Diverse Photochemistry of Sterically Congested α-Arylacetophenones: Ground-State Conformational Control of Reactivity

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Abstract: The effects of α and ortho substituents on the photoreactivity of various α-(*o*-tolyl)- and α-mesitylacetophenones have been measured. In general, both types of substitution lower the efficiency of cyclization to 2-indanol derivatives in solution. 1,3-Rearrangement of an α-mesityl group to form enol ethers and α-cleavage to radicals compete to various degrees, in some cases becoming dominant. Quenching studies in solution show that all three reactions occur from the same n,π* triplet state; α-substitution lowers rate constants for δ-hydrogen abstraction and increases those for α-cleavage and 1,3-rearrangement. X-ray crystal analysis and MMX calculations both show that any additional substitution at the α-carbon of α-aryl (phenyl, tolyl, or mesityl) ketones favors conformers in which the α-aryl groups have rotated 120° away from eclipsing the carbonyl. In agreement with this, α-phenyl and α-(*o*-tolyl) ketones undergo γ-hydrogen abstraction (Norrish type II reaction) with rate constants almost as large as those of the nonarylated ketones. NMR line-broadening studies show that, in most of the α-mesityl ketones, the rate constants for rotation around the mesityl-α-carbon bond (10^4-10^6 s^{-1}) are much slower than triplet decay. The same is true for rotations around the carbonyl-α-carbon bond in the α-arylisobutyrophenones. Consideration of the spectroscopic evidence, triplet lifetimes, and calculated rotational barriers indicates that ground-state conformational preferences determine which excited-state reactions can occur in most of these ketones. Many of the ketones that cyclize in low yield in solution do so in much higher yield when irradiated as solids, presumably because α-cleavage to radicals becomes mostly revertible. The solid-state reactivity demonstrates that hydrogen abstraction can occur from what are supposedly nonideal geometries: in particular, large values (60-70°) for the dihedral angle that the reacting hydrogen atom makes with the nodal plane of the carbonyl π system. The relationship between this angle and rate constants for hydrogen abstraction in solution is discussed. Rate constants for α-cleavage reveal the separate influences of steric congestion and conjugation of the developing benzyl radicals. The 1,3-aryl migration to oxygen appears to arise from initial CT complexation of the α-aryl to the carbonyl; subsequent bonding of oxygen to the benzene ring apparently relieves steric congestion. The 50:50 initial mixture of *Z* and *E* enol ethers suggests that the rearrangement is adiabatic, generating enol ether in its twisted triplet state. A large enhancement of indanol yields by alcoholic solvents is suggested to involve protonation of the same CT complex.

In the accompanying paper, we describe the facile photocyclization of several α-(*o*-tolyl)acetophenones to 2-indanols.[1] The reaction proceeds by rapid triplet-state δ-hydrogen abstraction that generates 1,5-biradical intermediates. These have 20-50-ns lifetimes and undergo cyclization in very high efficiency (80-100%). Increased alkyl substitution on the α-tolyl group lowers the quantum yield of cyclization; this fact suggests that some CT quenching of the triplet can compete with hydrogen abstraction.

In order to determine the scope of this new photocyclization, we have looked at the effects of additional substituents on the α and ortho carbons of the acetophenone. We have communicated some of our findings: (1) such substitution produces sufficient steric congestion that δ-hydrogen abstraction is suppressed in favor of competing α-cleavage to radicals and/or 1,3-aryl rearrangement;[2] (2) hydrogen abstraction occurs from nonideal geometries;[3] and (3) α-cleavage is the only photoreaction of several of these ketones.[4] This paper describes in full all of our studies on this interesting class of sterically crowded molecules and fills in the gaps between the simple α-arylacetophenones[1] and the highly congested ones studied by Hart[5] and by Rappoport.[6]

Results

General Procedures. The various α-arylacetophenone derivatives studied were synthesized, purified, and characterized by standard techniques as described in the Experimental Section. Photoproducts were prepared by Pyrex-filtered near-UV irradiation of 0.3 g of ketone in 500 mL of cyclohexane or benzene. Products were separated and isolated by either gas chromatography (GC) or preparative thin-layer chromatography (TLC). Structural assignments are based on IR, NMR, and MS spectroscopic identifications.

Table I. Photokinetics of α-Phenyl Ketones[a]

ketone	Φ_{II}[b,c]	Φ_{CB}[c,d]	Φ_{α}[e]	$k_q\tau$, M^{-1}[f]
1	0.02 (0.04)	0.03 (0.05)	0.035 (0.26)	295
2				53
3	0.10 (0.16)	0.05 (0.12)	0.014 (0.09)	26

[a] In benzene at room temperature; all values reproducible to ±10%. [b] α-Phenylacetophenone. [c] Values with 0.5 M added pyridine in parentheses. [d] Cyclobutanol. [e] Benzaldehyde; value with 0.05 M dodecanethiol in parentheses. [f] 2,5-Dimethyl-2,4-hexadiene quencher.

Photokinetics. Quantum yields were measured by irradiating equal-volume, degassed samples in parallel with valerophenone actinometers[7] and measuring product yields by GC or HPLC analysis. The samples contained 0.02-0.06 M ketone and typically 0.001 M internal standard and were irradiated at 313 or 365 nm to 5-12% conversion. Triplet lifetimes were measured by Stern-Volmer quenching.[8] Similar samples containing various concentrations of either naphthalene (365 nm) or 2,5-dimethyl-2,4-hexadiene (313 nm) were irradiated in parallel, and the relative quantum yields of product were measured. Plots of Φ^0/Φ versus quencher concentration were linear; their slopes provided the $k_q\tau$ values listed in Tables I-III. The triplet lifetime of one of the more congested ketones, α-mesityl-α-phenyl-*p*-methoxyacetophenone, *p*-MeO-**12**, was measured in benzene by laser flash kinetics (308 nm excimer, 5 ns pulse). The 410 nm transient characteristic of *p*-methoxyphenyl ketone triplets[9] showed a

(1) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) Zhou, B.; Wagner, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6796.
(3) Wagner, P. J.; Zhou, B. *Tetrahedron Lett.* **1989**, *30*, 5389.
(4) Wagner, P. J.; Zhou, B. *Tetrahedron Lett.* **1990**, *31*, 2251.
(5) Hart, H.; Giguere, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7775. Hart, H.; Lin, L.-T. W. *Tetrahedron Lett.* **1985**, *26*, 575.
(6) (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007. (b) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701.
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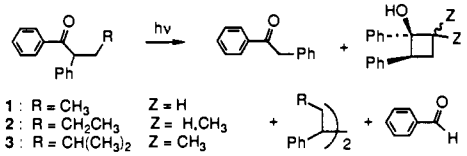
Table II. Photokinetics of α-(*o*-Tolyl) Ketones[a]

ketone	Φ_{cyc}[b]	Φ_α[c]	$k_q\tau$, M^{-1}[d]
4[e]	1.0	0	
5	0.05 (0.02)[f]	0.28	98 ± 10
6	0	0.38	121 ± 16
7	0.014[g] (0.34)[g,h]	0.03	28 ± 1

[a] In benzene at room temperature; values reproducible to ±10%. [b] Indanol. [c] Benzaldehyde with 0.005 M dodecanethiol present. [d] 2,5-Dimethyl-2,4-hexadiene quencher. [e] See ref 1. [f] In wet acetonitrile or *tert*-butyl alcohol. [g] Maximum value in methanol. [h] Type II products (α-tolylacetophenone plus cyclobutanol).

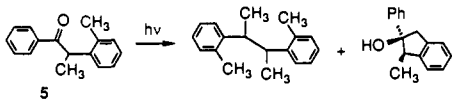
lifetime of 10 ns. This value, combined with our $k_q\tau$ value of 47 M^{-1}, indicates a k_q value of 4.7×10^9 M^{-1} s^{-1}, which is very similar to the "standard" value for exothermic energy transfer from triplet ketones to assorted polyenes.[10] Our earlier study[10] indicated that stereoelectronic factors but not steric congestion around the carbonyl lower k_q values. Therefore, we have used a value of 5×10^9 M^{-1} s^{-1} to calculate triplet lifetimes from our $k_q\tau$ values. Quantum yields of α-cleavage were measured from the benzaldehyde yields in the presence of approximately 0.05 M dodecanethiol or octadecanethiol, which trap all alkyl and acyl radicals that escape the solvent cage.[11,12] We verified with ketones **5** and **6** that benzaldehyde yields reach a maximum above 0.003 M thiol.

