Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 30. Rearrangement of the Benzoylmethyl Radical[1]

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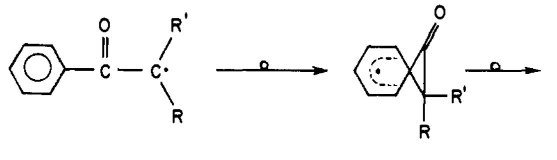
Abstract: The EPR spectra of benzoylmethyl, 1-benzoylethyl, and 2-benzoyl-2-propyl radicals in solution are reported. Barriers to rotation about the $C(O)-\dot{C}H_2$ and $C(O)-\dot{C}Me_2$ bonds have been measured. At low temperatures, benzoylmethyl radicals dimerize at rates close to the diffusion-controlled limit. At high temperatures decay occurs by a neophyl-like rearrangement and the benzyl radical is observed because the initially produced phenylacetyl radical is rapidly decarbonylated. The corresponding rearrangements of the 1-benzoylethyl and 2-benzoyl-2-propyl radicals are much slower than that of the benzoylmethyl radical at comparable temperatures. The results of kinetic studies on these dimerization, isomerization, and decarbonylation reactions are discussed in relation to the failure of early attempts[4] to obtain 1,4-diketones by dehydrodimerization of alkyl phenyl ketones.

In 1948 it was shown[4] that the reaction of aliphatic ketones with acetyl peroxide, at temperatures where the latter undergoes thermal decomposition, provides a convenient synthetic route to 1,4-diketones. However, all attempts to synthesize 1,2-dibenzoylethane and related diketones by dehydrodimerization of the appropriate alkyl phenyl ketones using the same procedure were unsuccessful, only resinous polymeric material being obtained. This was subsequently attributed[5] to a "neophyl-like" [6-9] rearrangement of the benzoylalkyl radicals, **1**, first to a 1-keto spiro[2.5]octadienyl radical, **2**, then to a phenylacetyl radical, **3**, which underwent α-scission to yield a benzylic radical, **4**, and carbon monoxide.



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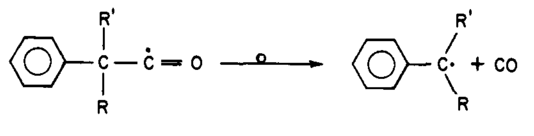

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a, R = R' = H b, R = H; R' = CH_3 c, R = R' = CH_3

In this paper we report a study of the three benzoylalkyl radicals, **1a**, **1b**, and **1c**, by kinetic EPR spectroscopy. The rate constant for the decarbonyation of **3a** at −116 °C has also been determined. Our kinetic data prove that the formation of polymeric products rather than dimers in the reaction of alkyl phenyl ketones with acetyl peroxide is unrelated to the neophyl-like rearrangement that the benzoylalkyl radicals can undergo.

Experimental Section

Commercially available materials were purified by normal procedures before use.

The benzoylalkyl radicals were produced either by reaction of the appropriate ketone with photochemically produced *tert*-butoxy radicals,[10] or by reaction of the appropriate α-bromo ketone with photochemically produced tri-*n*-butyltin radicals. The phenylacetyl radical, **3a**, was produced by reaction of phenylacetaldehyde with *tert*-butoxy radicals.

The general technique of kinetic EPR spectroscopy has been described in previous papers in this series.[1,11] In the present systems, a buildup of yellow-colored products, particularly at high temperatures, caused radical concentrations to decrease during the photolysis of static samples. This problem was overcome by flowing a solution of the reactants slowly through the photolytic zone within the EPR cavity.[11b]

Prolonged irradiation of α-bromoacetophenone and hexa-*n*-butylditin in solvents such as cyclopropane, isopentane, toluene, and *tert*-butylbenzene, at temperatures of −50 °C and below, gave a crystalline material which was shown to be 1,2-dibenzoylethane: pale yellow needles after recrystallization from CH_2Cl_2 and then from methanol, mp 145 °C (lit.[12] 144–145 °C). The identity of this compound was confirmed by treating the crystals with hydrazine in methanol which yielded 3,6-diphenyl-4,5-dihydropyridazine, mp 202 °C (lit.[12] 202 °C).

