spheres which have to be disrupted in the process of complex formation.

(E) Kinetic Identification of Reactive Species. (See paragraph at the end of paper about supplementary material.) In perchloric acid, k_{obsd} for the formation of the complex decreases from 10.2 to 0.405 s^{-1} as $[H^+]$ increases from 0.10 to 2.0 M. Inspection of data regarding the distribution of the major species of Ce(IV) in $HClO_4$ media reveals that whereas Ce^{4+} and $CeOH^{3+}$ concentrations increase with increasing $[H^+]$, $Ce(OH)_2^{2+}$ concentrations decrease. If these were the only changes in the system reflecting changes of acidity, one might have been tempted to draw a parallelism between the decreases in k_{obsd} and $Ce(OH)_2^{2+}$ and to propose that $Ce(OH)_2^{2+}$ is the kinetically significant species in Ce(IV)-BIDA reaction. However, BIDA also undergoes drastic changes with changes in $[H^+]$ (eq 12-14, where H_2L represents BIDA as a neutral

$$H_3L^+ \overset{K_1}{\rightleftharpoons} H_2L + H^+ \qquad (12)$$

$$H_2L \overset{K_2}{\rightleftharpoons} HL^- + H^+ \qquad (13)$$

$$HL^- \overset{K_3}{\rightleftharpoons} L^{2-} + H^+ \qquad (14)$$

species). With $pK_1 = 1.49$,[32] significant fractions of BIDA exist as a H_3L^+ species which is not readily amenable to complexation. For example, at 1.0 M $[H^+]$, over 96% of BIDA exists as H_3L^+. This will cause substantial reduction in the concentration of H_2L, HL^-, and L^{2-}, the species which are most readily complexed. It is conceivable, therefore, that a complexation between BIDA and Ce(IV) might involve $Ce(OH)^{3+}$ and even Ce^{4+} with H_2L, HL^-, and L^{2-}. Such complexes are expected to suffer drastic reduction in concentration with increasing acidity.

In acidic sulfate media, which consisted of $HClO_4$, Na_2SO_4, and $NaClO_4$ (to allow for the independent variation of $[H^+]$ and $[SO_4^{2-}]$),[16] k_{obsd} decreased by a factor of about 2100 as the sodium sulfate concentration increased from 0.002 00 to 0.600 M. Data on the distribution of Ce(IV) species in these media show a decrease by a factor of about 2700 in the concentration of $CeSO_4^{2+}$ as opposed to an increase in concentration for each of the other sulfato species of Ce(IV). This strongly suggests that in these media, $CeSO_4^{2+}$ is kinetically the most significant species.

(F) Temperature Effects. These were investigated for the BIDA-Ce(IV) reaction only in perchloric acid media. For the formation of the complex, $\Delta H^\ddagger$ is 14.2 kcal/mol, and $\Delta S^\ddagger$ is -9.3 eu. For complex decomposition $\Delta H^\ddagger$ is 15.6 kcal/mol, and $\Delta S^\ddagger$ is -17.3 eu. While a large negative $\Delta S^\ddagger$ is expected for the formation of the complex, the observed $\Delta S^\ddagger$ is small. On the other hand, one might expect to see a positive $\Delta S^\ddagger$ for the decomposition of the complex; instead, a $\Delta S^\ddagger$ which is even more negative than that for complex formation was observed. This could be indicative of a free radical process.[38] The interactions of all the product molecules with solvent could also be a contributing factor.

Registry No. 1, 3987-53-9; cerium(IV) perchlorate, 14338-93-3; cerium(IV) sulfate, 13590-82-4.

Supplementary Material Available: Detailed results of product identification, tables on time-dependent stoichiometry, quantitative determination of decarboxylation of BIDA, and distribution of species at various acidities and at various sulfate concentrations, an alternative method for analyzing the rate data, and four graphs pertaining to rate data (10 pages). Ordering information is given on any current masthead page.

---

(38) U. D. Gomwalk and A. McAuley, *J. Chem. Soc. A*, 2948 (1968).

