Boc-dmaPhe (40 mg, 0.11 mmol). EDC (21 mg, 0.11 mmol) and HOBt (15 mg, 0.11 mmol) were then added under cooling with ice. The stirring was continued overnight. The solvent was evaporated, and the residue was redissolved in chloroform. The chloroform solution was washed with 10% citric acid solution, water, 3% $NaHCO_3$ solution, and water and dried over $MgSO_4$. The solvent was evaporated. The residue was purified by column chromatography (silica gel/ethyl acetate) and recrystallized from ethyl acetate/hexane. Yield 41 mg (67%); mp 182–185 °C. Anal. Calcd for $C_{39}H_{44}N_4O_6$: C, 70.46; H, 6.67; N, 8.43. Found: 70.48; H, 6.88; N, 8.13.

Measurements. Spectroscopic measurements were carried out in TMP, THF, and a 1:1 mixture of THF and MTHF. The solvents were distilled before use. The sample solution was put into a quartz cuvette equipped with a Teflon stopcock. Argon gas was bubbled for 15 min before each measurement. The following spectrometers were used. Absorption, Jasco Ubest-50; fluorescence, Hitachi MPF-4; CD, Jasco J-600. The output of the spectrometers were interfaced to an NEC PC9801 personal computer. Fluorescence rise and decay curves were measured on a home-build single-photon-counting apparatus equipped with Ortec electronics. An air discharge lamp (fwhm = 3 ns) was used as the light source. The excitation and the emission wavelengths were selected by a combination of appropriate interference filters and glass filters. The excitation wavelength was 340–350 nm, and the emission wavelength was 380–390 nm for the monomer emissions and >550 nm for the exciplex emissions. The decay curves were analyzed by an iterative reconvolution method.

Conformational Analysis. The conformational calculation was carried out by using a set of programs for the conformational energy analysis of peptides of any amino acid sequence including the artificial ones. The software was developed by one of the authors (M.S.). The ECEPP parameters[15] were employed in the calculation, except for the two artificial amino acids, for which the structural parameters were taken from model compounds, and the energy parameters were calculated by a CNDO/ON MO calculations. The details of the parameters for the artificial amino acids will be reported elsewhere. The molecular model was drawn by using the NAMOD version 3 program.[16] The software was run on a NEC PC9801 personal computer.

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Registry No. I, 121445-62-3; II, 121445-60-1; III, 121445-63-4; IV, 121445-64-5; V, 121472-33-1; nitroPhe, 949-99-5; BOC-nitroPhe, 33305-77-0; BOC-dmaPhe, 105115-92-2; BOC-Glu(OBzl)·DCHA, 13574-84-0; Glu(OBzl)-OBzl·TosOH, 2791-84-6; BOC-Glu(OBzl)$_2$-OBzl, 89092-61-5; BOC-Glu(OBzl)$_3$-OBzl, 121445-54-3; BOC-Glu-(OBzl)$_4$-OBzl, 89107-69-7; pyrAla, 87147-90-8; BOC-pyrAla, 100442-89-5; BOC-pyrAla-Glu(OBzl)$_4$-OBzl, 121445-55-4; BOC-Ala, 15761-38-3; BOC-Ala-pyrAla-Glu(OBzl)$_4$-OBzl, 121445-56-5; BOC-dmaPhe-Ala-pyrAla-Glu(OBzl)$_4$-OBzl, 121445-57-6; Glu(OBzl) NCA, 3190-71-4; dmaPhe-Glu(OBzl)$_4$-OBzl, 121445-58-7; pyrAla-OMe·HCl, 107987-11-1; BOC-Ala-pyrAla-OMe, 121445-59-8; pyrAla-Glu(OBzl)$_4$-OBzl, 121472-34-2; Ala-pyrAla-OMe·HCl, 121445-61-2.

