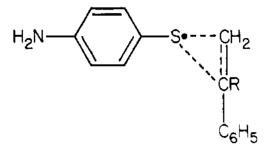
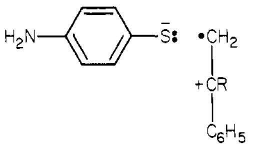
lower the energy of the electronic transition.

Reaction Mechanism. While there are no strong a priori reasons for correlating addition reactions of thiyl free radicals with σ^+ constants, nevertheless, negative ρ^+ values have been reported for thiyl-type addition reactions to substituted α-methylstyrenes,[17] and Ito and Matsuda have recently reported positive ρ^+ values of 1.37 for the addition reactions of para-substituted benzenethiyl radicals to styrene[4] and 1.72 for the addition reactions to α-methylstyrene.[18] Both sets of results indicate a somewhat polar nature of the transition state, with a small negative charge on sulfur, the transition state being represented by Ito and Matsuda[18] (for α-methylstyrene) as $[RS\cdots CH_2{=}C(CH_3)C_6H_5 \leftrightarrow RS^-,CH_2{=}C(CH_3)C_6H_5\cdot^+]$. Accordingly, for the addition of p-aminobenzenethiyl radical to styrene or α-methylstyrene, the important resonance structures would be **2a** and **2b** (R = H, CH_3). The higher ρ^+ value for the additions to α-methylstyrene would reasonably be due to stabilization of the positive charge in canonical structure **2b** by the α-methyl substituent.



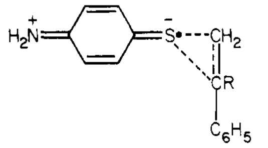
2a



2b

On this basis, hydrogen bonding by the amine protons of **1**, which displaces electron density in the direction of sulfur, thereby stabilizes reactant canonical structure **1b** and destabilizes transition-state canonical structure **2b**. The net result is a negative coefficients of β in eq 2 (i.e., rate retardation due to hydrogen bonding). The negative coefficient of π^* (i.e., reduced rates in more polar solvents) indicates that there is charge delocalization in the transition state compared with the reactants, which suggests in turn that **1b** is a more important contributor to the reactant ground state than **2b** to the transition state.

In the reverse reaction, going from p-$H_2NC_6H_4SCH_2\dot{C}HC_6H_5$ transition-state **2a,b** leads to slight charge localization, so that the positive but small coefficient of π^* in eq 4 is as expected. The positive (though small) coefficient of β is less readily rationalized and, from its magnitude, may be a second-order effect. Alternatively, resonance structure **2c** may be a minor contributor to the reaction transition state in solvents of high dipolarity and high HBA basicity.



2c

Registry No. p-Aminobenzenethiyl radical, 31053-95-9; styrene, 100-42-5; α-ethylstyrene, 2039-93-2; oxygen, 7782-44-7; p-$H_2NC_6H_4SCH_2\dot{C}HPh$, 84680-86-4.

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[17] (a) Walling, C.; Seymour, D.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1948**, *70*, 2558. (b) Cadogan, J. I. G.; Sadler, I. H. *J. Chem. Soc. B.* **1966**, 1191. (c) Church, D. F.; Gleicher, G. J. *J. Org. Chem.* **1975**, *40*, 536.

[18] Ito, O.; Matsuda, M. *J. Org. Chem.* **1982**, *47*, 2261.

A New Pathway for Cleavage of Some Phenacyl and Styryl Thioethers

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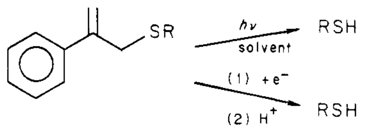
Ultraviolet photolysis or preparative electroreduction of 1-(benzylthio)-2-phenyl-2-propene results in both C–S and C–C bond cleavages. The analogous methyl thioether is nearly inert photochemically and does not give monomeric products upon electroreduction. The phenyl thioether gives exclusively C–S fragmentation. A mechanism involving photoinduced electron transfer followed by cleavage of the zwitterionic diradical is proposed for the novel C–C cleavage. Electrochemical peak potentials for the series of phenacyl and styryl thioethers are reported.

Introduction

The temporary blocking of a thiol in a multifunctional molecule is often necessary if sulfur-containing reagents are to be usefully exploited in organic synthesis. Although a number of routes for the protection of thiols are known, almost all involve deprotection either by strong Brønsted or Lewis acids or bases or by reductive electrolysis at highly negative applied potentials.[1-4] In our effort to find mild, selective deprotection routes for thioethers (by incorporating either a photosensitive or a more readily reducible functional group into the protected thiol), we have examined the photochemistry and electrochemistry of a series of substituted styrene derivatives. We hoped that the more easily reducible arene functionality might provide a more responsive chromophore and/or electrophore for easy deprotection of thiols (Scheme I).