Linear Solvation Energy Relationships. 24. Solvent Effects on the Transition State of the Addition Reaction of the *p*-Aminobenzenethiyl Free Radical to Styrene

Clifford W. Fong*

Weapons Systems Research Laboratory, Defence Research Centre Salisbury, GPO Box 2151 Adelaide, South Australia 5001

Mortimer J. Kamlet*

Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

Robert W. Taft*

Department of Chemistry, University of California, Irvine, California 92717

Received September 1, 1982

The solvatochromic equations have been successfully applied to the rate constants for the reversible addition of the *p*-aminobenzenethiyl radical to styrene, the relative equilibrium constants, and the electronic absorption spectra of the thiyl radical in 21 solvents. The resultant dissection of this data into solvent dipolarity and hydrogen bond acceptor basicity has been used in conjunction with literature substituent effect studies to provide a detailed picture of the transition state and its cybotactic environment.

Earlier studies of solvent effects on free-radical reaction rates[1] have generally found that the influence of solvent is usually small compared to that in analogous heterolytic reactions, since large differences in charge separation between the initial state and the transition state are not to be expected.[2] The small effect of solvent on reaction rate has invoked explanations ranging from similar solvation of the initial state and transition state, which have about

---

(1) (a) Martin, J. C. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol 2, Chapter 20. (b) Huyser, E. S. In "Advances in Free Radical Chemistry"; Williams, G. H., Ed.; Logos Press: New York, 1965. (c) Reichardt, D. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim/Bergstr., Germany, 1979; p 110.

(2) (a) Mayo, F. R.; Walling, C. *Chem. Rev.* **1950**, *46*, 191. (b) Huyser, C. S. "Free Radical Chain Reactions"; Interscience: New York, 1970; p 77. (c) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1967; p 132.

0022-3263/83/1948-0832$01.50/0

Table I. Absorption Peaks (ν_{max}) of p-$H_2NC_6H_4S\cdot$, the Addition Rate Constants (log k_1) to Styrene, the Relative Reverse Rate Constants (log $k_{-1}/k_2[O_2]$), the Solvents, and the Solvatochromic Parameters Used in the Correlational Analyses

no.[a]	solvent	ν_{max}[b] kK	log k_1,[b] M^{-1} s^{-1}	log $k_{-1}/k_2[O_2]$,[b] M^{-1} s^{-1}	π^*	β
2	cyclohexane	18.35	5.336	−1.131	0.00	0.00
14	benzene	17.54	4.769	−1.167	0.59	0.10
8	toluene	17.54	4.699	−1.319	0.54	0.11
53	mesitylene	17.54	4.709	−1.357	0.41	0.13
17	anisole	17.39	4.310	−1.284	0.73	0.22
97	fluorobenzene	17.54	4.638	−1.328	0.62	0.05
60	*o*-dichlorobenzene	17.30	4.420	−0.873	0.80	0.03
37	benzonitrile	17.24	4.049	−0.873	0.90	0.41
50	acetonitrile	16.39			0.75	0.20
9	dioxane	17.33	4.241	−1.036	0.55	0.37
13	tetrahydrofuran	17.24	4.017	−1.167	0.58	0.55
11	ethyl acetate	17.30	4.000	−1.143	0.55	0.45
47	ethyl benzoate	17.30	4.013	−0.967	0.74	0.41
25	*N,N*-dimethylformamide	16.39	2.845		0.88	0.69
29	dimethyl sulfoxide	16.39	2.477		1.00	0.76
6	carbon tetrachloride	18.18	5.301	−1.046	0.29	0.00
30	chloroform	17.54	4.594		0.77	0.00
20	dichloromethane	17.33	4.270		0.82	0.00
21	1,2-dichloroethane	17.33	4.021		0.81	0.00
24	pyridine	16.67	3.519	−0.879	0.87	0.64
3	triethylamine	17.39	4.140	−1.081	0.14	0.71
48	tributylamine	17.39	4.328	−1.060	0.16	0.62

