6$^-$; $\Delta BL \simeq 0.015$ Å, $\Delta OP \simeq -0.005$ (3G), -0.015 e (4-31G) for C-OH; $\Delta BL \simeq 0.015$ Å for C-O$^-$ (the changes in OP_{C-O^-} are in the opposite direction).

(20) Compare the C-OH bond in **1**$^-$ and **2**$^-$, **4**$^-$ and **5**$^-$, **7**$^-$ and **8**$^-$; $\Delta BL \simeq 0.014$ Å. This is not apparent from the ΔOPs.

(21) Compare, for example, the C-N bond in **1**$^-$ and **4**$^-$, **2**$^-$ and **5**$^-$, **3**$^-$ and **6**$^-$; compare the C-OH bond in **1**$^-$ and **2**$^-$, **4**$^-$ and **5**$^-$, **7**$^-$ and **8**$^-$.

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(23) For example, a least motion decomposition of the least stable **2**$^+$ species into $NH_3 + CH(OH)_2^+$ gives the least stable form of the protonated formic acid (trans,trans), while the more stable conformers **3**$^+$ and **4**$^+$ can lead to the most stable (cis,trans) protonated conformer ($\Delta E \simeq 7.6$ kcal/mol[15]); similar results hold with **7**$^+$ compared to **8**$^+$ which correlate respectively with the cis and trans protonated formamide.[12]

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(27) This can result in part from the anomeric type $|X\ lp, \sigma^*_{C-Y}|$ interaction which shifts charge from the X atom to the Y group. Indeed, in the T$^+$ conformers with respectively 0, 1, and 2 oxygen lp's app to the C-N bond, the electronic charge on the NH_3 group increases respectively by about 0.04 e (3G and 4-31G) per app lp. In the T$^-$ conformers, about 0.04 e (3G and 4-31G) is dispersed from the O$^-$ atom to the hydrogen atoms of the O-H or N-H app bonds (compare, for example, **1**$^-$ and **5**$^-$).

(28) Similar stereoelectronic control of α-proton abstraction from iminium ions[29] or from ketones[30] has been recently reported: the most acid CH bond is such that the charge of the incipient carbanion can interact with the vicinal π^* orbital; delocalization of the negative charge into empty orbitals has also been shown to be an important factor in the stereoselective formation of α-oxa, α-thia, and α-seleno carbanions.[31,32]

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Unusual Kinetic Behavior in the Self-Reactions of Acyl Methyl Nitroxides[1a]

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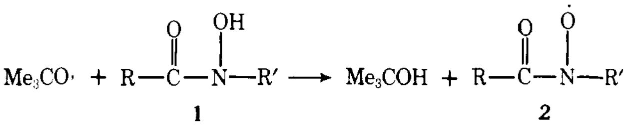
Abstract: The self-reactions of a series of acyl methyl nitroxides have been studied in solution. These reactions proceed by β-disproportionation, for which the measured rate contants lie in the range 10^1–10^3 M^{-1} s^{-1} at 298 K. Arrhenius parameters derived from the kinetic data are unusual, having low *A* factors (ca. 10^4 M^{-1} s^{-1}) and low activation energies (ca. 1–4 kcal/mol); such values indicate that the reactions do not proceed by a simple mechanism. These results are interpreted in terms of a strong dipole–dipole induced orientation within the caged radical pair which disfavors the disproportionation reaction.

Acyl nitroxides are persistent radicals which have been studied spectroscopically[2] for some years. It has recently been shown that some acyl *tert*-alkyl nitroxides may be isolated as pure materials,[7] and that such radicals have a potential synthetic role as mild oxidizing agents,[8] converting monohydric phenols to quinones and allylic alcohols to aldehydes. Thus, vitamin A alcohol can be oxidized to retinal by *tert*-butyl undecanoyl nitroxide in ca. 90% yield.[8b]

There are also strong indications that acyl nitroxides play a significant role in biological environments.[9] For example, it has been suggested that acyl aryl nitroxides are the active reagents formed in the metabolic transformation of certain carcinogenic amines.[10] This proposal has recently given cause for concern[11] since hydroxamic acids are used widely in chemotherapy and are easily oxidized to the corresponding acyl nitroxides.