Scheme I. Possible Routes for Mild Deprotection of Thiols



Although our quest for an effective deprotection sequence has not been realized, we have discovered a novel pathway for carbon–carbon reductive cleavage, which can be activated upon either photoexcitation or electroreduction. We report here results describing the photochemistry

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[1] Greene, T. W. "Protecting Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981; Chapter 6.

[2] Wolman, Y. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1974; p 669.

[3] Hiskey, R. G.; Rao, V. R.; Rhodes, W. G. In "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum Press: New York, 1973.

[4] McOmie, J. F. W. *Adv. Org. Chem.* **1963**, *3*, 251.

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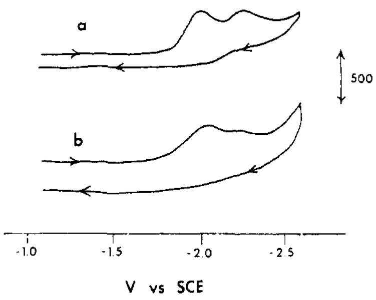
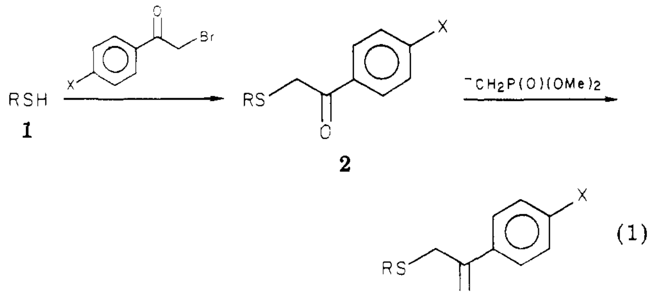


Figure 1. Cyclic voltammograms for **2c** (a) and **3c** (b). As 10^{-2} M solutions in dry, degassed acetonitrile containing 0.1 M tetrabutylammonium perchlorate, at Pt, room temperature, scan rate 0.1 V/s.

and the electroreduction of a series of phenacyl and styryl thioethers and suggest a mechanism for the unusual reaction course.

Results

Thiols (**1**) or thiolate anions could be protected as phenacyl thioethers (**2**) by treatment with α-bromoacetophenones. These in turn were converted to the corresponding styrenes **3** by methylenation with the anion of dimethyl methylphosphonate (eq 1).[5]



1

2

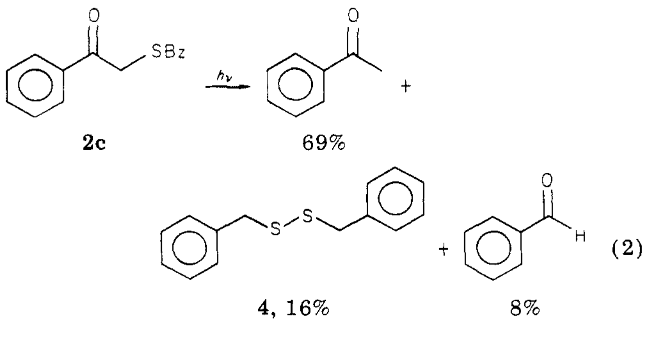
3

(1)

a, R = CH_3; X = H d, R = Bz; X = Cl
b, R = Ph; X = H e, R = Bz; X = NO_2
c, R = Bz; X = H f, R = Bz; X = OMe

The ultraviolet absorption spectra of **2** and **3** corresponded reasonably to those expected for substituted acetophenones or α-methylstyrenes. Compounds **2** exhibited weak n,π* (338 ± 5 nm) and strong π,π* (260 ± 20 nm) bands, while compounds **3** showed only π,π* bands at 240–300 nm. Irradiation of **2** and **3** as dilute methanolic solutions at 254 nm showed the compounds to be photoactive: specific absorption data and quantum yields for disappearance of starting material are listed in Table I.

The ketones **2** gave cleavage products analogous to those reported for **2a** by Caserio and co-workers.[6] Thus, **2c** gave rise to the products shown in eq 2.