α-Phenyl Ketones. Table I lists the three α-phenyl ketones that were studied to determine what effect, if any, α-aryl substitution has on the rate constants for hydrogen abstraction by triplet ketones. They all undergo type II elimination and cyclization in competition with α-cleavage to radicals, in the yields noted.

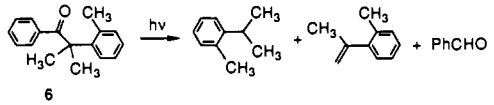


α-(*o*-Tolyl) Ketones. Table II compares the ketones that have been studied to α-(*o*-tolyl)acetophenone (**4**). It is apparent that additional α-substitution drastically cuts the quantum efficiency of cyclization.

α-(*o*-Tolyl)propiophenone (**5**) produced mainly a mixture of the diastereomeric 2,3-bis(*o*-tolyl)butanes and, in the presence of thiol, benzaldehyde. A 15% yield of (*Z*)-1-methyl-2-phenyl-2-indanol, identical to the major product from α-(*o*-ethylphenyl)acetophenone,[1] was also isolated. α-Deuteration of **5** did not affect this yield, but polar solvents decrease it. None of the (*E*)-indanol was detected.



α-(*o*-Tolyl)isobutyrophenone (**6**) forms only radical cleavage products in relatively high quantum efficiency. Benzaldehyde, *o*-cymene, and *o*,α-dimethylstyrene were collected by preparative GC after irradiation in the presence of 0.007 M dodecanethiol.



α-(*o*-Tolyl)valerophenone (**7**) undergoes primarily type II cleavage and cyclization together with small amounts of benzaldehyde formation and cyclization to (*Z*)-1-propyl-2-phenyl-2-indanol. The cyclobutanols were apparent in GC traces but were not specifically isolated. They are typically formed in 50% yield from α-substituted butyrophenones.[12] Total type II yields were quadrupled in wet acetonitrile.[7] When **7** is irradiated to high conversion, the major product is 2-phenyl-2-indanol, a secondary photoproduct from the **4** formed at low conversion.

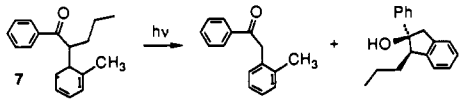


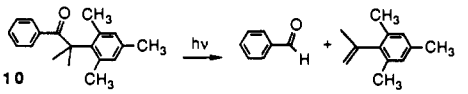
Table III. Photokinetics of α-Mesityl Ketones[a]

ketone	Φ_{cyc}[b]	Φ_α[c]	Φ_{EE}[d]	$k_q\tau$, M^{-1}[e]
8	0.44 (0.54)[f]			4.5
8-d_2	0.43			
9	0.24 (0.55,[g] 0.71[h])	0.02	0.012	17[b]
10		0.31		7.3[c]
11	0.12 (0.37,[g] 0.74[h])	0.006	0.005	5.0[i]
12	0.02 (0.03,[g] 0.06[h])	0.004	0.023	0.94,[b] 0.79[d]
12-*d*	0.02		0.021	
12-OMe	0.024 (0.041)[g]	0.005	0.010	47,[b] 42[d]
12-CN	0.008 (0.012)[g]	0.006	0.005	1.2[d]
13	0.035 (0.05)[j]	0.03		1.9[b]
14		0.016		3.8[c]
15		0.35		6.9[c]
16		0.33		0.6[c]

[a] In benzene at room temperature; values reproducible to ±10%. [b] Indanol. [c] Benzaldehyde, with 0.007 M dodecanethiol present. [d] *Z* and *E* enol ethers. [e] Naphthalene or 2,5-dimethyl-2,4-hexadiene quencher, 365 nm. [f] 1 M pyridine present. [g] 2 M dioxane present. [h] Wet acetonitrile or methanol. [i] Initial slope. [j] In dioxane or *tert*-butyl alcohol.

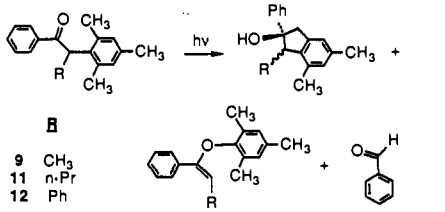
α-Mesityl Ketones. Table III compares the ketones that were studied to α-mesitylacetophenone (**8**). In most cases indanol yields are reduced by extra α-substitution, and enol ethers are formed in low yields. α-Cleavage is always competitive to various degrees.

Ketones **9–11** are analogous to **5–7**. Like **6**, α-mesitylisobutyrophenone **10** undergoes only radical cleavage. Benzaldehyde and 2-mesitylpropene were the major products detected and isolated by GC from irradiation in benzene.



Unlike **5**, α-mesitylpropiophenone (**9**) undergoes mainly cyclization to a 5:1 ratio of (*Z*)- and (*E*)-3,4,6-trimethyl-2-phenyl-2-indanols. The *Z*/*E* distinction is based on the 1.32 and 0.75 ppm chemical shifts of the doublets corresponding to the 3-methyl groups.[1] **9** undergoes only 2% α-cleavage, as detected by GC, and about 1% enol ether formation. A 1:4 *Z*/*E* mixture of the 1-mesitoxy-1-phenylpropenes was isolated by preparative GC.

α-Mesitylvalerophenone (**11**) behaves nearly the same as **9**, undergoing only a trace of type II cleavage, which was evident in the detection by GC of 4,6-dimethyl-2-phenyl-2-indanol, the photocyclization product of α-mesitylacetophenone. Only the *Z* isomer of the indanol where R = propyl could be detected and isolated. 1-Mesitoxy-1-phenylpentene was identified by GC–MS.



α-Mesityl-α-phenylacetophenone (**12**) undergoes only a trace of α-cleavage, forming comparable amounts of the indanol and the two 1-mesitoxystilbene isomers in low quantum yields. Only a single indanol isomer was isolated; it was assigned the *Z* stereochemistry because there were no aromatic resonances below 7 ppm, whereas two cis phenyls would shield each other and show signals in the 6.3–6.5 ppm range.[13] α-Deuteration does not

(9) Encina, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856.
(10) Scaiano, J. C.; Leigh, W.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806.
(11) Matsuura, T.; Kitaura, Y. *Tetrahedron* **1969**, *25*, 4487.
(12) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852.

Table IV. Dependence of Enol Ether Z/E Ratios on Conversion

ketone	isomer	ϵ^{365}, cm^{-1} M^{-1}	% (0.1% conv)	% (steady state)
12	*Z*	7	54.4	86.3
	E	47	45.6	13.7
12-OMe	*Z*	12	61.5	85.7
	E	63	38.5	14.3
12-CN	*Z*	1100	50.0	35.5
	E	620	50.0	64.5

[a] 0.1 M ketone irradiated at 365 nm in benzene at room temperature.

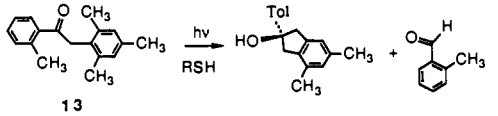
change, within experimental error, the indanol or stilbene quantum yields. Therefore, there cannot be significant enolization such as occurs with α-(triisopropylphenyl)acetophenone.[14] Precision was not sufficient to detect any secondary isotope effect on the indanol/stilbene ratio.

The *p*-methoxy and *p*-cyano versions of **12** also formed mixtures of indanol and two substituted mesitoxystilbenes, which were separated by preparative TLC. These ketones were studied primarily to determine the electronic origin of reactivity in terms of relative rate constants for hydrogen abstraction. For both **12** and *p*-MeO-**12**, indanol and enol ether formation were both quenched with comparable $k_q\tau$ values. Both substituents lowered enol ether yields and increased α-cleavage yields slightly.

