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.

Acknowledgment. This work was supported by the National Science Foundation.

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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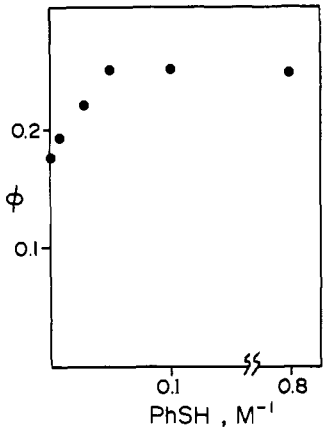


Figure 1. Effect of added benzenethiol on quantum yield for acetophenone formation from phenacyl phenyl sulfide **8**.

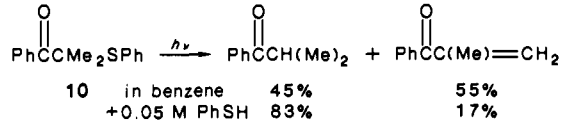
Table I. Photokinetic Data for Various Phenacyl Sulfides, Sulfoxides, and Sulfones $PhCOCH_2$–SZ[a]

compound	SZ	Φ_{-K}	Φ_p[b]	Φ_{max}[c]	$k_q\tau$[d]	$1/\tau$[e]
1	SCH_3	0.41	0.28	0.35	2.1	2.9
2	S-*n*-Bu	0.48	0.43	0.53	1.6	4.8
3	S-*t*-Bu		<0.001	0.04	3.9	1.5
4	$SOCH_3$		0.11	0.44	1.0	6.0
5	SO-*t*-Bu		0.15			
6	SO_2-*n*-Bu		0.20	0.24	214.	0.029
7	SO_2-*t*-Bu		0.08	0.17		

[a] Values reported represent averages of duplicate measurements, reproducibility ±5%. [b] Acetophenone formation in 1 M dioxane. [c] Acetophenone formation with 0.05 M benzenethiol. [d] M^{-1}. [e] 10^9 s^{-1}; $k_q = 6 \times 10^9$ M^{-1} s^{-1}.

such that it accounts, within experimental error, for all reacted ketone. Figure 1 displays the expected dependence on thiol concentration, the plateau indicating that all free phenacyl radicals have been trapped.[9] No thietanol could be detected, as has been reported previously.[3,5,10]

The second group gives only (substituted) acetophenones and disulfide in the presence of benzenethiol concentrations ≥0.05 M, with the material balance for the former accounting for all reactant disappearance. The third group gives good yields of monoketone products even in the absence of added thiol, yields that increase as the carbon bearing the SPh group becomes increasingly substituted. NMR analysis of a sample of **10** irradiated to high conversion showed that the proportion of saturated and unsaturated ketone products is changed by the addition of thiol.



Photokinetics. All reactions were run in benzene. For the quantitative measurement of product formation, degassed samples containing 0.1 M ketone and any additives were irradiated at 313 nm to 5–10% conversion. Yields of (substituted) acetophenone relative to 0.01 M hexadecane internal standard were then measured by GC analysis. Valerophenone actinometry[11] was employed for the measurement of quantum yields. Quenching studies were performed at room temperature with added 1-methylnaphthalene and 366-nm irradiation. In all cases where quenching was observed, Stern–Volmer plots were linear out to the largest Φ°/Φ values that were measured (usually at least 5); their slopes provided $k_q\tau$ values. Lifetimes were calculated on the basis of $k_q = 6 \times 10^9$ M^{-1} s^{-1}.[12] For many of the ketones, no quenching could be observed even with 2 M quencher. Ketone disappearance was measured at 20–30% conversion relative to eicosane internal standard. All the data are listed in Tables I–III as averages of duplicate measurements. Attempts to measure intersystem crossing yields by sensitized diene isomerization[13] were unsuccessful because of radical addition to the dienes.

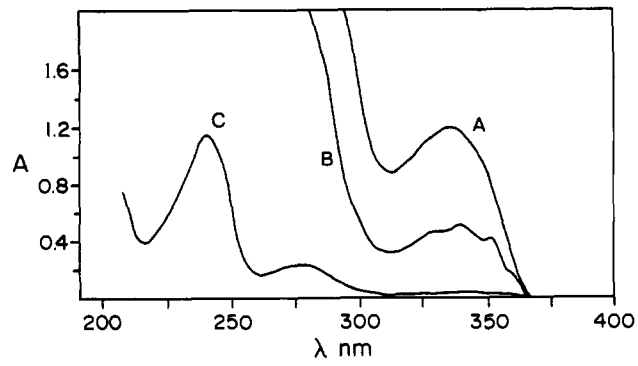


Figure 2. Absorption spectra of 1-phenyl-3-thia-1-heptanone (2): A, 0.0018 M in ethanol; B, 0.0014 M in heptane; C, 0.00014 M in heptane.

