and loss of the second RSR′ completes a sequence that leads to the generation of dibenzoylethylene. This alkene is a Michael acceptor, and its subsequent reaction with the starting ylide generates cyclopropane **1**—the exclusive product formed from phenacyl sulfonium ylidions that do not undergo homolytic carbon–sulfur bond cleavage.

The phenacyl sulfonium ylidions reveal their radical character in the presence of isobutene. We postulate that addition of the alkene to the ylidion forms a 1,4-radical cation intermediate. Addition of the radical to the ortho position of the benzoyl group followed by one-electron reduction (from $DCA^{\bullet-}$) of the newly formed 1,4-cation radical with following loss of sulfide leads to formation of tetralone **2**.

In previous work, Cu(II) was found to catalyze the formation of cyclopropanes in the reaction of phenacyl sulfonium ylides with alkenes.[7,11] An undetected "carbenoid" intermediate was postulated in this reaction. In light of our findings, it is reasonable to consider that the actual role of Cu(II) in this process is simply to convert the ylide to its ylidion, a thermodynamically feasible reaction. Formation of a cyclopropane- rather than a tetralone-like product in these cases may be due to the increased rate of reduction of the 1,4-radical cation intermediate by the associated copper. This proposal has added significance since the biosynthesis of cyclopropane rings by transfer of a methylene group from *S*-adenosinethione has been postulated to proceed through an intermediate sulfonium ylide.[19] Perhaps ylidions play the key role in this reaction.

Conclusions

The DCA-sensitized photolysis of phenacyl sulfonium ylides generates phenacyl sulfonium ylidions. The ylidions we examined cleave homolytically to form alkyl radicals and cations when an alkyl group bound to sulfur contains a radical-stabilizing group (i.e., benzyl). Phenacyl sulfonium ylidions that do not undergo rapid bond homolysis are attacked by nucleophiles and react with alkenes to give tetralones.

Experimental Section

General. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Varian XL-200 (200-MHz) or QE-300 (300-MHz) spectrometer in $CDCl_3$ solution with TMS as internal standard. Mass spectral data were obtained with a Varian MAT CH-5 or 731 mass spectrometer. IR spectra were recorded with an IBM IR32 FT-IR spectrometer. Direct photolyses were carried out in a Rayonet Photochemical reactor equipped with 350-nm lamps. The sensitization experiments were performed by irradiation with a medium-pressure mercury lamp arc (450 W) through a glass filter that cuts off light below 400 nm. Elemental analyses were performed by the Microanalysis Laboratory, University of Illinois. All melting points are uncorrected.

Quenching of Fluorescence of DCA in Acetonitrile Solution by the Ylides. The rate constant for fluorescence quenching of DCA by the phenacyl sulfonium ylides was determined in acetonitrile at room temperature. The concentration of DCA was adjusted to give an optical density of ca. 0.1 at the excitation wavelength (400 nm). The concentration of ylides in the solution was varied from 0.0 to 6×10^{-3} M. From the slopes of the linear Stern–Volmer plots, and the known lifetime of DCA^{*}[1] (15 ns),[20] the quenching rate constants were calculated to be ca. 2×10^{10} M^{-1} s^{-1}. The fluorescence of DCA was not quenched by 0.7 M isobutene.

Laser Flash Photolysis. The concentration of DCA was adjusted to give an optical density of ca. 3 at 388 nm, the excitation laser wavelength. In the first experiment, a nitrogen-purged acetonitrile solution of DABCO (0.1 M) in a 1.0-cm quartz cell equipped with a Teflon stopcock and a magnetic stir bar was irradiated. The transient spectrum showed the absorption of $DCA^{\bullet-}$ at 485 nm. This experiment was repeated with DMSY as the electron donor, and the spectrum of $DCA^{\bullet-}$ was similarly observed. Addition of isobutene to the solution did not affect the results.

