electrons ($S = {}^5/_2$). Only the transition between the lowest energies (M_s $+{}^1/_2 \rightarrow -{}^1/_2$) is measurable by ESR.[23] Since it is assumed that $g_x = g_y = g_\perp$ and $g_z = g_\parallel$, the simulation program is essentially the same as that used for Cu(II) porphyrins.[20] The superhyperfine interaction can be neglected, as the nuclear spin of iron is zero and the superhyperfine splitting with the ligand nitrogen atom is not observed. ϕ represents the tilt angle between the Z axis of the cast film and $g_\parallel$ with a standard deviation of σ. The spectral line shape was assumed to be Gaussian, and the spectral intensity was calculated from 600 to 3600 G at every 5 G.

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Acknowledgment. We are grateful to Dr. Yuichi Ishikawa for ESR spectra simulation and to Hideki Horiuchi for his skillful preparation of ESR quartz cells. We also thank Mr. Takahiro Takasaki for his detailed advice regarding preparation of the phosphate amphiphile **1**.

Photocyclization of α-(*o*-Tolyl)acetophenones: Triplet and 1,5-Biradical Reactivity

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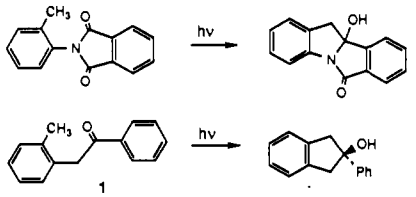
Abstract: Several ring-substituted α-(*o*-tolyl)acetophenones undergo photocyclization to 2-indanol derivatives in high quantum efficiency in solution and in high chemical yield as solids. The mechanism for reaction involves triplet state δ-hydrogen atom abstraction that generates 1,5-biradicals. Quenching studies indicate that the n,π* excited triplets of these ketones react, with rate constants $>10^8$ s^{-1}. Variations in triplet reactivity are ascribed to conformational equilibria that populate reactive and unreactive geometries to different extents. The α-aryl ring eclipses the carbonyl in the lowest energy geometry, from which the most favorable geometry for reaction can be reached by small bond rotations. α-(2,4,6-Triisopropylphenyl)acetophenone forms the relatively long lived enol as well as indanol in solvent-dependent ratios; deuterium labeling indicates that the 1,5-biradical disproportionates to form enol. This does not happen with α-mesitylacetophenone, so its 54% cyclization quantum efficiency is ascribed to an internal triplet quenching that competes with hydrogen abstraction. This internal quenching is presumed to be of the charge-transfer type and does not appear to lead directly to 1,5-biradicals. 1-Methyl-2-phenyl-2-indanol is formed from α-(*o*-ethylphenyl)acetophenone with a Z/E ratio of 20:1 in benzene and 2:1 in methanol. The 1,5-biradical intermediates were characterized by flash spectroscopy; they have lifetimes between 15 and 45 ns, with those derived from α-(*o*-isopropylphenyl) ketones being twice as long-lived as those derived from α-(*o*-methylphenyl) ketones, and show only a small solvent dependence. Biradical lifetimes and the diastereoselectivity of cyclization are interpreted in terms of biradical intersystem crossing occurring preferentially along the reaction coordinate for cyclization, such that the two processes effectively occur concurrently. The applicability of this concept to other biradicals is discussed.

For the past few years we have been conducting a systematic study of δ-hydrogen abstraction by triplet ketones and the competing reactions of the intermediate 1,5-biradicals.[1] Our studies began with a reinvestigation of the photocyclization of *o*-alkoxyphenyl ketones,[2,3] which we recently published in full.[4] A study of *o-tert*-butylbenzophenone[5] confirmed hints in the literature[6,7] that its triplet is highly reactive. Kanaoka's report that *N*-(*o*-tolyl)phthalimide undergoes photocyclization[8] prompted us to investigate α-(*o*-tolyl)acetophenone (**1**). We were delighted to discover that it and simple derivatives undergo highly efficient photocyclization to 2-indanols.[9]



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This paper reports in full our studies on the mechanism of this new photocyclization reaction, including flash spectroscopic characterization of the 1,5-biradical intermediates. The following paper[10] presents the much more complicated photochemistry that α-substituted α-(*o*-tolyl)acetophenones undergo.

Results

Product Identification. The ketones listed in Table I were all synthesized by standard procedures, as described in the Experimental Section. They all undergo clean photocyclization to 2-phenyl-2-indanols when irradiated at 313 or 365 nm or with the output of a medium-pressure mercury arc lamp filtered only by Pyrex. In all but one case the chemical yields were within experimental error of 100%. The exception is α-(2,4,6-triisopropylphenyl)acetophenone (**7**), which gives varying amounts of its enol as well. This fact was first established by irradiating a dioxane-d_8 solution of **7** with 350-nm Rayonet lamps and following the reaction by NMR. At high conversion, two separate signals for vinyl protons at 6.10 and 5.99 ppm, in a 4:1 ratio, indicated the formation of Z and E enols as the major products.[11,12] Integration of the vinyl signals and those of the indanol methyls indicated a 15:1 enol/indanol ratio. After one day, the E enol had disappeared; its NMR signals were replaced with those of the starting ketone. The Z enol was quite persistent and required treatment with acid or base to be tautomerized to the starting ketone. A portion of the unacidified solution of Z enol was

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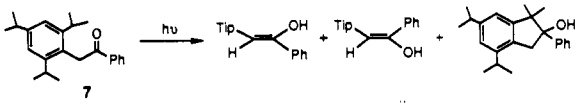
Table I. Photokinetics of Several α-(*o*-Tolyl)acetophenones $ArCH_2COAr'$[a]

ketone	Ar	Ar′	Φ_{cyc}[b]	Φ_{max}[b,c]	$k_q\tau$, M^{-1}[d]	k_H, 10^8 s^{-1}[e]
1	*o*-tolyl	phenyl	1.00 (0.05)		31 (1)	1.6
2	*o*-tolyl	*p*-anisyl	0.54 (0.04)		2900 (100)	0.010
3	*p*-xylyl	phenyl	0.62 (0.04)		19 (0.4)	1.9
4	mesityl	phenyl	0.44 (0.03)	0.54 (0.03)[f]	4.5 (0.2)	5.5
4-d_2			0.43			
5	*o*-EtPh	phenyl	0.80 (0.05)		5.4 (1.0)	8.0
6	dip[g]	phenyl	0.42 (0.07)		3.4 (0.1)	7.5
7	tip[i]	phenyl	0.04		3.2 (0.3)	8.5
7[h]			0.23[j]	0.016[k,l]		
7-d_2[h]			0.38	0.027[k]		

[a] In benzene, 313-nm irradiation unless otherwise noted. Average deviation of measurements noted in parentheses. [b] Indanol formation. [c] Maximum value with added Lewis base. [d] 2,5-Dimethyl-2,4-hexadiene quencher, $k_q = 5 \times 10^9$ M^{-1} s^{-1}. [e] $k = \Phi_{max}/\tau$. [f] 1 M pyridine. [g] 2,5-Diisopropylphenyl. [h] 365 nm. [i] 2,4,6-Triisopropylphenyl. [j] Φ(enol) also = 0.23. [k] Dioxane. [l] Φ(enol) = 0.24.

irradiated with 300-nm lamps; the resulting NMR spectrum showed singlets at 4.60 and 5.93 ppm, characteristic of starting ketone and of *E* enol. A solution containing mainly *Z* enol was strongly fluorescent, with an absorption maximum at 270 nm as would be expected for a stilbene; treatment with HCl removed the strong absorption and restored the ketone n,π* transition at 325 nm.

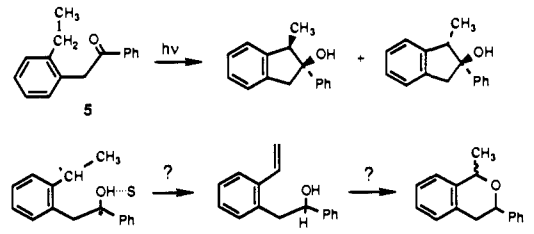


7

The photobehavior of **7** is strongly solvent and wavelength dependent. Irradiation of benzene-d_6 solutions at 365 nm produced an enol/indanol ratio of 1:1 at high conversion. In contrast, irradiation with 300-nm Rayonet lamps of both cyclopentane and toluene-d_8 solutions produced enol at low conversions but only indanol at complete reaction. Likewise, 313-nm irradiation in benzene produced only indanol in detectable amounts.

Irradiation of solid **7** produced a 3:1 enol/indanol ratio. Irradiation of both **1** and α-mesitylacetophenone (**4**) in the solid state also produced indanols in high yield.

