Integration of NMR spectra (300 and 60 MHz) of VPC purified material (185 °C) using the *tert*-butyl group as an internal standard (9H) indicated that the methyl groups on the aromatic ring were 96.5% labeled.

4,4-Dimethyl-1-phenyl-2-pentyn-1-one (17). A solution of *tert*-butylacetylene (3.0 g) in 5 mL of THF was added dropwise to a solution of ethylmagnesium bromide (1.0 equiv) in 30 mL of THF. After being stirred for 30 min, the mixture was treated dropwise with benzaldehyde (3.2 g) in 5 mL of THF. The mixture was worked up as for **7** to give the crude alcohol (85%) that was oxidized with Jones's reagent.[16] The crude ketone was purified by flash chromatography on silica gel using 4% EtOAc/hexane to give **17** as a colorless oil: NMR (500 MHz) δ 8.10–8.15 (m, 2 H), 7.62–7.42 (m, 3 H), 1.38 (s, 9 H); MS, *m/e* (%) 186 (30.3), 171 (11.4), 143 (43.1), 128 (30.8), 105 (100.0). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.02; H, 7.73.

Irradiation of 7. A solution of **7** (228 mg) in benzene (50 mL) was degassed and irradiated with a 450-W Hanovia lamp for 6 h through a uranium glass filter. Removal of solvent and flash chromatography[18] (5% Et_2O in hexanes) gave **11** (28 mg, 13%), **10** (140 mg, 66%), and **7** (18 mg, 8%). Yields are based on unrecovered **7**; longer irradiation increased the ratio **11**:**10**. Analytical samples of **10** and **11** were prepared by preparative gas chromatography. For (*E*)-5,7-dimethyl-2-(2,2-dimethylpropylidene)-1-indanone (**10**): mp 88–90 °C; IR 2970 (s), 1700 (s), 1650 (s), 1615 (s), 1325 (s), 1250 (s), 1190 (m), 1150 (m), 1108 (w) cm^{-1}; NMR (300 MHz) δ 7.090 (s, 1 H, ArH), 6.936 (d, J = 0.46 Hz, 1 H, ArH), 6.774 (t, J = 2.1 Hz, 1 H, olefinic), 3.747 (s, 2 H, CH_2), 2.656 (s, 3 H, CH_3), 2.392 (s, 3 H, CH_3), 1.231 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.27; H, 8.99. For (*Z*)-5,7-dimethyl-2-(2,2-dimethylpropylidene)-1-indanone (**11**): mp 86–88 °C; IR 2950 (s), 2920 (m), 2860 (m), 1695 (s), 1628 (s), 1610 (s), 1370 (m), 1320 (m), 1250 (m), 1190 (m), 1150 (m), 1025 (w) cm^{-1}; NMR (300 MHz) δ 7.025 (s, 1 H, ArH), 6.909 (s, 1 H, ArH), 6.186 (t, J = 1.6 Hz, 1 H, olefinic), 3.578 (s, 2 H, CH_2), 2.646 (s, 3 H, CH_3), 2.376 (s, 3 H, CH_3), 1.336 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: 83.77; H, 8.72.

Stern–Volmer Quenching of Rearrangement of 7 to 10. Degassed solutions of **7** (9.08 mM) in cyclohexane containing tetradecane (0.97 mM) as internal standard and containing different concentrations of 2,3-dimethyl-1,3-butadiene (0, 0.20, 0.80, 1.60, 2.40, and 3.20 M) were irradiated in duplicate at 25 °C through a 1-cm path of a K_2CrO_4 (0.002 M in 1% aqueous K_2CO_3) filter (~313 nm).[21] Products **10** and **11** were analyzed by gas chromatography; results were plotted in the usual fashion[22] and yielded $k_q\tau \approx 0.29$ M^{-1}.

Quantum Yield Determination. (a) 313 nm. Duplicate solutions (3.0 mL) of **7** (9.35 mM) in cyclohexane containing tetradecane (5 mM) as internal standard were placed in Pyrex test tubes, degassed with N_2, and sealed. These were irradiated on a merry-go-round apparatus simultaneously with duplicate tubes of valerophenone (10.3 mM) in ethanol containing tetradecane (5 mM), using the output of a 450-W Hanovia lamp filtered through the K_2CrO_4 filter described above. Conversion was ≤14%. Yields of **10** and **11** and acetophenone were determined by calibrated GC. From the known[21] quantum yield for formation of acetophenone from valerophenone, the quantum yield for products is ~0.097. **(b) Various Wavelengths.** Samples in hexane degassed by three or four freeze–pump–thaw cycles and sealed were irradiated with various combinations of UV and visible wavelengths isolated from Hg/Xe arc lamp sources by Bausch and Lomb SP-200 monochromators.

Irradiation of 7D. A solution of **7D** (117 mg) in anhydrous benzene (70 mL) was irradiated to 95% conversion in a toroidal vessel that was rinsed with D_2O before being dried in an oven for 1.25 h. The residue remaining after removal of solvent was purified by preparative GC (185 °C) to afford **11D** and **10D** in a ratio of 1:5. NMR spectra of these products indicated that in each case the olefinic hydrogen atom was 83% deuterium. Recovered starting acetylenic ketone was 95.5% labeled.