Cyclic Voltammetric Measurements. The oxidation potential of the ylides was measured by cyclic voltammetry using a Cybernetic potentiostat in acetonitrile solution with 10^{-3} M tetrabutylammonium perchlorate as supporting electrolyte. The reference electrode was a silver electrode saturated with $AgNO_3$. The working electrode was a platinum wire and the counter electrode was a platinum surface.

Preparation of Phenacylsulfonium Salts. The sulfonium salts were prepared by direct reaction of the alkyl sulfides with 2-bromoacetophenone[21] except in the case of the isopropylmethylphenacylsulfonium salt. Isopropylphenacyl sulfide (3.03 g, 15.6 mmol) and iodomethane (6.65 g, 47 mmol) were dissolved in 25 mL of methylene chloride, and the mixture was cooled to −78 °C. Then, rapidly, silver tetrafluoroborate (3.85 g, 20 mmol) was added. Once the solution was to room temperature, precipitation of silver iodide was observed. Continued stirring at room temperature under a nirogen atmosphere in the dark for 24 h resulted in a light-amber solution. The reaction mixture was filtered and the solid material washed with 200 mL of methylene chloride. Removal of the methylene chloride in vacuo gave the solid sulfonium salt mixed with excess unreacted starting materials. The mixture was triturated in ether to remove the starting material, and the resulting amber solid was recrystallized from 95% ethanol to give 3.47 g (75%) of the *S*-isopropyl-*S*-methylphenacylsulfonium tetrafluorborate: colorless crystal; mp 110–111 °C. ^{1}H NMR (CD_3OD): δ 1.60 (d, 6 H), 2.95 (s, 3 H), 3.88 (m, 1 H), 4.83 (s, 2 H), 7.59–8.08 (7, 5 H). Anal. Calcd for $C_{12}H_{17}OSBF_4$: C, 48.67; H, 5.79; S, 10.83; F, 25.66. Found: C, 48.70; H, 5.84; S, 10.88; F, 25.65.

Isopropylphenacyl Sulfide. Sodium (2.3 g, 0.1, mol) was dissolved in 40 mL of methanol, and propane-2-thiol (7.6 g, 0.1 mol) was added dropwise. When the addition of the thiol was complete, phenacyl bromide (19.9 g in 10 mL of methanol) was added, and the mixture was stirred for 2 h, heated at reflux for 2 h, and then cooled to room temperature. The mixture was filtered, and the residue was washed with methanol. Removal of solvent under reduced pressure gave a yellow liquid which was purified by radial chromatography using 5% ethyl acetate in hexane as eluant. After evaporation of the solvent, a yellow liquid (16.95 g, 89%) was obtained. ^{1}H NMR: δ 1.28 (d, 6 H, J = 7.4 Hz), 3.00 (m, 1 H), 3.83 (d, s, 2 H), 7.52–7.98 (m, 5 H). MS (EI): m/e 194 (M^+).

Preparation of Phenacyl Sulfonium Ylides. The ylides were prepared from their corresponding salts according to literature procedures.[21]

Dimethylsulfonium Phenacylide (DMSY) was obtained in 85% yield: mp 79–80 °C (lit.[21] mp 79–80 °C).[1] H NMR: δ 3.00 (s, 6 H), 4.33 (s, 1 H), 7.36–7.80 (m, 5 H). MS (EI): m/e (rel intensity) 180 (M^+, 63.5), 165 (31.4), 137 (100), 105 (41.8), 77 (78.4). Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; S, 17.78; H, 6.71. Found: C, 66.41; S, 17.74; H, 6.74.

Ethylmethylsulfonium Phenacylide (EMSY) was obtained in 90% yield: mp 82–83 °C. ^{1}H NMR: δ 1.31 (t, 3 H), 2.96 (s, 3 H), 2.97 (m, 1 H), 3.94 (m, 1 H), 4.22 (s, 1 H), 7.38–7.79 (m, 5 H). MS (EI): m/e (rel intensity) 194 (35.7), 166 (43.2), 137 (100) 105 (81.1), 77 (88.5). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; S, 16.50; H, 7.26. Found: C, 67.78; S, 16.31; H, 7.40.