Results and Interpretation

EPR Spectra. Although the EPR spectra of a number of alkanoylalkyl radicals have been described,[13-22] the spectra of only two benzoylalkyl radicals (**1a**[21,23] and benzoylbenzyl[21]) have been reported. The EPR parameters for the three benzoylalkyl radicals studied in this work are summarized in Table I, together with the parameters for the three comparable acetylalkyl radicals. The similarity in the hyperfine splitting constants (hfs) for the two sets of radicals implies that little or no spin density is delocalized into the aromatic ring of the benzoylalkyl radicals.[23]

At ca. −60 °C, the EPR spectrum of **1a** consists of four lines of equal intensity which indicates that the α-H's are magnetically inequivalent. As the temperature is raised, the central pair of lines first broaden and then collapse to a single sharp line. The quartet spectrum is thereby converted to a 1:2:1 triplet and the α-H's have become magnetically equivalent. Rotation about the $C(O)-\dot{C}H_2$ bond in **1a** is restricted at low temperatures because the unpaired electron is partly delocalized onto the oxygen, and this introduces some double bond character,[14,19,20] viz.

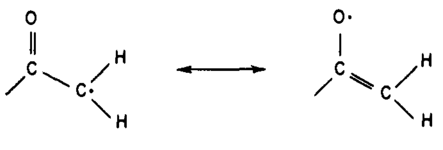


Table I. EPR Parameters for Some Benzoylalkyl and Acetylalkyl Radicals[a]

Radical	Temp, °C	a^{H_α}	a^{H_β}	g	Ref
$C_6H_5CO\dot{C}H_2$	25^b	19.60^c		2.0046	This work
	-60^b	19.20, 19.68		2.0046	This work
	-62^d	19.26, 19.70		2.0043	21
	-269^e	$19.83^{c,e}$		2.0045^e	23
$C_6H_5CO\dot{C}HCH_3$	25^f	18.70^g	$21.86^{g,h}$	2.0044	This work
$C_6H_5CO\dot{C}HC_6H_5$	23^i	14.04	4.94, $4.1,^c$ 1.4^c	2.0038	21
$C_6H_5CO\dot{C}(CH_3)_2$	25^f		$18.40,^h$ 20.63^h	2.0045	This work
	106^j		19.13^k		This work
$CH_3CO\dot{C}H_2$	25^l	19.75^c		2.0044	16
	-50^l	19.48, 19.95	m	2.0044	16
$CH_3CO\dot{C}HCH_3$	21^n	19.0^o	$23.0^{h,o,p}$	2.0045	20
	-30^q	19.0	$22.2^{h,r}$	2.0043	18
$CH_3CO\dot{C}(CH_3)_2$	-53^n		$19.5,^{h,s}$ $20.6^{h,s}$	2.0043	20

[a] Hfs are in gauss. [b] In toluene. [c] 2 H. [d] In CH_2Cl_2. [e] In argon matrix, averaged values. [f] In isooctane. [g] Independent of temperature from −35 to 125 °C. [h] 3 H. [i] In tetrahydrofuran. [j] In hexadecane. [k] 6 H. [l] In acetone. [m] Hfs due to CH_3CO = 0.27 G. [n] In adamantane matrix. [o] Independent of temperature from −103 to 21 °C. [p] Hfs due to CH_3CO = 0.8 G. [q] In CCl_3F. [r] Hfs due to CH_3CO = 0.9 G. [s] No change in the position or width of the lines from −91 to 85 °C, some broadening of the lines from 85 to 120 °C.