Irradiation of α-(*o*-ethylphenyl)acetophenone (**5**) produced both epimeric 1-methyl-2-phenyl-2-indanols, with a *Z*/*E* ratio of 20:1 in benzene, 4.6:1 in dioxane, and 2:1 in methanol. In the latter two solvents there were 7–15% of additional products, including a styrene. We tentatively suggest that they represent a small amount of biradical disproportionation competing with predominant cyclization. The *Z*/*E* ratios were determined from the



relative amounts of the methyl doublets at 1.16 and 0.72 ppm, respectively, in the ^1H NMR spectra of photolyzed solutions. It was assumed that a methyl cis to the phenyl is significantly shielded relative to one trans, as previously observed in a number of such products.[4,13,14] This assignment was bolstered by the different effects of shift reagents on the two indanol structures and by NOE analysis. The *E* isomer, with only hydrogens cis to the OH, complexed more strongly with $Eu(dpm)_3$; its methine cis to the OH and the more upfield of its two methylene protons were shifted much more than the methyl and the other methylene. In the *Z* isomer, the methyl cis to the OH and the upfield methylene undergo the largest shifts. The more upfield of the methylene

Table II. Lifetimes (ns) of Biradicals Formed from α-(*o*-Tolyl)acetophenones[a]

ketone	τ_{BR} (toluene)	τ_{BR} (MeOH)	k_q[b]
3	23	38	2.6 (0.6)
4	18	23	
6	34	40	1.8 (0.9)
7	45	51	1.1 (0.3)

[a] Mean deviation of lifetime measurements was ±4 ns. [b] Quenching by paraquat^{2+} in methanol, 10^9 M^{-1} s^{-1}; average deviation indicated in parentheses.

proton signals in both isomers must be cis to the OH. In the NOE experiments, the 7.6 (*Z*) and 7.4 (*E*) ppm doublets that correspond to the two ortho hydrogens on the 2-phenyl group were irradiated. Enhancement of only the more downfield of the two methylene resonances, which are cis to the phenyl group, was observed for both isomers. Thus the two types of NMR experiments agree. The two indanol structures have very little conformational freedom. In both isomers the most stable conformation presumably has the 2-carbon puckered to relieve torsional strain and to place the phenyl group pseudoequatorial.

Irradiation of both α-(*o*-tolyl)acetone[15] and α-(*o*-tolyl)acetaldehyde in solution produced only radical cleavage products. 1,2-Bis(*o*-tolyl)ethane was isolated from both.

Steady-State Photokinetics. Degassed benzene solutions 0.025 M in ketone and containing varying amounts of 2,5-dimethyl-2,4-hexadiene and a fixed amount of inert internal standard were irradiated at 313 nm. Product yields at 5–10% conversion were measured by gas chromatography and converted to quantum yields by analysis of valerophenone actinometers[16] that had been irradiated in parallel with the samples. Stern–Volmer plots[17] were linear, with slopes equal to $k_q\tau$. These and the quantum yields are listed in Table I. Triplet lifetimes, based on a k_q value of 5×10^9 M^{-1} s^{-1},[18] are also listed.

Test for Enolization. Ketone **4**-d_2 in CCl_4 was irradiated at 365 nm until the indanol/ketone ratio was 0.35. At this point no ^1H NMR signal at 4.30 ppm had appeared for a proton on the α-methylene group. With the conservative estimate that 10% exchange could be observed and with an indanol quantum yield of 44%, the maximum enolization quantum yield is 4%. In contrast, similar irradiation to 26% conversion of dilute **7**-d_2 in CCl_4 produced 22% α-H (4.46 ppm) in the unreacted ketone. ^2H NMR spectra of this sample showed peaks at 3.81 and 2.82 ppm, which correspond to the methylene deuteriums of the indanol and the benzylic deuteriums of the starting ketone, respectively. Given the broad signals of the ^2H spectra, the signal at 2.82 ppm could just as well represent an isopropyl group on an enol or indanol. In any event, the combined ^1H and ^2H NMR results corroborate

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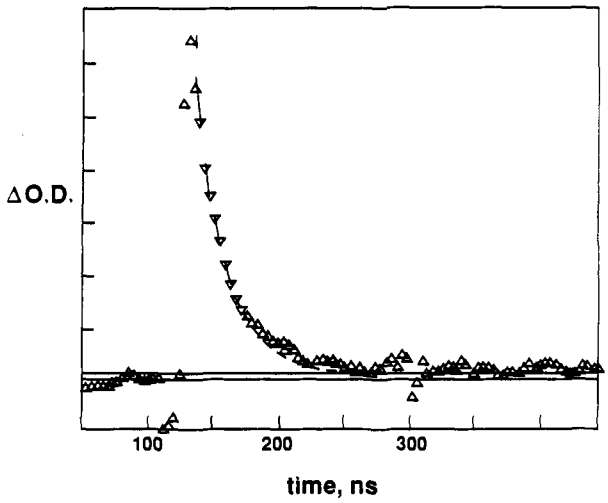


Figure 1. Time-resolved decay of the 1,5-biradical formed from α-(*p*-xylyl)acetophenone: solvent, cyclopentane; excitation, 337 nm; monitored, 320 nm.

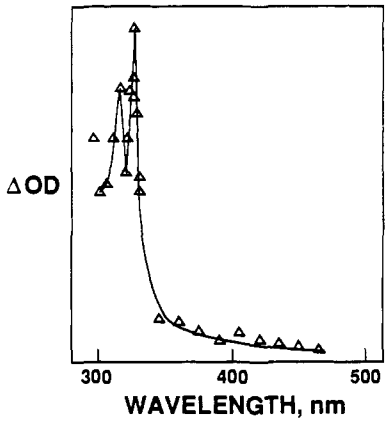
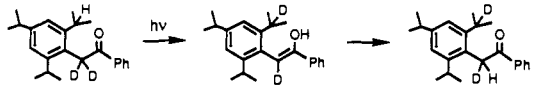


Figure 2. Transient absorption spectrum of the 1,5-biradical produced by flashing α-(*p*-xylyl)acetophenone in cyclopentane at 308 nm and observing 20–40 ns after the flash.

H–D exchange between the benzylic and α carbons, presumably via the enol.



Flash Kinetics. Ketones **3**, **4**, **6**, and **7** were flashed in several solvents, with both 308-nm excimer and 337-nm nitrogen laser excitation. Figure 1 shows a typical decay trace. The transients observed from all four ketones were assigned as 1,5-biradicals for the following reasons. Their lifetimes (listed in Table II) are much longer than those of the triplet ketones and were not changed by the addition of triplet quenchers such as conjugated dienes. Moreover, their absorption spectra show very sharp peaks in the 315–335-nm range, characteristic of benzylic radicals,[19] as exemplified in Figure 2. In fact, flashing a solution of 1,3,5-triisopropylbenzene containing 6% di-*tert*-butyl peroxide produced a transient absorption with a sharp peak at 335 nm identical to that observed from ketone **7**. A weaker absorption feature was also observed in all of the biradical transients, with λ_{max} at 410–420 nm, characteristic of the semipinacol radical site.[20] Further evidence for the presence of hydroxy biradicals was provided by the formation of paraquat radical cation.[21] It was monitored at 603 nm as a function of paraquat concentration; rate constants for the known redox reaction were derived from double reciprocal

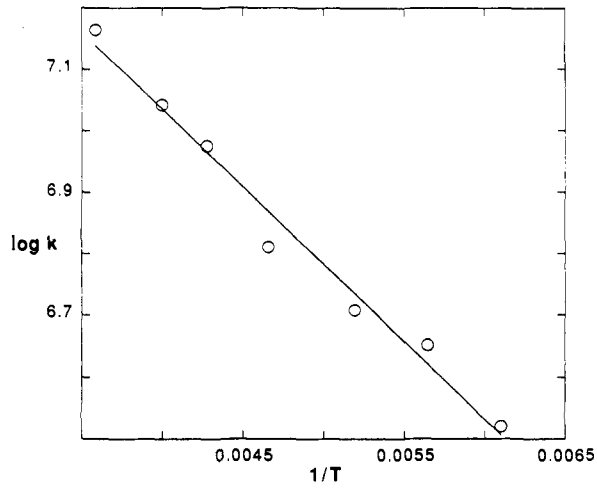
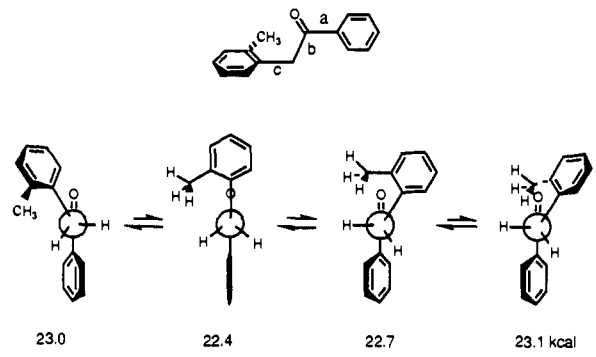


Figure 3. Arrhenius plot of temperature dependence of lifetime of the 1,5-biradical formed from α-(*p*-xylyl)acetophenone in ethanol: excitation, 337 nm; decay monitored, 298 nm.

Scheme I



sensitization plots and are included in Table II.

The temperature dependence for the decay of the biradical transient from **6** was measured at 415 nm in methanol and in isooctane between 255 and 340 K. In both cases, log $A = 8.1 \pm 0.2$ and $E_a = 1.0 \pm 0.3$ kcal/mol. Ketone **3** was monitored at 298 nm in ethanol, giving log $A = 8.0 \pm 0.15$ and $E_a = 1.15 \pm 0.14$ kcal/mol; Figure 3 shows an Arrhenius plot of the data.

When a high-power excimer laser was used, strong residual absorption was evident in the 330–400-nm range. The ratio of residual/total transient absorption for **7** depended linearly on excitation intensity, so the residual appears to be a secondary photoproduct of the biradical. The biradical is formed early in each laser pulse and is excited by the end of the laser pulse. This aspect of the results has been discussed separately.[22] Solutions of **7** also became highly fluorescent after a few flashes.

Spectroscopy. Phosphorescence spectra of all ketones were recorded in both EPA and 2-methyltetrahydrofuran glasses at 77 K. The spectra of all of the ketones except **2** are almost indistinguishable from that of acetophenone and have 0–0 bands at 388 ± 1 and 389 ± 1 nm, corresponding to triplet energies of 73.7 and 73.5 kcal/mol, respectively, in the two solvents. The spectrum of **2** is broader, with a 0–0 band at 406 nm (70.4 kcal/mol) in 2-methyltetrahydrofuran.