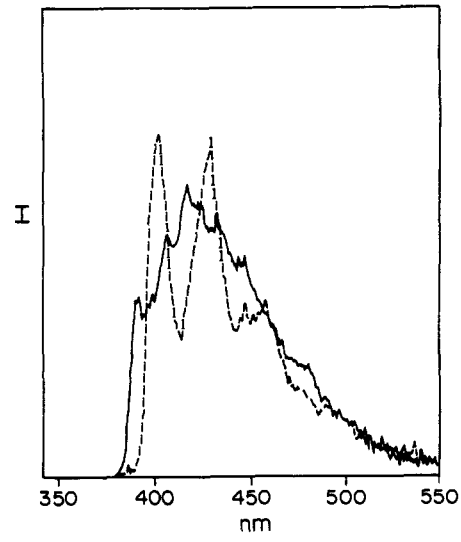


Figure 3. Phosphorescence spectra of **2** (dashed) and **8** (solid) in MTHF at 77 °K.

Spectroscopy. Uv spectra of the various phenacyl sulfides were measured in heptane. That for 1-phenyl-3-thia-1-heptanone (**2**) is typical and is shown in Figure 2. The n,π^* band shows distinct fine structure, which is blurred in ethanol. Phosphorescence spectra were measured in methyl–THF at 77 °C; triplet energies (E_T) were determined from the 0,0 bands. All of the thioalkoxy ketones showed sharp emission characteristic of n,π^* triplets, with a 0–0 band at 404 nm (70.9 kcal/mol), whereas all of the thiophenoxy ketones showed broad emission characteristic of π,π^* lowests triplets (Figure 3). All of the measured transition energies for compounds **8-X** are listed in Table II.

Discussion

The results indicate that the β-ketosulfides, -sulfoxides, and -sulfones all undergo excited state radical cleavage to generate α-keto radicals and sulfur-centered radicals. The former are trapped efficiently by benzenethiol, while the latter mainly couple. The reactions proceed at least partially from triplet states but are so rapid as to be quenched with difficulty. We shall discuss in turn competition with other excited state reactions, variations in the rate constants for cleavage, and the nature of the reactive excited state.

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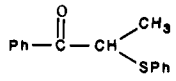
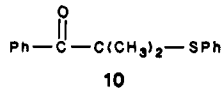
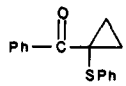
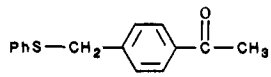
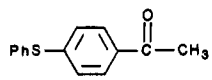
Table II. Effects of Para Substituents on Photocleavage of Phenacyl Phenyl Sulfides X-Ph-$COCH_2SPh$ (**8-X**)[a]

X	^1L_a[b]	$^1n,\pi^*$[b]	E_T[c]	Φ[d]	Φ_{max}[e]	$k_q\tau$[f]	$1/\tau$[g]
H	246	341	73.5	0.08	0.24[h]	UQ[i]	>20.
F				0.05	0.24	UQ	>20.
Cl				0.05	0.24	0.8	5.
Br				0.02	0.20	2.0	3.
CN	248	355	68.4	0.04	0.16	1.1	5.5
Me				0.05	0.30	UQ	>20.
OMe	257	336	70.4	0.09	0.41	2.2	2.7
SMe	307	340[j]		0.04	0.19	30.	0.2
NMe_2	325	330[j]	62.6	0.07	0.19	14.	0.5
Ph				0.05	0.27	40.	0.15

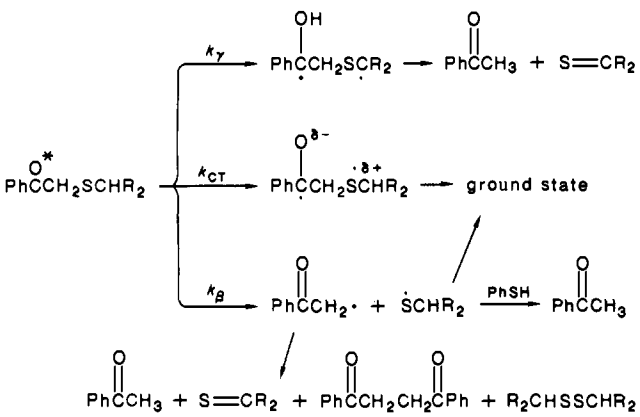
[a] Benzene solutions 0.1 M in ketone, 313 nm. [b] Absorption λ_{max}, nm. [c] 0-0 phosphorescence band, kcal/mol. [d] (Substituted) acetophenone formation. [e] With 0.05 M benzenethiol. [f] Methylnaphthalene quencher, 365 nm. [g] 10^9 s^{-1}, $k_q = 6 \times 10^9$ M^{-1} s^{-1}. [h] Quantum yield for disappearance of reactant = 0.26. [i] Unquenched by 2 M naphthalene. [j] Buried under ^1L_a band, estimated by comparison of fine structure with parent ketone.