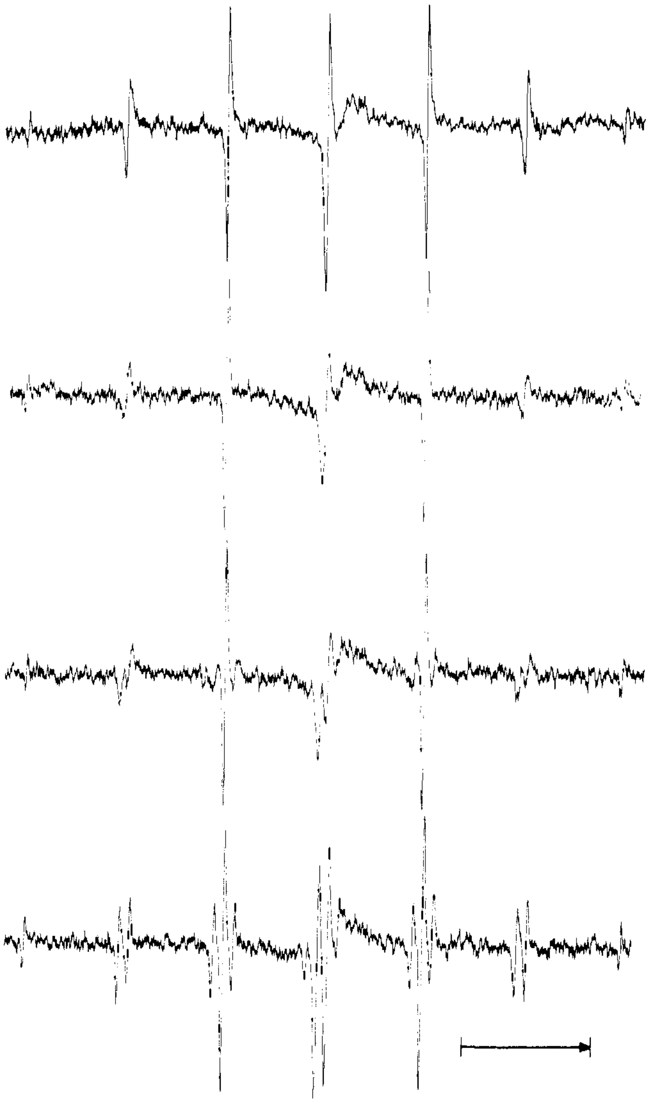


Figure 1. EPR spectrum of the 2-benzoyl-2-propyl radical at 132 (top), 97, 68, and 37 °C (bottom) in hexadecane. The arrow represents 25 G.

In the 2-cyclohexanoyl radical, the contribution of the canonical structure having the unpaired electron on oxygen has been reported[19,20] to be ca. 15%.

For a radical which shows an alternating line width effect in its EPR spectrum, the rate constant for the process which produces magnetic equivalence (rotation for **1a**) is given by[24]

$$k_{1a} = 6.22 \times 10^6\ \Delta a\ \mathrm{s}^{-1}$$

where Δa is the difference (in gauss) in hfs of the magnetically inequivalent atoms. For **1a**, Δa = 0.48 G and so $k_{1a} = 3 \times 10^6$ s^{-1} at −10 °C, the temperature of maximum broadening, and $\Delta G_{1a}^{\ddagger}$ is 7.5 kcal/mol. A complete line-shape analysis[25] of the spectra of **1a** in the temperature range from −30 to 20 °C gave the temperature dependence of k_{1a} as

$$\log (k_{1a}/\mathrm{s}^{-1}) = (13.0 \pm 0.4) - (8.3 \pm 0.5)/\theta$$

where $\theta = 2.3RT$ kcal/mol and the errors are standard deviations. The Arrhenius equation for the comparable rotational process in $CH_3\dot{C}OCH_2$ is[17]

$$\log (k/\mathrm{s}^{-1}) = (12.9 \pm 0.3) - (9.4 \pm 0.5)/\theta$$

and for $(CH_3)_3CCO\dot{C}H_2$ the activation energy for rotation has been estimated to be 8.6 ± 3.0 kcal/mol.[20] The similarity in the barriers to rotation in these $RCO\dot{C}H_2$ radicals supports the view that the nature of R has little effect on the properties of the radical.

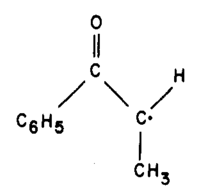
Radical **1c** also exhibits an alternating line width effect. At ambient temperatures, the hydrogens on the two methyl groups are inequivalent and the spectrum consists of a quartet of quartets (each 1:3:3:1, see Figure 1). As the temperature is raised the spectrum changes towards a 1:6:15:20:15:6:1 septet because the methyl groups become equivalent. The temperature of maximum broadening is 74 °C which, with Δa = 2.23 G, yields $k_{1c} = 1.4 \times 10^7$ s^{-1} and $\Delta G_{1c}^{\ddagger}$ = 9.1 kcal/mol. A complete line-shape analysis gives

$$\log (k_{1c}/\mathrm{s}^{-1}) = (13.0 \pm 0.3) - (9.5 \pm 0.5)/\theta$$

The activation energy for the comparable process in $CD_3CO\dot{C}(CH_3)_2$ has been estimated to be 9.1 ± 2.0 kcal/mol.[20]

Radical **1b** showed no alternating line width effect even at elevated temperatures and there was no indication that this radical existed in more than one conformation.[20] As Pratt and co-workers have pointed out,[20] unsymmetrically α-substituted acylalkyl radicals probably adopt a conformation in which the less bulky α substituent is cis to the oxygen. Comparison of the hfs for **1b** with the hfs of similar radicals[20] suggests that **1b** adopts a similar conformation, i.e.