Long-Range Triplet Hydrogen Abstraction. Photochemical Formation of 2-Tetralols from β-Arylpropiophenones

Boli Zhou and Peter J. Wagner*

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48824. *Received February 7, 1989*

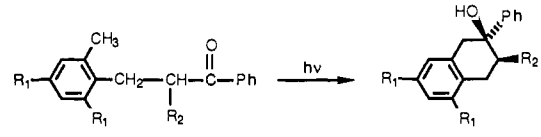
Abstract: The four ketones β-(*o*-tolyl)- and β-mesitylpropiophenone and -isobutyrophenone all undergo photocyclization to 2-tetralols via triplet-state ϵ-hydrogen abstraction. The intermediate 1,6-biradicals cyclize in 100% efficiency. The triplets react in very low quantum efficiency; rate constants for ϵ-hydrogen abstraction must compete with rapid (10^9 s^{-1}) CT quenching by the β-aryl group and range from $<3 \times 10^4$ for β-(*o*-tolyl)propiophenone to 3×10^6 s^{-1} for β-mesitylisobutyrophenone. The mesityl ketones are 10 times more reactive than the tolyl ketones; and the isobutyrophenones are 10 times more reactive than the propiophenones. The latter reactivity differences are ascribed to conformational constraints imposed by α-alkylation, contraints that actually increase the population of conformations close to that required for reaction.

The fortuitous preparation of β-(*o*-tolyl)propiophenone by the irradiation of the α isomer in the solid state[1] prompted us to investigate such structures for possible photoreactivity. We report that several β-(*o*-tolyl)propiophenones undergo triplet-state ϵ-hydrogen abstraction in competition with the well-known *rapid* internal CT quenching[2,3] to yield 1,2,3,4-tetrahydro-2-naphthols in high chemical but low quantum yields. These results add new information to two topics of considerable current interest: how rate constants for such remote hydrogen abstractions depend on molecular conformation[4,5] and how the behavior of triplet-generated biradicals varies with the distance between radical centers.[6]

Results

The four compounds in Scheme I have been studied. They were prepared by different procedures as described in the Experimental Section. Cyclohexane solutions approximately 0.003 M in ketone were irradiated for 2 weeks with only Pyrex filters. Compound **2** underwent only 25% conversion while compounds **3** and **4** were completely reacted. Collection by preparative gas chromatography

Scheme I



1 $R_1 = R_2 = H$
2 $R_1 = CH_3$ $R_2 = H$
3 $R_1 = H$ $R_2 = CH_3$
4 $R_1 = R_2 = CH_3$

Table I. Photokinetics of β-(*o*-Tolyl)propiophenones[a]

ketone	Φ(C_6H_6)	Φ(MeOH)	τ_T,[b] ns	$k_{\epsilon\text{-H}}$,[c] $\times 10^7$ s^{-1}
1	<0.000 05		1.4[d]	<0.003
2	0.000 17	0.0003	1.6	0.010
3	0.000 26	0.0012	1.0 (0.9)[d]	0.026
4	0.002 0	0.012	1.1	0.18

[a] All measurements represent the average of duplicate runs, with precision typically of ±8%. [b] Measured by quenching with 2,5-dimethyl-2,4-hexadiene in benzene. [c] $k = \Phi/\tau$. [d] From ref 3.

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(GC) provided 60–90% yields of cyclic products, which were identified as 2-tetralols by their spectroscopic properties. **1** reacts in such low quantum efficiency that product could be detected by GC but not in sufficient quantity to be isolated. Only one of the two possible epimeric products was detected from each of **2** and **4**. They were assigned as the *Z* isomers by analogy to the similar selectivity shown by α-methylbutyrophenone in its photocyclization.[7]

Quantum efficiencies are very low. They are considerably higher in methanol than in aprotic solvents, but they are the same within experimental error in acetonitrile, benzene, and benzene containing 2 M dioxane. Deuteration of the α-carbon in **3** and **4** does not alter the quantum yields of cyclization. Product formation is quenched by typical triplet quenchers such as 2,5-dimethyl-2,4-hexadiene. The measured $k_q\tau$ values range from 5 to 8 M^{-1}; such low quenching efficiencies indicate 1-ns triplet lifetimes in accord with earlier measurements of β-phenyl ketones.[2,3] All kinetic data are listed in Table I.