Isopropylmethylsulfonium Phenacylide (IMSY) was obtained in 63% yield: mp 98–99 °C. ^{1}H NMR: δ 1.34 (d, 6 H), 2.88 (s, 3 H), 4.15 (m, 1 H), 4.28 (s, 1 H), 7.34–7.80 (m, 5 H). MS (EI): m/e (rel intensity) 208 (27.0), 166 (92.0), 105 (100), 77 (70.0). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.29; S, 15.39; H, 7.74. Found: C, 69.10; S, 15.26; H, 7.69.

Benzylmethylsulfonium Phenacylide (BMSY) was obtained in 85% yield: mp 86–87 °C. ^{1}H NMR: δ 2.94 (s, 3 H), 4.20 (s, 1 H) 4.53 (d, 1 H, J = 12 Hz), 4.93 (d, 1 H, J = 12 Hz), 7.40 (m, 8 H), 7.80 (m, 2 H). MS (EI): m/e (rel intensity) 256 (6.3), 209 (54.7), 151 (100), 105 (62.7), 77 (38.0). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.86; S, 12.51; H, 6.29. Found: C, 74.33; S, 12.18; H, 6.37.

Tetramethylenesulfonium Phenacylide (TMSY) was obtained in 70% yield: mp 107–108 °C. ^{1}H NMR: δ 1.99 (m, 2 H), 2.74 (m, 2 H) 3.11 (m, 2 H), 3.60 (m, 2 H), 4.35 (s, 1 H), 7.33 (m, 3 H), 7.79 (m, 2 H). MS (EI): m/e (rel intensity) 206 (20.3), 105 (100), 77 (54.0). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; S, 15.54; H, 6.84. Found: C, 69.93; S, 15.46; H, 6.93.

3,4-Benzotetramethylenesulfonium Phenacylide (BTSY) was obtained in 66% yield: mp 109–110 °C. ^{1}H NMR: δ 4.22 (d, 2 H, J = 13.5 Hz), 4.50 (s, 1 H), 5.39 (d, 2 H, J = 13.5 Hz), 7.35–7.80 (m, 9 H). MS (EI): m/e (rel intensity) 254 (18.7), 135 (100), 105 (24.6), 77 (27.0). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; S, 12.61; H, 5.55. Found: C, 75.34; S, 12.43; H, 5.38.

2-(Methylthio)-3-phenylpropiophenone (3). A solution of lithium diisopropylamine (LDA, 1.73 mmol) in THF was added dropwise to a cold (−78 °C) solution of 2-(methylthio)acetophenone (1.7 mmol in 25

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mL of THF). The reaction mixture was stirred at −78 °C for 2 h and then warmed to −15 °C. A solution of benzyl bromide (2.6 mmol in 5 mL of THF) was added dropwise to the reaction mixture. After the addition, the solution was warmed to room temperature and 10 mL of water was added. Extractive workup with diethyl ether and evaporation of the solvent under reduced pressure gave a yellow oil. Purification by radial chromatography using 5% ethyl acetate in hexane as eluant gave a pale-yellow solid which was recrystallized from methanol to give colorless crystals, 0.31 g (70%): mp 66–67 °C (lit.[22] 68–69 °C). ^{1}H NMR: δ, 2.01 (s, 3 H), 3.07 (d, d, 1 H, J = 14, 8 Hz), 3.45 (d, d, 1 H, J = 14, 8 Hz), 4.40 (d, d, 1 H, J = 8, 6 Hz), 7.58 (d, m, 10 H). MS (EI): m/e (rel intensity) 256 (1.0), 151 (86) 105 (100), 91 (60), 77 (56).

2-(Methylthio)acetophenone. A solution of 2-bromoacetophenone (2.58 g, 13 mmol in 20 mL of methanol) was added dropwise to sodium methanethiolate (0.91 g, 13 mmol in 50 mL of methanol). The mixture was heated at reflux for 2 h, cooled, and diluted with two volumes of water. The mixture was extracted twice with 50-mL portions of ether; that ether extracts were combined and dried over potassium carbonate. Removal of solvent gave a yellow liquid that was purified by Kugelrohr distillation to give 1.81 g (84%) of a coloreless liquid. ^{1}H NMR: δ 2.12 (s, 3 H), 3.75 (s, 2 H), 7.5 (m, 3 H), 7.9 (m, 2 H). MS (EI): m/e 166 (M^+).