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Intramolecular Charge-Transfer Interactions in Triplet Keto Sulfides

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Abstract: The photochemistry of β-, γ- and δ-phenacyl sulfides, sulfoxides, and sulfones has been studied. The first group undergoes no irreversible reaction. The other two undergo type II photoelimination but in low quantum efficiency. Analysis of triplet lifetimes and product quantum yields indicates that all undergo rapid internal quenching, which is ascribed to a charge-transfer (CT) process. The positional dependence of rate constants for this CT reaction is $\beta > \gamma > \alpha \gg \delta > \epsilon$. Some rate constants (units of 10^8 s^{-1}) for $PhCO(CH_2)_nSBu$ are as follows: n = 1, 16; n = 2, 55; n = 3, 29; n = 4, 1.7; n = 5, ≤0.2. These values are interpreted as representing relative equilibrium constants for achieving cyclic orientations in which the sulfur lone pair and the half-empty oxygen n-orbital overlap substantially. The rate constants are very sensitive to the oxidation state of sulfur; for the n = 3 sulfoxide, $k = 35 \times 10^8$; for the n = 3 sulfone, $k = 0.35 \times 10^8$. The δ-substituted ketones undergo elimination to form 4-benzoyl-1-butene, by β-elimination of sulfur-centered radicals from the biradicals that intervene in the type II elimination. Actual radical cleavage rate constants lie in the order SNC > PhS ~ BuS(O) ≫ BuS, $BuSO_2$, CH_3CO–S and range from 10^9–3×10^5 s^{-1}. Rate constants for triplet state γ-hydrogen abstraction were found to correlate well with the σ_I values of the various sulfur groups, except for δ-sulfinyl, which apparently participates in the reaction.

As part of a systematic investigation of intramolecular charge-transfer (CT) quenching of triplet ketones, we have studied the photochemistry of ω-phenacyl sulfides of the structure $PhCO(CH_2)_nSR$, together with their corresponding sulfoxides and sulfones. Sulfides are known to quench triplet ketones bimolecularly.[1] The mechanism is thought to involve CT interactions, particularly since rate constants correlate with those of other electron donors.[1,2] Since the actual values of the bimolecular quenching rate constants are well below the diffusion limit,[1] rate constants for analogous intramolecular quenching processes should depend on the equilibrium constants for formation of the requisite cyclic orientations.[3,4] The donor orbital of sulfides is a lone pair

(1) Cohen, S. G.; Gutenplan, J. B. *J. Org. Chem.* **1973**, *38*, 2001. Cohen, S. G.; Ojanpera, S. *J. Am. Chem. Soc.* **1975**, *97*, 5633.

(2) (a) Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859; (b) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, 141.

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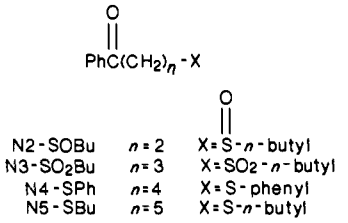
Table I. Photokinetic Data for Various Keto Sulfides, Sulfoxides, and Sulfones $PhCO(CH_2)_n-X$[a]

ketone	Φ_{-k}	Φ[b]	Φ_{II}^{max}[c]	$k_q\tau$[d]
N2–SBu	0	0	0	1.1[e]
N2–SOBu	0	0	0	1.7[e]
N2–SO_2Bu	0	0	0	176
N3–SBu	0.21	0.13	0.18	1.7 (2.0)[e]
N3–SOBu		0.03	0.035	16
N3–SO_2Bu		0.20		3750
N3–StBu		0.27		1.7 (2.3)[e]
N3–SPh		0.32	0.36	4.8
N4–SBu	0.25	0.18	0.21, 0.006[f]	28
N4–SOBu	0.36	0.03	0.03, 0.39[f]	21
N4–SO_2Bu	0.45		0.40, 0.03[f]	205
N4–SPh		0.02, 0.25[f]	0.02, 0.28[f]	38.5
N5–SBu	0.37	0.22	0.25	37 (40)[e]
N4–SCN		0.22[f]	0.003, 0.25[f]	106
N4–$SCOCH_3$		0.58, 0.02[f]	0.78	44

[a] Ketone (0.05 M) in benzene, 313 nm. [b] Acetophenone formation. [c] Dioxane or pyridine (1 m) added. [d] Stern–Volmer slope, M^{-1}, methylnaphthalene quencher, 365 nm. [e] Slope of double reciprocal sensitization plot, *cis*- to *-trans*-1,3-pentadiene. [f] 4-Benzoyl-1-butene formation.

Scheme I



on sulfur. The half-empty oxygen n-orbital is thought to be the acceptor orbital in excited ketones.[5-7] Therefore ketosulfides are particularly well suited to test the geometric requirements for intramolecular orbital overlap, since the two key orbitals are highly localized, primarily atomic p-orbitals with well understood directionality.

We have already reported a similar study for ketoamines[8] and have published a preliminary comparison.[2] In an accompanying paper[9] we describe the photocleavage of α-phenacyl sulfides. In this paper we describe the competing CT and γ-hydrogen abstraction reactions of β-, γ-, δ-, and ϵ-phenacyl sulfides. We first consider the effects of sulfur substituents in different oxidation states on rate constants for hydrogen atom abstraction. We then compare the CT rate constants for all (α through ϵ) phenacyl sulfides. Finally, we derive rate constants for β-elimination of sulfur-centered radicals from the efficiency of 4-benzoyl-1-butene formation from the δ-phenacyl sulfides, sulfoxides, and sulfones.[10,11]

Results

Keto sulfides were prepared by S_N2 displacement with sodium thiolates on the appropriate haloketone. Sulfoxides and sulfones were then prepared by oxidation of the sulfides. Table I lists all the compounds studied; Scheme I defines the abbreviations used.

The β-phenacyl compounds form no photoproducts in quantum yields $\geq$0.001 at 313 nm. The γ-phenacyl compounds all give acetophenone as the chief photoproduct, together with the expected 10–15% cyclobutanols as determined by characteristic GC retention times. The δ-phenacyl compounds also gave varying amounts of 4-benzoyl-1-butene product. For N4–SOBu and N4–SPh, butyl thiobutanesulfonate and phenyl disulfide were observed as byproducts in low yield, the latter accounting for only 3% of reacted N4–SPh.