Discussion

β-Aryl groups are known to quench the triplet states of ketones very rapidly by a CT process.[2,3] All four ketones studied here have triplet lifetimes on the order of 1 ns; our quenching studies give values in close agreement with those previously measured by flash kinetics. Scaiano has shown that the rate constant for this quenching process is determined primarily by how the conformational flexibility of the molecule allows overlap between the aryl π-electrons and the half-empty n orbital on oxygen.[3] Our results indicate that α-methylation does not decrease this flexibility. This conclusion is not surprising given that the most stable conformations of most noncongested ketones have the largest α-substituent (here CH_2Ar) eclipsing the carbonyl oxygen.[4]

The very low quantum yields for cyclization indicate that rate constants of hydrogen abstraction barely compete with the CT process. Fortunately, the overall chemical yields of cyclization do not seem to be adversely affected by the low quantum efficiency except in the case of **1**, so the overall reaction may have some synthetic potential. The results raise three main points of mechanistic interest: (1) the variations in $k_{\epsilon\text{-H}}$, the rate constant for ε-hydrogen abstraction; (2) the extent to which hydrogen abstraction competes with the rapid CT quenching of the $n\pi^*$ triplet; and (3) the cyclization efficiency of the presumed 1,6-biradical intermediates.

k_ϵ Values. The $k_{\epsilon\text{-H}}$ values listed in the table were calculated from $k = \phi/\tau$. The validity of this simple equation rests on three conditions: (1) that singlet → triplet intersystem crossing is 100% efficient; (2) that the 1,6-biradical intermediates cyclize quantitatively; and (3) that all cyclized product arises in a single process competitive with the CT quenching. It has already been shown that β-aryl ketones have unit intersystem crossing yields.[2,3] 1-Hydroxy-1,*x*-biradicals are known to revert to starting ketone by two separate disproportionation reactions.[9] The fact that the added aprotic Lewis bases dioxane and acetonitrile do not enhance cyclization quantum yields the way they enhance type II quantum yields indicates that the biradicals do not undergo significant reversion directly to starting ketone.[10] The fact that α-deuteration does not enhance Φ indicates that the biradicals do not undergo significant disproportionation to the enol form of starting ketone.[11] Therefore, given the high chemical yields of tetralols, it appears that cyclization is the only significant reaction of the 1,6-biradicals.

We have always analyzed rate constants for intramolecular hydrogen abstraction as reflecting the relative populations of conformations that require little (or no) bond rotation and distortion in order to reach the transition state for hydrogen transfer.[5,12] In this picture there are four classes of ketones: (1) those with reactive C–H bonds within bonding distance of the carbonyl oxygen in the most stable or only ground-state conformer; (2) those that have such a perfectly reactive conformation partially populated, in equilibrium with other unreactive conformations; (3) ones that have no such perfectly reactive conformation but can attain a conformation close enough to that needed for reaction that small amounts of bond distortion can lead to reaction; and (4) those that have no low-energy conformations in which a C–H bond can come within bonding distance of the carbonyl. These β-aryl ketones obviously are not in the first or fourth class.

Chart I

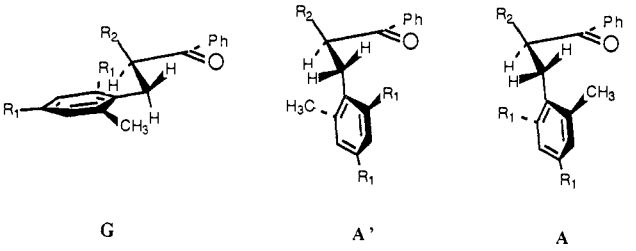

Table II. Conformational Energies Calculated by Molecular Mechanics

ketone	conformn	total energy,[a] kcal/mol
1	G	27.4
	A′	31.0
	A	29.5
2	G	28.5
	A′	31.3
	A	29.3
3	G	28.2
	A = A′	30.2
4	G	31.4
	A = A′	31.9

[a] Determined primarily by the steric energy contribution, since π resonance energies are almost identical throughout.