[a] Solvent numbering is the same in all papers of this series. [b] Values calculated from ref 7.

the same degree of charge separation, to a desolvation of the initial state compared to the transition state, which induces large but compensating changes in the enthalpy and entropy of activation. Alternatively, the transition state may involve only slight charge separation, as suggested by small ρ^+ values found in substituent-effect studies, though it has been argued that substituents may affect ground-state bond energies to the extent required to account for the small ρ^+ values observed.[3,4]

However, the vast majority of solvent-effect studies on free-radical reactions have been hampered by the lack of an adequate range of solvents and a comprehensive model of solvent effects that can effectively separate solvent dipolarity[5] from hydrogen-bonding effects. The solvatochromic comparison method and the solvatochromic equations and parameters, which provide such a model,[6] are applied in the present study to a recent report[7] dealing with solvent effects on the addition of *p*-aminobenzenethiyl radical to styrene.

We shall show that the application of the solvatochromic equations to the reaction rates for the forward and reverse reactions, coupled with the known substituent effect of the para-substituted benzenethiyl addition reaction,[4] gives a detailed picture of the transition state for the addition of *p*-aminobenzenethiyl radical to styrene.

Discussion

The reversible addition reaction of thiyl radicals to various alkenes is among the best documented examples of free-radical additions to multiple bonds.[8] For the addition of *p*-aminobenzenethiyl radical (**1**) to styrene under the conditions described by Ito and Matsuda,[7] the reaction can be written as in Scheme I.

Scheme I

$$p\text{-}\underset{\mathbf{1}}{H_2NC_6H_4S\cdot} + CH_2{=}CHPh \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$p\text{-}H_2NC_6H_4SCH_2\dot{C}HPh \underset{k_2}{\xrightarrow{O_2}} \text{peroxy radical}$$

The rate constants for the forward reaction (k_1), the reverse reaction ($k_{-1}/k_2[O_2]_s$), and the equilibrium constant ($Kk_2[O_2]_s$) were calculated by Ito and Matsuda in 26 solvents for k_1 and in 18 solvents for the relative k_{-1} and K constants. An attempted linear correlation of log k_1 with the Dimroth–Reichardt $E_T(30)$ parameters[1c,9] gave a poor fit, and it was suggested[7] that the solvents fell into three separate categories.

We have earlier shown[6] that the $E_T(30)$ scale measures a linear combination of effects attributable to solvent dipolarity (π^*) and hydrogen-donor acidity (α) but contains no contribution from solvent hydrogen bond acceptor basicity (β). The presence of the *p*-amino group on **1** indicates that the radical will act as a hydrogen-bond-donor (HBD) solute and interact with solvents that have hydrogen-bond-acceptor (HBA) properties. Hence, we expect that rate, equilibrium, and spectroscopic data in nonprotonic solvents ($\alpha = 0$) should be well-correlated by the general solvatochromic equation

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + b\beta \qquad (1)$$

where δ, a "polarizability correction term",[10] is 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.[11]

Correlations of Rate and Equilibrium Data. In contrast to the relationship between log k_1 and $E_T(30)$, the

---

[3] Semenov, N. N. "Some Problems in Chemical Kinetics and Reactivity"; translated by Bradly, J. E. S.; Pergamon: London, 1958; Vol 1.

[4] Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732.

[5] The term dipolarity is intended as a more specific description of the term solvent polarity.

[6] Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

[7] Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 568.

[8] (a) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 373. (b) Abell, P. I. In "Additions to Multiple Bonds"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol 2, Chapter 13.

[9] See figure 6 in ref 8.

[10] Taft, R. W.; Abboud, J. L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1080.

[11] The d term is estimated through the equations $d = 2XYZ/[s(\text{al}) + s(\text{ar})]$, where ΔXYZ is the difference between values calculated through the aliphatic and aromatic solvent regression equations at $\pi^* = 0.7$ and $s(\text{al})$ and $s(\text{ar})$ are the slopes of those regression equations.