As part of our general investigations of fundamental chemistry in this area we have now undertaken a kinetic study of the self-reactions of acyl methyl nitroxides, **2a–f**, in an attempt to understand the reasons for their persistence. The radicals were generated from the corresponding hydroxamic acids (**1a–f**) using *tert*-butoxy radicals which were produced by UV photolysis of di-*tert*-butyl peroxide.

$$\mathrm{Me_3COOCMe_3} \xrightarrow{h\nu} \mathrm{2Me_3CO\cdot} \qquad (1)$$

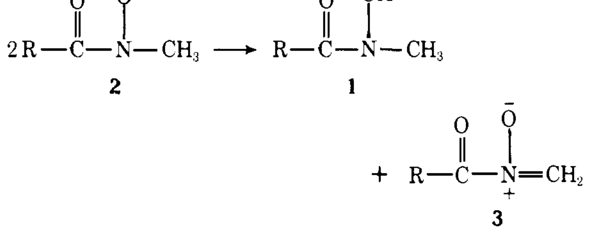


$$\mathrm{Me_3CO\cdot} + \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OH}{|}}{N}{-}R'} \longrightarrow \mathrm{Me_3COH} + \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle \dot{O}}{|}}{N}{-}R'}$$

1 **2**

1a, **2a**, R = *n*-hexyl; R' = CH_3 (2)
1b, **2b**, R = *sec*-butyl; R' = CH_3
1c, **2c**, R = *sec*-butyl; R' = CD_3
1d, **2d**, R = *tert*-butyl; R' = CH_3
1e, **2e**, R = 1-adamantyl; R' = CH_3
1f, **2f**, R = $(CH_3CH_2)_3C$; R' = CH_3

Our results show that compounds **2** decay by a comparatively slow bimolecular disproportionation to yield **1** and the corresponding nitrone **3**, e.g.



$$2\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle \dot{O}}{|}}{N}{-}CH_3} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OH}{|}}{N}{-}CH_3} + \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle \bar{O}}{|}}{\underset{+}{N}}{=}CH_2} \qquad (3)$$

2 **1** **3**

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The slowness of these radical-radical reactions does not arise because reaction 3 has an appreciable activation energy. Instead, there is a very low probability that two radicals forming an encounter pair will actually react with one another. We suggest that this comparatively unusual behavior in a radical-radical reaction is a consequence of the dipole-dipole interaction between the >N-O· groups of the encounter pair. Presumably this interaction disfavors orientations of the radicals which lead to reaction.

Experimental Section

Materials. Most of the hydroxamic acids were prepared from *N*-methylhydroxylamine and the appropriate acyl chloride using standard procedures.[12] They were generally purified by column chromatography over silica. Their mass spectra all showed a peak due to the parent ion and all **1** gave satisfactory NMR spectra[13] and elemental analysis.[13] Compounds **1e** and **1f** were kindly provided by A. H. Sharma.

The deuterated hydroxamic acid **1c** was prepared as follows. A mixture of *O*-benzylhydroxylamine hydrochloride (10 g) and α-methylbutyryl chloride (7.6 g) in pyridine (30 mL) was briefly heated to 60 °C, then cooled and quenched with ice water. On workup *N*-α-methylbutyryl-*O*-benzylhydroxylamine was obtained in 77% crude yield as a colorless solid. A portion of this unpurified material was methylated with CD_3I and sodium hydride in dry dimethoxyethane. The product was then hydrogenated over 10% Pd/C in ethanol under 1 atm of hydrogen. This gave **1c**, which was purified in the usual way.

Solvents were either reagent grade and were used as received or were distilled before use. Di-*tert*-butyl peroxide was distilled and was then passed through alumina in order to remove any traces of *tert*-butyl hydroperoxide.