Ketones **1** and **3**–**7** all have L_a UV absorption bands at 237–238 nm and n,π* bands around 325 nm, both typical of phenyl alkyl ketones.[23] For **2** the values are 265 and 319 nm, respectively, typical of *p*-methoxyphenyl ketones.[23]

Molecular mechanics calculations were performed on ketones **1**, **4**, and **7** using the MMX routines in PCModel.[24] Global minimizations were run with dihedral drivers for rotation around

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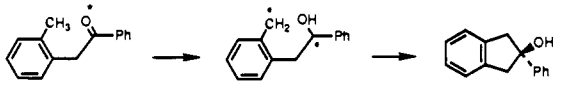
bonds a, b, and c. For all three ketones, the lowest energy conformer is predicted to be the one with the α-aryl group eclipsing the carbonyl and twisted such that its skeleton is perpendicular to bond b, as shown in Scheme I. In this geometry, the benzylic hydrogens closest to the carbonyl are 3.1 Å from the oxygen and make a dihedral angle ω of 75° with the nodal plane of the carbonyl π orbital.

There is a fairly flat potential for rotation 40° either way around bond b. For **1** and **4** the dihedral angles for rotation around bond b were fixed at both +30° and −30°; minimization indicated that opposite rotation around bond a and slight adjustments of the methyl groups resulted in energies no more than 0.5 kcal/mol above that of the minimum energy conformer. In those conformers that rotate so as to bring the benzylic hydrogens closer to the carbonyl, they are 2.8–2.9 Å from the oxygen and lie only 30–40° above the nodal plane of the carbonyl π orbital. Rotation in the opposite direction, which separates CH from carbonyl, appears equally likely.

Rotation ±20° around bond c also results in less than a 1 kcal/mol gain in energy, but only one direction of rotation brings a CH bond closer to oxygen. Minimization of the eclipsed conformer with bond c fixed at −20° brings the benzylic hydrogens within 2.7 Å of the oxygen, with an energy increase of only 0.5 kcal/mol. Rotation more than 20° such that the *o*-alkyl group bends in toward the carbonyl, which is required for the CH bonds to get any closer to the oxygen, produces a sharp increase in energy that is only partially mitigated by a comparable rotation about bonds a and b. Scheme I shows several minimum energy conformations of **1** with their MMX energies. The most favorable geometry for reaction appears to be 0.7 kcal/mol above the global minimum. There are several geometries having similar low energies, but approximately half of them have the methyl group rotated away from the carbonyl.

Discussion

Overall Mechanism. The fact of indanol formation suggests a δ-hydrogen atom abstraction by the excited carbonyl, followed by coupling of an intermediate 1,5-biradical. The quenching of product formation indicates the involvement of short-lived n,π* triplets, which are well-known to be highly reactive in hydrogen atom abstractions.[23,25,26] The flash spectroscopic detection of 18–50-ns transients that have the absorption characteristics of both semipinacol and benzyl radicals and that are readily oxidized by paraquat identifies the 1,5-biradicals.



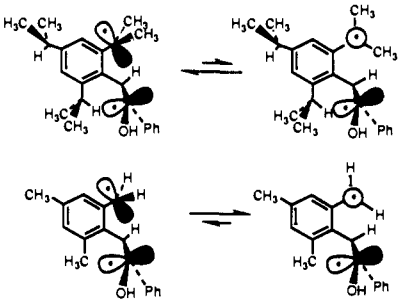
These α-(*o*-tolyl)acetophenones join the *o-tert*-butylphenyl ketones[5–7,27] and the *o*-alkoxyphenyl ketones[2–4] as classes of ketones that undergo facile δ-hydrogen abstraction from their triplets to generate 1,5-biradicals. It is now possible to compare triplet reactivity and biradical behavior in this range of compounds.

Biradical Reactions. The 100% quantum yield of indanol from **1** indicates that the 1,5-biradical undergoes no reactions that compete effectively with cyclization. The fact that added pyridine increases the cyclization quantum yield of **4** by only 20% indicates that only 20% disproportionation to starting ketone competes with cyclization of the intermediate biradical.[14,28] The high quantum yields from **1–6** indicate that in general only small fractions of the biradicals revert to starting ketone. We have pointed out two other cases of 1,5-[1,4,5] and 1,6-biradicals[29] that cyclize with very high efficiency. Unlike 1,4-biradicals, in which disproportionation through a 1,5-hydrogen shift competes strongly with cyclization to a strained ring, 1,5-biradicals cyclize to relatively strain-free rings in competition with a 1,6-hydrogen shift that requires a somewhat strained 7-atom transition state.

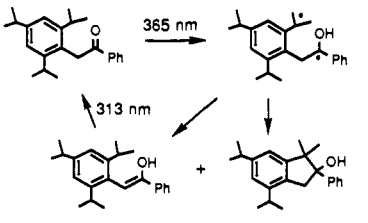
In the case of **7**, the formation of the enol of starting ketone and its reversion to ketone with H–D exchange between the benzylic and α carbons demonstrates that disproportionation involving a 1,4-hydrogen shift can compete with cyclization. This competition depends on solvent, as previously noted for the acyclic 1,5-biradical formed from β-ethoxypropiophenone.[28] Enol formation becomes the dominant reaction in a Lewis base solvent such as dioxane, whereas cyclization and enolization compete 50:50 in hydrocarbon solvents. As with β-ethoxypropiophenone,[28] α-deuteration of **7** enhances the quantum efficiency of cyclization, presumably at the expense of enol formation, although enol quantum yields were not measured directly. If the total product quantum yield is 0.46 in both **7** and **7**-d_2, then deuteration produces a 5-fold decrease in the enol/indanol ratio. This large primary isotope effect on biradical disproportionation also is similar to that observed for β-ethoxypropiophenone.

The lack of any H–D exchange in **4**-d_2 indicates that the biradical formed from **4** undergoes no appreciable enol formation. The difference between **4** and **7** in relative ease of cyclization and enol formation presumably reflects a standard steric effect on radical and biradical coupling, which will be discussed further below. The lack of enolization from **4** probably also reflects the unsubstituted benzyl radical site in the 1,5-biradical being fully conjugated and thus poorly oriented for disproportionation. Given the well-known propensity of isopropyl groups to adopt a geometry with the methyl groups 60° above and below the plane of the benzene ring, the 1,5-biradical from **7** probably has little difficulty adopting a geometry stereoelectronically suitable for disproportionation.

It is interesting that the biradical from **7** undergoes no disproportionation to a hydroxystyrene, as **4** is suspected of doing. Two other bis-tertiary biradicals are known to rearrange to hydroxyalkenes.[1,30] The biradical from **7** seems to have a geometry that would allow the transfer of a methyl hydrogen to the hydroxy radical site. Apparently the observed mode of disproportionation is much more facile.



There is a large wavelength effect on the photochemistry of **7**; at 313 nm and shorter wavelengths, quantum yields are low and enol yield depends on conversion, with none being formed at high conversion. The enol product is a substituted stilbene and absorbs strongly at 313 nm. Not only does it serve as an inner filter, lowering the quantum yield of cyclization, but it undergoes photoreversion to ketone, as has been found for similar enols.[12,31] The final consequence of such irradiation is slow formation of the only photostable product, the indanol.



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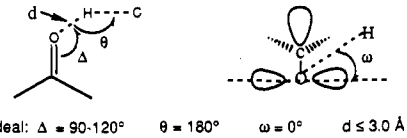
Scheme II



ideal: Δ = 90-120° θ = 180° ω = 0° d ≤ 3.0 Å

Triplet Hydrogen Abstraction Rate Constants. The rate constants in Table I equal the product of triplet lifetimes times the maximum cyclization (plus enol for **7**) quantum yields. δ-Hydrogen abstraction is the major decay path of all of these ketone triplets. Rate constants for intramolecular hydrogen abstraction are affected by the conformational flexibility of the molecule[32] as well as by inductive and conjugative effects of substituents,[33] which shall be discussed in turn.

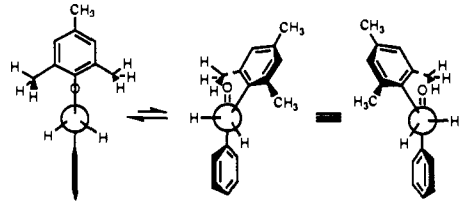
The 100-fold increase in triplet lifetime produced by a *p*-methoxy substituent is by now classic evidence for n,π* reactivity.[23,34,35] This 100-fold decrease in observed reactivity reflects the 1% population of n,π* triplets in equilibrium with the lowest π,π* triplet.[23] Its occurrence here means that the α-aryl group does not significantly alter either the electronic nature or the reactivity of the lowest triplets of these phenyl ketones.

Attack at the tertiary hydrogens in **6** is four times faster than at the primary hydrogens in **3**. This selectivity is comparable to the reactivity ratio of cumene/toluene toward both alkoxy radicals[36] and triplet ketones[37] and indicates that hydrogen abstraction occurs from conformationally equilibrated triplets.[32] If bond rotations were rate-determining, relative reactivities would not depend on C–H bond strength. The high quantum yields (unity for **1**) rule out the possibility that part of the ketone molecules are frozen in unreactive conformations unable to rotate into a reactive conformation, and there is no reason to expect such a situation.