The 2.5×10^5 s^{-1} rate constant for hydrogen abstraction in triplet **3** is only 0.05% that for δ-hydrogen abstraction in α-mesitylacetophenone.[13] The β-mesityl ketones are 1 order of magnitude more reactive than the β-tolyl ketones; and α-methylation provides another 1 order of magnitude acceleration. Rate constants for δ-hydrogen abstraction by α-arylacetophenones share the former characteristic[13] but are *depressed*, not enhanced, by additional α-substitution.[14] We must explain these substituent effects as well as the 2000-fold drop in reactivity afforded by one extra methylene group. We presume that the rate constants are dominated by conformational limitations imposed by the bulky aryl groups.[14] The entropic loss associated with forming an 8- vs 7-atom transition state would be only 1–2 orders of magnitude;[4] and α-methylation of valerophenone does not lower rate constants for triplet γ-hydrogen abstraction.[15]

The mesityl/tolyl ratio undoubtedly reflects a preference for conformations that hold the single methyl of the tolyl ketones away from the carbonyl, as is the case in α-aryl ketones.[13] We have performed MM2 calculations that reveal precisely this conclusion. Chart I shows the minimum energy conformations for **1**–**4** and their calculated energies. In both **1** and **2** the anti conformer A′ with the methyl pointed away from the carbonyl is 1.5–2.0 kcal/mol more stable than the anti conformer A required for reaction (Table II).

The gauche conformation G is predicted to be most stable for all of the ketones. The presence of additional methyl groups either on the α-carbon or as part of the mesityl group enlarges the nonbonded gauche interactions that destabilize conformation G. An α-mesityl destabilizes G by 1 kcal in the case of **2** vs **1** and 3 kcal in the case of **4** vs **3**. Likewise, the extra *o*-methyl on a mesityl group destabilizes G by 1 kcal in **3** vs **1** and by 3 kcal in

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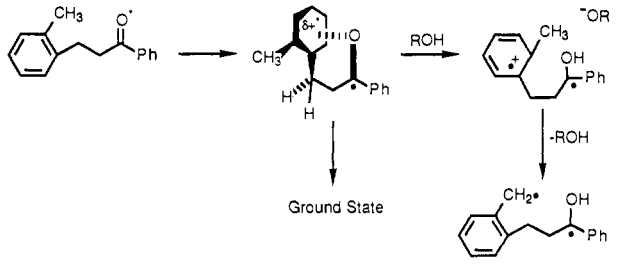
4 vs **2**. Both effects result in decreased energy differences between the G conformer and the reactive A conformer. The calculated percentage populations of the reactive A conformers of **1**–**4** are 0.2%, 0.7%, 2.6%, and 30%, respectively. The latter three parallel relative $k_{\epsilon\text{-H}}$ values very closely.

The decrease in reactivity for ϵ- vs δ-hydrogen abstraction is larger than the mere change in conformational populations. For example, α-mesitylacetophenone **5** exists in a conformation ideal for hydrogen abstraction as regards both orientation and distance.[1,9,14] Compound **4** apparently exists in a proper orientation much of the time yet is only 0.3% as reactive as **5**. There is an additional deactivation factor of 100 that must include the increased entropy loss for a larger cyclic transition state as well as the further strain required to bring the ϵ-carbon close enough to the carbonyl oxygen. In conformer G the ϵ-H is approximately 4 Å from the oxygen; it must get within 2.5–2.7 Å for reaction.[16]

These ketones belong to the third class outlined above. Their behavior exemplifies how class 3 represents a continuum that connects classes 2 and 4 and that there can be no simple rules based on transition-state ring size that satisfactorily predict reactivity in systems that involve the varying impediments to free bond rotation caused by rings and steric congestion. Since these ketones do not exist in conformations that can react without further bond distortion, their behavior adds no information to the question of orientational preferences[1,16] for hydrogen abstractions.

