and water. After the ether extracts were dried, evaporation and recrystallization from ethanol yielded 45 g of pure **5**, mp 76.5–77.5°. All other properties were reported.[4a] Synthesis of **6**, the cyclopentadiene adduct of **5**, was described recently.[5]

New Preparation of 4,5-Methylenephenanthrylene Ketone. Pyrene was submitted to ozonolysis by the normal procedure except that the reaction was stopped at the sodium salt of 5-formyl-4-phenanthroic acid since the next step was run in an alkaline solution. A mixture of 18 g of silver nitrate, 8 g of sodium hydroxide, and 10.3 g of sodium 5-formyl-4-phenanthroate in 300 ml of 50% ethanol was stirred and refluxed for 4 hr. The silver and excess silver oxide were filtered off and washed with hot water. The filtrate and washings were acidified with hydrochloric acid and the precipitated phenanthrene-4,5-dicarboxylic acid was collected and recrystallized from ethanol, mp 277–278°; ir (KBr) 3250 (OH stretch) and 1680 cm^{-1} (conjugated acid carbonyl). The calcium salt of the phenanthrene-4,5-dicarboxylic acid was prepared by boiling to dryness a mixture of equal weights of calcium oxide and acid in water. The calcium salt mixture was pyrolyzed in 30-g batches by heating the powdered solid in a beaker which was suspended inside another beaker containing boiling benzophenone (bp 306°). The subliming yellow 4,5-methylenephenanthrylene ketone was collected in a pure state on an erlenmeyer flask containing ether which kept the flask cool by refluxing from an efficient condenser attached to the flask. The average yield from 30 g of crude calcium salt mixture was 0.5 g, mp 167–170° (mixed with authentic ketone,[2,6] 168–170°).

endo,exo-**5,8-Dimethoxy-1,4-methano-9,10-methano-1,4,4a,9,10,-10a-hexahydroanthracene (6).** In a sealed tube were placed 11.3 g of 3′,6′-dimethoxybenzonorbornadiene (**5**) and 5.6 g of dicyclopentadiene. The tube was heated at 195° for 6 hr. The resultant oil crystallized from heptane to give 8.4 g (60%) of off-white solid. Several recrystallizations from heptane gave colorless needles, mp 128–129°; ν_{KBr} 3030, 2950, 2850, 1490, 1480, 1430, 1350, 1270, 1250, 1175, 1105, 1080, 1060, 990, 910, 900, 850, 820, 795, 785, 755, 730, and 705 cm^{-1}; nmr (CCl_4) δ 6.27 (2 H, $H_{6,7}$, singlet), 5.98 (2 H, $H_{2,3}$, triplet), 3.63 (6 H, OCH_3, singlet), 3.20 (2 H, $H_{9,10}$, triplet), 2.90–2.57 (3 H, $H_{1,4,11a}$, complex), 2.19 (2 H, $H_{4a,9a}$, broad singlet), and 1.70–0.95 ppm (3 H, $H_{11s,12a,12s}$, complex).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.16; H, 7.55.

endo,exo-**5,8-Dimethoxy-1,4-methano-9,10-methano-2,3-*exo*-(4′,5′-methylenephenanthrene-11′-spiro-1″-cyclopropane)-1,2,3,4,4a,9,9a,-10-octahydroanthracene (4).** A mixture of 4 g of 4,5-methylenephenanthrylene ketone, 6 ml of 95% hydrazine, and 100 ml of absolute alcohol was refluxed with stirring for 16 hr. The reaction mixture was then cooled and the 11-hydrazo-4,5-methylenephenanthrene product collected, mp 214–215°, yield 3 g; ir (KBr pellet) 3400 and 3325 cm^{-1} (N–H stretch). 11-Diazo-4,5-methylenephenanthrene was prepared by reaction of 0.3 g of 4,5-methylenephenanthrene-11-hydrazone with 0.6 g of yellow mercuric oxide and 0.2 g of anhydrous sodium sulfate in 50 ml of ether and several drops of saturated alcoholic potassium hydroxide solution. After the mixture was shaken for 30 min in the dark, the solution was filtered and the precipitate washed several times with ether. Into the combined ether solution of 11-diazo-4,5-methylenephenanthrene and washings was dissolved 0.4 g of **6** and the solution was set aside in the dark. After 2 months at room temperature, the reaction mixture had lost most of its color and the crystalline pyrazoline had precipitated. Nmr spectrum of the crude precipitate in deuteriochloroform showed δ 7.0–8.0 (8 H, $H_{1'-3'}$, $H_{6'-10'}$, complex), 6.43 (2 H, $H_{6,7}$, singlet), 5.6 (1 H, H_2, complex doublet), 3.76 (3 H, OCH_3, singlet), 3.59 (3 H, OCH_3), 3.2 (2 H, benzylic H, complex), and 1.5 3.0 ppm (9 H, complex).

