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Photochemical Anion-Promoted Carbon–Sulfur Cleavage Reactions of Diaryl Sulfides, Alkyl Aryl Sulfides, and Related Sulfoxides and Sulfones

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Diaryl sulfides and the related sulfoxides and sulfones react with substances such as diethyl phosphite anion, pinacolone enolate, and diphenylphosphide anion under irradiation to cleave one carbon–sulfur bond and form diethyl arylphosphonates, arylmethyl *tert*-butyl ketones, and aryldiphenylphosphines. Alkyl aryl sulfides and the related sulfones also experience carbon–sulfur bond cleavage under these conditions to produce arenethiols. Generally, these reactions occur in synthetically useful yields. The reactions of the anions with these sulfides, sulfoxides, and sulfones all require irradiation, but it is notable that the reactions of diphenylphosphide anion occur in the visible region of the spectrum. Several lines of evidence suggest that the reaction proceeds via the familiar $S_{RN}1$ pathway and that the photochemically-induced electron transfer occurs in an arene–anion complex. Thermochemical considerations dictate the cleavage direction in the anion radicals of unsymmetrical sulfides.

Introduction

The presence of sulfur in coal constitutes a major impediment to the environmentally sound utilization of this large resource. Certain physical methods can be used effectively for the removal of the dense mineral sulfides, principally iron pyrite, but no mild, selectively targeted strategies have been described for the removal of sulfur from the organic constituents.[1-3] We have been addressing this problem in our laboratory, and in the course of the work we have investigated the photochemically induced $S_{RN}1$ reactions of aryl sulfides and related compounds since it appeared that a knowledge of this chemistry might prove stimulating and extend the opportunities that are available for the reactions of organic sulfur compounds with alkali and alkaline-earth metals[4-12] and $S_{RN}1$ chemistry.[13,14] Further, Eisch and his associates have presented evidence that supports the involvement of electron transfer in the desulfurization of heterocyclic sulfur compounds[15,16] and unsaturated sulfones[17] with organometallic reagents.

The pioneering studies of Bunnett and his co-workers revealed that the carbon–sulfur bonds could be cleaved under $S_{RN}1$ conditions.[13,14] However, the scope and limitations of the reaction have not been explored, and we have therefore studied the reactions of selected aryl sulfides and their oxidized derivatives. The study was limited to the use of anions as electron sources. Without exception, photoexcitation was necessary to initiate electron transfer from the anions to the organic sulfur compounds. The reaction parameters, the product distributions, and certain mechanistic features are discussed.

Results

The aryl sulfides, alkyl aryl sulfides and their oxidized derivatives, and the other compounds that were needed to prove the structures of the reaction products were synthesized without difficulty as described in the Experimental Section.

Diaryl Sulfides. Diaryl sulfides such as diphenyl sulfide, naphthyl phenyl sulfide, and dinaphthyl sulfide reacted with anions such as diethyl phosphite (1), pinacolone enolate (2), and diphenylphosphide anion (3) under irradiation in aprotic solvents to form substitution products and arenethiolates as nucleofugic groups. The observations are summarized in Table I.

$$\underset{\mathbf{1}}{[(CH_3CH_2O)_2PO]^-} \quad \underset{\mathbf{2}}{[(CH_3)_3CCOCH_2]^-} \quad \underset{\mathbf{3}}{[(C_6H_5)_2P]^-}$$

The cleavage reactions were generally carried out by combining the sulfide with a 3–5-fold excess of the anions. The use of ammonia as the solvent generally gave the best yield of substitution products (compare entries 4 and 5), although its general usefulness is limited by the insolubility of most solid sulfides. The time required for complete disappearance of the sulfide varied from 2.5 h to more than 20 h. Whereas diphenyl sulfide and di-4-tolyl sulfide were generally completely cleaved after 3 h of irradiation, dinaphthyl sulfide required more than 20 h to undergo complete reaction.

Diphenyl sulfide reacted with 1, 2, and 3 to produce diethyl phenylphosphonate, 3,3-dimethyl-1-phenyl-2-butanone, and triphenylphosphine, which was partly or completely converted to the oxide, respectively, as substitution products. Although the conversions and yields were quite good, there were some side reactions. The reaction of diphenyl sulfide and diethyl phosphite yields ethyl phenyl sulfide, which probably was formed by the nucleophilic displacement reaction of benzenethiolate with diethyl phosphite, eq 1. Indeed, upon mixing equimolar

$$PhS^- + \mathbf{1} \rightarrow PhSCH_2CH_3 + [(CH_3CH_2O)PO_2]^{2-} \quad (1)$$

quantities of benzenethiolate ion and diethyl phosphite, ethyl phenyl sulfide was formed in 35% yield. The arenethiolates were usually detected after acid hydrolysis as the arenethiols and the corresponding disulfides that were formed through air oxidation reactions.[18] In some cases,

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Table I. Reactions of Diaryl Sulfides

entry	ArSAr (mmol)	anion (mmol)	conditions[a]	unreacted ArSAr (mmol)	products (mmol)
1	PhSPh (11.8)	1 (32)	DMSO, $h\nu$, 5, 25	0	$PhP(O)(OEt)_2$ (7.0) PhSSPh (2.7) $PhSCH_2CH_3$ (0.5) PhH (1.0)
2	PhSPh (2.9)	1 (15)	DMF, $h\nu$, 2.5, 25	0	$PhP(O)(OEt)_2$ (2.1) PhSH (0.6)
3	PhSPh (7.0)	1 (35)	NH_3, $h\nu$, 2.5, −76	0	$PhP(O)(OEt)_2$ (4.9) PhSH (5.2) $PhSCH_2CH_3$ (1.0)
4	PhSPh (3.0)	2 (15)	DMSO, $h\nu$, 3, 25	0.9	$PhCH_2C(O)C(CH_3)_3$ (2.0) PhSSPh (0.5) PhSH (0.5)
5	PhSPh (5.8)	2 (24)	NH_3, $h\nu$, 2.5, −76	0	$PhCH_2C(O)C(CH_3)_3$ (5.7) PhSSPh (2.5)
6	PhSPh (3.0)	3 (10)	DMSO, visible, 15, 25	0.5	Ph_3PO (2.1) PhSH (2.5)
7	$(4\text{-}CH_3Ph)_2S$ (2.8)	1 (15)	DMF, $h\nu$, 3, 25	0	$4\text{-}CH_3PhP(O)(OEt)_2$ (2.1) $PhCH_3$ (0.6)
8	$(4\text{-}CH_3Ph)_2S$ (2.9)	3 (9)	DMSO, visible, 8.5, 25	0.9	$4\text{-}CH_3PhPPh_2$ (1.6) $4\text{-}CH_3PhSH$ (1.9)
9	$(4\text{-}CH_3Ph)_2S$ (2.9)	3 (9)	DMSO, $h\nu$, 2.5, 25	0	$4\text{-}CH_3PhPPh_2$ (1.1) $4\text{-}CH_3PhP(O)Ph_2$ (1.0) $PhCH_3$ (trace) $4\text{-}CH_3PhSH$ (2.9)
10	1-NaphSPh (2.2)	2 (15)	DMSO, $h\nu$, 5, 25	0.1	$PhCH_2C(O)C(CH_3)_3$ (1.4) 1-NaphSH (1.4) $1\text{-}NaphCH_2C(O)C(CH_3)_3$ (0.4) PhSH (0.2) NaphH (0.2)
11	$(1\text{-}Naph)_2S$ (1.8)	1 (15)	DMF, $h\nu$, 20, 25	0.7	$1\text{-}NaphP(O)(OEt)_2$ (0.5) NaphH (0.6)
12	$(1\text{-}Naph)_2S$ (1.8)	2 (10)	DMF, $h\nu$, 19, 25	0.2	$1\text{-}NaphCH_2C(O)C(CH_3)_3$ (0.5) 1-NaphSH (1.2) NaphH (0.7) $(1\text{-}Naph)_2$ (0.2)