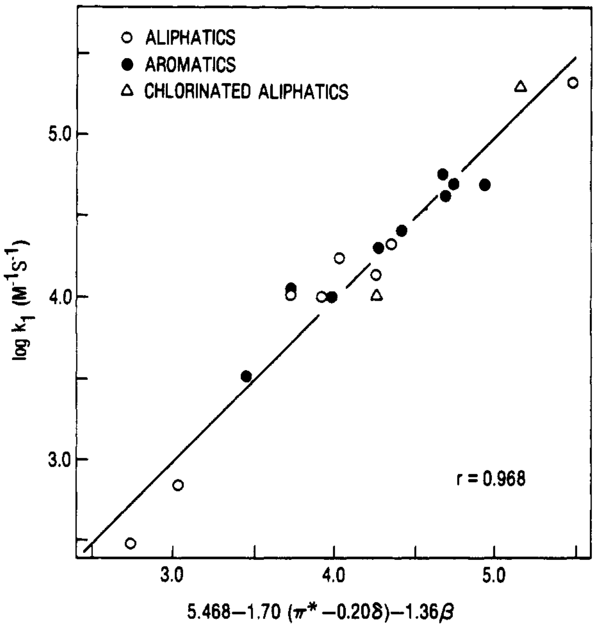


Figure 1.

correlation of log k_1 in eq 1 for the 21 solvents of known π and β values (Table I) is quite acceptable:

$$\log k_1 = 5.47 - 1.64(\pi^* - 0.20\delta) - 1.43\beta \quad (2)$$

$$r = 0.968,\ n = 21,\ \mathrm{SEE} = 0.18\ (6.3\%),\ \mathrm{SE}s = 0.16,\ \mathrm{SE}b = 0.15^{12}$$

A plot of the correlation is shown in Figure 1. To place the result in a context, the s value of −1.64 in eq 2 compares with s values of +4.4 for the Menschutkin reaction of Pr_3N with MeI[13] and 6.9–7.2 for heterolytic decompositions of the *tert*-butyl halides.[14]

Similarly, the correlation of the logarithm of the relative equilibrium constant $Kk_2[O_2]$ in eq 1 for the 16 solvents of known π and β values gives:

$$\log Kk_2[O_2] = 6.57 - 1.46(\pi^* - 0.20\delta) - 1.49\beta \quad (3)$$

$$r = 0.963,\ n = 16,\ \mathrm{SEE} = 0.16\ (8.0\%),\ \mathrm{SE}s = 0.20,\ \mathrm{SE}b = 0.17$$

The log of the relative reverse rate constant, $k_{-1}/k_2[O_2]$, gives a much poorer r value in the correlation according to eq 1:

$$\log k_1/k_2[O_2] = -1.26 + 0.25(\pi^* - 0.20\delta) + 0.18\beta \quad (4)$$

$$r = 0.483,\ n = 16,\ \mathrm{SEE} = 0.15\ (31.3\%),\ \mathrm{SE}s = 0.19,\ \mathrm{SE}b = 0.16$$

However, the lower r value very likely does not indicate poorer precision but probably reflects the smaller spread of the data. This conclusion is supported by the fact that the SEE, SEs and SEb values are quite similar for all the eq 2–4.

Correlations of Spectral Data. Ito and Matsuda[7] also noted that the bathochromic shifts of the absorption maxima of **1** in various solvents showed a rough qualitative relationship with Kosower's Z values and the $E_T(30)$ values, but the attempted correlations were poor. As we have previously shown,[6] Z, like $E_T(30)$, measures a linear combination of solvent dipolarity and HBD acidity effects but contains no β contribution. As before, we again find that the best correlation of $\nu(1)_{max}$[15] has terms in π^* and β, but, as with other p → π^* and $\pi \rightarrow \pi^*$ transitions of uncharged indicators (or, indeed, any spectra that are shifted bathochromically with increased solvent dipolarity),[10] the d term in eq 1 is in this case zero. The solvatochromic equation is given by eq 5. The precision of the