The entire solution was evaporated to dryness and the powdered residue covered with decalin. The solution was heated slowly to 160°, at which temperature the evolution of nitrogen ceased. Removal of the decalin under vacuum resulted in a red oil which was decolorized with charcoal in ethanol and recrystallized once from heptane and once from chloroform–alcohol yielding colorless cubic crystals, mp 210–211°; nmr ($CDCl_3$) δ 7.0–8.0 (8 H, $H_{1'-3'}$, $H_{6'-10'}$, complex), 6.54 (2 H, $H_{2,3}$, singlet), 3.78 (6 H, OCH_3, singlet), 3.63 (2 H, $H_{9,10}$, complex), and 1.0–3.0 ppm (10 H, complex).

Anal. Calcd for $C_{33}H_{28}O_2$: C, 86.84; H, 6.14. Found: C, 86.62; H, 6.23.

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Rates of Termination of Radicals in Solution. VI.[1] Ketyl Radicals Derived from Methyl-Substituted Phenylglyoxylic Acids

Takiko Fujisawa and George S. Hammond*

Contribution No. 4301 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

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Abstract: Phenylglyoxylic acid and five of its C-methylated derivatives have been studied by irradiation of isopropyl alcohol solutions of these compounds in the cavity of an electron paramagnetic resonance spectrometer. Ketyl radicals are produced when the aromatic ring has no ortho substituents or when both ortho positions are occupied by methyl groups. A single *o*-methyl group prevents the formation of a detectable concentration of radicals, presumably because of a competitive photoenolization reaction. Hyperfine coupling constants and rates of bimolecular radical decay are reported.

In previous papers in this series we have described our studies of structure–reactivity relationships of ketyl radicals, demonstrated by the rates of radical termination as measured by the esr-light intermittency technique.[1-4] We have now extended these studies to include the effect of methyl substituents on the photochemistry of the phenylglyoxylic acids, **1a–f**, and ketyl radicals, **2a–f**, derived from some of them.

Experimental Section

Materials. Phenylglyoxylic acid (Aldrich) was commercial material. Methyl-substituted phenylglyoxylic acids were prepared

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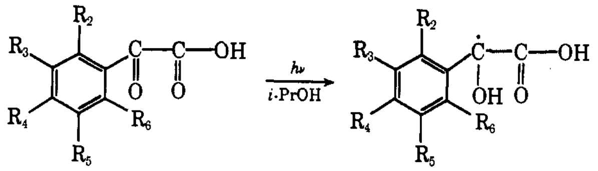


1 2

a, $R_2 = R_3 = R_4 = R_5 = R_6 = H$
b, $R_2 = R_5 = R_6 = H$; $R_3 = R_4 = CH_3$
c, $R_3 = R_5 = R_6 = H$; $R_2 = R_4 = CH_3$
d, $R_3 = R_4 = R_6 = H$; $R_2 = R_5 = CH_3$
e, $R_3 = R_5 = H$; $R_2 = R_4 = R_6 = CH_3$
f, $R_4 = H$; $R_2 = R_3 = R_5 = R_6 = CH_3$

by oxidation of the corresponding acetophenones.[5] Spectrograde isopropyl alcohol (MCB) was used as solvent.

Measurements. All solutions were 0.1–1.0 M in α-keto acid. The apparatus and procedure used for the measurement of esr spectra and determination of decay rate constants have been described elsewhere.[6] As previously discussed, the accuracy of determination of individual rate constants is ±20%.

Results and Discussion

Radicals were generated by ultraviolet irradiation of solutions of the phenylglyoxylic acids in isopropyl alcohol solution. The systems studied can be divided into three classes on the basis of their spectra: (a) compounds with no methyl group at the ortho positions (phenylglyoxylic acid (**1a**) and 3,4-dimethylphenylglyoxylic acid (**1b**)) which give esr spectra, steady-state radical concentrations and radical recombination rate constants which are very similar to those of the α-keto acids and esters reported previously;[1] (b) compounds having *o*-methyl groups (2,4-dimethyl- (**1c**) and 2,5-dimethyl- (**1d**) phenylglyoxylic acids) which give no esr spectra; and (c) compounds with methyl groups at both ortho positions (2,4,6-trimethyl- (**1e**) and 2,3,5,6-tetramethyl- (**1f**) phenylglyoxylic acids) which give high steady-state radical concentrations, and show decay rates two orders of magnitude lower than those of radicals derived from the α-keto acids in group a.

The hyperfine coupling constants for radicals **2a**, **2e**, and **2f** are given in Table I.