[a] The solvent, the nature of the light source, $h\nu$ indicates hanovia lamp and visible indicates room light, the reaction time (h), and temperature (°C) are noted.

arenes were obtained as byproducts. These compounds were undoubtedly formed by the abstraction of hydrogen atoms from the solvents. Work with labeled materials[19] and other experiments established that hydrogen atom donation occurred more readily from dimethylformamide than from dimethyl sulfoxide or ammonia.

The reaction of di-4-tolyl sulfide with **1** and **3** gave only para substitution products, thereby eliminating any need to consider benzyne intermediates. Entries 8 and 9 indicated that, although visible light promoted the cleavage of di-4-tolyl sulfide by diphenylphosphide anion, the reaction was clearly enhanced by exposure to UV light.

Competition experiments with diphenyl and di-4-tolyl sulfides and **1** and di-4-tolyl and di-4-anisyl sulfides with the same anion established the order of reactivity to be diphenyl sulfide, 1.00 > di-4-tolyl sulfide, 0.067 ± 0.004 > di-4-anisyl sulfide, 0.0098 ± 0.0014. These observations suggest that the Hammett reaction constant ρ is unusually large, ~ 7. The positive sign of ρ indicates that the overall rate of carbon–sulfur cleavage is decreased by electron-donating substituents such as the methyl and methoxy substituents.

The reactions of 1-naphthyl phenyl sulfide typically resulted in the cleavage of both phenyl and 1-naphthyl carbon–sulfur bonds (entry 10). However, there was a clear preference for the cleavage of the phenyl carbon–sulfur linkage.

Alkyl Aryl Sulfides. The selectivity of the carbon–sulfur bond cleavage process was even more apparent in the reactions of the alkyl aryl sulfides (Table II).

These reactions were carried out by irradiating a mixture of the sulfide and a 3–5-fold excess of the anion from 8 to 20 h. The reactions of alkyl aryl sulfides with the arenethiolates appeared to be considerably slower than the reactions of the same compounds with the other anions. Entries 1 and 7 illustrate this feature.

The course of the reaction was studied in the presence of arenethiolates as well as **2** and **3**. The alkyl carbon–sulfur bonds in the alkyl aryl sulfides were cleaved exclusively. The material balances for the arene fragments were very good in every instance, and, in most cases, the simple arenethiols were formed in good yields.

The material balances for the aliphatic portions of the sulfides were consistently low. This situation was not surprising inasmuch as the bond cleavage reactions of the alkyl aryl sulfide anion radicals liberate alkyl radicals such as methyl, ethyl, and benzyl radicals that presumably abstract hydrogen atoms from the solvents to form low-boiling hydrocarbons. Some of the radicals formed in the cleavage reactions were intercepted in subsequent reactions with the thiolate and phosphide anions. This aspect is particularly well illustrated in the reactions of the methyl, ethyl, and benzyl radicals with the phosphide anion (entries 6, 7, and 8). No products from reactions of this kind

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[19] The results of experiments involving the photochemical carbon–sulfur cleavage of various diaryl sulfides by deuterides, which were carried out in different hydrogen-donating solvents, indicate that the ease of hydrogen transfer from the solvents to aryl radicals parallels the bond energies. Cheng, C. Ph.D. dissertation, University of Chicago, 1989.

Table II. Reactions of Alkyl Aryl Sulfides

entry	ArSR (mmol)	anion (mmol)	conditions[a]	unreacted ArSR (mmol)	products (mmol)
1	PhSEt (3.3)	4-CH_3PhS^- (12)	DMSO, $h\nu$, 20, 25	1.7	PhSH (1.0) 4-CH_3PhSEt (0.2) 4-$CH_3PhSSPh$ (0.6)
2	4-CH_3PhSEt (3.3)	PhS^- (10)	DMF, $h\nu$, 15, 25	2.5	4-CH_3PhSH (0.6) PhSEt (0.1)
3	PhSEt (5.1)	**2** (15)	DMF, $h\nu$, 8, 25	1.4	PhSH (3.6)
4	4-CH_3PhSEt (3)	**2** (15)	DMF, $h\nu$, 15.5, 25	0.4	4-CH_3PhSH (2)
5	$PhSCH_2SPh$ (3.0)	**2** (15)	DMF, $h\nu$, 8, 25	0	$PhCH_3$ (1.3) $PhCH_2CH_2Ph$ (0.2) PhSH (2.5) $PhCH_2X$[b] (0.9)
6	$PhSCH_3$ (3.1)	**3** (9)	DMSO, visible, 19.5, 25	0	PhSH (2.7) $Ph_2P(O)CH_3$ (1.7)
7	PhSEt (3.2)	**3** (12)	DMSO, visible, 15, 25	0	PhSH (3.1) $Ph_2P(O)Et$ (2.2)
8	$PhSCH_2Ph$ (2.6)	**3** (7.5)	DMSO, visible, 19.5, 25	0	PhSH (2.5) $PhCH_3$ (0.3) $Ph_2P(O)CH_2Ph$ (1.5)

[a] Refer to Table I for an explanation of the notation. [b] An unknown compound having a molecular aweight of 232 and containing the benzyl group.