2c 69%

4, 16% 8%

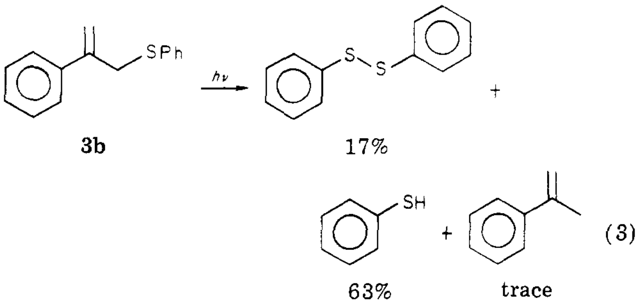
(2)

Table I. Absorption Maxima[a] and Quantum Efficiencies of Photochemical Disappearance of **2**, **3**, and **6**

compd	λ_{max}, nm/ε, 10^{-2} M^{-1} cm^{-1}	Φ_d
2c	243/118, 335/4.6	0.31
2d	252/167, 340/7.7	0.39
2e	261/135, 342/5.8	0.36
2f	274/144, 338/6.0	0.24
3a	239/71	<0.005
3b	243/94	0.17
3c	240/103	0.84
3d	245/104	0.47
3e	298/39	0.17
3f	260/81	0.68
6a	271/110	0.003
6b	247/194, 374/4.2	0.013

[a] Spectra determined in spectral grade methanol.

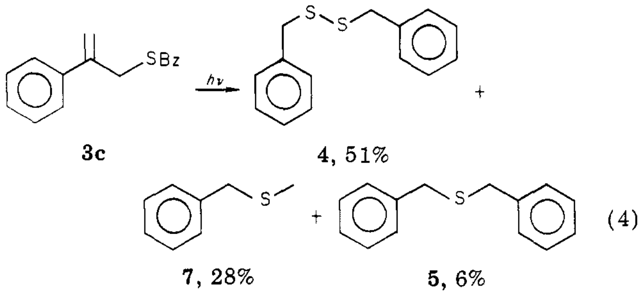
In contrast, **3a** proved to be nearly completely photostable, while **3b** gave respectable yields of thiyl radical derived products but only traces of styrene-derived products (eq 3). High yields of thiyl radical derived products were also obtained upon photolysis of **3c** (eq 4), along with traces of styrene and α-methylstyrene. Similar products were also obtained from **3d–f** (see Experimental Section).



3b 17%

63% trace

(3)



3c 4, 51%

7, 28% 5, 6%

(4)

Cyclic voltammograms for **2** and **3** exhibited irreversible oxidation waves in the region +1.4 to 2.2 V vs. SCE and irreversible reduction waves at −1.7 to −2.2 V. Typical cyclic voltammograms, for **2c** and **3c**, are shown in Figure 1. After the first scan, waves attributable to reaction products could be seen in the cyclic voltammogram. Specific redox data for families **2** and **3** are listed in Table II.

Preparative reductive electrolysis of compounds **2** and **3** gave products highly dependent on the identity of R. With **2a**, nearly no sulfur-containing products could be isolated and extensive polymerization had occurred. With **2b–f**, however, reasonable mass balance was achieved, acetophenone and radical-derived products being isolable in useful yields. The product distributions obtained for **2b** and **2c** are shown respectively in eq 5 and 6. Comparable product distributions were obtained for **2d–f**, details for which are listed in the Experimental Section.

Similarly, the electroreduction of **3a** gave poor yields of sulfur-containing products, in contrast to those obtained from **3b–f**. Poorer yields of α-methylstyrene (compared

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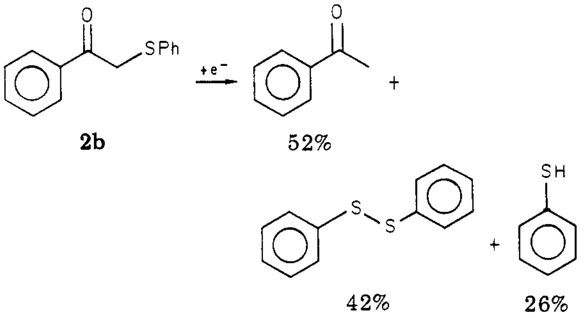
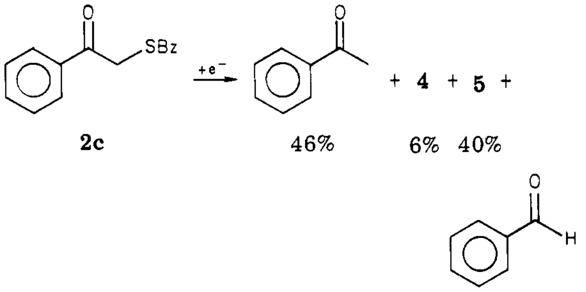
(5) Fox, M. A.; Triebel, C. A.; Rogers, R. *Synth. Commun.* **1982**, *12*, 1055.

(6) Caserio, M. J.; Lauer, W.; Novinson, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 6082.