Kinetics of Radical Decay. At temperatures of −50 °C and lower, radical **1a** decays with second-order kinetics at a rate



that is close to the diffusion-controlled limit (see Table II). The decay process must be a dimerization since 1,2-dibenzoylethane was isolated (see Experimental Section).

$$\underset{\textbf{1a}}{2C_6H_5CO\dot{C}H_2} \xrightarrow[T<-50\,°C]{(2k_t)_{1a}} (C_6H_5COCH_2)_2$$

At these temperatures, the concentration of **1a** under steady illumination is proportional to (incident light intensity)$^{0.5}$. At temperatures above −50 °C the light intensity exponent rises above 0.5 which indicates that there is a contribution to decay from a first-order process. At temperatures of ca. 100 °C the light exponent is 1.0 and decay occurs with "clean" first-order kinetics and the rate constant, $(k_d)_{1a}$, for this decay is 1.7×10^3 s^{-1} (see Table II). Using the flow system at somewhat higher temperatures (ca. 120 °C) and at low flow rates (ca. 5×10^{-4} mL/s) the EPR spectrum of **1a** was replaced by that of the benzyl radical,[26] **4a.** At faster flow rates the sample temperature decreased somewhat and eventually **1a** was again detected. However, we could find no conditions which allowed **1a** and **4a** to be observed simultaneously. Furthermore, we never observed any spectrum that could be attributed to **2a,** nor could the phenylacyl radical, **3a,** be detected at these temperatures (see below). The first-order decay process must correspond to the neophyl-like rearrangement of **1a** via **2a** to **3a** which then undergoes a rapid decarbonylation to give **4a.** Our failure to detect **2a,** combined with the prevailing view[8] that the analogous structure in the neophyl rearrangement may represent a transition state rather than a discrete intermediate, suggests that the overall process should be represented as

$$\underset{\textbf{1a}}{C_6H_5CO\dot{C}H_2} \xrightarrow{(k_d)_{1a}} \underset{\textbf{3a}}{C_6H_5CH_2\dot{C}O} \xrightarrow[\text{fast}]{(k_{CO})_{3a}} \underset{\textbf{4a}}{C_6H_5\dot{C}H_2} + CO$$

The phenylacetyl radical, **3a,** has been detected previously by EPR spectroscopy during the photolysis of dibenzyl ketone at low temperatures.[21] It is known to undergo very rapid decarbonylation.[21,27] For example, Robbins and Eastman[27a] measured the rate of decarbonylation of **3a** in benzene at room temperature relative to its rate of scavenging by the nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl. By assuming that the rate constant for trapping was 10^{10} M^{-1} s^{-1}, i.e., diffusion controlled, these authors estimated that $(k_{CO})_{3a}$ is ca. 10^8 s^{-1}. The assumed value for the trapping rate constant may have been overestimated by a factor of 2,[28] correction for which would give $(k_{CO})_{3a} \sim 5 \times 10^7$ s^{-1}. Similarly, Perkins and Roberts[27b] measured the competition between decarbonylation at 40 °C and addition to 2-methyl-2-nitrosopropane. It was assumed[29] that the rate constant for addition was the same as that found for addition of *tert*-butoxycarbonyl radicals, a revised value for which is 5.5×10^6 M^{-1} s^{-1}.[30] No phenylacyl adduct could be detected by Perkins and Roberts,[27b] which enabled these authors to estimate[30] that $(k_{CO})_{3a} > 3.5 \times 10^7$ s^{-1}.

We have confirmed that $(k_{CO})_{3a}$ is large at ambient temperatures by measuring this rate constant at temperatures sufficiently low that both **3a** and **4a** could be observed simultaneously when a cyclopropane solution of phenylacetaldehyde and di-*tert*-butyl peroxide was photolyzed. Radical concentrations were determined by double integration (by hand) of the single line due to **3a** and of a single line in the spectrum of **4a.** This was done at −116 °C, the temperature at which the best "mixed" spectrum was obtained. A well-established method[9,33] yields $(k_{CO})_{3a}$ in terms of the rate constant for the bimolecular self-reaction of **4a,** which was taken to be 10^9 M^{-1} s^{-1} under these conditions.[28,34] The value found for $(k_{CO})_{3a}$ at −116 °C was 9×10^2 s^{-1}. If a "normal" preexponential factor of 10^{13} s^{-1} is assumed,[37] then at 25 °C $(k_{CO})_{3a}$ will be ca. 5×10^7 s^{-1}, in excellent agreement with earlier estimates.[27] At 125 °C, the temperature at which the original attempt was made to prepare 1,2-dibenzoylethane from acetophenone,[4] $(k_{CO})_{3a}$ will be ca. 10^9 s^{-1}. Our failure to observe **3a** during the thermal rearrangement of **1a** is therefore not surprising since, at the required temperatures, the steady-state concentration of **3a** will be about 5 orders of magnitude below the limits of detection by EPR spectroscopy. Furthermore, the half-life of this radical at 125 °C is so short that only a diffusion-controlled reaction *with a species present in molar concentration* could compete with the decarbonylation. Radical **3a** cannot therefore be itself directly involved in any of the reactions that lead to polymeric materials in the acetophenone–acetyl peroxide reaction.