Table III. Photochemistry of Some Substituted Phenacyl Phenyl Sulfides[a]

compound	Φ[b]	Φ_{max}[c]	Φ_{-k}	$k_q\tau$[d]
 **9**	0.20	0.32	0.31	<0.1[e]
 **10**	0.33	0.34	0.35	<0.1[e]
 **11**	0.14	0.42		1.4
 **12**	0.11[f]	0.40		<0.1[e]
 **13**		0.001		

[a] In benzene, 0.1 M ketone, 313 nm. [b] Phenyl alkyl ketone formation. [c] With 0.05 M benzenethiol. [d] Methylnaphthalene quencher, 365 nm. [e] Unquenched by 2 M naphthalene. [f] *p*-Methylacetophenone formation.

Competition between β-Cleavage and Type II Cleavage. As discussed in our accompanying paper,[8] ketosulfides in general undergo two competitive intramolecular triplet reactions: CT quenching and γ-hydrogen abstraction. These β-keto sulfides undergo β-cleavage only to the extent that its rate competes with those of the other two reactions. Fortunately, all three rate constants can be extracted from the data in Table I.



The acetophenone product can arise from three separate pathways: γ-hydrogen abstraction followed by biradical cleavage,[14] β-cleavage followed by radical-radical disproportionation[9a] and β-cleavage followed by trapping of the phenacyl radicals. The thio-*tert*-butoxy compound **3** cannot react by the first two paths and forms very little acetophenone compared to the other two thioalkoxy compounds. The trapped quantum yield of 0.04 thus represents all of the phenacyl radicals that escape the original solvent cage following β-cleavage. Since several of the ketones that we have studied give maximum trapped quantum yields of 40% (Table III), we conclude that only 40% of the initial radical pairs diffuse apart in competition with in-cage reaction. Similar percentages have been determined for other triplet radical pairs.[9] By dividing the trapped yield by 0.4, we conclude that β-cleavage accounts for 10% of the total triplet decay rate of **3**, for a rate constant k_β of 1.5×10^8 s^{-1}. The remainder of the triplet decay is assigned to charge-transfer quenching and is discussed in the accompanying paper.[8]

Table IV. Rate Constants for Triplet State Reactions[a]

compd	$1/\tau$[b]	k_β[c]	k_γ[d]	k_{CT}[d]
1	29	1.5[e]	14	13.5[e]
2	48	1.5[e]	33	13.5[e]
3	15	1.5	0	13.5
4	60	54.	<1.	6
6	0.29	0.10	0.02	0.17
8	>100	>100		
11	43	43		
8-MeO	27	27.		
8-CN	55	22		33
8-SCH_3	2.0	1.0		1.0
8-Ph	1.5	1.0		0.5

[a] All in units of 10^8 s^{-1}. [b] From Tables I-III. [c] $\Phi_{max}/0.4\tau$. [d] See text. [e] Assumed the same as in **3**.

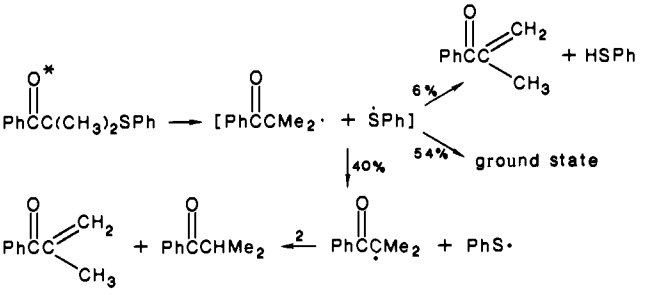
The majority of the acetophenone from **1** and **2** must arise by type II elimination. Addition of the radical trap benzenethiol causes **1** to form 7% more acetophenone, and **2** 10% more, than are formed in the absence of the radical trap. This extra acetophenone is concluded to represent the β-cleavage that does compete with hydrogen abstraction. Rate constants k_β for **1** and **2** calculated as just described equal 5 and 12×10^8 s^{-1}, respectively, much higher than for **3**. We feel that these latter two values are not very accurate, since they contan the errors associated with subtraction of large numbers. Moreover, if any of the three thioalkoxy groups were to cleave faster than the others, we would expet it to be the largest one (on **3**), which in fact has the smallest measured rate. Therefore we assume that **1** and **2** have the same values of k_β and k_{CT} as does **3** and that variations in triplet lifetimes reflect different values of k_γ. All the numbers are listed in Table IV; the k_γ values are discussed below.