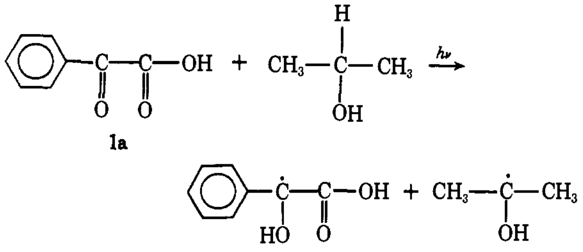
Table I. Hyperfine Coupling Constants for Ketyl Radicals at 30°

		Coupling constant, G[a]				
				Methyl proton		
Compd	Ketyl radical	Ring proton Ortho	Para	Ortho-substituted	Para-substituted	Hydroxyl proton
1a	**2a**	3.56[b]	3.56[b]			1.44[b]
1e	**2e**			1.12	1.12	0.56
1f	**2f**		2.38	0.96		0.48

[a] Accuracy ±0.1 G. [b] Reference 1.

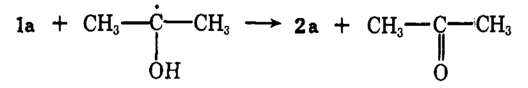
Group a. We have previously reported[1] that the intensity of esr signals obtained from phenylglyoxylic acids falls rapidly with time under intense irradiation, presumably because photolytic bond cleavage and photoreduction lead to rapid destruction of the parent compound. Because of this phenomenon, it was impossible to determine steady-state radical concentrations accurately. Under reduced light intensity we were able to estimate a steady-state radical concentration in experiments with **2a**. However, under these conditions, the radical concentration was too small to obtain the hyperfine coupling constants for **2a** which were determined previously.[1]

Photoreduction of **1a** in isopropyl alcohol leads to formation of the corresponding pinacol,[7] a result consistent with the mechanism shown in eq 1–3.

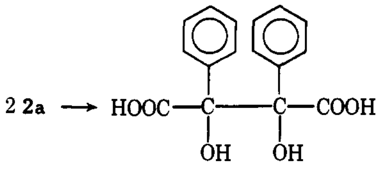


1a

2a (1)



$$\mathbf{1a} + CH_3-\underset{OH}{\underset{|}{\dot{C}}}-CH_3 \longrightarrow \mathbf{2a} + CH_3-\underset{O}{\underset{\|}{C}}-CH_3 \quad (2)$$



(3)

The acetone ketyl radical was not observed until the starting material (**1a**) had been nearly exhausted. The hydrogen transfer step (eq 2) is highly probable by analogy with the photoreduction of ketones when the concentration of ketone is rather high.[8,9] Although it is conceivable that some termination may occur by the reaction of **2a** with acetone ketyl radical, the contribution of this reaction to the observed decay of **2a** would be small.[3] Hence, the observed second-order decay rates should give the rate constants for coupling of radicals **2a**.

The esr spectra of radicals formed by irradiation of **1a** and **1b** appeared as unresolvable singlets. The steady-state radical concentrations and second-order decay rate constants for decay of **2a** and **2b** are given in Table II.

Table II. Decay Rates of Ketyl Radicals in Isopropyl Alcohol Solution at 30°

Compd	Ketyl radical	$[R\cdot]_0{}^a \times 10^5\ M$	$k_t{}^b[R\cdot]_0 \times 10^{-1}\ sec^{-1}$	$k_t \times 10^{-6}\ M^{-1}\ sec^{-1}$
1a	**2a**	0.17	64	380
1b	**2b**	0.30	64	210
1e	**2e**	3.2	9.3	2.9
1f	**2f**	1.1	5.2	4.7

[a] Concentration of radicals under steady illumination. [b] k_t is defined by $d[R\cdot]/dt = -2k_t[R\cdot]^2$.

Group b. *o*-Alkylbenzophenones of type **3** (R_1 = phenyl) do not undergo the usual facile photoreduction leading to ketyl radicals even in hydrogen-donating solvents, but yield photoenols **4** (R_1 = phenyl) by transfer of a hydrogen atom from the ortho substituents to the carbonyl group.[10–13] Although Heindel, *et al.*,

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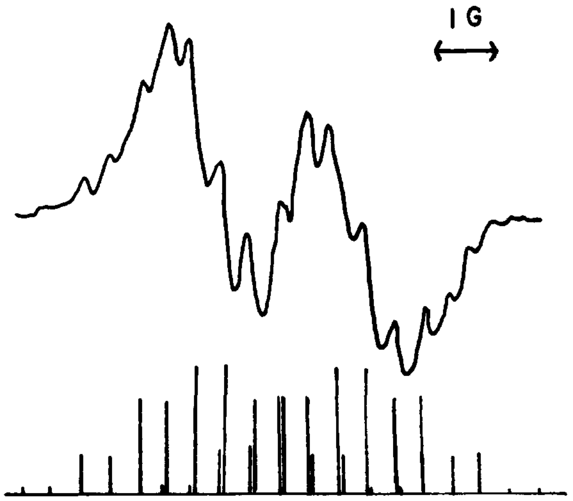
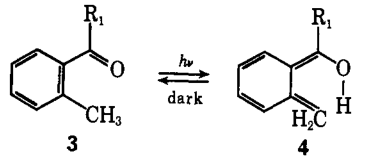