Kinetic Procedure. The kinetic EPR procedure has been described previously.[14] Samples were prepared in standard EPR tubes using a stock solution containing 20–25 mg of the appropriate hydroxamic acid, solvent (1.5–2 mL), and di-*tert*-butyl peroxide (7% v/v). They were deoxygenated using the usual "freeze-thaw" degassing procedure. Samples were irradiated with UV light for a few seconds, to generate nitroxide concentrations in the range $10^{-4.5}$–$10^{-7.0}$ M, and were then shaken in order to ensure uniform radical distribution. They were placed in the spectrometer and equilibrated to the operating temperature before measurements were made.

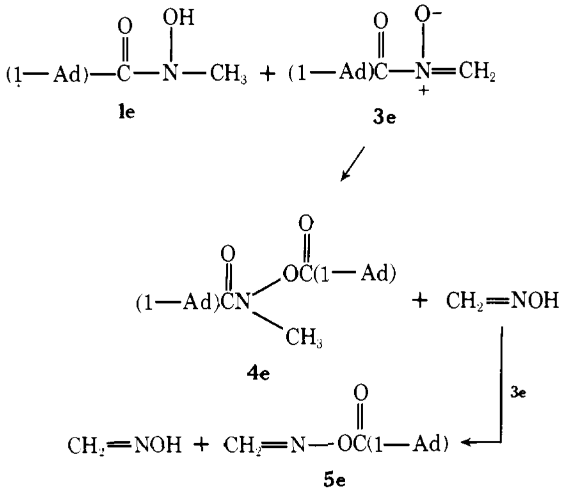
EPR Parameters. Spectroscopic parameters for radicals **2a–f** were obtained from measurements of the magnetic field position and microwave operating frequency for several lines of each spectrum. Solution of the isotropic Hamiltonian based on these data yielded *g* values and hyperfine splittings. This procedure has been described in greater detail elsewhere.[15]

Results and Discussion

Radical generation via reactions 1 and 2 is a standard and well-tested procedure.[16] The hydroxamic acids all gave clean EPR spectra of the corresponding acyl methyl nitroxides, the spectroscopic parameters for which are presented as supplementary material.

Radical decay via reaction 3 is supported by the following kinetic evidence: (a) decay occurred with "clean" second order kinetics; (b) rate constants were independent of the initial concentrations of radical, hydroxamic acid, and di-*tert*-butyl peroxide, when the concentration of each was changed by a factor of 10 or more; (c) the decay kinetics for the **2b**, **2c** pair of radicals show a large deuterium kinetic isotope effect; (d) no evidence was found for the formation of measurable quantities of nitroxide dimer in the temperature and concentration ranges studied.

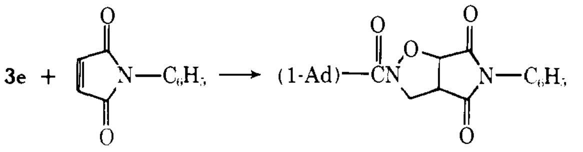
The products of the bimolecular self-reactions of **2** are difficult to identify because the nitrones, **3**, are extremely reactive. However, they do behave as powerful acylating agents which does allow *their* products to be identified. Thus, one-electron oxidation of *N*-methylhydroxamic acids[17,18] yields the *O*-acyl derivatives, **4**, and, in some cases, the *O*-acyloximes, **5**, have also been isolated. These two classes of compounds are formed by acylation of the hydroxamic acid and the oxime, respectively, e.g., eq 4 and 5.



$$(1\text{-Ad})C(=O)N(OH)CH_3 + (1\text{-Ad})C(=O)\overset{+}{N}(O^-)=CH_2 \rightarrow (1\text{-Ad})C(=O)N(OC(=O)(1\text{-Ad}))CH_3 + CH_2=NOH \quad (4)$$

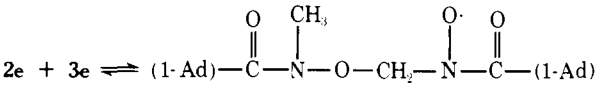
$$CH_2=NOH + CH_2=N-OC(=O)(1\text{-Ad}) \quad (5)$$

This general mechanism is supported by the observation[18] that addition of nucleophiles (including other oximes) to the reaction mixtures gives the corresponding acyl derivatives. Moreover, when the reaction is carried out in the presence of *N*-phenylmaleimide, the nitrone itself is trapped to give the cycloadduct **6**, e.g.,[18] eq 6.