The 3.5-fold larger rate constant for **4** compared to **1** must reflect more than simple inductive effects, since alkyl substitution does not produce much inductive enhancement of benzylic C–H bond reactivity,[37,38] as the **3**/**1** rate ratio attests.

Given the great current interest in the actual orientation of the carbonyl and the C–H bond during hydrogen transfer,[39-41] it is worth exploring what conformations these ketones may react from. Scheme II shows the orientational factors normally considered important.[39,40] Since triplet state hydrogen abstraction does not occur in solid ketones unless a hydrogen is within ~3 Å of the carbonyl oxygen in the ground state,[40] we presume that such proximity must also be achieved in solution for reaction to occur and may define a "reactive" geometry.[42]

It has been known for some time that the largest α-substituent on a ketone tends to eclipse the carbonyl.[43] Scheme I shows various such conformations for **1** with their MMX energies. The fully eclipsed symmetric geometry is predicted to be the most stable, but it does not hold the benzylic hydrogens close enough to the carbonyl oxygen for efficient reaction. Rotation around bond c or bond b improves this situation as regards both O–H distance and orientation, so *actual hydrogen transfer undoubtedly originates from such twisted, slightly higher energy conformers.* Depending on which direction the tolyl ring in **1** twists around bond b or c, the methyl group is brought either nearer to or farther from the carbonyl. The twisting produces reactive syn conformers and unreactive anti conformers, which have almost identical energies and thus identical populations at modest twist angles. This degeneracy in **1**, together with the small activating influence of the extra methyls on **4**, entirely explains the relative reactivities of **4** and **1**, since triplet **4** can twist only to reactive conformers.



It should be noted that triplet **5** undergoes δ-hydrogen abstraction almost as rapidly as triplet γ-phenylbutyrophenone undergoes γ-hydrogen abstraction.[33] Both reactions involve abstraction of a secondary benzylic hydrogen. Lewis has reported that the interposition of a ring improves the entropy requirements of internal hydrogen abstraction sufficiently to increase rate constants 10-fold.[44] This effect presumably offsets the normal 1:20 δ/γ reactivity ratio[45] for hydrogen transfer across an acyclic $(CH_2)_n$ chain. This cancelling effect would not be so likely if the α-alkyl or -aryl groups did not similarly eclipse the carbonyl during reaction of both ketones.

Competing Triplet Reactions. Benzyl phenyl ketone is known[46] to undergo triplet state Norrish type I cleavage to radicals with a rate constant of only 2×10^6 s^{-1}. Since all of our substituted acetophenones undergo δ-hydrogen abstraction with rate constants $>10^8$ s^{-1}, no α-cleavage competes. However, such is not the case for α-tolylacetone and α-tolylacetaldehyde, since α-cleavage of aliphatic ketone triplets is orders of magnitude faster than for phenyl ketones.[47-49] Mattay has found that irradiation of α-(*o*-tolyl)acetone in surfactant solution does lead to cyclization, presumably because the predominant α-cleavage reaction is mostly revertible in micelles.[50]

As the amount of alkyl substitution on the α-aryl group increases, the quantum yield for cyclization decreases. Although quantum yields for most ketone reactions are dominated by biradical partitioning,[42] such is not the case here. Very little disproportionation back to ground-state ketone occurs, and enolization is a competing product-forming reaction only with **7**. Therefore, we conclude that another internal chemical reaction must partially quench the triplets of these ketones. We believe that CT complexation is the most likely culprit. Internal CT quenching of n,π triplets by β-phenyl groups is known to be very rapid ($k \approx 10^9$ s^{-1})[51] and appears to be rotationally controlled because of the favorable orbital overlap possible.[52] Similar quenching by an α-aryl group is slower because of increased ring strain and poorer orbital overlap, a condition that can be offset by increased electron-donating ability of the aryl group. We considered testing our system with *p*-methoxy substituents, but the experiment has

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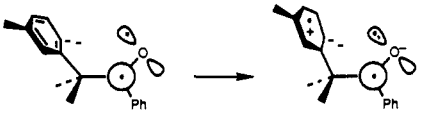
Table III. Comparison of Solvent Effects on Various Hydroxy Biradicals Formed by Triplet Ketone Intramolecular Hydrogen Abstraction

	hydrocarbon			Lewis base		
type	Φ	τ, ns	Z/E	Φ	τ, ns	Z/E
1,4[a]	0.4[b]	30	3:1	1.0[b]	100	2:1
1,5:*o*-*t*-Bu[c]	0.05[d]	~4		1.0[d]	45	
1,5:*o*-OR[e]	1[d]	<4	10:1	0.3[d]	~13	1:1
1,5:α-tol[f]	1[d]	18–45	20:1	1[d]	35–50	2:1

[a] Valerophenone. [b] Cyclization + elimination. [c] *o-tert*-Butylbenzophenone. [d] Cyclization. [e] *o*-(Benzyloxy)benzophenone. [f] α-(*o*-Ethylphenyl)acetophenone.

already been done. Heine and Lewis have reported that *p*-methoxybenzyl ketones undergo α-cleavage in only half the quantum efficiency of benzyl ketones.[46] We suspect that their observation is best explained by the same CT quenching. Since π orbital overlap with the half-occupied carbonyl n orbital is presumably most effective in the most stable, fully eclipsed conformations, which hold the benzylic hydrogens too far from the oxygen, and since the **4**/**1**, **6**/**3**, and **7**/**4** rate ratios indicate that hydrogen abstraction is rate-determining, we believe that little or no biradical formation arises *directly* from this CT process. However, we do observe protic solvent catalysis in more congested systems.[10] There is a good precedent for such behavior in the behavior of γ-amino ketones.[53]



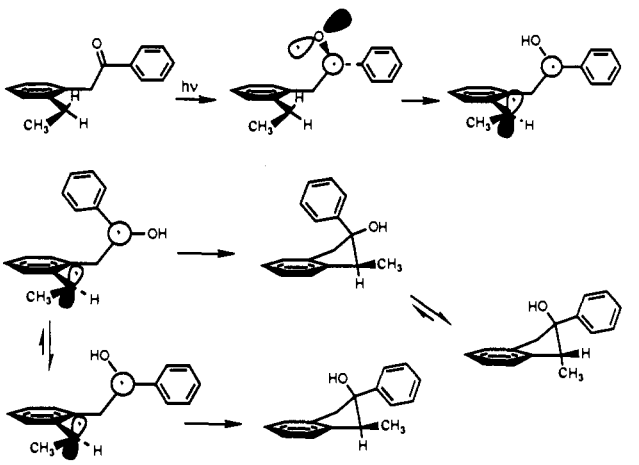
Biradicals. These α-(*o*-tolyl) ketones are precursors to the fourth distinct class of hydroxy biradicals that has now been studied systematically. The other classes are the 1,4-biradicals that intervene in Norrish type II reactions,[54] the 1,5-biradicals formed from *o-tert*-butylphenyl ketones,[5,27] and the 1,5-biradicals formed from *o*-alkoxyphenyl ketones.[4] These biradical types share many common features but also differ in important ways; they are compared in Table III.

Similarities of the biradical types: Small or zero temperature effects on lifetimes,[5,55] oxidative quenching by paraquat,[5,21] and disturbance by paramagnetic species.[5,56] The first two features are shared by the 1,5-biradicals described in this paper, and the third was not studied. It is widely accepted that the first and third characteristics indicate that triplet → singlet intersystem crossing (isc) determines the lifetimes of such triplet-generated biradicals.[54,57,58] Another characteristic shared by all hydroxy biradicals is the large solvent effect on cyclization diastereoselectivity, as demonstrated by ketone **5**.

Differences in the biradical types: Large variations in the effects that solvents have on biradical lifetimes and on quantum yields of product formation, and large variations in how structural features affect biradical lifetimes and product partitioning. However, these differences among biradicals do display parallels. In particular, the extent of solvent-induced variation in product quantum yields is always matched by a comparable variation in biradical lifetime.[1] In the case of these α-(*o*-tolyl)acetophenones, the biradicals show by far the smallest solvent dependence yet observed for hydroxy biradicals and also the smallest percentage of disproportionation back to starting ketone. A change from hydrocarbon to Lewis base solvent produces only 20–25% increases in cyclization quantum yields and biradical lifetimes. Lifetimes also depend on the extent of alkyl substitution at the site of hydrogen abstraction, unlike type II, 1,4-biradicals.[54]

We shall now examine the diastereoselectivity of cyclization and the lifetimes of these particular biradicals. In the process, we shall refine the picture of how intersystem crossing, cyclization, and biradical lifetimes are connected.