Table III. Reactions of Diphenyl Sulfone, Diphenyl Sulfoxide, and Ethyl Phenyl Sulfone

entry	substrate (mmol)	anion (mmol)	conditions[a]	unreacted substrate (mmol)	products (mmol)
1	$PhS(O)_2Ph$ (2.7)	**1** (15)	DMSO, $h\nu$, 4, 25	0.8	$PhP(O)(OEt)_2$ (1.7) PhH (0.2)
2	$PhS(O)_2Ph$ (2.7)	**2** (15)	DMF, $h\nu$, 14, 25	0.1	$PhCH_2C(O)C(CH_3)_3$ (1.9) PhH (0.3)
3	$PhS(O)_2Ph$ (2.5)	**3** (7.5)	DMSO, visible, 15, 25	0.2	Ph_3P (1.4) $Ph_3P(O)$ (0.6)
4	PhS(O)Ph (3.3)	**1** (12)	DMF, $h\nu$, 14, 25	0	$PhP(O)(OEt)_2$ (2.1) PhH (0.2) $PhSCH_2CH_3$ (0.9) PhSH (0.5) PhSPh (0.05) PhSSPh (0.1)
5	PhS(O)Ph (2.5)	**3** (7.5)	DMSO, visible, 15, 25	0	PhSH (0.4) Ph_3P (1.5) $Ph_3P(O)$ (0.5)
6	$PhS(O)_2Et$ (3)	**2** (15)	DMF, $h\nu$, 12, 25, + $PhCH_2Cl$ (3), Δ	0.7	$PhS(O)_2CH_2Ph$ (1.2)
7	$PhS(O)_2Et$ (2.8)	**3** (8)	DMSO, $h\nu$, 21, 25	0	$Ph_2P(O)Et$ (2.0)

[a] Refer to Table I for an explanation of the notation.

were detected when the enolate was used to promote the reaction. The product distribution for benzyl phenyl sulfide in this case (entry 5) included toluene and bibenzyl rather than adducts with the enolate.

Diphenyl Sulfone, Diphenyl Sulfoxide, and Ethyl Phenyl Sulfone. Representative results for the reactions of these compounds are summarized in Table III.

The cleavage reactions of diphenyl sulfone and diphenyl sulfoxide were best accomplished by treating the organic sulfur compound with a 3–5-fold excess of the anion in dimethylformamide or dimethyl sulfoxide; these compounds were not soluble in ammonia.

Diphenyl sulfone was cleaved by diethyl phosphite anion, pinacolone enolate, and diphenylphosphide anion in one of the two identical carbon–sulfur bonds to form products which, aside from the leaving group, were identical with the products formed from the corresponding sulfide. A comparison of entries 1–3 and 5 of Table I with the results shown in Table III indicated that diphenyl sulfone was somewhat less reactive than the corresponding sulfide. The material balances for the sulfur-free products were quite good. In a related experiment, diphenyl sulfone (3.2 mmol) was cleaved by **1** to give diethyl phenylphosphonate (0.9 mmol) and benzenesulfinate ion, which was subsequently trapped by excess benzyl chloride to give benzyl phenyl sulfone (1.3 mmol). This result indicated that the anion radical of diphenyl sulfone fragmented to form the phenyl radical and the benzenesulfinate ion. Entries 4 and 5 of Table III indicated that diphenyl sulfoxide reacted with anions to give derivatives of benzenethiolate instead of expected derivatives of benzenesulfenate ion, $PhSO^-$. Benzenethiolate ion was probably formed through the disproportionation reaction of benzenesulfenate ion,[20] the initial cleavage product of the anion radical of diphenyl sulfoxide, as noted in (2a) and (2b).

$$[PhSOPh]^{\bullet-} \rightarrow Ph^{\bullet} + PhSO^- \qquad (2a)$$

$$2\ PhSO^- \rightarrow PhS^- + PhSO_2^- \qquad (2b)$$

The reactions of ethyl phenyl sulfone with **2** and **3** gave products that indicated exclusive cleavage in the alkyl

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[20] Kice, J. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

carbon–sulfur bond (entries 6, 7, Table III). Experiments were carried out to demonstrate that pinacolone enolate did not react in visible light and to demonstrate that benzenesulfinate anion could be intercepted with benzyl chloride to form benzyl phenyl sulfone (entry 6, Table III). The ethyl fragment exhibited the same fate in the reaction of the sulfone as it did in the reaction of the related sulfide.

Discussion

The first anion-promoted carbon–sulfur bond cleavage was probably carried out by Bergmann and Tschudnowsky,[21] who used diphenylmethylsodium to convert diphenyl sulfoxide into triphenylmethane and benzenethiolate anion. Rossi and Bunnett[13,14] established that diphenyl sulfide reacted with acetone enolate following photochemical or potassium(0) initiation to form benzyl methyl ketone and benzenethiolate as well as the termination product, benzene (3). They formulated the reaction as

$$\mathrm{PhSPh} + \mathrm{CH_3COCH_2^-} \xrightarrow[\mathrm{K,\ NH_3}]{h\nu\ \mathrm{or}} \mathrm{PhCH_2COCH_3} + \mathrm{PhH} + \mathrm{PhS^-} \quad (3)$$

an $S_{RN}1$ process (4a–d). This well-known sequence is initiated by electron transfer to provide the anion radical of diphenyl sulfide, which fragments to produce the phenyl radical and the benzenethiolate ion. In the next step, acetone enolate adds nucleophilically to the phenyl radical to produce the anion radical of the ketone product. Subsequent electron transfer to diphenyl sulfide completes the propagation sequence. We shall use this as a paradigm in the discussion of our observations.

$$\mathrm{PhSPh} + \mathrm{CH_3COCH_2^-} \xrightarrow{h\nu} \mathrm{PhSPh^{\bullet-}} + \mathrm{CH_3COCH_2^{\bullet}} \quad (4a)$$

$$[\mathrm{PhSPh}]^{\bullet-} \rightarrow \mathrm{Ph^{\bullet}} + \mathrm{PhS^-} \quad (4b)$$

$$\mathrm{Ph^{\bullet}} + \mathrm{CH_3C(O)CH_2^-} \rightarrow [\mathrm{PhCH_2C(O)CH_3}]^{\bullet-} \quad (4c)$$

$$[\mathrm{PhCH_2C(O)CH_3}]^{\bullet-} + \mathrm{PhSPh} \rightarrow \mathrm{PhCH_2C(O)CH_3} + [\mathrm{PhSPh}]^{\bullet-} \quad (4d)$$

Scope and Limitations. Photochemical anion-promoted carbon–sulfur cleavage is applicable to a wide variety of organic sulfur compounds, namely diaryl sulfides, alkyl aryl sulfides, diaryl sulfoxides and sulfones, alkyl aryl sulfones, and, to a limited extent, aromatic heterocyclic sulfur compounds.[22] With the exception of dibenzyl sulfide, dialkyl sulfides are not cleaved by anions[22] even under photoexcitation by ultraviolet light. These compounds do not undergo anion-promoted carbon–sulfur cleavage presumably because of their low electron affinity, and, hence, low tendency to form anion radicals.