Table II. Rate Constants for Radical Decays

Radical	Solvent[a]	Temp, °C	$2k_t \times 10^{-9}$, M^{-1} s^{-1}	$k \times 10^{-3}$, s^{-1}
1a	C	−72	0.5	
	H	102		1.7 (k_d)
1b	C	−22	2.4	
1c	C	20	1.9	
	H	128	2.4	
3a	C	−116		0.9 (k_{CO})

[a] C = cyclopropane, H = hexadecane.

The 1-benzoylethyl radical, **1b,** decayed with second-order kinetics at ambient and subambient temperatures (Table II). On raising the temperature a simultaneous first-order decay process made its appearance. However, even at 195 °C there was an appreciable second-order component to the decay and so reliable rate constants for the isomerization of this radical could not be obtained. The isomerization of **1b** must be much slower than that of **1a.**

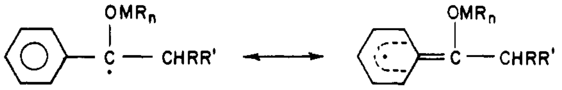
The 2-benzoyl-2-propyl radical, **1c,** decays with "clean" second-order kinetics even at temperatures as high as 130 °C (Table II). It is clear, therefore, that isomerization products of **1c** are *not* involved in the formation of polymeric material when acetyl peroxide reacts with phenyl isopropyl ketone at 115 °C.[4]

Discussion

The results presented above provide strong support for the previously proposed rearrangement of the benzoylmethyl radical.[5] They show that the rearrangement is disfavored as α hydrogens are replaced by methyl groups along the series, **1a, 1b, 1c.** This result can readily be understood since stabilization of the reactant radicals will increase along the same series (i.e., along the series primary, secondary, tertiary) and stabilization of the product radicals will, for steric reasons, decrease along the series **3a, 3b, 3c.**

On the other hand, it is clear from our results that the rearrangement of benzoylalkyl radicals is unrelated to the production in the acetyl peroxide–alkyl phenyl ketone reactions of polymeric materials rather than the anticipated[4] dimers. This is most clearly indicated by the fact that **1c** would not isomerize under the conditions used for the peroxide–phenyl isopropyl ketone reaction. Similarly, the extent of the isomerization of **1b** would not be large under the conditions used in the attempted dehydrodimerization of propiophenone. Moreover, although some of the benzoylmethyl radicals may have isomerized in the peroxide–acetophenone reaction, there is no evidence to indicate that **2a** (which may be a transition state only) was involved in the polymerization, while the phenylacetyl radical, **3a,** would have cleaved immediately to give benzyl. Since benzyl radicals are less reactive than the initiating methyl radicals from the acetyl peroxide there is no reason to suppose that they were responsible for polymer formation, though their involvement in this process cannot be ruled out.

We are therefore forced to the conclusion that polymer formation is a consequence of the basic structure of phenyl alkyl ketones and is unrelated to the nature of the radicals produced by hydrogen atom abstraction from these compounds. Presumably, radical additions to the carbonyl oxygen[38]



of phenyl ketones are facilitated by resonance stabilization of the adduct. Some polymerization at the temperatures of the attempted dehydrodimerizations is, after the event, perhaps not too surprising.

Finally, it should be noted that phenacyl bromide and related α-bromo ketones have been coupled using iron pentacarbonyl[39] or zinc dust[40] to the appropriate 1,4-diketones in appreciable yields at elevated temperatures. Our present results support the suggestions that these reactions involve the intermediacy of organoiron[39] and organozinc[40] complexes and do not occur by a simple radical-radical coupling, even though some radicals may be formed in these reactions.[40]

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