Effect of Sulfur Oxidation State on β-Cleavage. Table IV also contains rate constants for the three competing reactions of the keto sulfoxides and sulfones, calculated as just discussed. The behavior of **5** and **7** indicates that acetophenone formation now occurs primarily by β-cleavage rather than by γ-hydrogen abstraction, despite an early suggestion to the contrary.[6] In fact, there is no evidence for γ-hydrogen abstraction in the keto sul-

(14) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

foxide **4**. As will be discussed below, oxidation of the sulfur decreases both k_γ and k_{CT} tremendously. However, the RS(O) radical is eliminated much more rapidly than either RS or RSO_2, such that β-cleavage becomes the dominant reaction for the keto sulfoxides and a major reaction for the keto sulfones. Our findings here and for δ-substituted ketones reinforce all the evidence cited by Kice that sulfinyl radicals cleave much faster than thiyl or sulfonyl radicals.[15]

Effect of α-Substitution on β-Cleavage. Table III lists the quantum yields for a group of thiophenoxy-substituted ketones, most of which cleave in high quantum yield. For the four α-substituted ketones **8–11**, the yield of product ketone in the absence of any added trapping agent increases sharply with α-alkyl substitution. Addition of benzenethiol does not change the total yield of ketone product from **10** but does increase the ratio of saturated vs. unsaturated ketone. These observations indicate that the more substituted α-keto radicals undergo more disproportionation. Of course, disproportionation can proceed by reaction both of two α-keto radicals and of one α-keto radical with a thiyl radical. The quantum yield for formation of unsaturated product from **10** is only 6% in the presence of added thiol vs. 18% in its absence. The 6% must represent in-cage disproportionation between α-keto and thiyl radicals, which presumably is accompanied by some 50–60% coupling. The extra 12% then represents the two modes of disproportionation between radicals that have escaped the initial cage.

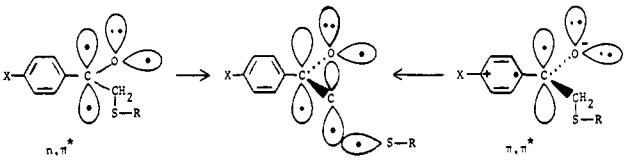


The benzenethiyl radical is cleaved so rapidly from the α-carbon that the overall reaction cannot be quenched with triplet quenchers, except in the case of the cyclopropyl ketone **11**. In this case, quenching indicates a k_β value of 4×10^9 s^{-1}. It is not unexpected that a cyclopropyl radical would be formed the least rapidly; it is remarkable that even the unsubstituted phenacyl radical is formed with $k_\beta > 10^{10}$ s^{-1}. Our independent work on δ-substituted ketones indicates that PhS is cleaved 1000 times more rapidly than is BuS,[8] so the rate constant could be as high as 10^{11} s^{-1}.

It is known that both ring halogens[16] and benzyl halogens[2] undergo rapid radical cleavage in various aryl ketones. Thus we were not surprised to find that **12** forms *p*-methylacetophenone in high yield in the presence of added benzenethiol, again in a very rapid excited state reaction. *p*-(Thiophenoxy)acetophenone (**13**), however, produces just a trace of acetophenone. In this case the lowest triplet probably contains a large charge-transfer component[17] and has intrinsically different reactivity from the ketones with weaker electron-donating substituents.

Nature of the Reactive Excited State. These phenacyl sulfides show n,π^* absorption that differs significantly from that of simple phenones such as acetophenone. The α-sulfur lowers the transition energy by some 4 kcal/mol (340 vs. 325 nm) and enhances its oscillator strength by almost an order of magnitude. That the lowest energy transition is n,π^* is evident from the hypsochromic shift in ethanol. It is unusual in showing a clear vibronic progression corresponding to the known excited state carbonyl stretching frequency of $\sim$1200 cm^{-1}.[18] Other examples of this rare vibronic structure are cyclobutanone[19] and *exo*-dicyclopentadienone.[20] All of these ketones have unusually large n,π^* extinction coefficients, such that only a small fraction of the intensity involves the rotational mixing that normally causes featureless n,π^* transitions.

It is well-known that α-heteratom substitution intensifies and shifts ketone n,π^* transitions.[21] The effect is believed to involve mixing of the carbonyl π^* and C–X σ^* orbitals, with the C–X bond parallel to the carbonyl π-orbital. The C–X bond becomes a partial acceptor of the excited n-electron density. The simplest picture of β-cleavage from an n,π^* state would also require the C–X bond (here C–S) to be perpendicular to the carbonyl.[22] In fact, NMR evidence does indicate that α-(thioalkoxy)aldehydes exist preferentially in such a conformation.[23] Inasmuch as electron transfer to carbon–halogen bonds is known to effect rapid cleavage,[24] the partial C–X σ character in the n,π^* state weakens the C–X bond and predisposes that excited state to cleave.



Whereas both thioalkoxy and thiophenoxy substitution lower the n,π^* transition energy, only the latter affects the π,π^* transitions. Thus the ^1L_a band for **2** has its λ_{max} at 240 nm vs. 238 nm for phenyl alkyl ketones,[17] whereas the corresponding transition for **8** occurs at 246 nm with double the intensity. Mixing of the carbonyl π orbitals with both the benzene π system and the α C–S σ^* orbital would in the lowest approximation produce the same energy shift for both n,π^* and π,π^* transitions, but the actual transitions are more complicated. Since the ^1L_a transition involves ring-to-carbonyl charge transfer,[17,25] the larger effect of the thiophenoxy substituent probably reflects its better electron-accepting ability. Again, inasmuch as the C–S bond is partially weakened, π,π^* states should also show some propensity to cleave.