With very few exceptions, complete sulfur removal is not accomplished. The anion radicals usually cleave only in one of the two carbon–sulfur bonds to form a thiolate as one of the products. The arenethiolates do not undergo further cleavage, presumably because of their reluctance to form dianions.

The anion is indispensable for the carbon–sulfur cleavage reactions that we have studied. The anions serve two important functions in their reactions with the organic sulfur compounds. Firstly, they function as electron donors. Secondly, they add nucleophilically to radical intermediates to produce anion radicals that are potentially capable of undergoing electron transfer with the organic sulfur compounds to ensure chain propagation. Some of the anions that are capable of functioning both as electron donors to organic sulfur compounds and as nucleophiles are **1**, **2**, **3**, and arenethiolates. Some other anions were not as suitable. Preliminary experiments with the trimethylsilyl anion revealed that although it promoted the cleavage of carbon–sulfur bonds of diaryl sulfides, the results were marked by poor material balances. Its study was therefore discontinued. Further, phenoxide ion promoted the reactions of di-4-tolyl sulfide to give toluene and 4-methylbenzenethiolate ion; however, the reaction occurred slowly, and only 22% of the sulfide was converted after 14 h of illumination. Ethereal products were not formed, and therefore, we inferred that the phenoxide ion functioned as electron donor (5a,b) but not as a nucleophile (5c). The lack of reactivity of the phenoxide ion in $S_{RN}1$ reactions has been reported by Rossi and associates,[23] although there are recent reports that naphthoxides[24] and substituted phenoxides[25] do add to aryl radicals.

$$\mathrm{PhO^-} + \mathrm{PhSPh} \xrightarrow{h\nu} \mathrm{PhO^{\bullet}} + [\mathrm{PhSPh}]^{\bullet-} \quad (5a)$$

$$[\mathrm{PhSPh}]^{\bullet-} \longrightarrow \mathrm{Ph^{\bullet}} + \mathrm{PhS^-} \quad (5b)$$

$$\mathrm{Ph^{\bullet}} + \mathrm{PhO^-} \not\longrightarrow [\mathrm{PhOPh}]^{\bullet-} \quad (5c)$$

Reaction Pathway. Initiation. The anion-promoted cleavage reactions that we have studied required photochemical activation either by ultraviolet or visible light. None of the cleavage reactions we have studied occurs in the dark. It is notable that the reactions with diphenylphosphide anion occur in visible light, whereas the reactions of the other anions require photostimulation by ultraviolet light. The absorption properties of the anions, therefore, need to be considered. Benzenethiolate,[26] pinacolone enolate, and diphenylphosphide anions absorb appreciably in the 300–400 nm region. Furthermore, diphenylphosphide anion, which absorbs strongly in the visible region (λ = 475 nm), promotes carbon–sulfur cleavage in ordinary laboratory light. These observations suggest that photoexcitation induces the anions to donate electrons to organic sulfur compounds of suitable electron affinity. Whereas the other anions require photostimulation by ultraviolet light to donate electrons, diphenylphosphide anion merely requires visible light.

Although numerous features of the photophysics and photochemistry remain unresolved, it is generally agreed that the photochemical initiation step of the $S_{RN}1$ reaction involves an electron transfer from a closed-shell anion to a suitable orbital of the substrate.[13,14,27-29] A variety of anions such as benzenethiolate, pinacolone enolate, diethyl phosphite, and diphenylphosphide anion have been found to be effective electron donors. Haloarenes have been frequently studied, but it is now clear that a variety of aryl sulfides and their derivatives are also suitable substrates.

In some cases, electron transfer may occur through the mediation of a complex between the sulfide and the anion. For instance, there is clear evidence for a charge-transfer

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[21] Bergmann, E.; Tschudnowsky, M. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 457.

[22] The photochemical carbon–sulfur cleavage reactions of phenyl styryl sulfides and benzothiophene were also investigated, the results of which are not reported in this paper, but are discussed in ref 19. Dibutyl sulfide did not react with diphenylphosphide anion even when irradiated with ultraviolet light.

[23] Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 3020.

[24] Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *Tetrahedron Lett.* **1988**, *29*, 3429.

[25] Beugelmans, R.; Bois-Choussy, M. *Tetrahedron Lett.* **1988**, *29*, 1289.

[26] Miyashita, T.; Aoki, T.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 231.

[27] Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690.

[28] Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663.

[29] Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660.

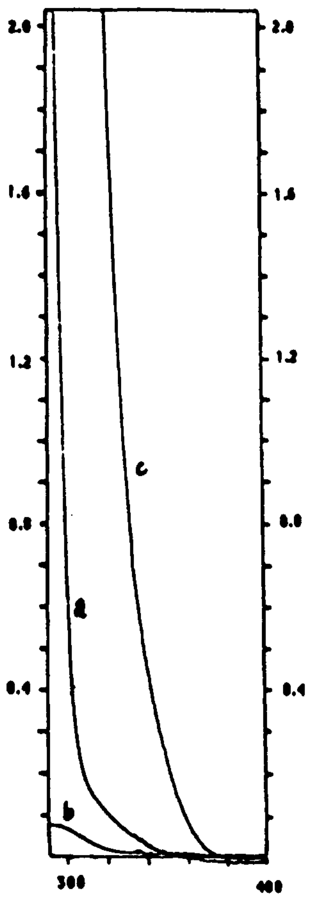


Figure 1. Superimposed UV spectra of (a) ethyl phenyl sulfide (7.7×10^{-3} M) in dimethylformamide, (b) diethyl phosphite (1.83×10^{-2} M) in dimethylformamide, (c) ethyl phenyl sulfide (6.5×10^{-3} M) and diethyl phosphite (1.83×10^{-2} M) in dimethylformamide.

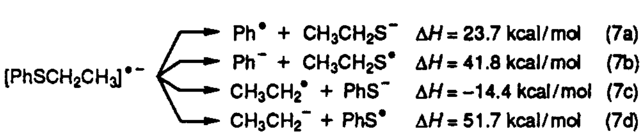
complex between ethyl phenyl sulfide and diethyl phosphite anion. Although diethyl phosphite anion by itself does not absorb appreciably at wavelengths greater than 300 nm, a solution that contains both ethyl phenyl sulfide and diethyl phosphite anion possesses an enhanced absorption much greater than the sum of the absorption of both species (Figure 1). The new species could very well be a complex of the sulfide and diethyl phosphite anion, a required precursor for electron transfer. A complex between iodobenzene and diethyl phosphite anion has been proposed by Hoz and Bunnett[27] to be probably responsible for the initiation of $S_{RN}1$ cleavage of iodobenzene. Moreover, they have reported that the reaction of iodobenzene and potassium diethyl phosphite occurred with a quantum yield of 20–50. Quantum yields of this magnitude imply that the electron-transfer process is an efficient one and that it is more efficient than expected for an initial excitation of an isolated anion in condensed matter. We, therefore, presume that electron transfer occurs within an associated complex of the anion and the sulfide, and more specifically, between a relatively energetic occupied orbital of the anion and a low-lying unoccupied orbital of the sulfide. In this situation, the energy levels of the anions become especially significant. Unfortunately, only limited information is available about the compounds of interest in this work. However, Brauman and co-workers[30–33] determined the ionization potentials of organic anions in the gas phase. Their work and the information that has been summarized in a recent critical compilation concerning electron detachment energies of anions indicate that enolates, arenethiolates, and phenoxides have electron detachment energies ranging from 40–60 kcal/mol. Although information about diphenylphosphide anion is lacking, the energy requirement for phosphide anion is only 28.9 kcal/mol.[34] Indeed, the values for the simple hydrogen-containing anions of the group IV, V, and VI elements of greatest interest parallel the results of our investigation and the investigations of other workers in this area and imply that electron transfer should be energetically more favorable in the order $PH_2^- > SH^- > NH_2^- > OH^-$. The data in the literature appear to be fully consistent with the experimental observations that visible light is adequate in the case of the diphenylphosphide anion.