Quantitative studies were performed by parallel 313-nm irradiation of degassed, sealed samples containing 0.05 M ketone together with any additives in benzene. Product yields after $\leq$10% conversion were determined by GC analysis and were converted to quantum yields by analysis of valerophenone actinometer solutions.[12] Several of the ketones were used to sensitize the cis–trans isomerization of 1,3-pentadiene.[13] Double reciprocal plots of isomerization quantum yield vs. diene concentration provided ketone intersystem crossing yields and $k_q\tau$ values.[14] Stern–Volmer quenching studies with 1,3-pentadiene or methylnaphthalene quencher yielded linear plots with slopes equal to $k_q\tau$. All the results are listed in Table I as averages of duplicate measurements. The agreement between $k_q\tau$ values measured by the two methods was excellent. Φ_{isc} values were unity for all ketones tested.

Dibutyl sulfide, sulfoxide, and sulfone were used to quench the type II reactions of butyrophenone and *p*-methoxyvalerophenone. The $k_q\tau$ values are listed in Table II together with k_q values calculated from literature triplet lifetimes.

Table II. Quenching of Triplet Ketones by Sulfide, Sulfoxide, and Sulfone

quencher	ketone	$k_q\tau$, M^{-1}	k_q, 10^7 M^{-1} s^{-1}
Bu_2S	$PhCOPr^a$	45	32.5
BuSOBu	$PhCOPr^a$	0.2	0.14
BuSOBu	*p*-MeOVP[b]	0.6	0.12
$BuSO_2Bu$	*p*-MeOVP[b]	<0.1	<0.02

[a] τ = 150 ns, ref 17. [b] τ = 500 ns, Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

Table III. Triplet Rate Constants for Keto Sulfides, Sulfoxides, and Sulfones

ketone	$1/\tau$[a]	$k_{\gamma\text{-H}}$[a]	k_{CT}[a]
N1–SBu	310	*b*	160
N1–SOBu	500	*b*	73
N1–SO_2Bu	2.8	*b*	1.7
N2–SBu	540	0	550
N2–SOBu	350	0	350
N2–SO_2Bu	3.4	0	3.4
N3–SBu	350	64	290
N3–SOBu	38	1.2	37
N3–SO_2Bu	0.16	0.035	0.125
N3–StBu	340	90	250
N3–SPh	125	45	80
N4–SBu	21.5	4.8	16.7
N4–SOBu	28	12	16
N4–SO_2Bu	3.0	1.2	1.8
N4–SPh	15.5	4.7	10.8
N5–SBu	16	14	2
N4–SCN	5.7	1.4	4.3

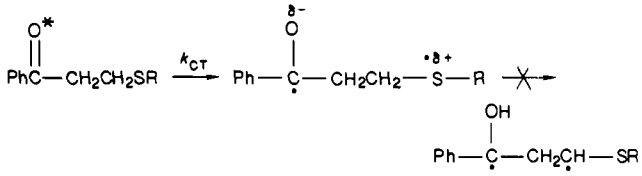
[a] Units of 10^7 s^{-1}, based on k_q = 6 × 10^9 M^{-1} s^{-1}; Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806. [b] See following paper.

Discussion

Separation of Rate Constants for Competing Reactions. Since thioalkoxy groups lower type II quantum yields and shorten triplet lifetimes of phenyl alkyl ketones, it is apparent that such substitution introduces reactions that compete with triplet state γ-hydrogen abstraction. Since sulfides are known to quench triplet ketones by a CT process,[1] some intramolecular CT quenching is inevitable in flexible keto sulfides[4] and is assumed to compete with triplet reaction in these ketones. Table III lists for all the ketones the rate constants for triplet reaction, which were separated as described in the following paragraphs.

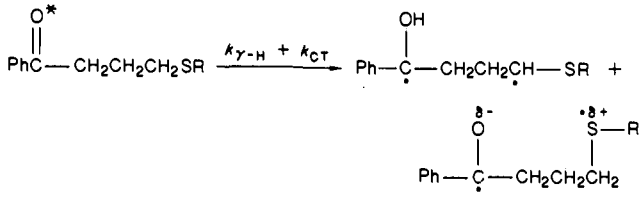
(3) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491.
(4) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.
(5) Turro, N. J.; Dalton, J. C.; Farington, G.; Niemczyk, M.; Pond, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 6978.
(6) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–52.
(7) Caldwell, R. A.; Creed, R. L. *Acc. Chem. Res.* **1980**, *13*, 45.
(8) Wagner, P. J.; Jellinek, T.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7512.
(9) Wagner, P. J.; Lindstrom, M. J. *J. Am. Chem. Soc.*, following paper in this issue.
(10) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579.
(11) Wagner, P. J.; Lindstrom, M. J.; Sedon, J. H.; Ward, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 3842.
(12) Wagner, P. J.; Kochevar, I.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
(13) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.
(14) Wagner, P. J. In *Creation and Detection of the Excited State*; Lamola, A., Ed.; Marcel Dekker: New York, 1971; Vol. 1A, p 173.

In the case of the β-substituted ketones, where there are no photoproducts, we conclude that CT quenching is the only triplet reaction. β-Ethoxypropiophenone undergoes efficient photocyclization to oxacyclopentanols, with the relatively long triplet lifetime of 70 ns.[15] The sensitization efficiency of N2–SBu indicates a triplet lifetime of only 0.2 ns. As concluded below, hydrogen abstraction from C–H bonds α to divalent sulfur occurs with much the same rate constants as from C–H bonds α to oxygen. Therefore δ-hydrogen abstraction in triplet N2–SBu can account for only ~0.3% of the total triplet decay. It is noteworthy that β-amino ketones provide cyclopropanol products,[16] presumably from 1,3-biradicals generated by proton transfer following internal CT. We see no evidence for any such products with these sulfides.