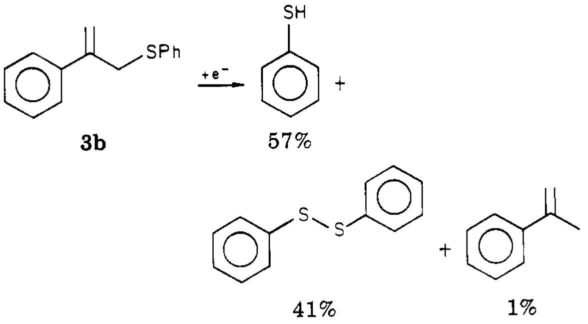


(5)

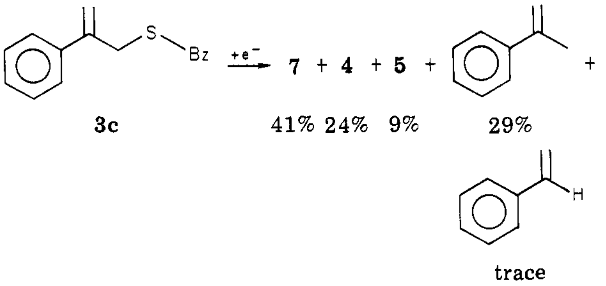


(6)

with that of acetophenone obtained from **2b–f**) are observed, however. Equations 7 and 8 show the products



(7)



(8)

obtained in the reductive electrolysis of **3b** and **3c**, respectively. Product distributions obtained for other members of the series are to be found in the Experimental Section.

Preparative electrooxidation of **2** and **3** did not give preparatively useful yields of products in the absence of oxygen. In the presence of oxygen, complex mixtures of compounds containing SO bonds were formed. No further elaboration of the oxidative processes was undertaken since only poor yields of cleavage products could be obtained.

Discussion

Photochemistry of 2. Photoexcitation of compounds **2c–f** led to efficient cleavage of the β-carbon–sulfur bond in the primary photoprocess. This mode of cleavage, which has analogy in previous studies of the photoreactions of β-keto sulfides,[6,7] probably occurs via Norrish type II hydrogen atom abstraction by the π,π^* triplet through a six-membered transition state.[8]

Table II. Electrochemical Peak Potentials[a] from Cyclic Voltammograms of 2, 3, and 6

compd	reduction waves, V vs. SCE	oxidation waves, V vs. SCE
2a	−2.0, −2.2	+1.8
2b	−2.0, −2.3	+1.7
2c	−2.0, −2.3	+2.2
2d	−1.9, −2.2	+1.8
2e	−1.0,[b] −1.7	+2.1
2f	−2.2, −2.4	+2.0
3a	−1.7	+2.4
3b	−2.0	+1.7
3c	−2.0	+2.2
3d	−2.0	+1.9
3e	−1.0,[b] −1.9	+1.7
3f	−1.9	+1.5
6a	−1.1[b]	+1.9
6b	−1.2[b]	+1.9

[a] Measures as 10^{-2} M solution in anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate at 0 °C and at ambient temperature; scan rates 0.1-1 V/s. [b] Quasi-reversible.

Photochemistry of 3. Derivatives **3** are bichromophoric, possessing transitions associated with locally excited styryl or thioether excited states. If the former (π,π^*) excited state is reactive, chemistry markedly different from that observed with **2** is probable, for π,π^* excited states are thought to be more polar and to exhibit markedly reduced biradical character.[8] There exists a report, nonetheless, that a styrene derivative can act as a hydrocarbon analogue to the type II photoelimination.[9]

With compounds **3**, we find, in contrast to ketones **2**, that the photoreactivity probably does not involve intramolecular hydrogen abstraction. Thus, while **2a** is reported[6] to efficiently cleave upon photoexcitation, **3a** is found to be nearly photoinert. The reactivity of **3b–f** should therefore be explained by an alternate, possibly polar, mechanism.

The products observed upon excitation of **3b** can be readily understood if the thiophenyl chromophore is excited directly upon irradiation or if it is generated by intramolecular energy transfer. It is known, for example, that dialkyl thioethers cleave, upon photolysis, to give thioalkyl radicals.[10–13] Such radicals are known precursors for both sulfur-containing products shown in eq 3. That irradiation of **3b** at 254 nm can indeed lead to excitation of the isolated phenylalkyl thioether, at least competitively with that of the isolated styryl chromophore, is consistent with the absorption spectra, λ_{max} for **3b** (243 nm) being close to that both for styrene (245 nm) and for thioanisole (253 nm). The low yield of α-methylstyrene from the photolysis mixture can reasonably be attributed to the well-known tendency for radical-initiated polymerization of the latter compound.

An analogous route can be postulated in the isolation of benzylthiyl radical derived products in the photolysis of **3c–f**. Thus, formation of major amounts of dibenzyl disulfide (**4**) may result from analogous radical–radical coupling. Some of the formation of dibenzyl sulfide (**5**) may also be derived from a radical process, since a control

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[7] Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1444.

[8] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

[9] Hornbeck, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6773.