Scheme III



Biradical Diastereoselectivity. The 20:1 *Z*/*E* product ratio from **5** demands a 1.8 kcal/mol difference between the two geometries for cyclization.[59] We originally suggested that this high selectivity might be developed as the two ends of the biradical form a bond.[1] However, Lewis' work first showed that the nonbonded interactions that cause such selectivity can either preexist in the biradicals or be created during cyclization as the methyl and phenyl groups on the biradical ends approach each other. The *Z* specificity seen in the photocyclization of α-methylbutyrophenone[47] exemplifies the former, and the *Z*/*E* cyclization selectivity of 3:1 for valerophenone[14,47] and 4:1 for β-ethoxypropiophenone[28] exemplifies the latter. When stereoselectivity is created during cyclization, the energy differences between the two isomeric products should be even greater than the energy differences between the transition states for cyclization. The thermodynamic energy difference between the *Z* and *E* indanols formed from **5** is not known, but MMX calculations suggest that puckering of the five-membered ring reduces the difference to near zero. Therefore, the discrimination between the two modes of cyclization probably reflects preexisting energy differences that persist during cyclization. This conclusion would be consistent with Lewis' observation that larger selectivity can be caused by preexisting steric effects than by those created during cyclization.[47]

We have tested this idea by performing MMX calculations on the biradical from **5**. After minimization with respect to rotation about all C–C single bonds, the two minimum energy geometries shown in Scheme III were calculated to differ in energy by 1.6 kcal/mol. The difference is easily understood in terms of a preference for the smaller group on the radical center, which was originally the carbonyl carbon, to point in over the benzene ring. Given the 25–50-ns lifetimes of these triplet 1,5-biradicals, they have plenty of time to establish such a conformational equilibrium, especially since the stablest conformation does not differ much in geometry from that required for the δ-hydrogen abstraction that forms the biradicals, as Scheme III shows. If the two biradical rotamers indeed differ by 1.6 kcal, most of the observed selectivity reflects this conformational equilibrium that is established in the biradical before cyclization. When the OH group is solvated by hydrogen bonding, it is comparable in size to the phenyl group such that the two rotamers are nearly equal in energy, and selectivity is lost. These results illustrate a different type of preexisting specificity from that shown by α-methylbutyrophenone,[47] since the phenyl and methyl groups' preferred orientations are determined by interactions not with each other but with the rest of the molecule. The phenyl group on one radical center prefers to be twisted away from the central benzene ring and the methyl group on the other radical center prefers to be twisted away from the large ortho substituent. We assume that

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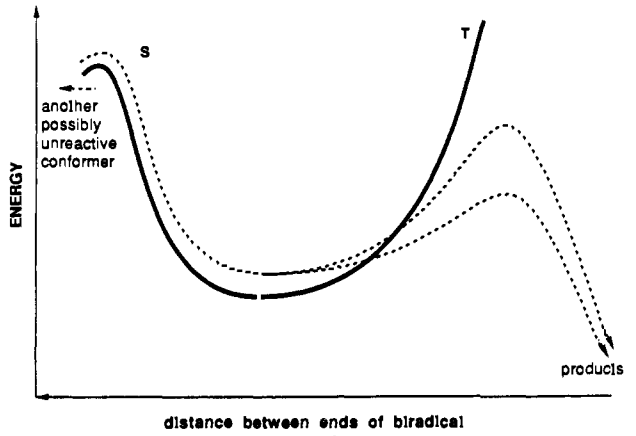

Figure 4. Energy of biradical surfaces along reaction coordinate for cyclization. The (dashed line) singlet surface splits into two levels to represent formation of two diastereomers in cases such as valerophenone. The barrier on the left represents rotation to a different conformation.

no rotation of the benzyl C–C bonds occurs within the biradical lifetimes, given the large barriers that seem to retard such deconjugation of benzyl radicals.[60]

Biradical Lifetimes. The above analysis assumes that cyclization of each rotamer involves the same motion and has the same rate constant. The first part seems reasonable here, since a simple disrotation around the two ortho bonds is all that is required for coupling. In fact, rotation in the opposite sense causes severe nonbonded interactions. The second part is a bit more complicated since it involves the timing of isc and cyclization. It is generally believed that rate-determining isc and chemical reaction of the biradicals are separate, consecutive steps.[54,57,58,61-63] How then does isc vary with structure and solvent? It appears that isc in short-chain biradicals is driven primarily by spin–orbit coupling, which depends on the distance between radical centers.[62,63] The two biradical conformations shown in Scheme III have exactly the same orientation of and distance between radical centers. Therefore they probably undergo isc at the same rate. Their two singly occupied p orbitals are nearly orthogonal in their lowest energy conformations. They fluctuate between parallel and perpendicular orientations as rapidly as the C–C bonds rotate. Adam and Wilson have proposed that the isc rates of various biradicals increase as their singly occupied p orbitals approach orthogonality,[64] in agreement with earlier proposals of Salem[65] and of Shaik and Epiotis.[66] The lifetimes of these biradicals do not support any strong connection between orthogonality and *rapid* isc, in accord with Caldwell's findings.[67] For example, the 1,4-biradical from γ-phenylbutyrophenone is structurally similar to these 1,5-biradicals in being bis-benzylic (phenyl substitution slightly lengthens 1-hydroxy biradical lifetimes[68]). It presumably favors a stretched conformation[69] in which the two p orbitals have no preference for orthogonality and the radical centers are 3.9 Å apart, compared to the 3.3 Å in these 1,5-biradicals to which benzylic conjugation imparts some 1,3-biradical character. Nonetheless, the 1,4-biradical is only twice as long-lived.[68]

What then actually induces isc? What has been missing is an understanding of how isc rates vary with biradical structure. Since isc is fastest when the biradical ends are proximate[63] and they come closest as they cyclize, can isc be connected with reaction? Kaptein first presented the notion of coupled isc and reaction in explaining the CIDNP observed upon irradiation of valerophenone.[70] Closs suggested that rates of biradical reactions reflect the percentage of singlet character in the biradical.[58] We recently suggested enhanced S–T splitting as the two radical sites approach each other, allowing isc at various points onto the potential surface that describes the reaction coordinate for singlet reaction.[1] Figure 4 presents what we now consider a better picture; it is based on the assumption that the biradicals have lowest triplet configurations until their ends come close enough to generate some bonding interaction. The basic idea is that both the singlet and triplet surfaces rise in energy as movement along the reaction coordinate develops electronic and steric strain, but the singlet surface is soon stabilized by the developing bond, such that the two surfaces cross at points that represent very low observed activation energies. This picture solves the puzzle pointed out by Closs: "the long lifetime of triplet biradicals must be attributed to the poor energy match of singlet and triplet levels rather than to a lack of mixing interactions."[58] We presume that isc along the reaction coordinate benefits from large spin–orbit interactions[63] as well as state degeneracy.

In terms of this model, the 1-kcal activation energies for 1,5-biradical cyclization represent such a surface crossing at a point where both states have begun to feel the steric and entropic strain of ring formation. The zero activation energies for decay of 1,4-biradicals[55] probably represent disproportionation and cleavage, which do not generate any particular steric strain, being the dominant reactions. Cyclization reactions, with their potential for ring strain, steric crowding around the forming bond, and a large loss in rotational entropy, are expected to have larger barriers even on the singlet surface than do other biradical reactions. Therefore, some product partitioning can occur *after* isc, otherwise no diastereoselectivity could develop during cyclization as discussed above. Figure 4 represents isc as a biradical undergoes two competing cyclizations, such as to epimeric products. Exactly how high up the cyclization barrier the triplet and singlet surfaces cross depends on the exchange energy; the larger it is, the higher up the barrier. The low observed activation energy for decay of our 1,5-biradicals suggests a small value, as normally assumed. Note that the stereoselectivity created during cyclization of these biradicals is presumed to take place on the singlet surface after isc, but with the molecule trapped in a conformational well deeper than the barrier to coupling.

We have already pointed out how biradical partitioning is usually explainable in terms of normal structural features such as increased barriers to coupling in sterically congested systems and primary isotope effects on disproportionations.[1] With the belief that isc and reaction must be separate, Scaiano[61] postulated that solvent and structurally induced changes in product composition from type II 1,4-biradicals arise from variations in isc rates of various biradical conformations. Our proposal attempts to provide a general explanation for why isc rates actually differ for different structures and solvation, such that normal barriers to product formation can still determine product partitioning. Intersystem crossing is still rate-determining, but it is induced by biradical reaction. Structural features that facilitate cyclization should then shorten biradical lifetimes. For example, the large increase in cyclization efficiency noted for α-alkoxyacetophenones relative to straight alkyl ketones was originally ascribed to the greater ease of forming oxetane rings relative to cyclobutane rings, the former having fewer eclipsing interactions.[71] Scaiano suggested that the shortening of both 1,4-[72] and 1,5-biradical[4] lifetimes by internal oxygen atoms probably reflects the same greater ease

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of bringing the biradical ends together into a cisoid geometry.[73] This suggestion conceptually connected biradical lifetimes with product distribution in terms of normal steric barriers to bond rotations, but it stopped just short of our picture. It should be noted that enhanced spin–orbit coupling has been suggested as an alternative explanation for the short lifetimes of 3-oxa-1,4-biradicals.[72b] However, we favor a conformational explanation since the biradical formed from γ-methoxyvalerophenone has almost the same lifetime as that from valerophenone.[74]

Let us now look at solvation. Why do the lifetimes of these 1,5-biradicals show such small solvent effects when other hydroxy biradicals[5,54] show such large ones? Clearly there cannot be a general polar solvent effect on isc. In fact, solvent effects are confined to hydroxy biradicals.[75,76] Caldwell recently concluded that there is no satisfactory explanation for these selective solvent effects on hydroxy biradicals within the framework of discrete isc and biradical coupling.[76] There is no reason that solvation of the hydroxy group would change the geometry of the most stable anti-stretched conformation of 1,4-biradicals. But the same solvation prevents the reversion to ketone that comprises typically two-thirds of the total 1,4-biradical reaction. In our picture, this solvation then also prevents two-thirds of the isc that is necessary for biradical decay. The small solvent effects on cyclization quantum yields and on biradical lifetimes of this paper's 1,5-biradicals reflect the fact that disproportionation back to ground-state ketone is a minor reaction. Eliminating this path can make only a small change in either measurement. In contrast, the 1,5-biradicals formed from *o-tert*-butylbenzophenone undergo 95% disproportionation in hydrocarbon solvents; alcohols suppress all of this reaction and increase the biradical lifetimes by a factor of at least 10.[5] This very type of reasoning had been rejected because solvent effects on 1,4-biradical lifetimes and reaction efficiencies are not exactly parallel.[77] However, whereas a rate-determining reaction following fast isc would require an exact parallel, *the model in Figure 4 does not*. According to our picture, when solvation eliminates a major pathway for biradical reaction, it also eliminates a major pathway for isc. With a lower probability for finding a successful isc path, the biradical's lifetime is entropically lengthened without acquiring any additional activation energy.