Table IV indicates the E/Z enol ether ratios measured for **12** and its para-substituted versions. Because the enol ethers absorb more strongly than the ketones, the ratios change with conversion even at 365 nm. At 0.1% reaction, the Z/E ratio approaches unity. At 6–8% reaction or after prolonged irradiation of either pure isomer, the Z/E ratio is determined by the extinction coefficient ratio, since most or all of the light is absorbed by the enol ethers. Hart found the same conversion dependence in his studies.[5] No evidence was found for any phenyl migration; only mesityl ethers were formed.

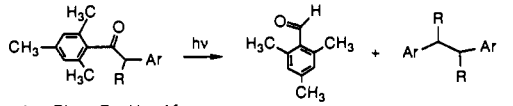
Whereas polar solvents decrease the indanol yield from **5** and only slightly increase it from **8**, they have much larger effects on **9**, **11**, and **12**. Dioxane (2 M) is normally sufficient to suppress back hydrogen transfer of hydroxy biradicals, and it doubles indanol quantum yields. However, protic solvents produce an even larger increase.

Ketones **13–16** were studied to determine how ortho substituents on the benzoyl group might affect reactivity. The effects are dramatic. From **13**, the indanol, *o*-tolualdehyde, and 1,2-dimesitylethane were isolated by prep GC. The single *o*-methyl decreases the quantum yield of cyclization 10-fold, such that α-cleavage occurs in comparable yield. The triplet lifetime is reduced by a factor of only 3, so the quantum yield changes are not merely due to the additional competing enolization reaction.[15]



13

All three α-aryl-2,4,6-trimethylacetophenones undergo only α-cleavage to radicals, generally in high efficiency except for **14**. Mesitaldehyde was detected from them all, 1,2-dimesitylethane from **15**, and 1,2-dimesityl-1,2-diphenylethane from **16**. No benzocyclobutenols[16] were detected from any of them, but some may not be stable to the GC analytical conditions.



Ar = Ph : R = H : **14**
Ar = Mes : R = H : **15**
Ar = Mes : R = Ph : **16**

(13) Knorr, R.; Ernst, L.; Friedrich, R.; Reibig, H.-U. *Chem. Ber.* **1981**, *114*, 1592.
(14) Wagner, P. J.; Meador, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 3684.
(15) Wagner, P. J.; Chen, C-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.
(16) Matsuura, T.; Kitaura, Y. *Tetrahedron* **1969**, *25*, 4487.

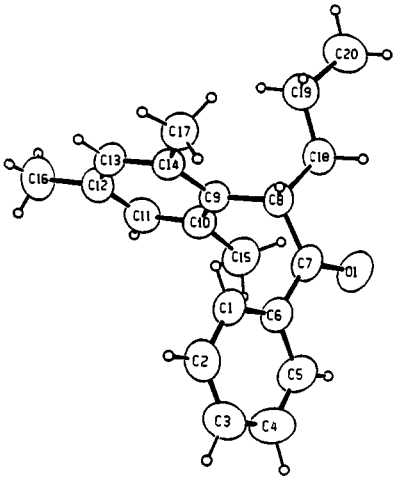


Figure 1. ORTEP for α-mesitylvalerophenone crystal.

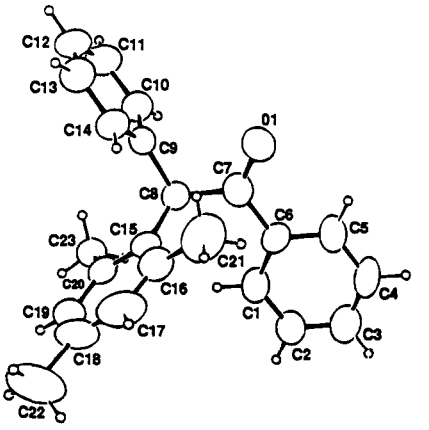


Figure 2. ORTEP for α-mesityl-α-phenylacetophenone crystal.

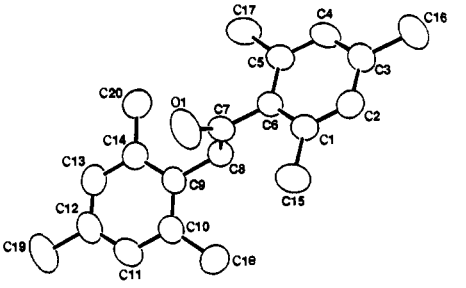


Figure 3. ORTEP for 1,2-dimesitylethanone crystal.

Solid-State Photochemistry. Crystals of ketones **5**, **9**, **11**, and **12** under argon were irradiated through Pyrex. The last three gave no benzaldehyde or enol ether products, which were prominent in solution. For **9** and **12**, indanol was the only product detected; **11** gave 6% of the type II product **8** and 94% indanol. Ketone **5** gave 67% indanol, 28% benzaldehyde, and 6% β-(*o*-tolyl)propiophenone. When **5** was irradiated in powder form deposited on a glass plate by evaporating a methylene chloride solution, the product yields were as follows: indanol, 50%; benzaldehyde, 25%; ditolylethane, 14%; β-(*o*-tolyl)propiophenone, 12%.

X-ray Structure Analysis. Figures 1–3 are ORTEP drawings of the crystal structures of ketones **11**, **12**, and **15**. Detailed crystallographic parameters are listed in the supplementary material.

NMR Line Broadening. In the room temperature ^1H NMR spectra of ketones **9** and **11**, the signals for the two ortho methyls and the two meta protons on the mesitylene ring are quite broad, suggestive of restricted rotation of the ring. Consequently, we studied these and several of the other ketones at low temperature and observed line broadening and coalescence in five of them: **6** and **9–12**. Figure 4 shows the results for **10**.

Table V. Dynamic NMR Line-Broadening Data

ketone	T, K	ω, Hz	k, 10^3 s^{-1}	ketone	T, K	ω, Hz	k, 10^3 s^{-1}
6[a]	185	50.0	0.65	**10** (α-Me)[d]	185	55.0	0.37
	190	22.5	1.22		190	30.0	0.63
	195	15.0	1.81		200	12.5	1.31
	200	7.5	3.99		210	7.5	2.20
9[b]	250	75.0	3.0	**11**[e]	280	50.0	2.9
	260	42.5	5.1		290	40.0	3.5
	270	22.5	9.9		300	22.5	6.5
	280	12.5	20.4		310	15.0	10.0
	290	7.5	44.3		320	10.0	16.5
10 (o-Me)[c]	210	35.0	6.2	**12** (meta)[f]	180	72.5	0.50
	220	15.0	14.9		185	47.5	0.75
	230	7.5	32.6		190	27.5	1.15
	240	5.0	54.3		210	5.0	8.00
					230	2.5	34.0

[a] ω_0 = 1.75 Hz. [b] ω_0 = 3.25 Hz. [c] ω_0 = 1.25 Hz. [d] ω_0 = 0.75 Hz. [e] ω_0 = 2.5 Hz. [f] ω_0 = 1.75 Hz.

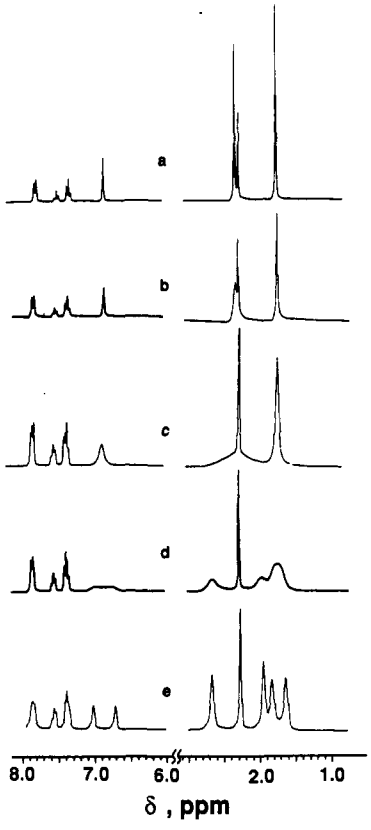


Figure 4. Temperature dependence of the 250-MHz NMR spectra of α-mesitylisobutyrophenone: methyl and aromatic resonances.