As detailed below, hydrogen abstraction from C–H bonds next to sulfoxide and sulfone groups is quite slow, so the measured triplet lifetimes for N2–SOBu and N2–SO2Bu again represent quenching by the sulfur functional group.

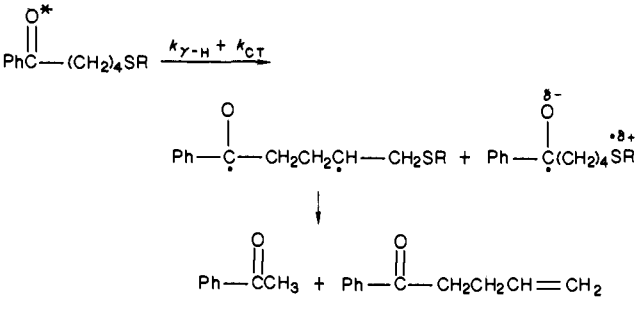
For the γ-substituted ketones, where only normal type II products are observed, we presume that CT quenching and γ-hydrogen abstraction are the only competing processes. In this case the triplet lifetime represents the sum of the rate constants for the two reactions. For the smaller ketones, the two rate constants can be separated by measuring the effects of added Lewis base on quantum yields. The maximum quantum yield indicates what fraction of the total decay is contributed by $k_{\gamma\text{-H}}$, eq 1.[17]



$$\phi_{II}^{max} = k_{\gamma\text{-H}}/\tau_R \quad (1)$$

$$1/\tau_T = k_{\gamma\text{-H}} + k_{CT} \quad (2)$$

Benzoylbutene formation occurs from δ-halo- as well as δ-thiyl ketones.[10] For the halo ketones it has been shown to arise by radical elimination in the 1,4-biradicals formed by triplet state γ-hydrogen abstraction.[11] Since β-cleavage of thiyl radicals is also well known,[18] we assume the same source of benzoylbutene here. Therefore competing triplet rate constants can be separated as for the γ-substituted ketones, the only difference being that the yields of acetophenone and benzoylbutene are summed to represent the total "type II" quantum yield.



(15) Wagner, P. J.; Kelso, P. A.; Kemmpainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.
(16) Roth, H. J.; El Raie, M. H. *Arch. Pharm. (Weinheim, Germany)* **1972**, *305*, 213, 219. Roth, H. J.; El Raie, M. H. *Tetrahedron Lett.* **1970**, 2445.
(17) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
(18) Hall, D. N.; Oswald, A. A.; Griesbaum, K. *J. Org. Chem.* **1965**, *30*, 3829.

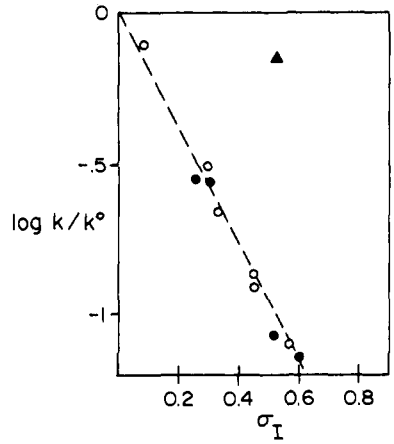


Figure 1. Hammett plot of $k_{\gamma\text{-H}}$ values for δ-substituted valerophenones. Dotted line represents plot of data in ref 17; ●, data from this work; ▲, sulfinyl; ○, non-sulfur substituents.

Table IV. Separation of Inductive and Conjugative Effects of γ-Substituents

γ-substituent	σ_I[a]	$10^{-4.3\sigma_I}$	k/k_0	RSF[b]
CH_3			1.0	1
OCH_3	0.30	0.051	5.0	98
SBu	0.25	0.084	4.5	54
SOBu	0.52	0.0058	0.077	13
SO_2Bu	0.60	0.0026	0.022	0.8
SPh	0.30	0.051	3.0	58

[a] From Kosower, E. *An Introduction to Physical Organic Chemistry*; Wiley: New York, p 49. [b] Resonance stabilization factor.

Substituent Effects on $k_{\gamma\text{-H}}$. Although the main thrust of this work was to determine k_{CT} values, we shall examine the derived k_H values first, since the consistency that their values display with respect to earlier work on substituent effects best defines the reliability of the actual k_{CT} values derived from eq 1 and 2.

It is obvious from the values in Table III that the sulfur functional groups vary tremendously in their effect on hydrogen abstraction. We shall consider first the δ-substituted ketones. Figure 1 shows how well these new values fit on a Hammett plot containing the values for other δ-substituents measured earlier.[17] With the exception of the sulfoxide, the fit is obviously excellent, an overall ρ value of −1.9 being displayed by a wide array of substituents. The thiyl groups produce the same inductive deactivation as alkoxy, while the stronger electron-withdrawing sulfone and thiocyanate groups slow down hydrogen abstraction by over an order of magnitude. Particularly for the sulfides, this excellent fit to expectation supports the accuracy of the rate constants.

The sulfoxide reacts almost as rapidly as the unsubstituted valerophenone. We have seen other examples of such acceleration (in reality reduced deceleration) in the δ-halo ketones.[11] This phenomenon provides further[19] evidence that the sulfinyl group, like bromo and iodo,[20] can participate in radical hydrogen abstraction by what is usually considered to be a weak bridging process.[20] It is interesting that the partially oxidized functional group produces this effect, whereas the sulfide does not. One might be tempted to connect this rate enhancement with the efficient elimination that produces benzoylbutene. However, we showed earlier[11] that kinetics and product ratios are independent for the δ-halo ketones, and the same is true here. For example, the δ-thiophenoxy ketones and thiocyanato ketones undergo as much elimination as does the δ-sulfinyl ketone, yet they display exactly the triplet reactivities expected for simple hydrogen abstraction.