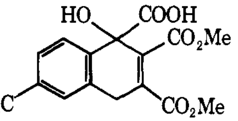
Figure 1. Esr spectrum of radical produced from **1f** on irradiation in isopropyl alcohol (top); block diagram of the expected lines based on the splitting constants given in Table I (bottom). Field increases from left to right.

have recently reported that photoreduction of 2-methylbenzophenone does occur in isopropyl alcohol, with unspecified quantum yield,[14] we were not surprised that



3 **4**

ortho-substituted phenylglyoxylic acids (**3**, $R_1 = CO_2H$) did not give large enough concentrations of ketyl radicals to yield esr spectra. We tried to isolate an adduct **5** from the reaction of **1c** with dimethyl acetylenedi-



5

carboxylate in benzene under irradiation,[10] but only starting materials were recovered.

Group c. Irradiation of **1f** gave rise to an intense esr spectrum (Figure 1) which was attributed to radical **2f**. Its decay rate was relatively slow. The spectrum shows 15 overlapping lines with a main doublet splitting of 2.38 G which was assigned to the para hydrogen atom. The additional splittings may be due to the six equivalent hydrogen atoms of the *o*- and *o'*-methyl groups with a coupling constant of 0.96 G (1:6:15:20:15:6:1 septet) and to the hydroxyl proton with a coupling constant of 0.48 G (doublet). The lines expected from this analysis are given below the trace of the spectrum.

The steady-state radical concentration and second-order radical decay rate were determined to be 1.1×10^{-5} *M* and 4.7×10^{6} M^{-1} sec^{-1}, respectively. This decay rate is two orders of magnitude lower than those for other α-keto acids[1] and α-diketones,[3] whose radicals are thought to decay by recombination, and one order of magnitude lower than the values for radicals from rigid α-diketones[3] which are believed to decay by disproportionation. The only photoproduct isolated from **1f** was a pinacol (mp 162–163°). None of the hydroxy ester was detected, indicating that radicals **2f** react by coupling. We find this result mildly surprising because we had anticipated that the highly hindered radicals might prefer reaction by disproportionation. The unusually low rate of reaction indicates that both modes of reaction of the radicals are subject to steric inhibition.

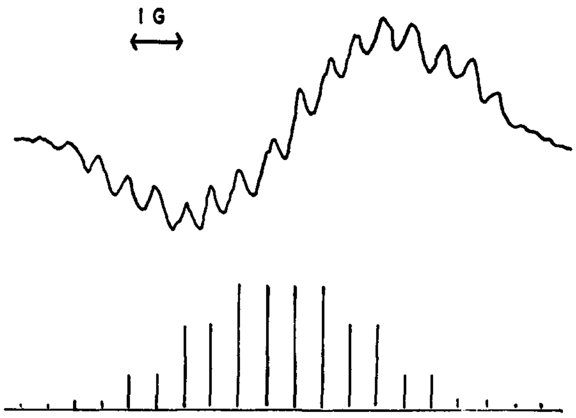


Figure 2. Esr spectrum of radical produced from **1e** on irradiation in isopropyl alcohol (top); block diagram of the expected lines based on the splitting constants given in Table I (bottom). Field increases from right to left.

The fact that radical **2f** is formed suggests that efficient hydrogen transfer to form the photoenol requires coplanar arrangement of the carbonyl group and the aromatic ring, a conformation inhibited by the second methyl group. However, the hyperfine splitting in the ketyl radical indicates that significant resonance interaction of the unpaired electron with the ring must occur. Although the radical may not be exactly planar, it is clear that the substituent bearing the unpaired spin cannot be held orthogonal to the ring.

The irradiation of **1e** gave a radical (**2e**) which behaved similarly to **2f**. The esr spectrum consists of 20 equally spaced lines. If we assume that the hydrogens of the *o*- and *p*-methyl groups have the same coupling constant, ten lines should be ascribable to these hydrogens. Then each of these lines may be split into a doublet by the hydroxyl proton. The indicated hyperfine coupling constants are 1.12 G for the hydrogens of the methyl groups and 0.56 G for the hydroxyl proton. The observed spectrum and that expected from the above assignment are given in Figure 2. The steady-state radical concentration and radical termination rate of **2e**, which are of the same order of magnitude as those for radical **2f**, are given in Table II.

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