Line widths of the *o*-methyl signals were measured at several temperatures above coalescence; the *m*-mesityl protons were measured for **12**, because the *p*-methyl and *o*-methyl signals overlap. Exchange rates were analyzed according to eq 1,[17] where ω is the measured line width at half-height, ω_0 is the natural line width (usually 1.25 Hz), and $\Delta\nu$ is the difference in chemical shifts of the two separated signals at low temperature, all in hertz. These are listed in Table V. The exchange rate at coalescence was determined from eq 2.[17] Figures 5 and 6 compare the Arrhenius

$$2k_{ex}(\omega - \omega_0) = \pi(\Delta\nu)^2[1 + 2(\omega/\Delta\nu)^2 - (\omega/\Delta\nu)^4]^{1/2} \quad (1)$$

$$k = \pi\Delta\nu/\sqrt{2} \quad (2)$$

plots. In those cases where coalescence was accurately measurable (no interference by overlapping signals), the exchange rate at the coalescence temperature is included on the Arrhenius plots. Table VI lists the derived activation parameters for the bond rotations that exchange the *o*-methyl, α-methyl, and meta protons.

For **6** (7:1 CD_2Cl_2/CD_3OD), the α-methyl signal at 1.67 ppm coalesced at 180 K and separated into two signals (1.52 and 1.78

(17) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 78.

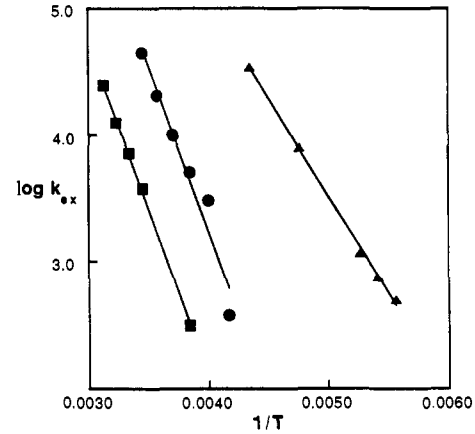


Figure 5. Arrhenius plots for exchange of *o*-methyl or *m*-mesityl protons in α-mesitylvalerophenone (■), α-mesitylpropiophenone (●), and α-mesityl-α-phenylacetophenone (▲).

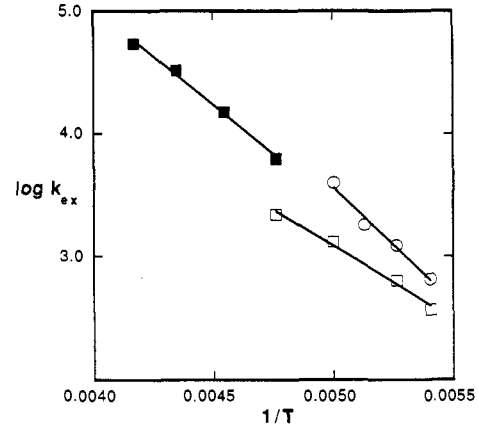


Figure 6. Arrhenius plots for exchange of (■) *o*-methyl protons and (□) α-methyl protons in α-mesitylisobutyrophenone and (○) α-methyl protons in α-(*o*-tolyl)isobutyrophenone.

Table VI. Kinetic Parameters from NMR Line-Broadening Studies

ketone	$\Delta\nu$, Hz	T_c, K	k_{coal}, s^{-1}	E_a, kcal	log A	k^{300}, s^{-1}
6	65	180	290	8.6	12.9	4.4×10^6
9	173	240	768	11.2	13.0	7.4×10^4
10 (o-Me)	178	200	800	7.3	11.4	1.2×10^6
10 (α-Me)	45	180	213	5.5	9.0	1.0×10^5
11	140	260	620	11.1	11.8	5.5×10^3
12	65 (meta)			7.1	11.3	1.2×10^6
	120 (o-Me)	188				

Table VII. Calculated Energies of Geometric Minima for α-Aryl Ketones

structure	energy, kcal/mol	structure	energy, kcal/mol
2E	26.4[a]	**7E** (syn)	33.3[b]
2G	23.8[a]	**7G**	30.7[b]
5E (syn)	30.2[b]	**9E**	32.8[b]
5G (syn)	29.2[b]	**9G**	30.8[b]
5G (anti)	28.3[b]	**10E**	36.2[b]
6E	>40[b]	**10G**	32.8[b]
6G (syn)	33.2[b]	**12E**	42.1,[b] 37.0[a]
6G (anti)	37.5[b]	**12G**	42.7,[b] 34.6[a]

[a] MMX. [b] MMPMI.

Table VIII. MMX Energies and Geometric Parameters for α-Mesitylpropiophenone **9** and α-Tolylpropiophenone **5**

β[a]	d, Å	ω	θ	MMXE, kcal
		9: No Restrictions		
135	2.72	70	120	24.4
127	2.67	65	114	24.3
120	2.61	61	105	24.6
105	2.56	50	101	25.7
90	2.54	35	96	27.3
75	2.58	14	93	29.7
60	2.58	9	97	30.4
45	2.62	21	127	28.0
30	2.60	35	125	28.4
10	2.63	74	113	26.7
		9: Benzoyl Planar		
140	2.82	76	119	26.4
130	2.73	67	113	25.2
120	2.64	59	108	24.8
110	2.57	50	108	25.1
100	2.53	41	99	26.2
90	2.52	32	96	27.9
80	2.54	21	93	30.0
60	2.63	9	94	32.6
40	2.64	17	126	28.6
20	2.60	26	124	28.6
		Hemipinacol Radical from **9**[b]		
123	2.67, 2.91	62, 99	109, 93	18.0
120	2.65, 2.91	60, 98	107, 93	18.1
110	2.56, 2.73	55, 93	104, 95	18.8
100	2.51, 2.61	48, 88	101, 96	20.2
90	2.49, 2.52	38, 80	98, 96	22.1
80	2.51, 2.48	26, 70	95, 97	24.2
70	2.66, 2.58	3, 44	90, 95	24.9
60	2.63, 2.81	24, −8	94, 85	23.6
50	2.71, 2.80	8, −19	91, 86	23.6
40	2.64	−30	125	20.5
30	2.64	−40	124	20.8
		syn-**5G**		
130	2.57	76	148	24.1
123	2.72	65	110	23.9
120	2.46	72	146	24.4
110	2.39	67	142	25.0
100	2.39	52	144	25.7
90	2.47	35	141	26.2
80	2.56	21	136	26.5
70	2.62	7	133	26.6
60	2.63	−5	130	26.7
50	2.63	−17	128	26.8
40	2.61	−28	126	27.0
30	2.57	−39	125	27.2
20	2.54	−48	124	26.6
10	2.55	−56	122	26.1
0	2.57	−64	120	25.7

[a] Dihedral angle for twist around bond b; 0° when α-aryl group eclipses carbonyl. [b] Two hydrogen atoms are within bonding distance at intermediate angles in all four species.

ppm) at 170 K. For **9** (acetone-d_6), the *o*-methyl signal at 2.16 ppm coalesced at 240 K and separated into two signals (1.90 and 2.59 ppm) at 200 K. The *m*-mesityl protons showed very similar temperature dependence, separating into two signals at 6.58 and 6.97 ppm. For **10** ($CDCl_3$), both the α-methyl and the *o*-methyl signals were temperature-dependent. The *o*-methyl signal at 2.30 ppm coalesced at 200 K and separated into two signals (1.91 and 2.62 ppm) at 185 K; the meta protons coalesced at 190 K and separated into signals at 6.62 and 6.94 ppm. The α-methyl signal at 1.72 ppm coalesced at 180 K and separated into two signals (1.60 and 1.78 ppm) at 175 K. For **11** (7:1 CD_2Cl_2/CD_3OD), the *o*-methyl signal at 2.28 ppm coalesced at 260 K and separated into two signals (2.01 and 2.59 ppm) at 230 K. The meta proton signal split into peaks at 6.62 and 6.94 ppm. For **12** (1:1 ethanol-d_6/acetone-d_6), the *o*-methyl signal at 2.19 ppm coalesced at 188 K and separated into two signals (1.96 and 2.44 ppm) at 170 K. The meta proton signal split into peaks at 6.79 and 7.05 ppm.