Table IV analyzes the effects of γ-substituents as we did earlier,[17] namely by assuming a ρ value of 4.3[17] for γ-substituents

(19) Shevlin, P. B.; Booth, T. E.; Greene, J. L.; Willcott, M. R.; Inners, R. R.; Cornelis, A. *J. Am. Chem. Soc.* **1978**, *100*, 3874.
(20) For a review, see: Skell, P. S.; Shea, K. J. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, p 809.

Table V. Comparison of Internal CT Quenching in Keto Sulfides and Ketoamines $PhCO(CH_2)_n$–X

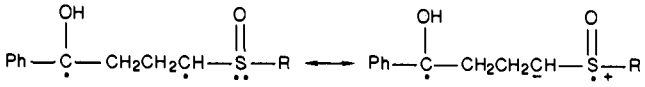
	X = SBu		X = NMe_2	
n	k_{CT}[a]	k_{CT}/k_2[b]	k_{CT}[a,c]	k_{CT}/k_2[d]
1	160	4.3	<10	<0.03
2	550	15	515	1.4
3	290	8	890	2.5
4	17	0.5	60	0.2
5	≤2	0.05	20	0.07

[a] Units of 10^7 s^{-1}. [b] $k_2 = 3.6 \times 10^8$ M^{-1} s^{-1}. [c] From ref 8 and 24. [d] $k_2 = 3.6 \times 10^9$ M^{-1} s^{-1}, ref 8.

in order to separate the inductive and conjugative effects of a substituent. The conjugative stabilization factor so deduced equals the actual relative reactivity divided by that expected based solely on the electron-withdrawing inductive effect of the substituent.

The thiyl groups produce strong conjugative enhancement of the rate constant for γ-hydrogen abstraction, about half as much as provided by an alkoxy group. The accuracy of this factor depends on the extent to which the type II reaction might proceed from a CT complex as well as by simple direct hydrogen abstraction. If it did, k_H values calculated from eq 1 and 2 would be too high and k_{CT} values too low. We have shown that the corresponding γ-amino ketones do not produce any type II products following CT interaction, presumably because the tight cyclic nature of the excited CT complex precludes hydrogen transfer.[21] That $k_{\gamma\text{-H}}$ values are lower than in γ-alkoxy ketones strongly suggests that the type II products arise only from simple hydrogen abstraction.

Not surprisingly, the fully oxidized γ-sulfonyl group produces no conjugative stabilization of the transition state for hydrogen abstraction. (The fact that the derived factor is within experimental error of unity testifies to the accuracy of this approach). The sulfinyl group again provides much less rate deceleration than would be expected from its inductive effect. Presumably the lone pair left on sulfur serves to conjugate with the developing radical center.



The effects of substituents on the ε carbon are correlated by the same Hammett plot displayed by δ-substituents if their σ values are multiplied by 0.43, the usual dampening factor for an insulating methylene.[17] The $k_{\gamma\text{-H}}$ value so calculated for N5–SBu is 1.4×10^8 s^{-1}. The measured rate of triplet decay is 1.6×10^8. Therefore k_{CT} was determined purely from eq 2. Other work has indicated that when the alkyl chain of phenyl ketones gets either too bulky or too long, Lewis bases do not solvate the intermediate biradicals effectively enough to fully maximize type II quantum yields.[22-24] In such cases eq 1 can no longer be used, but the predictability of $k_{\gamma\text{-H}}$ values allows precise calculation of competing rate constants.

The Effect of Separation on k_{CT} Values. Table V compares values of rate constants for internal quenching in triplet keto sulfides (including values from the following paper) with those that we have measured separately for ketoamines.[8,24] Values for bimolecular quenching rate constants are included. These latter values demonstrate that a sulfide intrinsicially is a worse CT quencher than is a tertiary amine because of their different oxidation potentials.

If we look first at the variation with n for these keto sulfides, we see a maximum for $n = 2$ and a dramatic falloff for $n > 3$. Assuming overlap of a sulfur lone pair orbital with the carbonyl oxygen n-orbital, there are $n + 3$ atoms in these cyclic quenching interactions. Since the quenching process is intrinsically inefficient, the rate constants are conformationally controlled[4] and reflect equilibrium stabilities of the cyclic conformations. Thus it is not surprising that five and six atom cycles are formed the fastest. As has already been noted,[4] the fact that these internal quenching rate constants parallel known ground-state conformational preferences so closely is unique evidence for the correctness of the simple HOMO–LUMO overlap model for such CT interactions.[7]

Orbital size and shape are expected to influence the distance and conformation required for effective overlap. In this regard, the differences between SR and NR_2 as internal CT quenchers is quite revealing. The sulfide group is actually a more effective quencher than is the dialkylamino group for small n, despite its higher oxidation potential. The ratio k_{intra}/k_{inter} for SR is larger than that for NR_2 for $n = 1$–4. This ratio represents the "effective molarity" of an internal quencher[25] and is now known to vary with the geometry of the particular reaction.[26] In this case we conclude that the longer reach of the sulfur 3p orbital compared to a nitrogen sp^3 orbital is responsible for the quantitative difference between SR and NR_2. Measurement of intramolecular CT rate constants obviously can give misleading estimates of relative redox potentials!

It is particularly interesting that k_{CT} is so high for the case of $n = 1$, where a four atom cycle is involved. In the corresponding amino ketone, k_{CT} is too low to measure.[8] Comparison of the effective molarities for the ketosulfides and ketoamines reveals that the sulfur/nitrogen ratio falls from 100 to 2.5 as n changes from 1–4. Obviously the greater size of the sulfur 3p orbital is most important for the shortest chains. As n gets larger, the entropic and conformational demands of the connecting methylene chain become more important and presumably dominate for $n \geq 5$. Unfortunately, we cannot measure k_{CT} values for n values greater than 5 for this type of ketosulfide since the type II reaction totally dominates triplet decay. The value in Table III for $n = 5$ is already an upper limit.