The bis-tertiary biradicals formed from **6** and **7** have lifetimes roughly twice as long as do the primary-tertiary biradicals formed from **3** and **4**. The increased steric barrier to the coupling of tertiary centers would then slow down isc slightly as modeled in Figure 4. The competing enolization from **7** likewise reflects the barrier to cyclization. We presume that the solvent effects on the competition between enolization and cyclization reflect an increased barrier to cyclization when the hydroxy group is solvated, since two tertiary radical centers must couple. This partitioning probably takes place on the singlet surface after isc. Since both reactions involve close approach of the radical centers, only minor molecular motion is necessary to switch between them, so that biradical lifetimes may not be greatly affected by solvation.

Finally, we must emphasize that our model for reaction-induced isc is not intended to fit all biradicals, merely those whose structures allow fairly facile product formation. Thus the widely varying lifetimes reported for several cyclic biradicals[64] apparently highlight the factors that come into play when cyclization is not facile.

Experimental Section

Chemicals. All solvents were purified reagent grade materials. Benzene was distilled from P_2O_5 after having been repeatedly washed with sulfuric acid. Dioxane was distilled from lithium aluminum hydride. *tert*-Butyl alcohol was distilled from sodium. Methanol was distilled from magnesium turnings. Pyridine was distilled from barium oxide. Mallinkrodt spectral grade cyclohexane was used as received for preparative irradiations. Merck dioxane-d_8 and Aldrich benzene-d_6 were used as received. Various higher alkanes for use as internal standards were washed with sulfuric acid and then distilled or recrystallized.

Aldrich 2,5-dimethyl-2,4-hexadiene was allowed to sublime in a refrigerator. Aldrich *cis*-stilbene and piperylene were used as received. Naphthalene was recrystallized from methanol.

Analyses. ^1H NMR and ^{13}C NMR spectra were recorded primarily on a Bruker WM-250 FT spectrometer in $CDCl_3$ except where noted, IR spectra on a Perkin-Elmer 599 spectrometer, UV spectra on either a Varian Carey 219 or a Shimadzu UV-160 spectrometer, mass spectra on a Finnigan 4000 GC/MS, and phosphorescence spectra on a Perkin-Elmer MPF-44A spectrofluorimeter.

Gas chromatographic analyses were performed on Varian 1400 machines with flame ionization detectors. Preparative collections were done on a Varian 900 equipped with a 20% SE-30 column. HPLC analyses were performed on a Beckman 332 gradient system on a silica column equipped with a Perkin-Elmer LC-75 UV detector.

Preparation of Ketones. All new compounds were analyzed by high-resolution MS on a JEOL HX-110 instrument by FAB with 6 keV xenon excitation of samples in nitrobenzyl alcohol matrices. The ketones were all purified to >99% as determined from their clear NMR spectra and by GC or HPLC analysis.

α-(o-Tolyl)acetophenone. *o*-Xylyllithium was prepared, as described by Broaddus,[78] from *o*-xylene, butyllithium, and tetraethylenediamine in 100 mL of ether. One-half mol equiv of benzoic acid in 100 mL of ether was added slowly; the solution was refluxed under nitrogen for 4 h. Normal aqueous workup afforded an oil; vacuum distillation provided a 36% yield of ketone, which was recrystallized from ethanol to yield white platelets, mp 67–68 °C (lit. mp 67–68 °C):[79] IR (CCl_4) 1690 cm^{-1}; ^1H NMR δ 2.30 (s, 3 H, aryl CH_3), 4.2 (s, 2 H, CH_2), 6.9–8.1 (m, 9 H, aromatic); ^{13}C NMR δ 19.7, 43.4, 126.1, 127.2, 128.3, 128.6, 130.2, 130.3, 133.1, 133.4, 136.8, 197.4; MS *m/z* 210 (M^+), 105 (base), 89, 77; (FAB) *m/z* 211.1123 (MH^+).

α-(o-Tolyl)-p-methoxyacetophenone. α-(*o*-Tolyl)acetic acid was heated with 1 equiv of phosphorous trichloride at 70–80 °C for 2 h. The cooled mixture was added to an excess of anisole containing 1 equiv of aluminum chloride at 0 °C. This mixture was heated at 75 °C for 2 h. Workup produced colorless crystals that were recrystallized from ethanol, mp 76–77 °C: Ir (CCl_4) 3080–2860, 1685, 1605, 1512, 1465, 1262, 1170 cm^{-1}; ^1H NMR δ 2.27 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 4.26 (s, 2 H, CH_2), 6.80, 7.82 (AB quart, J = 7 Hz, 4 H, *p*-MeO-benzoyl), 7.2–7.5 (m, 4 H, tolyl); ^{13}C NMR δ 19.7, 43.0, 55.3, 113.7, 126.0, 127.0, 129.8, 130.1, 130.2, 130.5, 133.8, 136.9, 163.4, 196.0; MS *m/z* 240 (M^+), 135 (base), 105, 91, 77.

α-Mesitylacetophenone. α-Mesitylacetonitrile was prepared by the procedure of Fuson and Rabjohn.[80] First, mesitylene was chloromethylated with formaldehyde and HCl; the distilled chloromethylmesitylene was then reacted with sodium cyanide in ethanol. The nitrile was vacuum distilled. Phenyllithium (70 mmol) was added to 63 mmol of the nitrile in 250 mL of ether. The solution was refluxed for 3 h. Workup afforded a 61% yield of crystals, which were recrystallized from ethanol to give white needles, mp 146.5–148 °C (lit. mp 147–148 °C):[81] IR (CCl_4) 1700 cm^{-1}; ^1H NMR δ 2.2 (s, 6 H, *o*-CH_3), 2.3 (s, 3 H, *p*-CH_3), 4.3 (s, 2 H, CH_2), 6.8 (s, 2 H, mesityl meta C-H), 7.5–7.8 (m, 3 H, phenyl), 8.1 (d, 2 H, phenyl); ^{13}C NMR δ 20.2, 20.9, 39.2, 128.0, 128.6, 128.8, 129.2, 129.5, 133.1, 136.3, 136.8, 137.1, 197.1; MS *m/z* 238 (M^+), 223, 209, 147 (base), 119, 105, 91, 77; (FAB) *m/z* 239.1436 (MH^+).

α-(2,5-Dimethylphenyl)acetophenone. 2,5-Dimethylbenzoic acid was prepared by treating the Grignard of 2-bromo-*p*-xylene with CO_2. The acid was reduced to the alcohol with $LiAlH_4$ in ether. The alcohol was converted to the chloride with thionyl chloride; the nitrile was prepared by treating the chloride with sodium cyanide in DMSO. The crude cyanide in ether was added to an ether solution of phenylmagnesium bromide. After 4 h of reflux and workup, the crude product was purified by chromatography through 50 g of alumina with petroleum ether as eluent to give white crystals, mp 52–53 °C: IR (CCl_4) 1690 cm^{-1}; ^1H NMR δ 2.21 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 4.62 (s, 2 H, CH_2), 6.9–7.2 (m, 3 H, xylyl), 7.3–8.2 (m, 5 H, phenyl); ^{13}C NMR δ 19.2, 20.8, 43.4, 128.0, 128.7, 130.3, 131.0, 133.1, 133.3, 135.5, 198.0; MS *m/z* 224 (M^+), 119, 105 (base), 91, 77; (FAB) *m/z* 225.1279 (MH^+).

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α-(o-Ethylphenyl)acetophenone. Aldrich o-bromoethylbenzene was reacted with magnesium and then carbon dioxide in ether to generate the acid. The acid was reduced to the alcohol with LAH, the alcohol was converted to the chloride with thionyl chloride in benzene, and the chloride was converted to the nitrile with sodium cyanide in DMSO. Phenyl Grignard reagent was added to the nitrile in ether. Normal workup provided the ketone, which was recrystallized from either methanol or 95% ethanol, mp 35 °C: IR (CCl_4) 1698, 1688, 1449, 1208, 992, cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.5 Hz, 3 H), 2.62 (quar, J = 7.5 Hz, 2 H), 4.36 (s, 2 H), 7.14–7.23 (m, 2 H), 7.27 (dd, J = 4.8, 1.5 Hz, 2 H), 7.50 (tt, J = 7.3, 1.4 Hz, 2 H), 7.60 (tt, J = 7.3, 1.4 Hz, 1 H), 8.04 (dd, J = 7.1, 1.4 Hz, 2 H); ^{13}C NMR δ 14.5, 25.8, 42.7, 126.2, 127.6, 128.5, 128.6, 128.8, 130.7, 132.1, 133.3, 137.1, 142.8, 198.2; MS (FAB) m/z 225.1279 (MH^+).