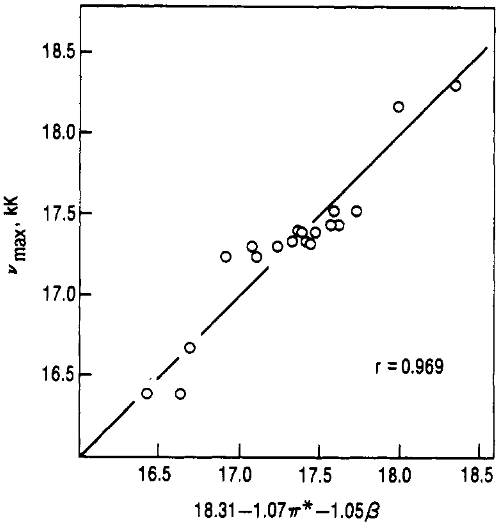


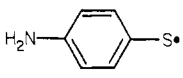
Figure 2.

$$\nu(1)_{max}\ (\times 10^{-3}\ \mathrm{cm}^{-1}) = 18.34 - 1.15\pi^* - 1.07\beta \quad (5)$$

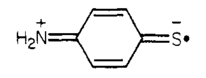
$$r = 0.969,\ n = 20,\ \mathrm{SEE} = 0.12\ (6.3\%),\ \mathrm{SE}s = 0.10,\ \mathrm{SE}b = 0.10$$

correlation is quite good, considering that the $\nu(1)_{max}$ values are derived from transient absorption spectra obtained by flash photolysis, and some of the absorption bands are quite unsymmetrical. A plot of the correlation is shown in Figure 2.

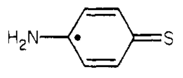
The ground and excited states of the *p*-aminobenzenethiyl radical may be considered in terms of differing contributions of canonical resonance structures **1a–c**.



1a



1b



1c

Ground-state delocalization of the unpaired electron on sulfur (structure **1a**) into the benzene ring (as in structure **1c** or the analogous canonical forms with the unpaired electron in the ortho positions) has been shown to occur to only a minor extent by ESR spectroscopy.[16]

The electronic excited state presumably includes a substantially increased contribution from structure **1b**, which becomes progressively more important as the dipolarity (π^*) and HBA basicity (β) of the solvent increase in magnitude. The bathochromic effect of solvent basicity is consistent with the hydrogen bond increasing the ground-state electron density on the amine nitrogen and with hydrogen-bond strengthening in the electronic excitation. From the b/s ratio of 0.93 in eq 5, we note that solvent dipolarity and HBA basicity show comparable abilities to stabilize resonance contributor **1b** and hence

---

[12] r = multiple correlation coefficient, n = number of solvents, SEE = standard error of the estimate, and the value in parentheses is the SEE as a percentage of the range of the observed variable (XYZ), SEs = standard error of s, SEb = standard error of b.

[13] Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053.

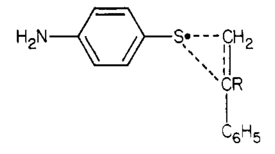
[14] Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

[15] ν_{max}, which is a measure of the energy of the electronic transition, is used rather than λ_{max}.[7]

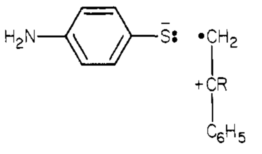
[16] (a) Schmidt, U. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 602. (b) Schmidt, U. *Ber. Dtsch. Chem. Ges.* **1969**, *97*, 405.

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.



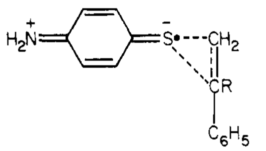
2a



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.

---

[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

Marye Anne Fox* and Carol A. Triebel

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

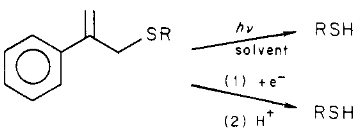
Received July 16, 1982

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

---

[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.

0022-3263/83/1948-0835$01.50/0