Those ketones whose reactions are readily quenched react primarily from their triplets. However, the α-thiophenoxy ketones undergo cleavage so rapidly that their n,π^* singles may cleave competitively with intersystem crossing. The relative energies of the n,π^* and ^1L_a singlets is relevant to the nature of the lowest triplet, since the lowest π,π^* triplet is primarily L_a,[17] and the n,π^* and π,π^* triplets of phenyl ketones are nearly degenerate.[17,26] What with exclusive n,π^* stabilization by RS, we presume that the n,π^* triplets of **1–3** lie far enough below the π,π^* triplets that the rate constants in Table IV reflect pure n,π^* reactivity. This conclusion is borne out by the characteristic vibronic structure of their phosphorescence spectra and the 2.6 kcal/mol lower E_T value relative to acetophenone. With the PhS group affording comparable stabilization of both n,π^* and π,π^* states, ring substituents should promote lowest π,π^* triplets just as for acetophenones and valerophenones.[17] In fact the phosphorescence of all the ketones in Table II lack the normal n,π^* vibronic structure, so that they all probably have lowest triplets that are π,π^*. However, the 0–0 bands correspond closely to those of the comparable valerophenones. Given the huge rate constants for β-cleavage of these ketones, it is conceivable that they themselves do not phosphoresce strongly even at 77 K but instead cleave. In that case the observed emission may in fact be from products present as impurities.

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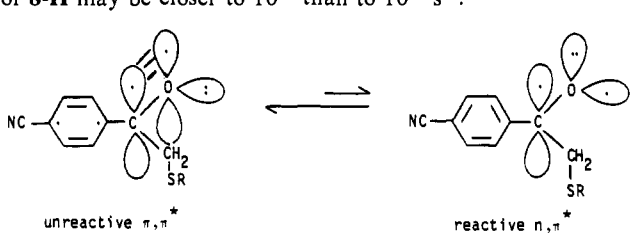
Effect of Ring Substitution on β-Cleavage. Since PhS is a worse electron donor than RS,[8] it is unlikely that charge-transfer quenching (S to C=O) would have rate constants competitive with the large k_β values for the α-thiophenoxy ketones, except possibly in the case of **8-CN**. Since the quantum yields of trapped acetophenone are mostly in the range of 0.2–0.3, whereas the α-substituted ketones in Table III and **8-MeO** give values closer to the "maximum" of 0.4, it appears that there is some competitive decay process, the nature of which is not clear. Nonetheless, the triplet decay rates in Table II must represent primarily (≥50%) k_β values.

It is clear that those ring substitutents that lower π,π* triplet energies substantially also lower rate constants for β-cleavage. Since the unsubstituted k_β value is not known, the magnitude of the rate decreases cannot be determined exactly. Therefore it is unclear to what extent, if any, the measured reactivity of these phenacyl phenyl sulfides represents reaction from small equilibrium concentrations of upper n,π* triplets, as is the case for γ-hydrogen abstraction in substituted valerophenones.[17] If that were the case here, one could apply the normal "*p*-methoxy kinetic effect"[17,27,28] of 100 to derive a k_β for **8-H** of 3×10^{11} s^{-1}. As described above, this value is three times greater than what might have been extrapolated from the behavior of n,π* α-thioalkoxyketone triplets. The slowest reacting triplets (**8-Ph** and **8-SMe**) have rate constants on the order of 1×10^8 s^{-1}, 1/3000 the value extrapolated for triplet **8-H**. These molecules undergo β-cleavage considerably more rapidly than would be the case if all reactivity came from low populations of upper n,π* triplets. Comparably substituted valerophenones show no measurable triplet reactivity but, as discussed above, probably have the same n,π*–π,π* separations, which exceed 6 kcal/mol.

The C–S bond energy in phenacyl sulfides is on the order of 55–60 kcal/mol.[29] Since all of the ketones studied have higher triplet energies, we do not consinder it likely that the rate decreases reflect the homolytic cleavage becoming somewhat endothermic as the triplet energy of the ketone decreases. We suggest tentatively that the π,π* triplets of compounds **8-X** can undergo β-cleavage directly but with variable intrinsic reactivities lower that that of n,π* states. As is well-known,[30,31] the lowest π,π* triplets of phenyl ketones have mixed character. Inasmuch as internal ring-to-carbonyl charge transfer contributes, the triplet should be reactive, as discussed above. Inasmuch as excitation is localized on the benzene ring, reactivity would be diminished. That this latter conclusion is correct is suggested by the reactivity of **8-CN**, which is comparable to that of **8-MeO**. In contrast, *p*-cyanovalerophenone is 50 times more reactive than *p*-methoxyvalerophenone in triplet γ-hydrogen abstraction,[31] which depends on n,π* population.[17] We interpret this dichotomy to mean that **8-MeO** is reacting mainly from its π,π* state, which has significant CT character, while **8-CN** reacts mainly from its upper n,π* state, since the π,π* triplet excitation is largely localized on the ring.[31] Inasmuch as this picture is correct, the actual k_β value of **8-H** may be closer to 10^{10} than to 10^{11} s^{-1}.