Special Effect of Methanol. The large increases in Φ observed in methanol solvent suggest an additional mechanism for cyclization, since dioxane is as efficient as alcohols at solvating other hydroxybiradicals.[10] The effect resembles the behavior of 2-naphthyl-γ-(dimethylamino)propyl ketone, which undergoes triplet-state type II elimination only in protic solvents. In that case internal CT quenching is rapid and the lowest $\pi\pi^*$ triplets do not abstract hydrogen atoms, so no biradicals are formed in aprotic solvents.[17] We suggested that solvent protonation of the triplet exciplex formed by charge transfer from nitrogen to carbonyl leads to the same biradical that could have been formed by direct hydrogen atom abstraction. The exciplex formed by CT interaction between β-aryl and carbonyl apparently also can be protonated on oxygen, with the resulting ion pair undergoing a second proton transfer to generate the 1,6-biradical. There have not been many examples of this phenomenon. We presume that the overlap between the β-aryl ring and the carbonyl n orbital produces a cyclic geometry that holds the *o*-methyls too far from the oxygen for direct transfer; instead only an acid-catalyzed transfer takes place. We cannot directly prove that no product arises from prior internal CT complexation in aprotic solvents, but the fact that $k_{\epsilon\text{-H}}$ values are so low suggests that no significant product arises from this path in aprotic solvents.



Biradical Behavior. It is becoming increasingly obvious that the 1,4-biradicals that intervene in the Norrish type II reaction, which normally revert to ketone in high efficiency,[10] are not good models for "longer" biradicals. Whereas some 1,5-biradicals also disproportionate directly back to ketone,[11,18] others disproportionate through a 1,4 hydrogen transfer to produce enols[11,19] and some cyclize in 100% efficiency.[9,13,20] In particular, the 1,5-biradical formed from α-(*o*-tolyl)acetophenone cyclizes to the exclusion of any competing disproportionation involving 1,4 or 1,6 hydrogen transfers.[13] In these homologous 1,6-biradicals, cyclization to a six-membered ring predominates over disproportionations involving 1,5 and 1,7 hydrogen transfers. That a reaction involving an 8-atom ring might be slow is not surprising, but enol formation would involve a 6-atom transition state yet does not compete.

Scaiano has proposed that product partitioning is determined by differential intersystem crossing rates for different biradical conformations.[21] Cyclization and disproportionation of these 1,6-biradicals both involve bringing the two ends of the biradicals within almost the same distance of each other. Therefore, it is difficult to envision how biradical partitioning might be governed by conformationally controlled intersystem crossing, unless movement along competing reaction coordinates is the discriminating factor. Consequently, we prefer to analyze the high cyclization efficiency for these 1,6-biradicals in terms of relative barriers for chemical reaction. In that case the additional rotational entropy loss associated with aligning the C–H bond with both half-occupied p orbitals and some serious eclipsing interactions make disproportionation uncompetitive with formation of a relatively strain-free six-membered ring, which requires alignment only of the two p orbitals.

Experimental Section

Preparation of Ketones. β-(*o*-Tolyl)propiophenone was prepared by alkylation of *tert*-butyl malonate with α-bromo-*o*-xylene followed by acylation with benzoyl chloride.[22] A mineral oil suspension of sodium hydride (0.083 mol) was added to a solution of 22 g (0.083 mol) of *tert*-butyl malonate in 100 mL of *tert*-butyl alcohol. After 3 h, 15 g (0.081 mol) of α-bromo-*o*-xylene in 40 mL of *tert*-butyl alcohol was added; the solution was stirred at 65 °C for 2 h. Crude *tert*-butyl α-(methylbenzyl)malonate was obtained quantitatively following aqueous workup. This was dissolved in 450 mL of benzene, 0.11 mol of sodium hydride suspension was added, the mixture was stirred at 80 °C for 4 h, 11 g (0.08 mol) of benzoyl chloride in 150 mL of benzene was added, and the mixture was heated for another 4 h. The cooled solution was neutralized with 4 g of *p*-toluenesulfonic acid and filtered. After removal of solvent, the residue was refluxed with 2 g of *p*-toluenesulfonic acid in 450 mL of glacial acetic acid containing 9 mL of acetic anhydride. The cooled solution was neutralized with KOH in ice. Normal workup was followed by vacuum distillation and recrystallization from ethanol to yield 5 g (30%) of colorless crystals, mp 46.5–47.5 °C: IR (CCl_4) 1704, 1615, 1210, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H, $ArCH_3$), 3.07, 3.24 (A_2B_2, J = 8.5 Hz, 4 H, $-CH_2CH_2-$), 7.1–8.0 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 19.18, 27.32, 38.89, 126.03, 126.17, 127.88, 128.46, 128.58, 130.19, 132.90, 135.79, 136.70, 139.23, 199.06; MS *m/z* 224, 206, 119, 105 (base), 91, 77.