Table IX. Spectroscopic Properties of α-Tolyl and α-Mesityl Ketones

ketone	$\delta_{C=O}$, ppm	$\nu_{C=O}$, cm^{-1}	λ_{max} (L_a), nm[a]	E_T, kcal[b]
4	197.4	1697	238 (14 000)	73.5
5	200.4	1693	239 (13 000)	72.8
6	203.9	1692	240 (10 900)	72.4
7	200.2	1690	240 (9 100)	72.6
8	197.1	1700	237 (15 200)	73.5
9	202.3	1693	239 (12 100)	73.1
10	201.6	1689	240 (12 100)	72.6
11	204.0	1686	239 (12 300)	72.9
12	199.6	1697	238 (13 800)	72.9
12-OMe	198.2	1690	270 (16 500)	70.3
12-CN	198.6	1700	247 (23 800)	68.1
13	201.1	1692	235 (8 300)	73.7
14	207.2	1704		
15	206.1	1710	218 (21 700)	72.9
16	204.5	1705		72.8

[a] In heptane. [b] 0,0 phosphorescence band in 2-methyltetrahydrofuran at 77 K.

Molecular Mechanics Calculations. Given that most of these ketones appear to be so sterically congested that bond rotations are relatively slow, we calculated various energy-minimized conformations of each. Two versions of molecular mechanics were used, first MMPMI and later MMX as embodied in PCModel.[18]

Scheme I shows various local conformational minima for each ketone, and Table VII lists the calculated energies for each. These energies include both steric and π resonance energy. Dihedral drivers were used for rotations about two key bonds: the α-aryl–α-carbon bond c and the carbonyl–α-carbon bond b. The E and G labels refer to whether the α-aryl group eclipses (or nearly eclipses) the carbonyl or is twisted some 120°. No E minima were found for compounds **6** and **10**. Table VIII lists the minimized MMX energies at various rotation angles β around bond b in ketone **9**, in **9** with the benzoyl group held coplanar, in the hemipinacol radical of **9**, and in the syn form of ketone **5**.

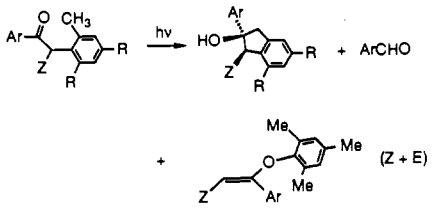
Spectroscopy. Table IX lists three spectroscopic measurements for these ketones that normally relate to the degree of conjugation between a benzoyl group's phenyl ring and its carbonyl group: (1) the chemical shift of the carbonyl carbon; (2) the position and intensity of the L_a band in the UV spectrum; and (3) the frequency of the carbonyl IR absorption. The table also lists the positions and energies of the 0,0 phosphorescence bands of most of the ketones at 77 K in 2-methyltetrahydrofuran. Although several of the ketones show absorption shifts in one or more categories, only **15**, with an L_a band at 218 nm and the highest energy carbonyl stretch, appears to have a nonconjugated trimethylbenzoyl group, as the X-ray structure revealed. Ketone **13** also has a relatively high energy L_a band and the highest energy phosphorescence; it may have a highly twisted chromophore. The table does not list data for the n,π* bands, which remain relatively unaffected by steric congestion.

Discussion

As described above, these ketones undergo three reactions in varying proportions: cyclization to 2-indanols, cleavage to radicals, and rearrangement to enol ethers. Some of the ketones undergo only one of the three, while others undergo all three competitively.

(18) Both programs were obtained from Serena Software, Bloomington, IN.

The main goal of this discussion is to establish molecular geometries and to then explain why these reactions compete to such different extents for the various ketones by determining how rate constants vary with structure and molecular geometry.

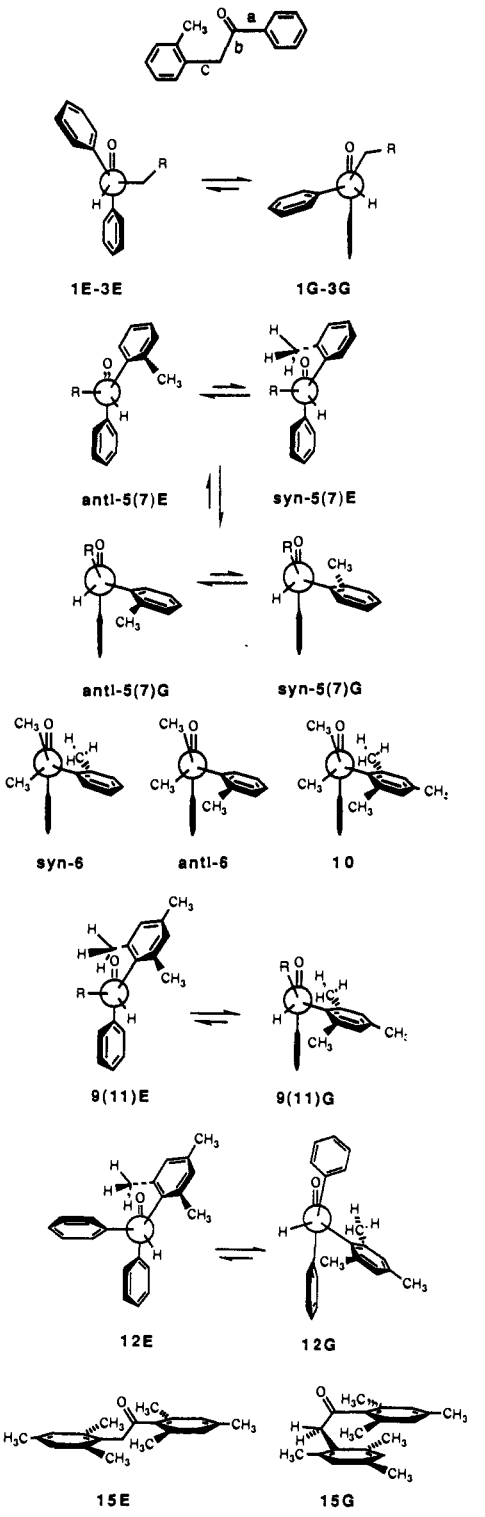


Basic Mechanisms. The cyclization is known to proceed by triplet-state δ-hydrogen abstraction that generates a 1,5-biradical.[1] Aldehyde formation involves triplet-state α-cleavage to benzylic and acyl radicals, which are trapped quantitatively by thiols.[11,12] In the absence of trapping agent, normal radical coupling and disproportionation products are formed. Enol ether formation involves a 1,3-aryl shift and has been observed previously only for α,α,α-triphenylacetophenone[19] and two α,α-dimesityl ketones.[5] Although the rearrangement of the two latter ketones was not quenched by modest concentrations of piperylene,[5] the fact that this reaction is quenched for **12** and its two derivatives indicates that it too is a triplet reaction. The triplet lifetimes are so short that relatively high quencher concentrations are required for significant quenching.