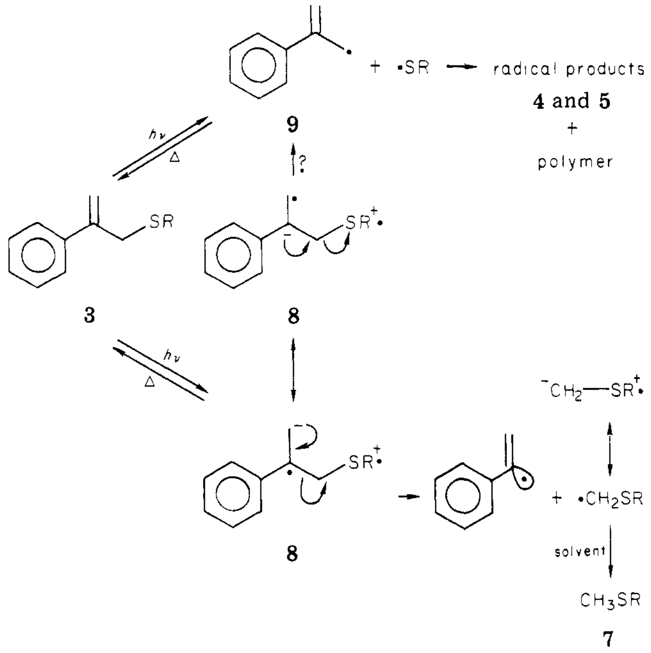
[10] Laarhoven, W. H.; Cuppen, T. J. H. M. *Tetrahedron Lett.* **1966**, 5003.

[11] Laarhoven, W. H.; Cuppen, T. J. H. M.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 821.

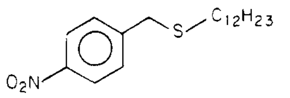
[12] Carruthers, W. *Nature (London)* **1966**, *209*, 908.

[13] Block, E. *Q. Rev. Sulfur Chem.* **1969**, *4*, 230.

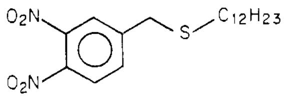
Scheme II. Possible Routes for C-S and C-C Cleavage in the Photolysis of 3



reaction established that benzyl mercaptan in the presence of starting material does indeed give rise to this product. Furthermore, excitation of aryl alkyl thioethers, e.g., **6a** and **6b**, gives traces of disulfide along with disproportionation products derived from the C_{12} chain.



6a



6b

In **3c–f**, however, the radical products are accompanied by an additional significant product, **7**, in which the bond adjacent to the styrene has been cleaved. That the methyl group of **7** is derived from the carbon originally located adjacent to the styryl group was established by the failure of **4** or **5** to produce **7** under mimicked reaction conditions. While α cleavage adjacent to an excited carbonyl chromophore is well precedented (Norrish type I reaction),[14] its occurrence adjacent to a vinyl group is much more unusual.

More probable than this direct α cleavage is the possibility of photoinduced electron transfer, with the thioether acting as a donor and the styryl group acting as an electron acceptor, leading to chemistry summarized in Scheme II. Thioethers function effectively as excited electron donors,[15] and arenes have been thoroughly characterized as excited-state electron donors or acceptors, depending on the electron demand of the reaction partner.[16] Photoexcitation of a bifunctional molecule like **3** might therefore be expected to produce zwitterionic diradical **8**. Such a species can be considered an intramolecular exciplex if the positive and negative centers remain in close proximity. If so, back electron transfer would surely be facile. If, however, the two charged centers become physically separated by a bond rotation, chemistry characteristic of the individual ion radicals might be observed.

A common chemical fate of radical ions is the cleavage of a β σ-bond to relieve the extant charge. Cleavage of the C–C or the C–S bonds separating the ion radical centers in **8** would simultaneously relieve charge at each center, producing a pair of neutral radicals. Hydrogen abstraction and/or radical coupling from solvent would then lead to the observed products.

Scheme II requires a strong interaction between the thioether and styryl groups in the excited state. Although no exciplex-like emission could be detected from dilute solutions of **3a** or **3c**, the characteristic emission of α-methylstyrene was nearly completely absent, as might be expected if intramolecular fluorescence quenching between the two chromophores were important.

The importance of charge separation in the excited state of **3c** could, in principle, be probed by studying the effect of substituents on the efficiency of the photochemical cleavage. Unfortunately, the reduction peak potentials of **3c–f** were nearly identical (see Table II), so it is hardly surprising, even if there is substantial charge separation in the photoexcited state, that the quantum yields for cleavage of **3c–f** were identical within a factor of 2 (0.5 ± 0.3; see Table I).

If Scheme II were operative, the variation in photorectivity of **3a–c** could be explained as a combination of steric effects on the conformation of the zwitterionic biradical **8** and of electronic stabilization of the radical ion centers in **8** by the substituent on sulfur.