β-Mesitylpropiophenone was prepared by the same procedure, the malonate ester being alkylated first with 2,4,6-trimethylbenzyl chloride; mp 81–82 °C: IR (CL_4) 1695, 1602, 1490, 1290, 1208 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H, *p*-CH_3), 2.32 (s, 6 H, *o*-CH_3), 3.08, 3.24 (A_2B_2, 4 H, $-CH_2CH_2-$), 6.78–8.0 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 19.66, 20.72, 23.63, 37.82, 127.93, 128.55, 128.99, 132.99, 134.72, 135.37, 135.96, 136.72, 199.45; MS *m/z* 252, 234, 219, 147, 132, 117, 105, 91, 77 (base).

β-(*o*-Tolyl)isobutyrophenone was prepared by alkylation of propiophenone enolate. The ketone (19 g, 0.14 mol) was added to a solution of 0.15 mol of LDA in 100 mL of THF at −78 °C. After 30 min, 20 g (0.14 mol) of α-chloro-*o*-xylene in 100 mL of THF was added. The solution was refluxed for 4 h after being allowed to warm for 2 h. Normal workup and distillation under reduced pressure afforded 15 g (42%) of a colorless liquid: IR (CCl_4) 1695, 1600, 1492, 1450, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 2.34 (s, 3 H, $ArCH_3$), 2.74 (a), 3.14 (b), 3.78 (x) (ABX, J_{AB} = 14.9 Hz, J_{BX} = 7.7 Hz, 3 H, $-CH_2CH-$), 7.06–7.92 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 17.42, 19.42, 36.17, 41.03, 125.67, 126.10, 127.99, 128.38, 129.50, 130.11, 132.66, 135.89, 136.33, 137.86, 203.65; MS *m/z* 238, 220, 133, 117, 105 (base), 91, 77.

β-Mesitylisobutyrophenone was prepared by the Friedel–Crafts acylation of mesitylene with α-chloroisobutyrophenone. The latter was prepared by stirring 30 g of isobutyrophenone with 28 g of sulfuryl

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chloride at 25 °C for 3 h. Aqueous workup afforded 25 g (67%). The α-chloroketone (15 g) was added to 60 mL of mesitylene containing 13.5 g of $AlCl_3$. The mixture was heated at 50–60 °C overnight. Normal aqueous workup was followed with column chromatography on silica with 30:70 benzene–hexane eluent and recrystallization from methanol to yield 10.6 g (49%) of colorless crystals, mp 53–54 °C: IR (CCl_4) 1693, 1600, 1482, 1450, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (d, J = 7.3 Hz, 3 H, $CHCH_3$), 2.22 (s, 3 H, p-CH_3), 2.32 (s, 6 H, o-CH_3), 2.96 (m, 2 H, CH_2), 3.76 (m, 1 H, CH), 6.82–7.86 (m, 7 H); ^{13}C NMR ($CDCl_3$) 17.27, 20.29, 20.62, 32.33, 40.67, 128.02, 128.39, 129.01, 132.69, 133.56, 135.22, 136.42, 136.59, 204.62; MS m/z 266, 248, 233, 161, 145, 133 (base), 105, 91, 77.

Deuterated ketones were prepared by treating dioxane–D_2O solutions of the ketones with dilute sodium hydroxide, followed by standard extraction and recrystallization.

β-Mesitylpropiophenone-α-d_2 was shown to be 94% d_2 and 6% d_1 by MS; the methylene ^1H NMR resonance at δ 3.24 had disappeared and that at 3.08 had become a singlet.

β-Mesitylisobutyrophenone-d was shown to be <1% d_0 by MS; in the ^1H NMR, the methylene signal had become a clear AB quartet at δ 2.86 and 3.03 and the α-methyl a singlet.

Isolation of Photoproducts. In general, 0.3 g of a given ketone in 500 mL of cyclohexane was irradiated with a Pyrex-filtered, water-cooled 450-W Hanovia medium-pressure mercury arc for 2 weeks. After solvent had been removed, products were isolated by being passed through a 5 ft × $^1/_4$ in. GC column containing 15% SE-30 held at 260 °C. The major product was further isolated by preparative TLC on silica.