6e (6)

Finally, the nitrone can act as a spin trap for the acyl nitroxide when oxidation of the hydroxamic acid is carried out to high conversion using alkaline $K_3Fe(CN)_6$ at 25 °C as oxidant.[18,19] Under these conditions the EPR signals due to **2** and **7** are observed, e.g., eq 7.



$$\mathbf{2e} + \mathbf{3e} \rightleftharpoons (1\text{-Ad})-C(=O)-N(CH_3)-O-CH_2-N(O\cdot)-C(=O)-(1\text{-Ad}) \quad (7)$$

7e

All this evidence supports our conclusion that the bimolecular self-reaction of acyl methyl nitroxides can be represented by reaction 3.

Arrhenius parameters for the decay of **2a–f** are presented in Table I. The errors given for *E* correspond to one standard deviation, while those for the *A* factor include an allowance for the error involved in measuring the absolute radical concentrations. Individual rate constants at specific temperatures are available as supplementary material.

Arrhenius parameters for the self-reactions of **2** show the following features: (a) the measured *A* factors are substantially lower than those normally found for radical-radical reactions (which are generally 10^8–10^{10} M^{-1} s^{-1});[20] (b) in two instances the observed activation energy is *less* than that expected if the reaction were diffusion controlled,[21] i.e., it is *less* than that conferred by the temperature dependence of solvent viscosity; (c) the kinetic isotope effect observed with radical pair **2b** and **2c** is approximately equal to the theoretical maximum established by classical theory;[23] (d) activation energies *increase* as the steric protection afforded by the acyl group is *increased*;[24] (e) activation energies are smaller in heptane than in toluene.

These reaction kinetics are most distinctive and are quite unusual. An obvious explanation for the low activation energies and low *A* factors would be that the H-atom transfer proceeds by quantum-mechanical tunneling. However, this seems im-

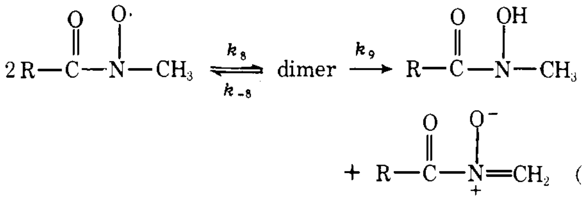
Table I. Arrhenius Parameters for the Self-Reactions of Acyl Methyl Nitroxides, RC(=O)N(O·)R′, in Toluene Unless Otherwise Noted

	radical R	radical R′	$k_3^{298\mathrm{K}}$, M^{-1} s^{-1} [a]	log (A/M^{-1} s^{-1})	E, kcal/mol
2a	*n*-hexyl	CH_3	3700	4.6 ± 0.5	1.4 ± 0.3
2b	*sec*-butyl	CH_3	390	4.2 ± 0.6	2.2 ± 0.4
2c	*sec*-butyl	CD_3	26	4.2 ± 0.6	3.8 ± 0.5
2d	*tert*-butyl	CH_3	53	4.0 ± 0.4	3.1 ± 0.3
2e	1-adamantyl	CH_3	33	3.5 ± 0.4	2.7 ± 0.3
2f	$(CH_3CH_2)_3C$	CH_3	46	4.3 ± 0.3	3.6 ± 0.2
2b	*sec*-butyl	CH_3	1200[b]	3.6 ± 0.4[b]	0.7 ± 0.3[b]
2c	*sec*-butyl	CD_3	74[b]	3.7 ± 0.6[b]	2.5 ± 0.5[b]

[a] Calculated from Arrhenius parameters. [b] In *n*-heptane as solvent.

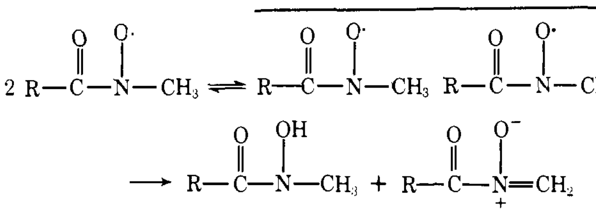
probable because authentic examples of reactions proceeding by quantum-mechanical tunneling are characterized by A_D/A_H ratios *much* greater than unity and by kinetic isotope effects, k_H/k_D, significantly larger than the "classical" maximum.[25] Neither of these phenomena is observed with the acyl methyl nitroxides.