Substituent Effects on γ-Hydrogen Abstraction. The sulfides **1** and **2** have rate constants for triplet state γ-hydrogen abstraction about $^1/_3$ those measured for the corresponding α-alkoxy ketones[32] and show the dampened secondary/primary selectivity expected for such high reactivity. In contrast, γ-alkoxy and γ-thioalkoxy ketones have the same k_γ values,[8] which are only $^1/_6$–$^1/_{20}$ those for the α-substituted ketones. The latter are more reactive because of a substantial inductive effect on reactivity, as demonstrated by the enhanced triplet reactivity of α-fluoro ketones[33] and by the fact that triplet α-methoxybutyrophenone is five times more reactive than is triplet butyrophenone itself.[32] The difference between α-alkoxy and α-thioalkoxy reflects the greater electronegativity of oxygen.

It was concluded earlier that α-(thiobenzyloxy)acetophenone undergoes only type II elimination with no β-cleavage, and it was suggested that its short triplet lifetime reflected an internal CT interaction that facilitated γ-hydrogen transfer.[10] Our measured rate constants do verify that this ketone should undergo only a few percent β-cleavage. However, since α-thioalkoxy ketones undergo triplet γ-hydrogen abstraction more slowly than do α-alkoxy ketones, the suggestion of CT induced reaction seems incorrect. In fact, we have shown that internal CT interactions in amino ketones can *prevent* hydrogen transfer.[34]

Sulfoxide **4** and sulfone **6** undergo γ-hydrogen abstraction with rate constants much lower than in the sulfides, as expected because of the positive charges on sulfur. We cannot assign an actual rate constant to triplet **4**, but **6** is deactivated by a factor of 1750 relative to **2**. The corresponding factor for γ-sulfonyl ketones is 1760;[8] such internal consistency supports the accuracy of these measurements. The 55-fold deactivation produced by γ-sulfinyl substitution thus suggests a k_γ value for triplet **4** of 2.5×10^7 s^{-1}, only 0.5% its rate of β-cleavage.

1,4-Biradical Behavior. The addition of dioxane or other Lewis base normally increases type II quantum yields considerably[35] but produces no change in these sulfur-containing ketones. Similar behavior already has been reported for α-alkoxy ketones.[32] Therefore we conclude that the 1,4-biradicals formed from both kinds of α-hetero ketones form product in high efficiency even when not solvated. However, the thia ketones produce no detectable thietanol, whereas the oxa ketones produce primarily oxetanols. Although this disparity already has been noted,[9] it becomes even more interesting in light of recent thoughts about biradical behavior.

Originally, substituent effects on the partitioning of biradicals were interpreted as reflecting relative product energies.[36] The absence of thietanol could reeflect thermodynamic instability due to long C–S bonds, but the weak C—S double bond should also disfavor biradical cleavage. It is now thought that biradical lifetimes are determined primarily by rates of intersystem crossing[37] and that product ratios may reflect varying intersystem crossing rates for different biradical conformations.[38] α-Alkoxyacetophenones form triplet biradicals with unusually short lifetimes, presumably because of enhanced spin-orbit coupling.[39] The large amount of oxetanol formed from such ketones[32] might then reflect rapid intersystem crossing occurring from the conformation in which the biradical is formed immediately after γ-hydrogen abstraction. However, it has been known for years that triplet sulfur atoms add to alkenes with greater stereospecificity[40] than do triplet oxygen atoms,[41] and this disparity has been explained as reflecting greater spin-orbit coupling and faster intersystem crossing for the sulfur-containing 1,3-biradical. One

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might therefore expeect even more cyclization from the sulfur-containing 1,4-biradicals instead of none! It is apparent that the model relating biradical lifetimes and product partitioning is not yet complete.[42]

Summary. Triplet state β-cleavage of phenacyl alkyl sulfides is very rapid, $k_\beta = 1.5 \times 10^8$ s^{-1}. The rate is lower for the analogous sulfones but 40 times higher for the sulfoxides. These variations with sulfur oxidation state reflect known kinetic preferences for formation of sulfur-centered radicals. All of the sulfides have n,π^* lowest triplets that are stablized by coupling of the benzoyl π^* orbital with the C–S σ^* orbital. This coupling weakens the C–S bond.

The phenacyl and thiyl radicals mainly couple to give dibenzoylethanes and disulfides. The extent of disproportionation to give acetophenone increases with increasing α-alkyl substitution on the ketones. The phenacyl radicals can be trapped efficiently with added benzenethiol; maximum quantum yields of 40% suggest that approximately 60% of the initially formed radical pairs undergo in-cage coupling and disproportionation.

Triplet phenacyl phenyl sulfides cleave so rapidly that only those substituted ketones with π,π^* lowest triplets and excitation energies <70 kcal/mol react slowly enough to be quenched by triplet quenchers. The enhanced rate constants reflect both the greater kinetic stability of thiophenoxy radicals and the stabilization of π,π^* states by the α-thiophenoxy group. It is concluded that both n,π^* and π,π^* triplets are intrinsically reactive in these β-cleavage reactions, with the reactivity of the former dependent on how much free spin density resides on the carbonyl.