3-Methyl-2-phenyl-1,2,3,4-tetrahydro-2-naphthol from β-(*o*-tolyl)isobutyrophenone: IR ($CDCl_3$) 3510, 1450, 1180, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (d, J = 6.7 Hz, 3 H, $CHCH_3$), 2.35 (s, 1 H, OH), 2.37–2.81 (m, 3 H, $-CH_2CH-$), 2.95, 3.37 (AB quartet, J = 17.3 Hz, 2 H, $ArCH_2$), 7.06–7.53 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 15.87, 34.67, 36.83, 45.60, 74.81, 124.94, 124.95, 126.01, 126.14, 126.61, 128.28, 129.34, 134.29, 136.20, 146.81, MS m/z 238, 220, 205, 133, 105 (base).

5,7-Dimethyl-2-phenyl-1,2,3,4-tetrahydro-2-naphthol from β-mesitylpropiophenone: IR ($CDCl_3$) 3580, 1445, 1225, 1175, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3 H, $ArCH_3$), 2.12 (s, 1 H, CH), 2.26 (s, 3 H, $ArCH_3$), 2.35–2.82 (m, 4 H, CH_2CH_2), 2.94, 3.28 (AB quartet, J = 17.5 Hz, 2 H, $ArCH_2$), 6.75–7.50 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 19.35, 20.77, 23.72, 35.34, 43.85, 72.14, 124.84, 126.93, 127.63, 128.23, 128.56, 130.64, 133.32, 134.10, 135.13, 147.55; MS m/z 252, 234, 219, 202, 143, 132, 105, (base).

3,5,7-Trimethyl-2-phenyl-1,2,3,4-tetrahydro-2-naphthol from β-mesitylisobutyrophenone: IR ($CDCl_3$) 3610, 1605, 1490, 1180 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (d, J = 7.1 Hz, 3 H, $CHCH_3$), 1.78 (s, 1 H, OH), 2.27 (s, 3 H, $ArCH_3$), 2.30 (s, 3 H, $ArCH_3$), 2.38–2.82 (m, 3 H, $-CH_2CH-$), 2.92, 3.48 (AB quartet, J = 17.1 Hz, 2 H, $ArCH_2$), 6.77–7.55 (m, 7 H); MS m/z 266, 248, 233, 132, 117, 105 (base).

Procedures for Quantitative Measurements. In general, samples of known ketone (0.03–0.06 M) and internal standard (0.007 M eicosane or nonadecane) concentration were prepared in purified solvents with volumetric glassware. Aliquots of 2.8 mL were transferred with syringes to 13 × 100 Pyrex tubes, which were then degassed in two freeze–thaw–pump cycles and sealed. Samples were irradiated in parallel on a "merry-go-round" apparatus[23] along with actinometer tubes containing 0.1 M *o*-methylvalerophenone, for which the quantum yield of *o*-methylacetophenone formation is 0.016.[24] Light at 313 nm was isolated with a basic potassium chromate filter solution. Because of the long irradiation times (2–4 days), several independent batches of actinometers were used; the total *o*-methylacetophenone obtained was added together to calculate the overall absorbed light intensity. Product yields and ketone disappearance were measured by GC on 15-m Megabore DB1 or DB210 columns held at 155–160 °C.

Molecular mechanics calculations were performed on an IBM XT with the MMPMI software produced by Serena Software, Bloomington, IN. Structural input was generated with MIO and then submitted to MMPMI for calculation. The resulting output structure was resubmitted to MMPMI in three steps: first with one dihedral angle drive operating for the C_α–CO bond rotation; then, with this rotation fixed at angles of minimized energy, with a second dihedral angle drive applied to rotation about the C_α–C_β bond. Finally, a third dihedral angle drive was applied to rotation about the C_β–aryl bond, without fixing the other two dihedral angles. Rotation of the β-aryl group did not change the first two dihedral angles from their input values. The energy-minimized structures were used as input for calculations without dihedral angle drive for verification that true minima had been obtained.

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