Fragmentation and Thermochemistry. Elementary thermochemical considerations indicate that the energy requirements for the dissociation of diphenyl sulfide anion radical into phenyl radical and benzenethiolate ion should be much less than the bond dissociation energy of the neutral sulfide, 80 kcal mol^{-1}.[35,36] Gas-phase information suggests a more than 70 kcal mol^{-1} reduction (6).[33,35–37] This estimated gas-phase value[38] has recently been verified by Bausch and associates.[39]

$$[PhSPh]^{\bullet -} \rightarrow Ph^{\bullet} + PhS^- \qquad \Delta H = 4 \text{ kcal/mol} \quad (6)$$

The results of Table II indicated that the alkyl aryl sulfides cleaved consistently and selectively in the alkyl–sulfur bond regardless of the identity of the anion. These results are fully consistent with the well-known alkali and the alkaline-earth metal induced carbon–sulfur cleavage reactions of alkyl aryl sulfides.[8–10,40] Since the cleavage reactions induced by alkali and alkaline-earth metals undoubtedly involve anion radicals as intermediates, the similar mode of cleavage exhibited by the alkyl aryl sulfides in our study further supports the intermediacy of anion radicals in the anion-promoted cleavage reactions.

Furthermore, the mode of cleavage of the alkyl aryl sulfides is well explained by thermochemistry. The anion radical of ethyl phenyl sulfide can cleave in four possible modes (7a–d). The heats of reaction for the four cleavage modes can be calculated by using a conventional thermochemical cycle. Benson's Additivity Rules[35–36] and available thermochemical information such as the electron affinities of alkyl aryl sulfides,[37] phenyl,[41,42] and thiyl



$[PhSCH_2CH_3]^{\bullet -} \rightarrow Ph^{\bullet} + CH_3CH_2S^- \quad \Delta H = 23.7$ kcal/mol (7a)

$[PhSCH_2CH_3]^{\bullet -} \rightarrow Ph^- + CH_3CH_2S^{\bullet} \quad \Delta H = 41.8$ kcal/mol (7b)

$[PhSCH_2CH_3]^{\bullet -} \rightarrow CH_3CH_2^{\bullet} + PhS^- \quad \Delta H = -14.4$ kcal/mol (7c)

$[PhSCH_2CH_3]^{\bullet -} \rightarrow CH_3CH_2^- + PhS^{\bullet} \quad \Delta H = 51.7$ kcal/mol (7d)

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radicals[43] yield the values shown in the equations. The calculated heats of reaction indicate that the most thermochemically favorable mode of cleavage of the anion radical of ethyl phenyl sulfide is the formation of the ethyl radical and the benzenethiolate ion (7c), a conclusion that is in accord with the experimental results. In fact, (7c) is the only cleavage mode that is exothermic.

A similar thermochemical analysis shows that the anion radical of ethyl phenyl sulfone should cleave to give the ethyl radical and benzenesulfinate anion, a prediction that is borne out by entries 6 and 7 of Table III.

It is significant that the anion radicals of alkyl aryl sulfides and alkyl aryl sulfones cleave in the weaker carbon–sulfur bond, namely, the alkyl carbon–sulfur bond. To be more specific, for methyl phenyl sulfide, the methyl carbon–sulfur bond is weaker than the phenyl carbon–sulfur bond by at least 20 kcal/mol.[35,36] For the corresponding sulfone, the methyl carbon–sulfur bond is weaker by 30 kcal/mol.[35,36]

The results in Table I reveal the following order of reactivity of diaryl sulfides toward photostimulated anionic cleavage: PhSPh > PhSNaph > NaphSNaph. This order of reactivity can be rationalized by the relative heats of reaction that we have estimated for the fragmentation steps (6) and (8).[37,44] The fragmentation of dinaphthyl

$$[\mathrm{NaphSNaph}]^{\bullet -} \rightarrow \mathrm{Naph}^{\bullet} + \mathrm{NaphS}^{-} \qquad \Delta H \geq 4 \text{ kcal/mol} \quad (8)$$

sulfide anion radical to form the naphthyl radical and naphthalenethiolate ion (8) is probably more endothermic than the corresponding fragmentation of the diphenyl sulfide anion radical to form the phenyl radical and the benzenethiolate ion (6). This trend in the heat of reaction as the sulfide substituent changes from phenyl to more condensed aryl moieties is supported by the work of Bausch and associates.[39] The greater heat of reaction of (8) compared to (6) is actually due to the greater electron affinity to the naphthyl-substituted sulfide compared to diphenyl sulfide.

Coupling of Radicals and Anions. The reactions of ethyl phenyl sulfide and ethyl 4-tolyl sulfide with 2 (entries 3 and 4, Table II) did not provide *tert*-butyl *n*-propyl ketone. Thus, 2 does not readily add to the ethyl radical (10).

$$\mathrm{CH_3CH_2}^{\bullet} + \mathbf{2} \nrightarrow [\mathrm{CH_3(CH_2)_2C(O)C(CH_3)_3}]^{\bullet -} \quad (10)$$

On the other hand, the formation of relatively large quantities of alkyldiphenylphosphine oxides in the reactions of 3 with methyl phenyl sulfide (entry 6, Table II), ethyl phenyl sulfide (entry 7, Table II), and benzyl phenyl sulfide (entry 8, Table II) suggests that, in contrast to 2, *3 adds nucleophilically to the alkyl radicals* (11).

$$\mathrm{CH_3}^{\bullet} + \mathbf{3} \rightarrow [\mathrm{Ph_2PCH_3}]^{\bullet -} \quad (11)$$

Inhibition by Dinitrobenzenes and Substituent Effect. The carbon–sulfur cleavage reactions we have studied were inhibited by dinitrobenzenes. To cite a specific example, diphenyl sulfoxide (3 mmol) was irradiated with excess diethyl phosphite (12 mmol) for 40 min to give diethyl phenylphosphonate (1.6 mmol) and benzene (0.1 mmol). The reactant was 70% converted. When the same reaction was repeated in the presence of 1,4-dinitrobenzene (0.5 mmol), the sulfoxide was recovered almost quantitatively after 2.5 h of irradiation.