α-(2,5-Diisopropylphenyl)acetophenone. p-Diisopropylbenzene was dissolved in dry DMF and cooled to −20 °C. A solution of bromine in DMF at −20 °C was added and the solution was stirred at −20 °C for 3 h. (*Caution: Addition of Br_2 to DMF must be done at low temperature to avoid a violently exothermic reaction.*) After quenching with sodium sulfite and workup, the 2,5-diisopropylbromobenzene[82] was distilled at 4 Torr. Preparation of the Grignard reagent and reaction with CO_2 produced 2,5-diisopropylbenzoic acid. The acid was reduced with $LiAlH_4$; the resulting alcohol was treated with thionyl chloride in chloroform to produce 2,5-diisopropylbenzyl chloride. 2-Phenyl-1,3-dithiane[83] was reacted with phenyllithium in dry THF at −50 °C for 6 h.[84] The benzyl chloride in THF was added and the solution was allowed to stir under nitrogen overnight. Workup provided an oil that was added to a stirred suspension of mercuric chloride (2 mol equiv) and mercuric oxide (3 mol equiv) in a 1:1 mixture of acetonitrile and water.[85] The mixture was refluxed for 4.5 h, during which time its color changed from milky yellow to milky white. After filtration and workup, vacuum distillation produced the pure ketone, bp 180–5 °C (1 Torr): IR (CCl_4) 1700 cm^{-1}; ^1H NMR δ 1.17 (d, 6 H, p-$CHMe_2$), 1.19 (d, 6 H, o-$CHMe_2$), 2.82 (m, 1 H, $CHMe_2$), 2.92 (m, 1 H, $CHMe_2$), 4.32 (s, 2 H, CH_2), 6.95–7.2 (m, 3 H, diisopropylphenyl), 7.3–8.0 (m, 5 H, phenyl); ^{13}C NMR δ 23.7, 23.8, 29.2, 33.4, 43.1, 125.3, 125.4, 128.1, 128.5, 128.9, 131.4, 132.9, 136.9, 145.8, 197.7; MS m/z 280 (M^+), 175, 105 (base), 77; (FAB) m/z 281.1905 (MH^+).

α-(2,4,6-Triisopropylphenyl)acetophenone was prepared by adding phenyl Grignard to 2,4,6-triisopropylbenzyl cyanide, prepared from triisopropylbenzene by the procedure described for 2,5-dimethylbenzyl cyanide. The ketone was recrystallized from methanol, mp 101.5–102.5 °C (lit. mp 113.5–114.5 °C):[86] IR (CCl_4) 1710 cm^{-1}; ^1H NMR δ 1.20 (d, J = 7 Hz, 12 H, o-iPr), 1.27 (d, J = 7 Hz, 6 H, p-iPr), 2.86 (sept, 3 H, $CHMe_2$), 4.46 (s, 2 H, CH_2), 7.05 (s, 2 H, m-tip), 7.52 (t, J = 7 Hz, 2 H), 7.62 (t, J = 7 Hz, 1 H), 8.1 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 24.0, 30.2, 34.2, 37.6, 120.9, 126.5, 128.0, 128.7, 133.1, 137.1, 147.1, 197.7; MS m/z 322 (M^+), 217, 203, 105 (base); (FAB) m/z 323.2375 (MH^+).

α-(o-Tolyl)acetaldehyde. o-Tolylacetic acid (Aldrich) was reduced to the alcohol with $LiAlH_4$. The alcohol was oxidized with chromium trioxide/pyridine in methylene chloride.[87] The aldehyde was purified by distillation: IR (neat) 1725 cm^{-1}; ^1H NMR δ 2.2 (s, 3 H, CH_3), 3.6 (d, 2 H, CH_2), 7.1 (br s, 4 H, aromatic), 9.4 (s, 1 H, CHO); MS m/z 134 (M^+), 91 (base), 77.

α-(o-Tolyl)acetone. Phenyllithium was reacted with 2-methyl-1,3-dithiane[85] in THF at −20 °C for 2 h. The solution was cooled to −70 °C, and o-methylbenzyl bromide in THF was added and allowed to react for 2 h.[84] After workup, the solvent was removed. The crude dithiane was oxidized as described for (diisopropylphenyl)acetophenone. Workup and vacuum distillation produced pure ketone, bp 104–114 °C (12 Torr) (lit. bp 110–113 °C at 14 Torr):[15] ^1H NMR δ 2.1 (s, 3 H, $ArCH_3$), 2.2 (s, 3 H, $COCH_3$), 3.5 (s, 2 H, CH_2), 7.0 (br s, 4 H, aromatic); MS m/z 148 (M^+), 133, 119, 105, 91, 77.

α-Deuterated ketones were prepared by refluxing 0.01 mol of ketone in a mixture of 100 mL of dioxane and 85 mL of D_2O containing 0.2 mol of sodium carbonate.[88] After workup, the ketones were recrystallized either from hexane or from ethanol-O-d_1. Percent deuterium incorporation was determined by comparison of mass spectra for the parent ions and for the M − 105 ions (loss of benzoyl).

α-Mesitylacetophenone-d_2: ^1H NMR, same as for **6** except no peak at δ 4.3; 2.4% d_1, 97.8% d_2.

α-(2,4,6-Triisopropylphenyl)acetophenone-d_2: ^1H NMR, same as for **17** except no peak at δ 4.46; 3.7% d_1, 96.3% d_2.

Identification of Photoproducts. In general, 200-mg samples of ketone in 300 mL of cyclohexane were irradiated under nitrogen in an immersion well with a Pyrex-filtered 450-W Hanovia medium-pressure mercury arc. Removal of solvent left products that were judged to be >99% pure by HPLC analysis.

2-Phenyl-2-indanol. From α-(o-tolyl)acetophenone: IR (neat) 3770, 3080–2850 cm^{-1}; ^1H NMR δ 2.15 (br s, 1 H, OH), 3.24, 3.49 (AB quartet, J = 16.4 Hz, 4 H, CH_2), 7.2–7.4 (m, 7 H), 7.56 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 49.1, 83.3, 125.0, 125.2, 126.9, 127.2, 128.4, 140.9, 145.8; MS m/z 210 (M^+), 192, 105 (base), 91, 77.

2-(p-Methoxyphenyl)-2-indanol. From α-(o-tolyl)-p-methoxyacetophenone: mp 206–208 °C (recrystallized from hexane); IR (CCl_4) 3600, 3080–2880, 1612, 1515, 1250, 1180, 1042 cm^{-1}; ^1H NMR δ 2.12 (s, 1 H, OH), 3.24, 3.47 (AB quar, 4 H, J = 16.6 Hz, CH_2), 3.82 (s, 3 H, OCH_3), 6.83, 7.48 (AB quar, 4 H, J = 8 Hz), 7.16–7.36 (m, 4 H); ^{13}C NMR δ 48.7, 55.1, 82.8, 113.5, 124.8, 126.3, 126.6, 137.9, 141.0, 159.0; MS m/z 240, 222, 207, 178, 135 (base), 107, 77.

2-Phenyl-2-hydroxy-5-methylindan. From α-(2,5-dimethylphenyl)-acetophenone: IR (neat) 3540, 3420, 3080–2920 cm^{-1}; ^1H NMR δ 2.2 (br s, 1 H, OH), 2.21 (s, 3 H, CH_3), 3.02, 3.29 (AB quartet, J = 16.3 Hz, 4 H, CH_2), 6.88–7.01 (m, 3 H), 7.1–7.2 (m, 3 H), 7.39 (d, J = 7.3 Hz, 2 H); ^{13}C NMR δ 21.2, 48.8, 49.0, 83.4, 124.7, 125.2, 125.7, 127.0, 127.6, 128.2, 128.3, 136.4, 138.0, 141.2, 145.9; MS m/z 224 (M^+), 206, 191, 119, 105 (base), 91, 77.

2-Phenyl-2-hydroxy-4,6-dimethylindan. From α-mesitylacetophenone: IR (neat) 3520, 3370, 3080–2860 cm^{-1}; ^1H NMR δ 1.26 (br s, 1 H, OH), 2.16 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 3.07, 3.37 (AB quartet, J = 16.4 Hz, 2 H, CH_2), 3.08, 3.24 (AB quar, J = 16.3 Hz, 2 H, CH_2), 6.81, 6.83 (each s, 1 H, meta), 7.2–7.3 (m, 3 H), 7.47 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 18.8, 21.1, 47.6, 49.3, 82.8, 122.8, 125.0, 126.8, 128.1, 128.5, 133.7, 136.4, 136.7, 140.8, 147.6; MS m/z 238 (M^+), 220, 133, 105 (base), 91, 77.