Electrochemistry of 2 and 3. While electrochemical redox reactions can model simultaneously only one of the charge centers of **8**, they can establish whether ion radical generation can effect the projected C–C cleavage. If so, parallel reactivity might be observed upon photolysis and upon preparative electrolysis.

Inspection of eq 2–8 makes immediately obvious the striking similarity between the products obtained upon photolysis and upon electroreduction of **2** and **3**. Since the observed reduction peak potentials of **2** and **3** (Table II) resemble the reported reduction potentials of acetophenone (−1.87 vs. SCE)[17] or styrene (−1.96 V vs. SCE[18]) more closely than those of aryl alkyl or dialkyl thioethers (ca. −2.5 V vs. SCE[19]), the initial electroreduction probably populates the phenacyl or styryl electrophore. This radical anion thus mimics, at least partially, the electron distribution in the styryl portion of **8**. The irreversibility of the cyclic voltammetric waves, indicating instability of the reduced species, is consistent with rapid chemical reaction following electroreduction and with the formation of high yields of cleavage products.

The isolation of substantial quantities of acetophenone from the electroreduction of both **2b** and **2c** is indicative of directed C–S cleavage from the radical anion. Rupture of the C–S bond could generate the acetophenone enolate and a thiyl radical through a β cleavage analogous to that encountered in the familiar Norrish type II reaction.

As with **2**, the electroreduction of **3** gives rise to product distributions highly reminiscent of those obtained upon photolysis. Analogous reductive cleavage routes can be envisioned to occur in similar fashion.

Substituted Phenacyl of α-Methylstyryl as Protecting Groups. The complexity of the mixtures obtained by either photolysis or electroreduction of **2** and **3** obviates the phenacyl or α-methylstyryl functionalities as efficient protecting groups. Furthermore, the very modest shifts

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(14) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92.

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(16) Mataga, N.; Kubota, T. "Molecular Interactions and Electronic Spectra"; Marcel Dekker: New York, 1970.

(17) Andrieux, C. P.; Saveant, J. M. *Bull. Chim. Soc. Fr.* **1972**, 3281.

(18) Wawzonek, S.; Berkey, R.; Blaha, E. W.; Runner, M. E. *J. Electrochem. Soc.* **1955**, *102*, 235.

(19) Gerdil, R. *J. Chem. Soc. B* **1966**, 1071.

in redox potentials (Table II) and in absorption spectra (Table I) for para substitution of the ring makes selective activation of a particular derivative difficult. This method does not offer a clear advantage, then, over conventional techniques for deprotection of thioethers, despite the less negative potentials required for the electroreduction and the high photosensitivity of **2** and **3**.

The discovery of the unusual C–C reductive cleavage in **3c–f**, initiated either by photochemical electron transfer or by application of about a −2-V potential, represents a new reaction pathway for styrene radical anions. Whether such radical anion fragmentations will provide a general route for synthetically interesting transformations is a question of continuing interest to our group.

Experimental Section

The syntheses of **2** and **3** have been described elsewhere.[5] Ultraviolet and visible spectra were obtained as dilute solutions in reagent grade methanol by using a Varian DMS 90 spectrophotometer in 1-cm quartz cells. Fluorescence spectra were measured in the same cells with a Spex spectrofluorometer. Proton spectra were obtained as carbon tetrachloride solutions on a Varian 390 spectrometer.

Photochemistry. Compounds **2** and **3** (0.1 M in spectral grade methanol) were irradiated in deaerated quartz test tubes. The irradiation was carried out in a Rayonet photochemical reactor using low-pressure mercury arcs (254 nm). The ketones **2** were irradiated for 10 min before GC–MS analysis. Styrenes **3** were irradiated for 3 min, and thioethers **6** were irradiated for 20 min. The progress of the reaction was monitored by repetitive UV scans every 10 s for **2** and **3**. Quantum yields for the disappearance of starting material were obtained by irradiating the samples of interest in a double-baffle merry-go-round apparatus with solutions of potassium ferrioxalate after the method of Hatchard and Parker.[20]

Product analyses were conducted with a gas chromatograph–mass spectrometer (GC–MS, Finnigan 4023 automated GC–MS) equipped with a 50-m SE-30-coated fused silica capillary column. Peak characterizations were made by comparison with known fragmentation patterns from the library of an INCOS data system and by co-injection with known compounds. Yields were calculated by comparison with an internal standard added after the completion of the reaction but before workup and concentration (acetophenone for the photolysis and electrolysis of **3**). Yields are based on moles of reacted thioether.

Photolysis of 2c. Photolysis of **2c** using the above photolysis procedure gave rise to the products listed in eq 2.