Inhibition was not limited to any particular substrate or anion. Moreover, relatively small amounts were sufficient to inhibit the cleavage reactions. In most cases, one dinitrobenzene per five molecules of the sulfur compounds was sufficient to inhibit the cleavage reactions. Both 1,3- and 1,4-dinitrobenzenes have high electron affinities (1,3-dinitrobenzene = 1.65 eV, 1,4-dinitrobenzene = 2.0 eV).[45] 1,4-Dinitrobenzene appeared to be a better inhibitor than 1,3-dinitrobenzene due to its higher electron affinity. This distinctive property of the dinitrobenzenes lends credence to electron capture as the mechanism for inhibiting anion-promoted cleavage reactions. The dinitrobenzenes inhibit these cleavage reactions by competing with the organic sulfur compounds for electrons in the initiation and in the chain-propagating electron transfer from the substituted aromatic anion radical.

The competition experiments with substituted diphenyl sulfides yield a large positive Hammett ρ value. Inasmuch as electron-donating substituents should reduce the rates of the first two steps in the reaction sequence (4a–d), we infer that the large ρ reflects the influence of the substituents on these two reactions. However, further work will be needed to determine whether reaction 4a or 4b is quantitatively more important.

Conclusions

Diaryl sulfides, sulfoxides, and sulfones and alkyl aryl sulfides and sulfones, among other organic sulfur compounds, undergo photochemical anion-promoted carbon–sulfur cleavage reactions. Light and the anion are the indispensable elements for these cleavage reactions. Photoexcitation is necessary to induce electron transfer from the anions to the organic sulfur compounds. Initial electron transfer probably occurs within a sulfide-anion complex. The anions also function as radical-trapping nucleophiles. The product distribution, substituent effects, inhibition by a strong electron acceptor (dinitrobenzene), thermochemistry, and spectroscopic evidence strongly suggest that these cleavage reactions involve the familiar $\mathrm{S_{RN}1}$ pathway.

Experimental Section

Materials and Equipment. Diphenyl sulfoxide was recrystallized from an ethanol/water mixture. Benzyl phenyl sulfide and diphenyl sulfone were recrystallized from ethanol. Dimethylformamide, dimethyl sulfoxide, and diethyl phosphite were dried by vacuum distillation over calcium hydride. All other starting materials and reagents were purchased commercially and used without purification.

Proton NMR spectra were recorded on the Bruker HX-270 and University of Chicago 500-MHz spectrometers. Carbon-13 NMR spectra were recorded on the Varian XL-400 spectrometer. NMR spectra were recorded with deuterated chloroform as the solvent and tetramethylsilane as internal standard. Infrared spectra were recorded on the Nicolet 20 SXB spectrometer.

Gas chromatographic analyses were carried out on a Perkin-Elmer Sigma-3B FID chromatograph coupled to a Perkin-Elmer Sigma 15 printer/plotter using a 6 ft × $^1/_8$ in. column packed with 10% OV-101 as stationary phase. Melting points were taken with a Hoover capillary melting point apparatus.

Preparation of Ethyl Phenyl Sulfide, Ethyl 4-Tolyl Sulfide, and Ethyl 2-Naphthyl Sulfide.[46] Ethyl phenyl sulfide, ethyl 4-tolyl sulfide, and ethyl 2-naphthyl sulfide were prepared from bromoethane, the corresponding arenethiolate, and trioctylmethylammonium chloride as phase-transfer catalyst.[46] The

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preparation of ethyl 2-naphthyl sulfide, which was subsequently utilized in the preparation of 2-naphthyl phenyl sulfide, is representative.

2-Naphthalenethiol (4.81 g, 0.03 mol) and trioctylmethylammonium chloride (0.3 g) were added to an aqueous solution of potassium hydroxide (2.32 g, 0.035 mol + 20 mL H_2O). Ethyl bromide (2.6 mL, 0.035 mol) was added into the stirred mixture, upon which heat was evolved. The solution was stirred for 2 h. More water (30 mL) was added, and the mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with water. Ether was removed to yield ethyl 2-naphthyl sulfide as a brown, oily liquid. The crude, oily sulfide was used immediately in the preparation of 2-naphthyl phenyl sulfide: ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, $J = 8$ Hz), 3.04 (q, 2 H, $J = 8$ Hz), 7.38–8.46 (complex, 7 H).

Preparation of 2-Naphthyl Phenyl Sulfide. 2-Naphthyl phenyl sulfide was prepared according to the method of Nakayama, Fujita and Hoshino.[46]

Ethyl 2-naphthyl sulfide (5.6 g, 0.03 mol) and isoamyl nitrite (8.3 mL, 0.06 mol) were dissolved in 1,2-dichloroethane (40 mL). The mixture was gently refluxed. A solution of anthranilic acid (8.5 g, 0.06 mol) in dioxane (30 mL) was added dropwise via an addition funnel over a period of 15 min to the refluxing mixture. After the addition was completed, the mixture was refluxed further for 1 h. The resulting brown solution was concentrated under rotary evaporation, and the resulting oily residue was purified by column chromatography with silica gel as adsorbent and hexane as eluent. 2-Naphthyl phenyl sulfide was obtained as a white solid (4.6 g, 86% yield). The sulfide was recrystallized from ethanol to give a white crystalline solid, mp 51 °C (lit.[47] mp 51 °C): IR (KBr) 688, 737, 816, 862, 1025, 1477, 1579, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–7.82 (complex, 12 H).

Preparation of Di-4-tolyl Sulfide, Di-4-anisyl Sulfide, 1-Naphthyl Phenyl Sulfide, 1,1′-Dinaphthyl Sulfide, and 2,2′-Dinaphthyl Sulfide.[48] 1-Naphthalenethiol was prepared according to the following procedure[49] and subsequently used in the preparation of 1-naphthyl phenyl sulfide.

Crushed ice (~30 g) was added to a solution of 1-aminonaphthalene (10 g, 0.07 mol) in concentrated sulfuric acid (15 mL). The solution was maintained at 0 °C while the amine was diazotized by the dropwise addition of a solution of sodium nitrite (6 g, 0.09 mol) in water (10 mL).