(Z)-1-Methyl-2-phenyl-2-hydroxyindan was the major product obtained upon irradiation (Pyrex filter: >300 nm) to 100% conversion of 0.02 M α-(o-ethylphenyl)acetophenone in benzene-d_6: ^1H NMR (C_6H_6, 300 MHz) δ 1.18 (d, J = 6.8 Hz, 3 H), 2.97, 3.34 (AB quar, J = 16 Hz, 2 H), 3.39 (quar, J = 6.8 Hz, 1 H), 7.07–7.30 (m, 7 H), 7.48 (d, J = 7.8 Hz, 2 H). A doublet (J = 7.2 Hz) at δ 0.84 was assigned to the (*E*)-indanol methyl group by comparison to the chemical shifts of the two methyls in 1,1-dimethyl-2-phenyl-2-indanol below. Its integration was only 5% that of the doublet for the methyl group of the *Z* isomer. A similar solution in dioxane-d_8 was irradiated to 90% conversion. The *Z* and *E* methyl groups appeared at δ 1.16 and 0.75, respectively, in a 4.6:1 ratio. Two other doublets at δ 1.48 and 1.80 for a byproduct represented about 7% of the total product yield. Another sample of ketone in methanol was irradiated to 85% conversion. The solvent was removed and an NMR spectrum was obtained in $CDCl_3$. The (*Z*)- and (*E*)-indanols were present in a 2:1 ratio; the two unassigned doublets at δ 1.33 and 1.73 accounted for ~15% of the total, and a group of signals between 5.30 and 5.80 ppm suggested the presence of a few percent styrene. The two indanols were isolated as liquids by column chromatography on silica. *Z* isomer: IR (CCl_4) 3596, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 6.9 Hz, 3 H), 3.05, 3.39 (AB quar, J = 16.3 Hz, 2 H), 3.47 (quar, J = 6.9 Hz, 1 H), 7.18–7.30 (m, 5 H), 7.37 (t, J = 7 Hz, 2 H), 7.60 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 10.31, 49.31, 50.39, 85.44, 123.69, 124.87, 125.36, 126.95, 127.01, 127.06, 128.17, 140.09, 144.14, 145.0. *E* isomer: IR (CCl_4) 3603, 3450 (br), 1050 cm^{-1}; ^1H NMR δ 0.72 (d, J = 7.3 Hz, 3 H), 3.10, 3.68 (AB quar, J = 15.9 Hz, 2 H), 3.32 (quar, J = 7.3 Hz, 1 H), 7.21 (m, 4 H), 7.29 (m, 1 H), 7.34 (t, J = 6.5 Hz, 2 H), 7.45 (d, J = 6.3 Hz, 2 H); ^{13}C NMR δ 17.63, 44.58, 52.39, 86.10, 124.34, 124.88, 126.16, 126.92, 126.97, 127.36, 128.16, 140.1, 143.2, 146.7. Their stereochemistry was ascertained by addition of $Eu(dpm)_3$. The maximum downfield shifts recorded for the 2-phenyl ortho protons, the methyl, the methine, the upfield CH_2, and the downfield CH_2 were as follows: for *Z*, 0.30, 0.36, 0.25, 0.40, 0.25 ppm; for *E*, 0.85, 0.56, 1.40, 1.25, 0.78 ppm. The *E* isomer complexed with this shift reagent about ten times more strongly than did the *Z* and, unlike the *Z*, showed a hydrogen-bonded OH stretch in its FTIR spectrum.

1,1-Dimethyl-2-phenyl-2-hydroxy-5-isopropylindan. From α-(2,5-diisopropylphenyl)acetophenone: IR (neat) 3420, 3080–2860 cm^{-1}; ^1H NMR δ 0.76 (s, 3 H, CH_3), 1.27 (d, J = 6.9 Hz, 6 H, iPr), 1.35 (s, 3 H, CH_3), 2.03 (br s, 1 H, OH), 2.90 (m, 1 H, iPr), 2.99, 3.29 (AB quartet, J = 16.0 Hz, 2 H, CH_2), 7.10–7.28 (m, 3 H), 7.31–7.39 (m, 3 H), 7.58 (d, J = 7.0 Hz, 2 H); ^{13}C NMR δ 19.5, 24.1, 27.8, 33.9, 44.0, 51.3, 87.2, 122.6, 123.1, 123.2, 125.2, 126.4, 127.0, 127.6, 138.8, 141.9,

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147.4; MS *m/z* 280 (M^+), 161, 105 (base), 91, 77.

1,1-Dimethyl-2-phenyl-2-hydroxy-4,6-diisopropylindan. From α-(2,4,6-triisopropylphenyl)acetophenone: IR (neat) 3420, 3080–2850 cm^{-1}; ^1H NMR δ 0.78 (s, 3 H, CH_3), 1.29 (d, *J* = 7.3 Hz, 12 H, iPr), 1.36 (s, 3 H, CH_3), 2.14 (br s, 1 H, OH), 2.92 (m, 2 H, iPr), 3.08, 3.81 (AB quartet, *J* = 16.1 Hz, 2 H, CH_2), 6.90 (s, 1 H), 7.00 (s, 1 H), 7.24–7.38 (m, 3 H), 7.60 (d, *J* = 7 Hz, 2 H); ^{13}C NMR δ 19.6, 22.9, 23.1, 24.3, 28.1, 31.1, 34.4, 42.2, 51.6, 87.2, 118.4, 121.5, 124.1, 126.6, 127.1, 127.7, 133.6, 140.8, 144.8, 148.4; MS *m/z* 322 (M^+), 231, 217, 203 (base), 105, 91, 77.

A dioxane-d_8 solution of the ketone was prepared in an NMR tube: ^1H NMR δ (relative to dioxane at 3.70) 1.32 (d, *J* = 7.8 Hz, 12 H, *o*-iPr), 1.42 (d, *J* = 7.8 Hz, 6 H, *p*-iPr), 3.00 (sept, *J* = 7.8 Hz, 3 H, iPr), 4.56 (s, 2 H, CH_2), 7.13 (s, 2 H, *m*-tip), 7.60 (m, 3 H), 8.20 (dd, 2 H). The sample was irradiated with Rayonet 350-nm lamps until all the ketone had disappeared. Two singlets appeared in the vinyl region at δ 6.10 and 5.93 in a 4:1 ratio; a singlet at δ 0.78, with one-tenth the intensity of the vinyl signals, corresponded to one methyl of the indanol product. After sitting overnight, the signal at 5.93 ppm disappeared and was replaced with a singlet at 4.53 ppm, corresponding to the methylene group of the starting ketone, and a doublet at 8.20 ppm, corresponding to the ortho protons of the ketone. The remaining product, the major one formed, was concluded to be (*Z*)-1-phenyl-2-(2,4,6-triisopropylphenyl)ethanol: ^1H NMR δ 1.29 (d, *J* = 7.5 Hz), 1.36 (d, *J* = 7.5 Hz), 2.58 (br s, 1 H, OH), 2.76–3.46 (m, *J* = 7.8 Hz, C*H*Me_2), 6.10 (s, 1 H, vinyl), 7.12 (s, 2 H, *m*-tip), 7.35–7.95 (m, 5 H). The minor, unstable product was concluded to be the *E* enol, which displayed its vinyl proton at δ 5.93 and two aromatic proton singlets at δ 7.27 and 7.08. One drop of HCl was added to the solution of *Z* enol, which then was poured onto some sodium bicarbonate and allowed to evaporate. The solid was extracted with CCl_4; the resulting solution displayed the NMR spectrum of starting ketone with weak indanol peaks but no peak at 6.10 ppm.

A 10^{-2} M methanol solution of ketone was irradiated with 350-nm lamps until no ketone remained. Its UV spectrum showed the growth of a strong absorption with λ_{max} at 270 nm. Addition of one drop of concentrated HCl to the UV cell caused the UV spectrum to return to that of the starting ketone, with a distinct peak at 325 nm.

A 10^{-2} M toluene-d_8 solution of ketone was irradiated with 300-nm lamps; reaction progress was followed by NMR. At 10–20% conversion, the enol vinyl signal and the indanol methylene signal were formed in comparable amounts. By 80% conversion, no enol peak remained; only indanol signals were present.

α-(2,4,6-Triisopropylphenyl)acetophenone in benzene-d_6 was irradiated in a Pyrex NMR tube at 365 nm. Two separate samples were reacted to 59% and 64% conversion, as determined by integration of the δ 0.78 methyl signal of the indanol and the δ 4.32 α-methylene signal of the ketone (^1H NMR). Integration of the δ 6.13 vinyl signal of the enol product and the methyl signal of indanol indicated an average enol/indanol ratio of 1.0.

α-(2,4,6-Triisopropylphenyl)acetophenone-d_2 in CCl_4 was irradiated similarly. An indanol/ketone ratio of 0.35 was determined by comparison of the δ 0.78 methyl signal to the δ 8.1 doublet for the ortho protons on the benzoyl group. Integration of the δ 4.45 α-methylene signal and the δ 8.1 signal indicated 22% incorporation of ^1H in unreacted ketone. The ^2H NMR of a separately irradiated sample was recorded on a Bruker WH-180 spectrometer with a 10-mm broadband probe. The α-methylene deuterium signal of unreacted ketone appeared at δ 4.45 by reference to added $CDCl_3$. In the irradiated sample there were also ^2H absorptions at δ 3.82 and 2.82, corresponding to the ring CD_2 in indanol product and to the tertiary benzylic isopropyl proton in starting ketone and/or enol.

Procedures for Quantitative Measurements. Solutions containing ketone, internal standard, and any additive were prepared in volumetric glassware. Equal 2.8 mL volumes were transferred to 13 × 100 mm Pyrex or Kimax tubes. These were attached to a vacuum line where they underwent at least three freeze (liquid nitrogen)–pump (10^{-3} Torr)–thaw cycles, before being sealed under vacuum.

Samples were irradiated in parallel with actinometers on a merry-go-round apparatus[89] immersed in a room temperature water bath. A water-cooled Hanovia 450-W medium-pressure mercury arc was used as the light source. The immersion well containing it was placed in a filter solution containing 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3 to isolate 313-nm radiation. A set of Corning CS 7-37 filters were used to isolate the 365-nm band.

Samples were then analyzed either by GC or HPLC analysis. Response factors in relation to internal standards were measured with the isolated products. Solutions 0.1 M in either valerophenone or *o*-methylvalerophenone in benzene were used as actinometers. Quantum yields for formation of either acetophenone or *o*-methylacetophenone were 0.33[14] and 0.016,[90] respectively.

Flash Kinetics Measurements. Samples were prepared in 7 × 7 mm Suprasil cells and were degassed by bubbling purified nitrogen through them for several minutes. The apparatus has been described.[91] Excitation was provided by either an excimer laser operating at 308 nm or a nitrogen laser at 337 nm.

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