Experimental Section

Solvents and Additives. Solvents were purified as described in the accompanying paper.[8] Benzenethiol (Aldrich) was used as received. Various *n*-alkanes from dodecane to nonadecane, previously purified and distilled, were used as internal standards for GC analysis. Naphthalene was recrystallized from ethanol. *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 by valeryl chloride.

Preparation of Ketones. Most phenacyl sulfides were prepared by reacting the appropriate commercial phenacyl halide with the sodium salt of the appropriate thiol. The thiol was added to an ethanol solution of sodium hydroxide and stirred at room temperature for an hour. Phenacyl halide (1 equiv) was added, and the mixture was stirred overnight at room temperature. The mixture was then poured into water and extracted with ether. After normal workup, crude products were either distilled at reduced pressure or recrystallized from ethanol. The following compounds were so prepared: ^{1}H NMR spectra were taken in $CDCl_3$ and UV spectra in heptane; from their mass spectra, only the parent ions are reported.

α-(Methylthio)acetophenone: bp 80 °C (0.05 torr); IR (neat) 2900, 1695, 1360 cm^{-1}; NMR δ 2.05 (s, 3 H), 6.05 (s, 3 H), 7.3 (m, 3 H), 7.8 (m, 2 H); *m/e* 166.

α-(Butylthio)acetophenone: bp 120 °C (0.5 torr); IR (neat) 2950, 1690, 1275 cm^{-1}; NMR δ 0.9 (m, 3 H), 1.4 (m, 4 H), 2.5 (t, 2 H), 3.7 (s, 2 H), 7.3 (m, 3 H), 7.8 (m, 2 H); *m/e* 208; UV λ_{max} 340 nm (ϵ = 370), 240 nm (8200); in ethanol, 336 (630), 242 (10 400).

α-(*tert*-Butylthio)acetophenone: bp 100 °C (0.05 torr); IR (neat) 2950, 1695, 1280 cm^{-1}; NMR δ 1.3 (s, 9 H), 3.8 (s, 2 H), 7.3, 7.8; *m/e* 208.

α-(Phenylthio)propiophenone: bp 135 °C (0.05 torr); IR (neat) 3025, 1695, 1230 cm^{-1}; NMR δ 1.5 (d, 3 H), 4.5 (m, 1 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/e* 242.

α-(Phenylthio)isobutyrophenone: bp 130 °C (0.07 torr); IR (neat) 3025, 1695, 1230 cm^{-1}; NMR δ 1.5 (s, 6 H), 7.3 (m, 8 H), 7.8 (m, 2 H); *m/e* 256.

α-(Phenylthio)-2-phenylacetophenone: mp 77 °C; NMR δ 5.7 (s, 1 H), 7.2 (m, 13 H), 7.8 (m, 2 H); *m/e* 304.

α-(Phenylthio)acetophenone: mp 49 °C; IR ($CHCl_3$) 1685, 1605, 1205 cm^{-1}; NMR δ 4.2 (s, 2 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/e* 228; UV λ_{max} 341 nm (450), 246 (19 500).

α-(Phenylthio)-*p*-fluoroacetophenone: bp 150–155 °C (0.25 torr); IR (neat) 1685, 1605, 1205 cm^{-1}; NMR δ 4.05 (s, 2 H), 7.08 (m, 8 H), 7.8 (m, 2 H); *m/e* 246.

α-(Phenylthio)-*p*-chloroacetophenone: mp 65 °C; IR 1680, 1600, 1275 cm^{-1}; NMR δ 4.1 (s, 2 H), 7.1 (m, 8 H), 7.7 (m, 2 H); *m/e* 262.

α-(Phenylthio)-*p*-bromoacetophenone: mp 60 °C; IR ($CHCl_3$) 1680, 1595, 1280 cm^{-1}; NMR δ 4.1 (s, 2 H), 7.1 (m, 5 H), 7.5 (m, 4 H); *m/e* 307, 309.

α-(Phenylthio)-*p*-methylacetophenone: mp 61 °C; IR ($CHCl_3$) 1660, 1605, 1275 cm^{-1}; NMR δ 2.3 (s, 3 H), 4.1 (s, 2 H), 7.1 (m, 8 H), 7.6 (d, 2 H); *m/e* 242.

α-(Phenylthio)-*p*-methoxyacetophenone: mp 86 °C; IR ($CHCl_3$) 1670, 1600, 1265 cm^{-1}; NMR δ 3.7 (s, 3 H), 4.1 (s, 2 H), 6.8 (d, 2 H), 7.1 (m, 5 H), 7.8 (d, 2 H); *m/e* 258; UV λ_{max} 336 (650), 257 (19 600).