Photolysis of 3. Photolysis of **3b** and **3c** using the general photolysis procedure gave the products listed in eq 3 and 4. Prolonged photolysis of **3a** gave only recovered starting material. Analogous photolyses of **3d–f** gave the following products, respectively.

3d: 54% methyl benzyl sulfide (**7**); 37% dibenzyl sulfide (**5**); 6% dibenzyl disulfide (**4**); traces of substituted styrene and α-methylstyrene.

3e: 59% **7**; 35% **5**; traces of substituted styrene and α-methylstyrene.

3f: 75% **7**; 23% **5**; traces of substituted styrene and α-methylstyrene.

Photolysis of 6. Photolysis of **6a** and **6b** by the general procedure gave mixtures of $C_{12}H_{24}$ and $C_{12}H_{22}$ isomers. No quantitative characterization of this photoreaction was attempted. Traces of substituted disulfide were also formed.

Electrochemistry. Acetonitrile was freshly distilled from calcium hydride and degassed using a three-cycle, freeze–pump–thaw sequence before each experiment. Tetrabutylammonium perchlorate (TBAP) was obtained from Southwestern Analytical Chemicals, Inc. TBAP was recrystallized by the dropwise addition of ether to a solution of the crude solid in a minimal amount of methanol until white crystals precipitated from the solution. The crystals were vacuum filtered and dried under vacuum for 24 h. The electrolyte was dried for 4 h under high vacuum before each experiment.

The electrochemistry was performed with a Princeton Applied Research Model 173 potentiostat equipped with a universal programmer (PAR Model 175). The current–voltage curves were recorded on a Houston Instruments x–y recorder. The electrochemical cell was a standard three-electrode cell with an adaptor attached to the side for adding liquids or solids.

For cyclic voltammetry, the cell was equipped with a platinum disk working electrode (0.05 cm^2), a platinum coil counterelectrode, and a silver wire reference electrode. For preparative electrolysis, the cell was equipped with a platinum mesh working electrode, a platinum coil counterelectrode, and a silver wire reference electrode. All platinum electrodes were cleaned by soaking in hot nitric acid and then rinsing with distilled water. The silver and platinum disk electrodes were polished with polishing powder (0.3 μm) before each experiment.

Cyclic Voltammetry. The degassed solvent, acetonitrile (7 mL), was added via syringe to the cell containing TBAP (0.24 g, 0.1 M). The solvent window (between +2.4 and −2.5 V) was scanned to ensure the absence of air, water, or other impurities. The compound (0.05 M) was added to the cell, and electrochemical measurements were carried out at various scan rates (0.1, 0.2, 0.5, 1.0 V/s) and temperatures (0 °C and ambient). After each experiment ferrocene (5 mM), whose redox behavior is known,[21] was added as an internal reference.

Preparative Electrolysis. Degassed solvent, acetonitrile (7 mL), was added via syringe to the cell containing TBAP (0.24 g, 0.1 M). To remove any impurities that may be present, the solvent was preelectrolyzed at the desired reduction potential until no current was detected. The compound (0.07 mmol, 0.1 M) was added, and the reduction was initiated at a controlled potential held 0.1 V negative of the peak potential observed by cyclic voltammetry. The electrolysis was terminated when one electron/molecule (0.068 mF) had passed through the solution. The electrolyzed solution was analyzed by GC–MS following replacement of the solvent by methanol.

Electroreduction of 2, 3, and 6. Upon following the general procedure for preparative electrolysis, the following product distributions were obtained.

2a. Extensive polymerization of **2a** was obtained, and no quantitative analysis of the reaction mixture was attempted. Trace quantities of acetophenone were also formed.

2b and 2c. Product distributions are listed in eq 5 and 6, respectively.

2d: 34% **5**; 1% **7**; 5% substituted styrene; 6% substituted acetophenone.

2e: 56% **5**; 3% **7**; 3% substituted styrene; 57% substituted acetophenone.

2f: 24% **4**; 9% **5**; 61% substituted acetophenone.

3a: No sulfur-containing products; traces of α-methylstyrene.

3b and 3c: Product distributions listed in eq 7 and 8, respectively.

3d: 18% **5**; 49% **7**; 4% substituted styrene; 14% substituted α-methylstyrene.

3e: 29% **5**; 51% **7**; 12% substituted styrene; trace of substituted α-methylstyrene.

3f: 8% **5**; 38% **7**; trace quantities of substituted styrene and α-methylstyrene.

6a and 6b: Mixtures of $C_{12}H_{22}$ an $C_{12}H_{24}$ isomers were obtained. No sulfur-containing products could be detected.