Dibenzoyl-1,2-dibromoethane. A 1.18-g (5 mmol) portion of *trans*-dibenzoylethylene was dissolved in 20 mL of acetic acid by warming the mixture slightly, and 0.79 g (5 mmol) of bromine was added to the solution dropwise. The mixture was stirred at room temperature for 1 h and cooled to 0 °C. The resulting crystalline precipitate was filtered as a pale-yellow solid in quantitative yield: mp 185–186 °C (lit.[24] 184–185 °C). ^{1}H NMR: δ 5.97 (s, 2 H), 7.40 (m, 6 H), 8.01 (m, 4 H). MS (EI): m/e (rel intensity) 315 (55), 105 (100).

Dibenzoylacetylene. A solution of 1.40 g (3.54 mmol) of dibenzoyl-1,2-dibromoethane in 15 mL of acetone and 0.75 g (7.4 mmol) of purified triethylamine was heated at reflux for 1 h. The precipitated triethylammonium bromide was removed by filtration, and the solvent was evaporated under reduced pressure. The resulting orange-red residue was recrystallized from absolute ethanol twice to give 0.66 g (80%) of a pale-yellow solid: mp 109–110 °C (lit.[25] 110–111 °C).[25] ^{1}H NMR: δ 7.65 (m, 6 H), 8.23 (m, 4 H). IR ($CHCl_3$, cm^{-1}): 2252 (w), 1652 (s). MS (EI): m/e (rel intensity) 234 (100), 178 (91.2), 105 (87.4).

1,2-(Dibenzoyl)vinyl Methyl Sulfide (4). A solution of 1,2-dibenzoylacetylene (0.2 g, 0.86 mmol in 10 mL of methanol) was added to a solution of sodium methanethiolate (0.06 g, 0.86 mmol in 30 mL of methanol). The mixture was heated at reflux for 2 h, cooled to room temperature, and quenched with water and then with a saturated calcium bicarbonate solution. Extractive workup with methylene chloride and evaporation of the solvent gave an orange oil which was purified by radial chromatography using 5% ethyl acetate in hexane as an eluant to give 0.048 g (20%, a mixture of E and Z isomers): mp 60–61 °C. ^{1}H NMR for one of the isomers: δ 2.46 (s, 3 H), 7.04 (s, 1 H), 7.47–7.95 (d, m, 5 H). ^{1}H NMR for other isomer: δ 2.16 (s, 3 H), 7.09 (s, 1 H), 7.50–8.00 (m, 5 H). MS (EI): m/e 282, 267, 235, 177, 105.

2-(Acetoxy)acetophenone (5). A solution of 2-bromoacetophenone (3.96 g, 20 mmol) and sodium acetate (1.64 g, 20 mmol) in 20 mL of DMF was heated at 100 °C for 12 h. The reaction mixture was cooled to room temperature, and 15 mL of water was added. Extractive workup with diethyl ether and evaporation of solvent gave a yellow solid which was purified by radial chromatography using 5% ethyl acetate in hexane as eluant. Recrystallization from diethyl ether and petroleum ether gave 2.14 g (60%) of colorless crystal: mp 44–45 °C. ^{1}H NMR: δ 2.24 (s, 3 H), 5.35 (s, 2 H) 7.50–7.92 (m, 5 H). MS/EI: m/e 178 (M^+). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.41; H, 5.54. IR (cm^{-1}): 1750 (s), 1706 (s).

Direct Irradiation of the Ylides in Acetonitrile Solution at 350 nm. Typical Procedure. A solution of the ylide in acetonitrile was placed in a Pyrex round-bottomed flask equipped with a stir bar and rubber septum. The solution was purged with nitrogen for 30 min and irradiated in a Rayonet photochemical reactor with 350-nm lamps while being stirred. The reaction was periodically monitored by UV–vis spectroscopy until ca. 50% of the UV absorption band of the ylide had disappeared. The solvent was removed under reduced pressure, and the product yields were determined by ^{1}H NMR spectroscopy with an internal standard.