A solution of potassium ethyl xanthate (20 g, 0.120 mol) in water (~25 mL) was heated to 40 °C in a three-necked flask equipped with a condenser, a dropping funnel, and a magnetic stirrer. The cold diazonium solution obtained above was added dropwise with stirring at such a rate that the temperature did not exceed 40 °C. After addition, the solution was allowed to stand for 30 min. The cooled mixture was extracted with ether (3 × 50 mL). The combined ether extracts were washed with 10% sodium carbonate solution (16 mL) then with water (2 × 25 mL) and subsequently dried over anhydrous magnesium sulfate. The ether was partially removed by rotary evaporation to give ethyl 1-naphthyl xanthate. The xanthate solution was reduced immediately to the thiol.

Lithium aluminum hydride (2.7 g, 0.07 mol) was stirred in dry ether (140 mL). The ether solution of ethyl 1-naphthyl xanthate obtained above was added dropwise at such a rate to maintain a gentle reflux of the ether solution. After addition, the mixture was stirred for 3.5 h. The remaining hydride was then quenched by the dropwise addition (very carefully) of water (21 mL). The resulting thick mixture was hydrolyzed with 10% sulfuric acid (~70 mL). The ether layer was separated, and the aqueous layer was extracted further with ether (2 × 50 mL). The combined ether extracts were washed thoroughly with water (2 × 50 mL) and dried over calcium chloride. The solvent was removed, and the oily residue was purified by column chromatography over silica gel as adsorbent and with hexane as eluent. 1-Naphthalenethiol was obtained as a yellowish oil (6.9 g, 62%): IR (neat) 768, 790, 1504, 1565, 1589, 2569, 3054 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.55 (s, 1 H), 7.25–8.15 (complex, 10 H).

Di-4-tolyl sulfide, di-4-anisyl sulfide, 1-naphthyl phenyl sulfide, 1,1′-dinaphthyl sulfide, and 2,2′-dinaphthyl sulfide were prepared according to the literature.[48] The preparation of di-4-tolyl sulfide is representative.

A three-necked flask (500 mL) was equipped with a magnetic stirrer, reflux condenser, and a nitrogen inlet. A solution of alkoxide was prepared by stirring sodium (2.3 g, 0.10 mol) in isobutyl alcohol (~150 mL) under nitrogen. To the cooled solution was added 4-methylbenzenethiol (6.21 g, 0.05 mol), 4-bromotoluene (8.55 g, 0.05 mol), and tetrakis(triphenylphosphine)palladium(0) (0.58 g, 0.0005 mol). The reaction mixture was refluxed for 8 h, after which almost all of the solvent was distilled off to give a dark slurry. Water (50 mL) was added, and the mixture was extracted with ether (3 × 50 mL). The combined ether extracts were separated and washed with water (2 × 25 mL), after which the solvent was removed by rotary evaporation. The crude product was recrystallized from methanol to give white crystals of di-4-tolyl sulfide (7.9 g, 73% yield), mp 56–57 °C (lit.[47] mp 57 °C): IR (KBr) 806, 1492, 2864, 2947, 3022 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H), 7.11 (d, 4 H, $J = 9$ Hz), 7.24 (d, 4 H, $J = 9$ Hz).

Reaction of Di-4-tolyl Sulfide with Diethyl Phosphite. Photostimulated cleavage reactions were typically carried out in a three-necked Pyrex flask equipped with a nitrogen inlet and a magnetic stirrer. The light source was usually a Pyrex-filtered medium-pressure 450-W Hanovia lamp fitted in a water-cooled immersion well.

Potassium *tert*-butoxide (1.97 g, 17 mmol) was carefully weighed out under argon (glove bag) and dissolved in dimethylformamide (30–40 mL). Diethyl phosphite (2 mL, 15 mmol) was then added to the solution, followed by di-4-tolyl sulfide (0.6518 g, 3 mmol). Illumination was started. After 3 h, the lamp was turned off and water (75 mL) was added to the solution. The solution was acidified with dilute hydrochloric acid and extracted with ether (4 × 50 mL). The combined ether extracts were washed with water (2 × 25 mL), dried and anhydrous magnesium sulfate, filtered, and concentrated in a rotary evaporator. The concentrated solution was then analyzed by gas chromatography or another appropriate method. Analysis showed the presence of toluene (0.6 mmol) and diethyl 4-tolylphosphonate (2.2 mmol).

In another experiment, the reaction of di-4-tolyl sulfide (0.6320 g, 2.9 mmol) with diethyl phosphite (2 mL, 15 mmol) for 3.5 h under photoexcitation in dimethylformide gave diethyl 4-tolylphosphonate, among other products. The concentrated reaction mixture was purified through a column filled with basic alumina, Brockmann 1, and eluted successively with hexane, chloroform, and ether. Diethyl 4-tolylphosphonate (0.31 g, 47% yield) was eluted with ether: IR (neat) 794, 816, 1029, 1055, 1129, 1251, 1445, 1607, 2983, 3026 cm^{-1}. ^1H NMR ($CDCl_3$) 1.26 (t, 6 H, $J_{OCH_2-CH_3} = 7$ Hz), 2.36 (s, 3 H), 4.06 (m, 4 H), 7.23 (dd, 2 H, $J_{PhH_a-H_b} = 8$ Hz, $J_{P-PhH_a} = 4$ Hz), 7.66 (dd, 2 H, $J_{P-PhH_b} = 12$ Hz).[50]

A similar reaction of diphenyl sulfide and diethyl phosphite gave, among other products, diethyl phenylphosphonate: IR (neat) 697, 750, 796, 967, 1023, 1051, 1132, 1252, 1440, 2907, 2933, 2984 cm^{-1}. ^1H NMR δ 1.19 (t, 6 H, $J_{OCH_2-CH_3} = 8$ Hz), 3.98 (m, 4 H), 7.30–7.73 (complex, 5 H).[51]

The reaction of 1,1′-dinaphthyl sulfide with diethyl phosphite gave, among other products, diethyl 1-naphthylphosphonate: IR (neat) 777, 802, 965, 1020, 1050, 1154, 1249, 1508, 2905, 2934, 2982 cm^{-1}.[52] ^1H NMR δ 1.29 (t, 6 H, $J_{OCH_2-CH_3} = 7$ Hz), 4.14 (qd, 4 H), 7.48–8.56 (complex, 7 H).

Reaction of Diphenyl Sulfide with Diphenylphosphide. An orange-red solution of potassium diphenylphosphide (10 mmol) was prepared by adding diphenylphosphine (pyrophoric!)(1.7 mL, 10 mmol) to a solution of potassium *tert*-butoxide (1.21 g, 10 mmol) in dimethyl sulfoxide. Diphenyl sulfide (0.57 g, 3 mmol) was finally added. The solution was allowed to stand for 15–20 h after which water (75 mL) was added to quench the reaction. The solution was acidified with dilute hydrochloric acid and repeatedly extracted with methylene chloride (3 × 50 mL). The combined methylene chloride extracts were washed with water

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(2 × 25 mL), followed by excess 30% aqueous hydrogen peroxide, dried with anhydrous magnesium sulfate, filtered, and concentrated with a rotary evaporator. The concentrated solution was then analyzed by gas chromatography. Analysis showed the presence of unreacted diphenyl sulfide (0.5 mmol), triphenylphosphine oxide (2.1 mmol) and benzenethiol (2.5 mmol).