Both hydrogen atom abstraction and α-cleavage are well-known to be n,π* reactions.[9,20] Ketones **12** and *p*-MeO-**12** have n,π* and π,π* lowest triplets, respectively,[21] but each undergoes hydrogen abstraction only from its n,π* triplet.[22] Since cyclization and enol ether formation occur in similar ratios from both ketones, both reactions must arise from n,π* triplets. Since cyclization is quenched with the same efficiency as is enol ether formation in both ketones, both reactions must arise from either the same n,π* triplet or an equilibrium mixture of different n,π* triplets. No mechanism has been postulated for this 1,3-shift; we suggest that it is initiated by charge-transfer (CT) complexation of the donor α-aryl group to the n,π* triplet,[2] a reaction that we believe is common to ketones with electron-rich α-aryl groups[1] but that is not generally as fast as CT quenching by β-phenyl groups.[23]

There is additional evidence for such CT complexation: the extra increases in indanol quantum yields associated with protic solvents. Lewis base solvents always maximize product formation from hydroxy biradicals, but dioxane normally is as good as methanol.[7,15] The only other similar photoreactions in which such large, specifically protic solvent enhancements have been observed are the type II reactions of γ-amino ketones[24] and the cyclization of β-mesitylpropiophenones.[25] In both cases, the remote substituent is known to react with the triplet ketone by rapid CT complex formation. We have postulated that the protic solvent catalyzes hydrogen transfer by protonating the negative carbonyl oxygen in the CT complex.[24] The same thing apparently happens here. This conclusion opens to question the extent to which indanol formation in aprotic solvents may arise from CT interaction followed by proton transfer. The behavior of simple α-aryl ketones[1] suggests that competing CT quenching in the α-mesityl ketones does not lead to enhanced indanol yields. Therefore, we feel confident in using indanol quantum yields in aprotic Lewis base solvents to determine the amount of triplet decay attributable to direct δ-hydrogen atom abstraction.

Scheme I



Dissection of Rate Constants. The quenching studies indicate that most of these ketones have triplet lifetimes shorter than 10 ns. Since rate constants for unimolecular radiationless decay of simple phenyl ketones, as well as of α-phenylacetophenone,[26,27] are lower than 5×10^5 s^{-1}, we conclude that the triplet lifetimes are determined solely by rates of the various competing chemical reactions. Consequently the lower than unity total quantum yields represent significant reversion of intermediate to reactant, as is

(19) Heine, H. G. *Tetrahedron Lett.* **1971**, 1473.
(20) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.
(21) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.
(22) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.
(23) (a) Whitten, D. G.; Punch, W. E. *Mol. Photochem.* **1970**, *2*, 77. (b) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Haug, A.; Graber, D. R. *Ibid.*, 81. (c) Stermitz, F. R.; Niicodem, D. E.; Muralidharan, V. P.; O'Donnell, C. M. *Ibid.*, 87.
(24) Wagner, P. J.; Ersfeld, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4515.
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(26) Lewis, F. D.; Magyar, J. G. *J. Org. Chem.* **1972**, *37*, 2102.
(27) (a) Heine, H.-G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691. (b) Lewis, F. D.; Hoyle, C. H.; Magyar, J. G. *J. Org. Chem.* **1975**, *40*, 488.

Table X. Rate Constants for Competing Triplet Reactions of α-Arylacetophenones[a]

ketone	$1/\tau_T$	k_H[b]	k_α	k_{CT}
α-PhAP[c]	0.2		0.2	
α-PhPP[c]	2		2	
α-PhiBP[c]	12		12	
α-Ph_2AP[c]	10		10	
1	2.0	0.2	2	
2	10	8	(2)[d]	
3	23	21	(2)[d]	
4	16	16	<0.8	<0.8
5	5	0.25	2.8	≤2
6	4	<0.2	3.0	≤1
7	18	0.25 (6–12)[e]	~3	≤2
8	110	60	<1.0	50
9	30	16	1.2	12
10	70	<2	42	27
11	100	37	1.3	62
12	550	17	5	530
12-OMe	11	0.4	0.11	10
12-CN	420	5	5	410
13	260	15	16	230[f]
14	130	<2	4	126
15	73	<1	51	22
16	830	<10	540	270

[a] All in units of 10^7 s^{-1}. [b] k_δ or k_γ. [c] Reference 27a. [d] Assumed. [e] γ-Hydrogen abstraction. [f] Includes any enolization.

normal for triplet ketone reactions.[20] In such cases, minimum rate constants for the individual competing reactions can be determined from eq 3, where the Φ_{max} values represent quantum yields under conditions in which all of an intermediate has been trapped in some way.

$$k = \Phi_{max}/\tau_T \quad (3)$$

Deduction of actual rate constants requires that the amount of reversion by intermediate to ground-state reactant be determined. In many cases only estimates can be made. Quantum yields for α-cleavage were estimated by doubling the trapped benzaldehyde yields to correct for in-cage recombination.[28] For δ-hydrogen abstraction, the quantum yields in the presence of 2 M dioxane, which suppresses reversion of hydroxy biradicals to ketone, were used in eq 3. The values of k_H for **2** and **3** were calculated by simply subtracting 2×10^7, the rate of α-cleavage,[27a] from their overall triplet decay rates. The type II quantum yield in methanol was used to calculate k_γ for **7**. That portion of the total $1/\tau$ value not assigned to α-cleavage or hydrogen abstraction was assigned to internal CT quenching by the α-aryl group. The quantum yields for enol ether formation are assumed to represent the fraction of such CT interactions that result in actual bonding, as discussed below. All of the rate constants so calculated are listed in Table X.

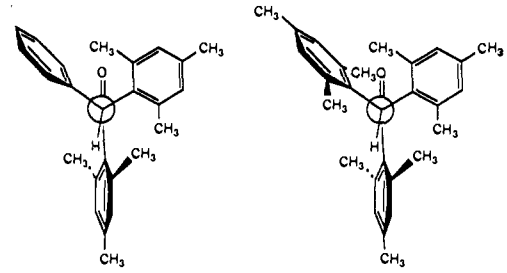
Effects of Substitution on Competing Reactions of α-(*o*-Tolyl) and α-Mesityl Ketones. We shall first summarize how rate constants vary for the α-(*o*-tolyl) ketones and the α-mesityl ketones. Then we shall consider how structural changes affect each independent competing reaction. Ketones **4** and **8** are the models for δ-hydrogen abstraction, while α-phenyl ketones are the models for α-cleavage.

The α-methyl group in **5** and the propyl group in **7** lower the rate constant for δ-hydrogen abstraction by a factor of 50 from that in **4**. Consequently, γ-hydrogen abstraction dominates in **7** while α-cleavage dominates in **5** as well as in **6**. The estimated rate constant for γ-hydrogen abstraction in **7** is good only to ±100% because of the overall low quantum yields, but the range brackets the value found for **2**.

The single extra α-groups in **9**, **11**, and **12** lower k_H by factors of 2–4 and accelerate α-cleavage and the 1,3-mesityl shift, such that all three reactions compete. δ-Hydrogen abstraction remains the major reaction in **9** and **11**, but the quantum efficiency of total product formation drops as the α-substituent gets larger. α-

(28) Lewis, F. D.; Magyar, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 5973.

Scheme II



16 17

Cleavage is the exclusive reaction for **10** because of the very high value for k_α, and the same is true for **14–16**. In **13** α-cleavage is faster and δ-hydrogen abstraction slower than in **8**, so that both occur with the same rate constant, but other reactions account for 90% of triplet decay, probably mostly enolization of the *o*-methylbenzoyl group.[15] In **15** and **16** α-cleavage and the presumed CT quenching are so rapid that hydrogen abstraction does not compete.

Molecular Geometries. Rappoport has quantitated and expanded the pioneering work of Fuson[29] by conducting an elegant investigation of various α-mesityl ketones that are so sterically congested that their enol forms are kinetically and often thermodynamically stable with respect to their keto form.[6] The ketones that we have studied display their steric congestion in a variety of ways. The dynamic NMR studies show that some of them undergo key bond rotations very slowly, with rate constants of only 10^4–10^6 s^{-1}. The molecular mechanics calculations show that the molecules often have restricted conformational freedom, with highly preferred conformations that minimize internal nonbonded interactions.

As shown in our accompanying paper,[1] α-tolylacetophenone **4** and α-mesitylacetophenone (**8**) exist preferentially in conformations with the α-aryl group eclipsing the carbonyl group and held perpendicular to the α-carbon–carbonyl bond. This is not a good geometry for hydrogen abstraction, but low-energy 20–30° twists around bonds b and c bring the δ C–H bonds into a highly favorable position for reaction. For all of the α-aryl ketones, any substituent on the α-carbon, from methyl to phenyl, causes bonds b and c (Scheme I) to twist substantially. The twists around bond c occur because the α-aryl ring is a substituted cumene.[30] The C–H bond of the ArCOCHR group prefers to be aligned parallel to the plane of the α-benzene ring with the ArCO and R groups held above and below the plane, so as to minimize interactions with ortho substituents. With the α-aryl group eclipsing the carbonyl, the required twisting of bond c can proceed only some 20° before causing severe nonbonded interactions. Rotation around bond b so that the R group nearly eclipses the carbonyl allows full twisting of bond c. Bond a also twists to minimize interaction of the benzoyl group's ortho substituent with the substituents on the α-carbon, at the expense of some conjugation. Only when R is phenyl do the calculations predict any significant population of E geometries. Scheme I depicts the various predicted stable conformations of these ketones.