α-(Phenylthio)-*p*-(methylthio)acetophenone: mp 48 °C; IR ($CHCl_3$) 1670, 1590, 1095 cm^{-1}; NMR δ 2.4 (s, 3 H), 4.2 (s, 2 H), 7.1 (m, 8 H), 7.6 (d, 2 H); *m/e* 274; UV λ_{max} 307 (20 200).

α-(Phenylthio)-*p*-cyanoacetophenone: mp 65 °C; IR ($CHCl_3$) 2225, 1700, 1275 cm^{-1}; NMR δ 4.2 (s, 2 H), 7.2 (s, 5 H), 7.7 (m, 4 H); *m/e* 253; UV λ_{max} 355 (810), 248 (31 200).

α-(Phenylthio)-*p*-phenylacetophenone: mp 92 °C; IR ($CHCl_3$) 1700, 1275 cm^{-1}; NMR δ 4.2 (s, 2 H), 7.0–7.5 (m, 12 H), 7.8 (d, 2 H); *m/e* 304.

α-(Phenylthio)-*p*-(dimethylamino)acetophenone was prepared by reacting dimethylamine with β-(phenylthio)-*p*-fluoroacetophenone. This ketone (10 g) in 50 mL of xylene was placed in a pressure bomb and cooled in an ice/salt bath. Then 25 mL of anhydrous amine (Aldrich) was added; the bomb was sealed and heated at 80 °C for 24 h while being shaken vigorously. After the usual workup, pure crystals were obtained in 85% yield by recrystallization from ethanol: mp 78 °C; IR ($CHCl_3$) 1660, 1600, 1375 cm^{-1}; NMR δ 2.9 (s, 6 H), 4.1 (s, 2 H), 6.5 (d, 2 H), 7.1 (m, 5 H), 7.7 (d, 2 H); *m/e* 271; UV λ_{max} 325 (27 100).

1-Benzoyl-1-(phenylthio)cyclopropane was prepared by reacting sodium thiophenoxide with 4-chlorobutyrophenone and subsequent base-catalyzed cyclization. First, 4-chlorobutyrophenone (Eastman) was treated with bromine in acetic acid. To 100 mL of ethanol containing 28 g of the resulting 2-bromo ketone was added an equimolar amount of thiophenoxide. The solution was stirred for 4 h; 1.1 equiv of sodium methoxide were then added. After a few minutes, normal workup and recrystallization form ethanol provided a 91% yield: mp 62 °C; NMR δ 1.3 (m, 2 H), 1.7 (m, 2 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/e* 254.

***p*-((Phenylthio)methyl)acetophenone** was prepared from sodium thiophenoxide and *p*-(bromomethyl)acetophenone. The latter was prepared by a routine bromination of *p*-methylacetophenone with NBS. The displacement reaction was performed in the same manner as with the phenacyl halides. Product was recrystallized from ethanol in 95% yield, mp 91 °C; IR ($CHCl_3$) 1685, 1265 cm^{-1}; NMR δ 2.5 (s, 3 H), 4.1 (s, 2 H), 7.2 (m, 8 H), 7.7 (m, 2 H); *m/e* 242.

α-(Methylsulfinyl)acetophenone was prepared by a slight modification of the method of Corey and Chaykovsky.[43] To a slurry of 37 g potassium *tert*-butoxide in 200 mL of Me_2SO was added 50 g of ethyl benzoate dropwise. The mixture was stirred vigorously at 70 °C for 1 h and then poured into ice water containing excess HCl. Product was extracted into chloroform and worked up normally. A 70% yield was obtained after recrystallization form ether–$CHCl_3$: mp 84 °C; IR ($CHCl_3$) 1680, 1275, 1050 cm^{-1}; NMR δ 2.7 (s, 3 H), 4.3 (s, 2 H), 7.3 (m, 3 H), 7.8 (m, 2 H); *m/e* 182.

α-(Methylsulfonyl)acetophenone was prepared in the same manner as the sulfoxide except that the initial slurry contained a 10% excess of dimethylsulfone (Aldrich) relative to the ethyl benzoate. Recrystallization from ether–$CHCl_3$ afforded a 75% yield: mp 105 °C; IR ($CHCl_3$) 1695, 1325 cm^{-1}; NMR δ 3.1 (s, 3 H), 4.5 (s, 2 H), 7.3 (m, 3 H), 7.8 (m, 2 H); *m/e* 198.

Procedures are descirbed in the preceding paper.[8] The 366-nm region of a 450-W mercury arc 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. The substituted acetophenone products were identified by comparison of their retention times with those of authentic samples. Acetophenone was actually isolated by preparative GC from irradiated samples of **8-H** and identified by its spectroscopic features. For **9** and **10**, the analytical conditions used did not separate acrylophenone or α-methylacrylophenone from propiophenone or isobutyrophenone, respectively. NMR analysis of irradiated samples of **10** showed product absorbances at δ 1.6 (singlet) and 1.0 (doublet) corresponding to α-methylacrylophenone and isobutyrophenone. The ratios of the two products were determined by integration of these peaks.

Acknowledgment. This work was supported by the National Science Foundation.

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