The reaction of methyl phenyl sulfide (0.5081 g, 4 mmol) and diphenylphosphide (2.1 mL, 12 mmol) for 20 h gave, among other products, methyldiphenylphosphine oxide. The concentrated reaction mixture was passed through a column of basic alumina, Brockmann 1, and eluted successively with hexane, chloroform, and ethyl acetate. Methyldiphenylphosphine oxide (0.51 g, 59% yield) was eluted with ethyl acetate as a white solid and recrystallized from a mixture of ethyl acetate and petroleum ether: mp 111–112 °C[53]; IR (KBr) 696, 754, 774, 1125, 1175, 1304, 1320, 1440, 2912, 2979, 3054 cm^{-1}; ^{1}H NMR δ 2.0 (d, 3 H, J = 13 Hz), 7.42–7.71 (complex, 10 H).

The reaction of di-4-tolyl sulfide with diphenylphosphide gave diphenyl(4-tolyl)phosphine oxide, among other products: IR (KBr) 700, 725, 752, 817, 1120, 1186, 1440, 1602, 3053 cm^{-1}; ^{1}H NMR δ 2.38 (s, 3 H), 7.25–7.68 (complex, 14 H).[54]

The reaction of benzyl phenyl sulfide gave benzyldiphenylphosphine oxide (recrystallized from a mixture of ethanol and water, mp 192–194 °C,[55] among other products: IR (KBr) 695, 723, 754, 1120, 1182, 1437, 2944, 3061 cm^{-1}; ^{1}H NMR δ 3.60 (d, 2 H, J = 8 Hz), 7.03–7.69 (complex, 15 H).

The reaction of ethyl phenyl sulfide with diphenylphosphide gave ethyldiphenylphosphine oxide (recrystallized from a mixture of ethyl acetate and petroleum ether, mp 120–121 °C),[53] among other products: IR (KBr) 699, 721, 742, 764, 1123, 1180, 1439, 2937, 3057 cm^{-1}; ^{1}H NMR δ 1.20 (td, 3 H, $J_{\mathrm{CH_2-CH_3}}$ = 8 Hz, J_{PCCP} = 17 Hz), 2.28 (qd, 2 H, $J_{\mathrm{CH_2-CH_3}}$ = 8 Hz, J_{PCP} = 12 Hz), 7.41–7.77 (complex, 10 H).

Photostimulated Reaction of Diphenyl Sulfide with Pinacolone Enolate in Ammonia. Reactions in ammonia were typically carried out in a three-necked flask equipped with a magnetic stirrer, an addition funnel, a dry ice condenser whose vent serves as a nitrogen inlet, and an inlet for ammonia.

The dry ice condenser was filled with acetone and dry ice. Ammonia was condensed into the flask until it was half-full. Potassium *tert*-butoxide (3 g, 27 mmol) was carefully weighed out under argon and dissolved in ammonia. Pinacolone enolate (3.2 mL, 24 mmol) was added slowly through the addition funnel, followed by diphenyl sulfide (1.10 g, 5.8 mmol). Illumination was started. The light source was turned off every half-hour to remove the ice that had condensed on the walls of the flask and to replenish the dry ice–acetone bath. After a total illumination time of 2.5 h, the light was turned off and the reaction was quenched with ammonium chloride. The reaction flask was allowed to stand overnight to remove all ammonia. Water (75 mL) was added to the mixture, which was subsequently acidified with dilute hydrochloric acid and extracted with ether (3 × 50 mL). The combined ether extracts were washed with water (2 × 25 mL), dried with anhydrous magnesium sulfate, filtered, and concentrated with the rotary evaporator. The concentrated solution was then analyzed by gas chromatography and other appropriate methods.

In another experiment, the reaction of diphenyl sulfide (1.10 g, 5.8 mmol) with pinacolone enolate (3.2 mL, 24 mmol) for 2.5 h under photoexcitation gave 3,3-dimethyl-1-phenyl-2-butanone, among other products. The reaction mixture was passed through a column filled with basic alumina, Brockmann 1, as adsorbent and eluted successively with hexane, chloroform, and ether. 3,3-Dimethyl-1-phenyl-2-butanone (0.54 g, 53% yield) was eluted with ether: IR (neat) 696, 725, 1478, 1497, 1712, 2934, 2969 cm^{-1}; ^{1}H NMR δ 1.23 (s, 9 H), 3.81 (s, 2 H), 7.17–7.34 (complex, 5 H);[56] ^{13}C NMR δ 26.5, 43.1, 44.5, 126.4, 128.2, 129.4, 134.8, 212.6.

Competition Experiment between Diphenyl Sulfide and Di-4-tolyl Sulfide. Potassium *tert*-butoxide (1.26 g, 11 mmol) was weighed out under argon and dissolved in dimethylformamide (35 mL). Diethyl phosphite (1 mL, 8 mmol) was added to the flask, followed by diphenyl sulfide (0.3909 g, 2 mmol) and di-4-tolyl sulfide (0.4461 g, 2 mmol). Illumination was started. Meanwhile, aliquots (5 mL) were withdrawn (at 0, 15, 30, and 50 min) and delivered into flasks containing water (10 mL) and preweighed quantities of dioctyl sulfide and benzyl phenyl sulfide as standards. Each of the aliquots was acidified with dilute hydrochloric acid and extracted with ether (3 × 10 mL). The combined ether extracts were washed with water (2 × 5 mL), dried with anhydrous magnesium sulfate, and concentrated by a rotary evaporator. The aliquot solutions were analyzed by gas chromatography, from which the concentrations of the reactants were determined. The relative reactivity of diphenyl sulfide to di-4-tolyl sulfide was estimated to be 14.[57]

Competition Experiment between Di-4-tolyl Sulfide and Di-4-anisyl Sulfide. The procedure in the preceding paragraph was repeated with the use of potassium *tert*-butoxide (2.54 g, 23 mmol), diethyl phosphite (2.2 mL, 17 mmol), di-4-tolyl sulfide (0.4254 g, 1.9 mmol), and di-4-anisyl sulfide (0.5105 g, 2 mmol). A 45-mL portion of dimethylformamide was added. Aliquots (10 mL) were withdrawn at 0, 20, and 35 min. The relative reactivity of di-4-tolyl sulfide to di-4-anisyl sulfide was estimated to be 7.[57]

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