Low activation energies and low A factors *can* also arise in radical-radical reactions if the radicals are in equilibrium with a dimer which can decay irreversibly, i.e., eq 8 and 9. Under



$$2\,\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O\cdot}{|}}{N}{-}CH_3} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \text{dimer} \xrightarrow{k_9} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OH}{|}}{N}{-}CH_3} + \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\underset{+}{\overset{\overset{O^-}{|}}{N}}{=}CH_2} \qquad (8), (9)$$

such conditions the measured rate constant for radical decay is a composite rate constant. In particular, if $2k_8[\mathrm{RCON(\dot{O})CH_3}]/k_{-8} < 1$, the observed decay will proceed with second-order kinetics and $k_3(\text{apparent}) = k_9k_8/k_{-8}$. This type of kinetic scheme has been applied to the self-reactions of certain iminoxy radicals[26] and has also been invoked to account for the low A factors and low activation energies observed in the bimolecular self-reaction of dialkyl nitroxides.[14,27] We believe that it also applies to the acyl methyl nitroxides examined in this work. However, we suggest that the "dimer" does not involve a species having a formal chemical bond between the two acyl nitroxide radicals. All that is actually required, kinetically, is that there be only a low probability that the encounter pair of radicals within a solvent cage assume a configuration suitable for chemical reaction. Such a situation does not require the formation of a chemical bond. It could also be produced by a dipole-dipole interaction which holds the caged pair of radicals in an orientation which does not allow the β-disproportionation reaction to occur.



$$2\,\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O\cdot}{|}}{N}{-}CH_3} \rightleftharpoons \overline{\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O\cdot}{|}}{N}{-}CH_3\quad R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O\cdot}{|}}{N}{-}CH_3}}$$
$$\longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OH}{|}}{N}{-}CH_3} + \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\underset{+}{\overset{\overset{O^-}{|}}{N}}{=}CH_2} \qquad (10)$$

Though the following picture is undoubtedly an oversimplification, we suggest that the actual radical decay reaction can be viewed as occurring only in those rare encounters which bring the two radicals directly together in some highly specific mutual orientation in which β-disproportionation can occur. In this "reactive" orientation there is a small but significant activation energy for H-atom transfer and, naturally, a larger activation energy for D-atom transfer—hence the kinetic isotope effect. However, in the same solvent the probability of a "reactive" orientational encounter will be the same for the normal and for the deuterated radical and hence $A_H = A_D$. The vast majority of radical-radical encounters occur with "unreactive" orientations and such orientations are maintained by strong dipole-dipole forces not only as the radicals approach one another, but also while they remain in close encounter within the solvent cage, and as they diffuse apart once again. That is, reorientation of an "unreactive" to a "reactive" orientation does not easily occur within the solvent cage. The degree of solvation of the radicals could influence (1) the probability that an encounter will occur along a "reactive" orientation and (2) the activation energy for reaction in such encounters. Furthermore, solvent viscosity could affect the number of encounters and the lifetime of the encounter pair. For these reasons, the effect that a change in the solvent would have on the rate constant and Arrhenius parameters for decay cannot, a priori, be predicted. In fact, it is even questionable if the Arrhenius parameters should be interpreted in simple terms since the "solvation" of these nitroxide radicals even in a single solvent will be dependent on the solvent density and hence on the temperature.[28] For this reason, we are not disturbed by activation energies for decay that in some cases[29] are less than the activation energy for diffusion.

A similar picture can be applied to the bimolecular decay of dialkyl nitroxides. These are comparatively slow reactions that also have low A factors and low activation energies.[14,27,29] In addition, there was evidence of "dimer" formation at low temperatures.[14,27,28,30,31] However, the experimental observations are quite consistent with a "dimer" formed by dipole-dipole forces and, in fact, ΔH for "dimer" formation is of the magnitude expected for such an interaction.[31] That is, we would now argue that the Arrhenius parameters obtained for the bimolecular decay of dialkyl nitroxides arise because nitroxide radicals have large dipole moments[31,32] rather than because a chemically bonded dimer is produced. A similar model may apply to other dipolar radicals which undergo slow bimolecular self-reactions.