Direct Irradiation of DMSY. **(A)** A 6.67 × 10^{-3} M solution of DMSY in acetonitrile was irradiated at 350 nm for 40 min. The UV–vis absorption spectrum of the solution remained unchanged. Evaporation of solvent under reduced pressure gave a yellow residue whose ^{1}H NMR spectrum showed only DMSY. The same result was obtained after 20 h of irradiation.

(B) A 0.20-g (1.11 mmol) sample of DMSY in 25 mL of absolute ethanol was placed in a round-bottomed flask. The sample was purged with nitrogen for 30 min and irradiated at 350 nm (Rayonet reactor) for 12 h under a nitrogen atmosphere. The precipitate that formed during the photolysis was collected by filtration (11 mg) and was shown to be cyclopropane **1**. Removal of the solvent from the filtrate gave a brown solid. ^{1}H NMR spectral analysis of the solid revealed residual DMSY which was recovered by recrystallization from diethyl ether (0.12 g). No evidence for formation of acetophenone or ethyl phenylacetate was obtained by ^{1}H NMR spectral analysis or by GC/MS analysis of the photolysis mixture. Essentially identical results were obtained when DMSY was irradiated in an isopropyl alcohol solution. When DMSY was irradiated in benzene solution, the ^{1}H NMR spectrum of the reaction mixture revealed only formation of a trace amount of **1**.

Direct Irradiation of IMSY. A 4.29 × 10^{-3} M solution of IMSY was irradiated for 9 h. Evaporation of solvent under reduced pressure gave an orange liquid. TLC and ^{1}H NMR analysis of the crude product showed unreacted ylide, 2-(ethylthio)-3-methylbutyrophenone (the Stevens rearrangement product). ^{1}H NMR: δ 0.958 (d, 3 H, J = 5.4 Hz), 1.19 (d, 3 H, J = 6.6 Hz), 1.03 (s, 3 H), 2.32 (m, 1 H), 3.75 d, d, 1 H, J = 10 Hz), 7.48–7.96 (m, 5 H). GC/MS: m/e 208 (M^+). ^{1}H NMR analysis also showed secondary photolysis product 3-methylbutyrophenone.

Direct Irradiation of BMSY. A 3.98 × 10^{-3} M solution of the ylide was irradiated until its UV–vis absorption band at 318 nm had decayed to 50% of the initial value. Evaporation of solvent under vacuum gave a yellow solid. The ^{1}H NMR spectrum of the crude product showed starting ylide, minor amounts of bibenzyl, and the Stevens rearrangement product 2-(benzyloxy)-2-phenylethene methyl sulfide. The secondary photolysis product 2-benzylacetophenone was also detected. Calculation of yields based on integration with an internal standard gave 78% Stevens product **3**, 11% 2-(benzyloxy)-2-phenylethene methyl sulfide, and 9% bibenzyl.

Direct Irradiation of TMSY. A 3.75 × 10^{-3} M solution of the ylide was irradiated for 4.5 h. Evaporation of solvent under vacuum gave a yellow residue. The ^{1}H NMR spectrum of the residue showed residual ylide and new absorptions from the product that was isolated by radial chromatography using 10% ethyl acetate as an eluant and identified as the Stevens rearrangement product 2-benzoyltetrahydrothiopyran (**6**) by spectroscopic data (64% at 22% conversion of TMSY). ^{1}H NMR: δ 1.60–1.89 (m, 4 H), 2.12 (m, 2 H), 2.75 (m, 2 H), 4.42 (m, 1 H), 7.50–8.02 (m, 5 H). MS (EI): m/e (rel intensity) int 206 (M^+, 9.4), 105 (29.7), 101 (100), 77 (31.2).