Effect of Sulfur Oxidation State on k_{CT}. As Tables II and III show, the sulfide group is only 2–8 times better than the sulfoxide group as an internal quencher but 250 times better as a bimolecular quencher. Rate constants for the sulfone group are so small that they could not be measured for some of the ketones. Of course, the fully oxidized sulfur atom has no remaining lone pairs to serve as donor electrons, so no CT quenching was expected by such an electron-deficient center. We do not know whether the low values measured for N2–SO_2Bu and N4–SO_2Bu represent some real reaction of a sulfonyl group or the presence of minor impurities, perhaps incompletely oxidized sulfides.

The sulfinyl group has one lone pair left on sulfur, but its energy is lowered by the net positive charge on sulfur, as evidenced by the 0.4 eV higher ionization potential of dimethyl sulfoxide relative to dimethyl sulfide.[27] The lowered bimolecular quenching rate for sulfoxide was expected for a CT process. It is not so clear what process produces such rapid intramolecular quenching in the various keto sulfoxides. The fact that k_{CT} values for sulfoxide and sulfide for a given n are comparable for $n = 1$–4 indicates that the intramolecular quenching ability of a sulfinyl group is real and not due to an isolated experimental error. It is not clear from calculations whether the highest energy occupied orbital of sulfoxides resides primarily on S or O.[27] The apparent huge "effective molarity" of a sulfinyl group is reminiscent of that of

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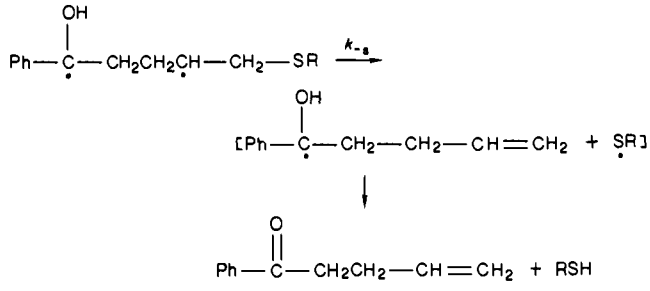
β-vinyl[28] and phenyl groups[29] and suggests electron donation by the S=O bond instead of by a single lone pair. Of course, the quenching may not involve charge transfer but instead some other reversible chemical process favored by the arrangement of functional groups.

The phenylthiyl group is only half as good a quencher as are the alkylthiyl groups, presumably because the lone pair electron density of the sulfur atom is slightly delocalized onto the benzene ring. The thiocyanate group is an even worse donor, as expected.

β-Cleavage of Biradicals. We have already published a full report on this reaction of δ-halo ketones.[11] Table I lists the product quantum yields observed for the sulfur containing ketones. We have already published relative values of k_{-S} derived from these product ratios, compared to that found for δ-chloro.[10] Since we concluded that $k_{-S} = 4 \times 10^6$ s^{-1} for the chloro-substituted biradical,[11] we can derive the following estimates of actual k_{-S} values for sulfur-centered radicals: SBu, 6×10^5; SOBu, 3×10^8; SO_2Bu, 1.5×10^6; SPh, 4.4×10^8; SCN, 2×10^9. The only assumptions involved are that all of the benzoylbutene is formed by the same mechanism as for the chloro ketone and that the sulfur-containing biradicals have lifetimes the same as that of the chloro biradical, 27 ns. We have no direct experimental evidence in support of these reasonable assumptions. However, since thiyl radicals are well known to add reversibly to alkenes,[30] some β-cleavage from the 1,4-biradical followed by radical–radical disproportionation is expected for the sulfur-substituted biradicals. Likewise, biradical lifetimes appear to be dominated by intersystem crossing.[31] Sulfur and chlorine should produce comparably small heavy atom effects.



The observation of only 3% PhSSPh radical coupling product indicates that the postulated in-cage disproportionation is nearly 100% efficient, just as we observed for the corresponding reaction of δ-halo ketones[11] and for the trapping of 1,4-biradicals by thiols.[32] A combination of heavy-atom effects and electron-transfer results in rapid reaction of the hemi-pinacol and thiyl radicals within the solvent cage and thus high yields of benzoylbutene.

The rate constant that we derive for alkanethiyl radical cleavage explains why thiols add efficiently to olefins. We have determined a bimolecular rate constant of 10^7 M^{-1} s^{-1} for hydrogen abstraction from alkanethiols by alkyl radicals.[33] Therefore concentrations of thiol above 0.1 M trap over half the β-thiyl radicals formed by radical addition.

The relative propensities of the different sulfur-centered radicals to cleave are in accord with what is known about the various types of sulfur radicals.[34,35] Sulfinyl and phenylthiyl have comparable rate constants over 100 times faster than either alkylthiyl or sulfonyl. Sulfinyl radical is known to be the fastest formed oxidation state,[34] and formation of benzenethiyl is aided by resonance.[35] We described in our earlier papers why these cleavages represent monoradical reactions of the biradicals.[10,11] Thiocyanato radical cleaves even faster, whereas thioacetate has a rate $<10^6$, as does alkylthiyl. The slow rate for the latter certainly provides additional evidence that this elimination is a radical as opposed to ionic process.