Generation of 5 from 2c. At room temperature, benzyl mercaptan (13 mg, 0.1 mmol) was added to a solution containing potassium *tert*-butoxide (14 mg, 0.1 mmol) in 5 mL of THF. The resulting solution was transferred via syringe to a solution of **2c** (20 mg, 0.1 mmol) in 5 mL of THF. The mixture was stirred for 4 h, washed with three 20-mL portions of brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, to yield approximately 10 mg of dibenzyl sulfide (60% yield) along with recovered **2c**.

Attempted Generation of 7 from 4 or 5. 1. At room temperature, *n*-BuLi (2.4 mmol, 1.5 M hexane) was added to a solution of **5** (0.5 g, 2 mmol) in 5 mL of THF. After 4 h of stirring, the

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solution was washed with three 20-mL portions of brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was found to contain only dibenzyl sulfide (by ^1H NMR analysis).

2. Sodium (0.05 g, 2 mmol) was added to a solution of **5** (0.5 g, 2 mmol) in 5 mL of toluene. The mixture was heated at reflux for 8 h and was then allowed to cool to room temperature. The solution was washed with three 20-mL portions of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, giving a complex mixture from which **7** was specifically absent (GC–MS analysis).

Parallel reactions with **4** also failed to produce **7**. (The yield of **7** was less than 1% by GC–MS analysis.)

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Registry No. **2a**, 5398-93-6; **2b**, 16222-10-9; **2c**, 2408-88-0; **2d**, 52264-85-4; **2e**, 84538-92-1; **2f**, 21875-74-1; **3a**, 79992-70-4; **3b**, 84538-93-2; **3c**, 84538-94-3; **3d**, 84538-95-4; **3e**, 84538-96-5; **3f**, 84538-97-6; **6a**, 84538-99-8; **6b**, 84539-01-5.

Activated Metallic Nickel as a Reagent for the Dehalogenative Coupling of Halobenzenes

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Activated metallic nickel powder, prepared by the reduction of nickel halides with lithium and with naphthalene as an electron carrier, is a simple and a convenient reagent for the dehalogenative coupling of iodobenzenes and bromobenzenes under mild conditions. The intermediates, ArNiX and Ar_2Ni species (Ar = C_6F_5), were isolated as the phosphine complexes.

Recently, considerable interest has centered on the use of zerovalent transition metals and their complexes as selective and mild reagents in organic synthesis.[1] However, some of the useful complexes coordinated with ligands such as phosphine or carbon monoxide are unstable and not easy to prepare or are toxic. Other studies using the metal atom vaporization technique have also been successful in employing transition metals in synthesis.[2] In many cases, however, this approach does not lend itself to being completely general.

There are few reports of oxidative addition of metallic transition metals under mild conditions;[3] two reports involving group 8 elements have appeared. Fischer and Bürger reported the preparation of π-allylpalladium complex by the reaction of palladium sponge with allyl bromide.[4] The Grignard-type addition of allyl halides to aldehydes has been carried out by reacting allylic halides with cobalt or nickel metal prepared by reduction of cobalt or nickel halides with manganese/iron alloy–thiourea.[5]

In a series of our studies on the chemistry of activated metals, we have shown that the transition-metal powders prepared by the reduction of metal halides with alkali metal in an ethereal or a hydrocarbon solvent have high reactivities in their metallic state toward organic and inorganic substrates.[6] In a previous paper, we reported preliminary results showing that activated nickel powder can induce the dehalogenative coupling of iodo- or bromobenzene.[7] We report here the application of activated metalic nickel as a reagent for the homo coupling of a variety of halobenzenes. In addition, the mechanistic considerations will be discussed on the basis of the isolation of intermediates, ArNiX and Ar_2Ni species (Ar = C_6F_5), as their phosphine complexes.

Results and Discussion

Activated nickel powder employed for the reactions was simply prepared by stirring a 1:2.3 mixture of nickel halide and lithium metal (eq 1) under argon with a catalytic

$$\mathrm{NiX_2} \xrightarrow[\text{glyme}]{\text{Li (2.3 equiv)/C}_{10}\text{H}_8\text{ (0.1 equiv)}} [\mathrm{Ni}] \tag{1}$$

$$\mathrm{ArX'} \xrightarrow[\text{glyme (Me}_2\text{SO or DMF)}]{[\mathrm{Ni}]} {}^1/_2\mathrm{ArAr} \tag{2}$$

amount of naphthalene (10 mol % based on nickel halide) at room temperature for 12 h in 1,2-dimethoxyethane (glyme). The resulting black slurry, which slowly settled after the stirring was stopped, was washed with freshly distilled glyme to remove the naphthalene and was used for the reaction with halobenzenes. As the presence of the naphthalene did not disturb the following reaction, the removal procedure is optional. The dehalogenative coupling reactions were carried out at 80 °C by using a 0.7–0.8:1 mixture of halobenzene and the nickel powder (eq 2). The course of the reaction was followed, and the yields were determined by GLC.

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