Direct Irradiation of BTSY. A 2.86 × 10^{-3} M solution of BTSY was irradiated for 1 h; the UV–vis absorption band of the ylide at 320 nm had disappeared completely. Evaporation of solvent under vacuum gave a yellow solid. The product was isolated by radial chromatography using 5% ethyl acetate in hexane as an eluant and purified by recrystallization from methanol to give colorless crystals: mp 72–73 °C. It was identified as the expected Stevens rearrangement product, 2-benzoyl-3,6-dihydro-4,5-benzothiopyran. ^{1}H NMR: δ 3.18 (d, d, 1 H, J = 15.2, 5.2 Hz), 3.35 (d, d, 1 H, J = 15.2, 8.8 Hz), 3.61 (d, 1 H, J = 14.6 Hz), 3.84 (d, 1 H, J = 14.6 Hz), 4.58 (d, d, 1 H, J = 8.8, 5.2 Hz) 7.22 (m, 4 H), 7.50 (m, 3 H), 7.96 (m, 2 H). ^{13}C NMR: δ 192.65, 136.42, 135.58, 135.55, 133.34, 129.02, 128.67, 128.59, 127.29, 126.64, 126.45, 43.42, 30.71, 29.68. MS (EI): m/e (rel intensity) 254 (8.8), 149 (85), 105 (100), 77 (66).

Electron-Transfer Sensitization. Typical Procedure. A DCA-saturated acetonitrile solution of the ylides was placed in a Pyrex cell equipped as in the procedure for the direct irradiation. The sample was purged with nitrogen for 30 min and irradiated with a medium-pressure mercury arc lamp (450 W) equipped with a glass filter that cuts out light below 400 nm. DCA was the only species in the irradiated solution that absorbs light in this region. The sample was irradiated for several hours, the nitrogen atmosphere was maintained throughout the photolysis, and product formation was monitored by GC/MS.

Sensitization of BMSY. A 5 × 10^{-3} M solution of the ylide in 20 mL of DCA-saturated acetonitrile was irradiated for 6 h. Evaporation of solvent under reduced pressure gave an orange residue. Analysis of the residue by ^{1}H NMR spectroscopy revealed ylide, DCA, and several products. The products were isolated by radial chromatography using 5% ethyl acetate in hexane as the eluant to give **4** and cyclopropane **1**: mp 211–212 °C (lit. mp 218–219 °C;[26] 212–213 °C[27]). ^{1}H NMR: δ

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(3.77 d, d, 2 H, J = 5.4 Hz), 4.24 (t, 1 H, J = 5.4 Hz), 7.49 (m, 9 H), 8.01 (m, 4 H), 8.29 (m, 2 H). MS (EI): m/e 354 (M^+). MS (FAB): m/e 355 ($M^+ + 1$). The yields of the products were determined by ^1H NMR spectroscopy to be **4** (52%), **1** (26%), and benzyl methyl sulfide (18%).

Sensitization of IMSY. A 7.5×10^{-3} M solution of the ylide in 20 mL of DCA-saturated acetonitrile was irradiated for 6 h. Evaporation of the solvent gave an orange solid. Its ^1H NMR spectrum revealed residual ylide and compounds **4** and **5**. The products were identified by GC/MS analysis and isolated by radial chromatography. The products yields were determined by ^1H NMR spectroscopy to be 38% **4** and 10% **5** at 30% conversion of IMSY.

Sensitization of DMSY, EMSY, TMSY, and BTSY. Solutions of the ylides (7.5×10^{-3} M in 20 mL of DCA-saturated acetonitrile) were irradiated. Evaporation of solvent in each case gave an orange solid. Analysis by ^1H NMR spectroscopy and GC/MS revealed residual ylide and formation of cyclopropane **1**: formed in 91% yield at 30% conversion from DMSY, 82% yield at 31% conversion from EMSY, 85% yield at 31% conversion of TMSY, and 65% yield at 33% conversion of BTSY. In this case, 2,7-dihydrobenzothiophene was formed in 33% yield.