Experimental Section

Solvents and Additives. Benzene was purified by repeated washing with sulfuric acid, neutralization, drying, and distillation from P_2O_5. Dioxane was distilled through a short Vigraux column. Pyridine was distilled from barium oxide. Various *n*-alkanes from dodecane to nonadecane, previously purified and distilled, were used as internal standards for GC analysis. *cis*-1,3-Pentadiene (Chemical Samples) was used as received (99.8% pure by GC analysis), as were the mixed isomers. Valerophenone was prepared by standard Friedel–Crafts acylation of benzene with valeryl chloride.

Procedures. For kinetic measurements, all solutions were prepared in volumetric flasks; 2.8-mL aliquots were placed in 13 × 100 Pyrex or Kimax tubes. The samples were degassed to 10^{-3} torr by several freeze–pump–thaw cycles and then irradiated in parallel in a "merry-go-round" apparatus[36] immersed in a water bath. Actinometer samples containing 0.1 M valerophenone were irradiated at the same time. The 313-nm region of a Hanovia 450-W medium pressure mercury arc was isolated with an aqueous filter solution containing 0.0002 M potassium chromate in 0.1 M potassium carbonate. The 366-nm region was isolated with a set of Corning no. 7-83 glass filters. Analyses were done by gas chromatography (GC), usually on a 6 ft × $^1/_8$ in. column containing 3% QF-1 on 60/80 Chromosorb G held at 145 °C.

Acetophenone usually was identified by its characteristic retention time. It was actually isolated by preparative GC from irradiated samples of 4-SBu and 5-SPh and identified by its spectroscopic features. 4-Benzoyl-1-butene was isolated by preparative-scale irradiation (Pyrex filter) of 160 mL of 0.05 M 5-SPh in nitrogen-flushed benzene for 24 h. It was also isolated by preparative GC of a partially irradiated 3-mL sample. In both cases the product had spectra identical to authentic material prepared by adding the Grignard of 4-bromo-1-butene to benzonitrile.[37] For other ketones it was identified by its GC retention time.

Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter connected to a differential corrected spectrum unit, on samples 10^{-3} M in ketone. UV spectra were measured on a Cary 14 spectrophotometer.

Preparation of the Keto Sulfides. Various benzoylalkyl halides were first prepared by straightforward Friedel–Crafts acylations of benzene with the appropriate ω-chloro acid chloride or with β-bromopropionyl chloride. The appropriate ω-benzoylalkyl halide was then refluxed for 5–12 h with the sodium salt of the appropriate thiol in ethanol. For preparation of the δ-benzoyl sulfides, the ethylene glycol ketal of γ-chlorobutyrophenone was employed. Products were purified by distillation under reduced pressure or by recrystallization from ethanol. Only the parent mass spectral peaks are listed below. All NMRs (proton) were run in $CDCl_3$.

β(Butylthio)propiophenone: IR (neat) 1680, 1450, 1350 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.4 (m, 4 H), 2.4–3.4 (m, 6 H), 7.3 (m, 3 H), 7.8 (m, 2 H); *m/e* 222.

γ-(Butylthio)butyrophenone: bp 145 °C (0.3 torr); IR (neat) 1695, 1450, 1230 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.4 (m, 4 H), 1.9 (m, 2 H), 2.5 (m, 4 H), 3.1 (t, 2 H), 7.3, 7.8; *m/e* 236.

γ-(*tert*-Butylthio)butyrophenone: bp 125 °C, (0.15 torr); IR (neat) 1695, 1225 cm^{-1}; NMR δ 1.25 (s, 9 H), 2.0 (m, 2 H), 2.6 (t, 2 H), 3.1 (t, 2 H), 7.3, 7.8; *m/e* 236.

γ-(Phenylthio)butyrophenone: mp 35 °C; IR ($CHCl_3$) 1675, 1225 cm^{-1}; NMR δ 2.0 (m, 2 H), 3.0 (m, 4 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/e* 254.

δ-(Butylthio)valerophenone: bp 155 °C (0.3 torr); Ir (neat) 1685, 1450, 1220 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.6 (m, 8 H), 2.4–3.0 (m, 6 H), 7.3, 7.8; *m/e* 250.

δ-(*tert*-Butylthio)valerophenone: bp 140 °C (0.3 torr); IR (neat) 1685, 1220 cm^{-1}; NMR δ 1.2 (s, 9 H), 1.7 (m, 4 H), 2.5 (t, 2 H), 2.9 (t, 2 H) 7.3, 7.8; *m/e* 250.

δ-(Phenylthio)valerophenone: mp 87 °C; IR ($CHCl_3$) 1675, 1200 cm^{-1}; NMR δ 1.9 (m, 4 H), 2.9 (t, 4 H), 7.3, 7.8; *m/e* 270.

ε-(Butylthio)hexanophenone: bp 145–160 °C (0.4–0.5 torr); IR (neat) 1695, 1450, 1220 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–1.9 (m, 10 H), 2.5 (t,

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4 H), 2.9 (t, 2 H), 7.3, 7.8; *m/e* 264.

Preparation of Keto Sulfoxides. The benzoyl sulfide was dissolved in acetone, and 1 equiv of 30% hydrogen peroxide was added slowly behind a safety shield. The reaction was stirred overnight. After workup, products were recrystallized from ether–chloroform mixtures.

β-(Butylsulfinyl)propiophenone: mp 78 °C; IR ($CHCl_3$) 1695, 1225, 1025 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–1.9 (m, 4 H), 2.5–3.5 (m, 6 H), 7.3, 7.8; *m/e* 238.

γ-(Butylsulfinyl)butyrophenone: mp 47 °C; IR ($CHCl_3$) 1698, 1225, 1030 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–2.0 (m, 4 H), 2.2 (m, 2 H), 2.7 (m, 4 H), 3.2 (t, 2 H), 7.3, 7.8; *m/e* 252.