Rappoport has reported the structures shown in Scheme II for **16** and **17**;[6] Hart has reported that **17** and 1-phenyl-2,2-dimesitylethanone (**18**) undergo only 1,3-mesityl shifts to produce enol ethers.[5] Interestingly, the two α-mesityl groups in **17** undergo much freer rotation than do the single α-mesityl groups in ketones **9–12**, since no line broadening was observed at the lowest temperature obtainable.[6] In contrast, rotation around the mesityl–carbonyl bond in **17** is hindered.

It is important to point out that the predicted lowest energy conformations of **11**, **12**, and **15** closely match the measured crystal structures. For example, the MMX calculations predict a β value of 127° in the lowest energy G conformer of **9**, in excellent

(29) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. R.; Shenk, W. J.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.
(30) Mannschreck, A.; Ernst, L. *Tetrahedron Lett.* **1968**, 5939.

agreement with the measured value of 129° in crystals of **11**. This correspondence speaks well for the accuracy of the molecular mechanics calculations on all of these ketones. The chemical shifts of ~1.9 and ~2.6 ppm for the ortho methyls in **9–12** indicate that one methyl group is shielded and the other deshielded by the benzoyl π system as expected for the twisted G geometry, which places one methyl group in the plane of the benzoyl phenyl ring and the other above it. Since the single methyl group of **5** appears at 2.5 ppm, we conclude that it spends most of its time in the anti conformation shown in Scheme I, where it is deshielded.

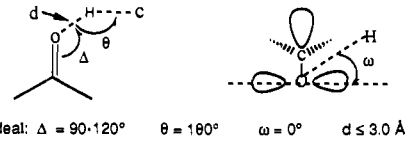
Our study of the α-phenyl ketones **1–3** revealed that the average value of k_H for the abstraction of a γ-hydrogen is 45% that for the comparable ketone without an α-phenyl.[7] This finding upholds the molecular mechanics calculations that indicate that an α-alkyl group rather than the α-phenyl prefers to eclipse the carbonyl. If the α-alkyl groups had been twisted 120° away from the carbonyl, the γ-hydrogens would spend very little time near the carbonyl and the rate constant for hydrogen abstraction would be much lower. The factor of 2 decrease in reactivity may reflect some population of the E rotamer or a small diminution of intrinsic n,π* reactivity because of electronic mixing with the α-aryl π system. It is interesting that a similar G geometric preference has been computed for *O*-methylmandelate esters,[31] supporting Siegel and Thornton's "perpendicular phenyl" explanation[32] for the facial selectivity observed in Diels–Alder additions to dienes containing such esters. The conformational preference favoring rotation of the α-aryl group of α,α-disubstituted carbonyl compounds some 120° away from the carbonyl apparently does not require an ortho substituent on the α-aryl ring.

The calculations in Table VIII indicate that there is a 6 kcal/mol barrier between the G and E geometries of **9**, with the former being some 2 kcal more stable than the latter and 4 kcal more stable than the conformations thought to be reactive in **4** and **8**.[1] The slow rotation around bond c in the α-mesityl ketones (10^3 to 4×10^4 s^{-1}) reflects the substantial steric hindrance that occurs when an *o*-methyl and an α-alkyl or α-phenyl group pass each other. The measured activation energies (7–11 kcal/mol) presumably measure that steric destabilization. Similar activation energies have been measured for other 2,6-dimethyl-*sec*-alkylbenzenes.[33] The slow rotation around bond b in **6** indicates that the slower rotation around b in **10** is independent of rotation around c. For the two α-methyls to become equivalent, the tolyl or mesityl group must eclipse either the carbonyl, such that the *o*-methyls interact unfavorably with the carbonyl oxygen or with an α-methyl, or—even worse—the benzoyl benzene ring. Consequently, the NMR results and the calculations agree that the lowest energy geometry has nonequivalent methyls, with one of them nearly eclipsing the carbonyl.

We did not perform the NMR line-broadening studies in order to obtain precise values for rotational activation parameters, and the values in Table VI are probably accurate to only 15%. Nonetheless, perusal of Table V and Figures 5 and 6 reveals that rotation of a mesityl group around bond c has similar activation energies in all of the ketones. The observed dependence of rate constants on the second α-substituent, phenyl > methyl > propyl, is determined mainly by the *A* factors; thus, the differential steric effects are largely entropic in origin. Likewise the faster rotation around bond b for **6** relative to **10** appears to be mainly entropic.

Ground-State Control of Photoreactivity. As just explained, a single extra α-substituent forces α-tolyl or mesityl groups to twist such that the highly reactive conformations with the aryl group nearly eclipsing the carbonyl are destabilized and barely populated (~0.1–1.0%) in the ground states. The reactive triplets do not have exactly the same geometries as the ground states. Since n,π* excitation is known to lengthen C–O bonds[34] and thought to make the benzoyl group more nearly coplanar,[35] and since Rappoport found that even small structural changes can greatly affect the orientations of remote atoms with respect to each other in such sterically congested molecules,[6] we performed the comparisons listed in Table VIII. Constraining the benzoyl group to be coplanar produces only negligible changes in the energies and orientational parameters of **9**. The MMX calculations on the hydroxy radical of **9** produced a C–O bond length of 1.33 Å, much closer to the expected triplet value than the 1.22 Å of ground-state ketone, and kept the benzene–C–O dihedral angle between 0 and 14°. The calculated minimum energy conformation of the radical has an angle β of 123° and a 7 kcal/mol barrier for rotation to a 2.8 kcal higher E conformer. Thus, altering the structure of **9** so as to closely mimic the geometry of the triplet makes little difference in the calculated barriers between and the relative energies of the E and G conformations. Even though a more precise calculation of transition-state energies for the triplets clearly is desirable, we feel safe in using the ground-state geometries to analyze excited-state reactivity. It apparently remains true that n,π* excitation is so localized on the carbonyl group that the rest of even such a sterically crowded molecule undergoes relatively small changes in geometry.

Scheme III



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

As noted above, all of the mesityl ketones undergo such slow rotation about the mesityl–α-carbon bond that the mesitylene ring can undergo only very limited twisting on the excited-state time scale of a few ns. Likewise, the α-arylisobutyrophenones undergo sufficiently slow rotation around the carbonyl–α-carbon bond that this rotation is also frozen on the triplet time scale. Given the calculated 6-kcal barrier to rotation from G to E conformers, the short-lived triplets of the sterically congested α-mesityl ketones probably can react only from the G conformations that are populated in the ground state.[36–39] Even when bond rotations may be fast enough to allow some interconversion of excited-state conformations, as in the α-tolyl ketones, the E rotamers would appear to be strongly disfavored. We shall rely on the molecular mechanics calculations, as summarized in Scheme I, to interpret how reactivity depends on molecular geometry, since the calculated structures were corroborated by X-ray structure determinations and by various spectroscopic characteristics.