Sensitization of BMSY in the Presence of Tetra-*n*-butylammonium Acetate. A 5×10^{-3} M solution of BMSY in 20 mL of DCA-saturated acetonitrile containing 5×10^{-3} M tetra-*n*-butylammonium acetate was placed in a Pyrex vessel and purged with nitrogen for 30 min. The sample was irradiated ($\lambda > 400$ nm) for 10 h. Evaporation of solvent gave an orange solid. ^1H NMR spectral analysis of the crude product revealed residual BMSY, **4**, **1**, and 2-acetoxyacetophenone: mp 44-45 °C, identified by comparison with an authentic sample.

Sensitization of DMSY in the Presence of Isobutene. Isobutene was bubbled into a 5×10^{-3} M solution of BMSY in 18 mL of DCA-saturated acetonitrile (0 °C) in a Pyrex vessel until the solution volume had increased by ca. 2 mL. The vessel was sealed and irradiated ($\lambda > 400$ nm) for 8 h. The ^1H NMR spectrum and a GC/MS analysis of the crude product revealed residual DMSY, cyclopropane **1**, and a new product identified as 4,4-dimethyl-1-tetralone (**2**) based on its spectral properties and the preparation of a derivative:[26] ^1H NMR: δ 1.396 (s, 6 H), 2.02 (t, 2 H, J = 7 Hz), 2.74 (t, 2 H, J = 7 Hz), 7.28-7.52 (m, 3 H), 8.02 (d, 1 H). GC/MS: m/e 174 ($M^{\bullet+}$), 159, 131, 91.

The 2,4-dinitrophenylhydrazone of **2** was prepared and recrystallized from ethyl acetate: mp 121-125 °C (lit.[27] 125-126 °C). ^1H NMR: δ 1.36 (s, 6 H), 1.96 (t, 2 H, J = 7 Hz), 2.86 (t, 2 H, J = 7 Hz), 7.42 (m, 2 H), 8.20-8.46 (m, 4 H), 9.18 (d, 1 H)9 MS (FI): m/e 354 ($M^{\bullet+}$).

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Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solvent[1]

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Abstract: Long-chain alkanethiols, $HS(CH_2)_nX$, adsorb from solution onto gold and form oriented, ordered monolayers. Monolayers exposing more than one functional group at the surface can be generated by coadsorption of two or more thiols from solution. In general, the ratio of the concentration of the two components in a mixed monolayer is not the same as in solution but reflects the relative solubilities of the components in solution and interactions between the tail groups, X, in the monolayers. Multicomponent monolayers do not phase-segregate into single-component domains large enough to influence the contact angle (a few tens of angstroms across) and also do not act as ideal two-dimensional solutions. In the two-component system $HS(CH_2)_nX/HS(CH_2)_nCH_3$ in ethanol, where X is a polar tail group such as CH_2OH or CN, adsorption of the polar component is particularly disfavored at low concentrations of the polar component in the monolayer. These isotherms may arise from poor solvation of the polar tail groups in the quasi-two-dimensional alkane solution provided by the methyl tail groups. From dilute solutions in alkanes, adsorption of $HS(CH_2)_{10}CH_2OH$ is strongly preferred over $HS(CH_2)_{10}CH_3$, probably due to the stabilization afforded by intramonolayer hydrogen bonds between the hydroxyl tail groups. The wettability of mixed monolayers is not linear in the composition of the surface. In a surface comprised of a polar and a nonpolar component, the polar component is more hydrophilic when its concentration in the monolayer is low than when the monolayer is composed largely of the polar component.

The formation of oriented monolayer films on a surface by the spontaneous adsorption of molecules from solution has become known as self-assembly. Of all the types of self-assembled monolayers that have been studied,[3] two systems have shown the greatest promise as a means of controlling the chemical structure of organic surfaces: adsorption of organosulfur compounds on noble metals such as gold[4-8] and silver,[9] and reaction of alkyltrichlorosilanes with silicon or glass.[10] Our research has concentrated on the first of these systems.[11] In a previous paper,[8] we presented a study of the formation, characterization, and properties of monolayers generated by the adsorption of *n*-alka-

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