δ-(Butylsulfinyl)valerophenone: mp 79 °C; IR ($CHCl_3$) 1695, 1010 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–2.0 (m, 8 H), 2.6 (t, 4 H), 3.8 (t, 2 H), 7.3, 7.8; *m/e* 266.

δ-(Phenylsulfinyl)valerophenone: mp 60 °C; IR ($CHCl_3$) 1698, 1050 cm^{-1}; NMR δ 1.8 (m, 4 H), 2.9 (m, 4 H), 7.3 (m, 8 H), 7.8; *m/e* 286.

Preparation of Keto Sulfones. A large excess of 30% hydrogen peroxide was added behind a safety shield to either the benzoylsulfide or -sulfoxide in glacial acetic acid. The mixture was allowed to stir for 1–2 days. Following extraction into chloroform and normal workup, the products were recrystallized from ether–chloroform mixtures.

β-(Butylsulfonyl)propiophenone: mp 116 °C; IR ($CHCl_3$) 1695, 1315, 1225, 1125 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–2.0 (m, 4 H), 3.0 (t, 2 H), 3,4 (m, 4 H), 7.3, 7.8; *m/e* 254.

γ-(Butylsulfonyl)butyrophenone: mp 65 °C; IR ($CHCl_3$) 1695, 1300, 1125 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.2–2.5 (m, 6 H), 2.8 (m, 6 H), 7.3, 7.8; *m/e* 268.

δ-(Butylsulfonyl)valerophenone: mp 66 °C; IR ($CHCl_3$) 1695, 1305, 1150 cm^{-1}; NMR δ 0.9 (t, 3 H), 1.5–2.1 (m, 8 H), 3.0 (m, 6 H), 7.4, 7.8; *m/e* 282.

δ-(Phenylsulfonyl)valerophenone: mp 90 °C; IR ($CHCl_3$) 1695, 1305, 1150 cm^{-1}; NMR δ 1.9 (m, 4 H), 3.0 (m, 4 H), 7.3 (m, 8 H), 7.2; *m/e* 302.

δ-(Thioacetoxy)valerophenone was prepared by the free-radical addition of thiolacetic acid to 4-benzoyl-1-butene. A twofold excess of the acid and the benzoylbutene were dissolved in benzene containing a pinch of benzoyl peroxide; the mixture was refluxed overnight. After workup, the product was recrystallized from ethanol: mp 63 °C; IR ($CHCl_3$) 1690, 1220 cm^{-1}; NMR δ 1.7 (m, 4 H), 2.2 (s, 3 H), 2.9 (m, 4 H), 7.3, 7.8; *m/e* 236.

δ-(Thiocyanato)valerophenone was prepared by heating a mixture of δ-chlorovalerophenone and 10% excess potassium thiocyanate in DMF at 80 °C for 24 h. After being distilled, the product was recrystallized from hexane, mp 47.5–48.5 °C; IR ($CHCl_3$) 2150, 1690 cm^{-1}; NMR δ 1.4–2.0 (m, 4 H), 2.7 (t, 2 H), 3.1 (t, 3 H), 7.3, 7.8; *m/e* 219.

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Radical Cleavage and Competing Photoreactions of Phenacyl Sulfides

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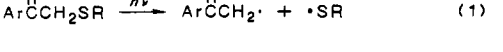
Abstract: The photochemistry of ketones with the structures $PhCOCH_2SR$, $PhCOCH_2S(O)R$, $PhCOCH_2SO_2R$, and *p*-X-$PhCOCH_2SPh$ has been studied. They all give primarily acetophenone as product when irradiated in the presence of benzenethiol, which traps free phenacyl radicals formed by excited state β-cleavage. The sulfur-centered radicals give coupling products. The maximum quantum yield for this β-cleavage is 0.40; apparently 60% of the initially formed radical pairs undergo in-cage reaction. When R = methyl or butyl, some acetophenone is formed by γ-hydrogen abstraction as well. Alkyl substituents on the α-carbon enhance the disproportionation reactions of the phenacyl radicals. Measurements of quantum yields and triplet lifetimes (by Stern–Volmer quenching of acetophenone formation) allowed determination of rate constants for β-cleavage as follows: PhS, 10^{10}–10^{11}; MeS(O), 6×10^9; BuS, 1.5×10^8; $BuSO_2$, 1×10^7 s^{-1}. Ring substituents increase triplet lifetimes. Absorpton and phosphorescence spectra indicate that the n,π* and π,π* transitions both involve some population of the C–S σ* orbital. This mixing, together with the free spin density on the excited carbonyl carbon, appears to determine the rate constant for cleavage. Radical cleavage is also very fast and efficient for *p*-((phenylthio)methyl)acetophenone.

A common photoreaction of ketones containing good radical leaving groups on the α-carbon is β-cleavage.[1] Although there are several isolated reports of phenacyl sulfides cleaving to radicals photochemically,[2-7] there has been no systematic study reported of how structural variation affects this photoreaction. Since our related investigation of internal charge transfer in triplet ketosulfides revealed that β-cleavage competes with the other triplet reactions of phenacyl sulfides,[8] we have studied the quantitative effect of ring- and α-substituents, and of sulfur oxidaton state, on this cleavage.



$$ArCCH_2SR \xrightarrow{h\nu} ArCCH_2\cdot + \cdot SR \qquad (1)$$

Results

Three separate sets of sulfur-containing ketones were synthesized and studied: (1) phenacyl alkyl sulfides, sulfoxides, and sulfones (compounds **1–7**); (2) ring-substituted phenacyl phenyl sulfides (compounds **8-X**); and (3) α-substituted phenacyl phenyl sulfides (**8–14**). Each group was characterized spectroscopically and kinetically.

Photoproducts. The first group gives acetophenone as well as the dibenzoylethane already reported.[4,6] In the presence of sufficient added benzenethiol, the yields of acetophehone are enhanced

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