In conclusion, the present work emphasizes once again that radical-radical reactions show far more diverse and interesting chemistry and kinetics in solution than do radical-radical reactions in the gas phase. This can be attributed partly to the fact that very few classes of radicals have as yet been carefully examined in the gas phase and partly to the fact that there is no gas-phase techniques which has anything like the power and versatility of kinetic EPR spectroscopy. We hope that the unusual kinetic behavior of acyl methyl nitroxides in solution will stimulate studies of these radicals in the gas phase.

Acknowledgment. We thank NATO for the award of a Research Grant which made this collaboration possible.

Supplementary Material Available: A list of NMR parameters and elemental analyses for hydroxamic acids **1a–f** and tables of rate constants at different temperatures for the self-reactions of acyl nitroxides **2a–f** (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) In this paper we focus attention upon *N*-acyl *N*-alkyl nitroxides.[3] However, simple acyl,[4] acyl aryl,[5] and diacyl[6] nitroxides have been characterized by EPR spectroscopy.

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Hydrogen Abstraction by Biradicals. Reactions with Tri-*n*-butylstannane and Octanethiol

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Abstract: The biradicals generated in the Norrish type II reaction abstract hydrogen atoms from mercaptans and Bu_3SnH with rate constants of 9×10^6 and 1.1×10^6 M^{-1} s^{-1}, respectively (for the biradical from γ-methylvalerophenone). The data from competitive and time-resolved experiments are in excellent agreement. The results suggest that the reactivity of radical sites in biradicals is identical with that of the same sites in monoradicals.

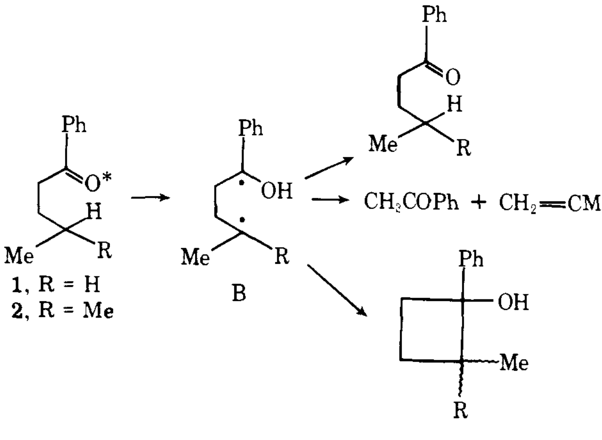
Introduction

Triplet-derived biradicals produced in the Norrish type II reaction have been the subject of several recent studies.[3-10] The first trapping studies were reported in 1972 and involved the abstraction of hydrogen atoms from mercaptans;[3] these studies also led to the first estimate of biradical lifetimes. While mercaptans proved to be excellent biradical scavengers because of their high reactivity toward radical centers and low reactivity toward carbonyl triplets,[11] they also led to considerable uncertainty in the biradical lifetimes because of the unusually large spread in the reported values for the rate constants for the reactions of S–H bonds with carbon-centered radicals.[12] The direct detection of biradicals[7,13] offers now the possibility of a direct, time-resolved measurement of their rates of reaction with mercaptans.

In this paper we report the results of a laser flash photolysis study of the reactions of biradicals generated in the Norrish type II reaction of phenyl alkyl ketones with octanethiol and tri-*n*-butylstannane. We have been able to establish that (a) biradicals react in hydrogen-abstraction reactions with the same rate constants as monoradicals having the same reactive center; (b) the biradical lifetimes obtained from direct or competitive studies are in full agreement if the correct rates of the competitive reactions are known; and (c) we have obtained absolute rate constants for the reactions of secondary and tertiary carbon radical centers with mercaptans.

Results

Our experiments have been carried out using the biradicals generated in the Norrish type II process (reaction 1) of valerophenone (**1**) and γ-methylvalerophenone (**2**).



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