Orientational Requirements for Hydrogen Abstraction. Scheme III depicts the various geometric features that must affect the transition-state energy for hydrogen abstractions. The most important are thought to be the linearity of the O–H–C alignment[40,41] as expressed by angle θ, the angles that the developing O–H bond makes with respect to the nodal plane of the carbonyl π system (ω) and with the long axis of the carbonyl (Δ), and the distance *d* from H to O. (We have maintained Scheffer's symbols[42] for everything except τ, which we label ω to avoid any confusion with lifetimes.) Various theoretical studies of the reaction agree that the optimal value of ω should be 0°; θ, 180°; and Δ, 90–120°.[41,43–45] These values provide maximum overlap of the hydrogen s orbital

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(34) Chandler, W. D.; Goodman, L. *J. Mol. Spectr.* **1970**, *35*, 232.
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(36) (a) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1969**, *91*, 6444. (b) Dauben, W. G.; Kellogg, N. S. *J. Am. Chem. Soc.* **1980**, *102*, 4456.
(37) Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090.
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(40) Corey, E. J.; Hertler, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1657.
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(45) (a) Sauers, R. R.; Scimone, A.; Shams, H. *J. Org. Chem.* **1988**, *53*, 6084. (b) Sauers, R. R.; Krogh-Jerperson, K. *Tetrahedron Lett.* **1989**, *30*, 527.

with the singly occupied oxygen n orbital, which is universally recognized as the locus of radical reactivity in n,π^* states.

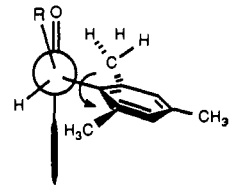
Solid-State Reactivity. Scheffer has reported several examples of ketones that undergo efficient intramolecular hydrogen abstraction in their crystalline states.[42] He has pointed out two structural features required for such behavior, both of which reflect the restrictions on molecular motion peculiar to the crystalline state: (1) the ketone must possess a geometry suitable for intramolecular hydrogen abstraction, i.e., one in which the molecule can proceed through the transition state to the biradical within the considerable constraints of the crystal lattice, and (2) the biradical must be able to proceed to stable product within the same constraints. He has observed a large number of γ-hydrogen abstractions in crystals in which the ketone molecules possess a wide range of values for all three important angles and d values up to 3 Å. He has concluded that the occurrence of all of these solid-state rearrangements indicates that reaction can occur with transition structures that cover a correspondingly wide gamut of orientations. Unfortunately, such studies do not give any indication as to how rate constants may vary as d and the angles change.

With regard to our studies, we observe efficient indanol formation upon solid-state irradiation of several ketones, some of which undergo competing reactions in solution. We concur with Scheffer that the mere occurrence of these hydrogen abstractions in the solid state means that the molecular structure measured for each of these ketones in their crystalline states represents a reactive geometry, one in which only minimal molecular motion is required, probably primarily along the C–H–O bond-stretching coordinate, in order for the molecule to proceed to the transition state. For the specific case of **11**, the solid-state geometric parameters are as follows: d = 2.72 Å; ω = 66°; Δ = 75°; θ = 115°; and β = 129°. Reaction obviously can occur from both the E (in **4** and **8**) and G (in **5**, **9**, **11**, and **12**) orientations of the α-aryl group. We conclude that reaction of all of these sterically congested ketones in solution can occur from either geometry but probably with different rate constants because of different component orientations.[20]

The absence of significant α-cleavage and enol ether formation in the solid state presumably derives from the rigidity of the crystal environment. A 1,3-rearrangement apparently requires too much molecular motion. α-Cleavage undoubtedly does occur, but the radical pairs cannot diffuse apart and instead recouple. The formation of β-tolylpropiophenone as a side product in the solid-state irradiation of its α isomer presumably indicates the expected disproportionation of the geminate radical pairs and the subsequent addition of benzoyl radicals to the styrene.[3] We need to perform additional experiments to substantiate this pathway.

Conformational Effects on Hydrogen Abstraction. It is clear from Table X that extra α-substitution on the α-aryl ketones depresses the rate constant for δ-hydrogen abstraction in solution. However, there is a large difference between the α-tolyl and α-mesityl systems in the extent to which k_H is depressed. Its value in **5** and **7** is only one-fiftieth what it is in **4**, whereas its average value in **9–12** is one-third that in **8**. Since both series of ketones exist primarily in the G conformation, we must carefully examine whether they are both subject to ground-state control and react only from G conformations or whether the large deactivation for **5** and **7** means that they react only from barely populated E geometries.

As discussed above, the α-mesityl ketones **9–12** must be reacting from their ground-state G conformations. We used a dihedral driver to calculate the effects of rotation about the mesityl–α-carbon bond in **9G**. The MMX energies gradually rose to 1.4 kcal/mol larger than that of the calculated global minimum over a 20° rotation in either direction. Interestingly, the distance between O and H varied no more than 0.1 Å, and the value of ω either stayed the same or *rose* as the molecule adjusted various bond lengths and angles to accommodate the twist. In particular, the degree of coplanarity of the benzoyl group decreased as the anti *o*-methyl swung down. This particular motion should be more disfavored in the triplet state. In any event, the key distance and angular aspects of hydrogen transfer do not vary much in those portions of the rotational well that are energetically accessible. Larger rotations increase the energy rapidly as an *o*-methyl gets close to the alkyl group R.



As shown in Table VIII, we estimated the barrier for rotation about bond b between the G and E conformations of **9**. The value of 6 kcal/mol would produce an actual G → E rate constant $\leq 10^8$ s^{-1}, if log A = 12. At the moment of excitation, at least 99% of the molecules are within 20° of the favored 127° value of β; very few of them would reach conformation E in their 3-ns lifetime. Since k_H for **9–12** is ~35% as fast as for **8**, little reaction can occur from geometries that are even 0.5 kcal/mol higher that the conformational minimum, unless those geometries are intrinsically *more* reactive than **8**. In fact, the best orbital alignment for reaction occurs at $\beta \approx 60°$, which is the *maximum* energy point for bond b rotation.

These calculations indicate that *all energetically accessible geometries of* ***9*** *have a benzylic C–H bond at a distance* $d < 3$ *Å from the carbonyl oxygen.* Since there is no unreactive conformer for the α-mesityl ketones, we believe that the 3-fold decrease in k_H values relative to **8** primarily reflects the high (65–70°) values of ω in **9–12**. The rotational barriers measured by NMR and the MMX calculations indicate that no conformation with an ω value near 0° can possibly be sufficiently populated to contribute to the observed rate constant. *All of the reactivity of the* α*-alkyl-*α*-mesityl ketones appears to arise from geometries with "nonideal" values of* ω *and none from partial population of a highly reactive eclipsed geometry similar to that of* ***8***. These measurements appear to provide the first quantitative evidence that rate constants for n,π^* hydrogen abstraction may show the predicted $\cos^2$ dependence[20] on the value of ω, since $\cos^2$ (65°) = 0.18, half the measured deactivation factor. An exact dependence on $\cos^2 \omega$ for the ground state could not be expected given the longer C–O bond in the triplet,[38] the likelihood of slight molecular reorganization in going to the transition state, and the unknown but presumed low value of ω for the model **8**. Moreover, the simple $\cos^2$ dependence only takes into account the n orbital spin density and not any possible decreasing spin delocalization onto oxygen in the developing hydroxy radical. *What is important is the fact that hydrogen abstraction does occur when* ω *is far from the ideal 0° but with a lower rate constant than when* ω *is close to 0°.* It must be stressed that the correlation of reactivity with ω values is intended merely to establish how wide a range of molecular geometries can undergo internal hydrogen transfer and not to insinuate actual transition-state structures.

Ito and Matsuura have drawn very different conclusions from their observation that 2,4,6-triisopropylbenzophenone undergoes photocyclization to a benzocyclobutenol in the solid state as well as in solution.[46] The trisubstituted benzene ring is twisted out of conjugation with the carbonyl so that the benzylic hydrogen is at an angle ω of some 56°. They conclude that this angle is too large for the n,π^* triplet to react and that therefore a π,π^* triplet must be involved. We see no reason for such a conclusion either in their work or in ours.

We have not explicitly considered θ and Δ values. The latter have near-ideal values of 80–110° in the various ground-state geometries, whereas the former tend to have very nonideal values of 90–120°. We pointed out long ago the apparent unimportance of ideal θ values,[47] and Scheffer's work[42] reinforces this conclusion, at least as regards reactant geometry. In fact, the distance d

(46) Ito, Y.; Matsuura, T.; Fukuyama, K. *Tetrahedron Lett.* **1988**, *29*, 3087.

(47) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.

appears to be far and away the most crucial factor in determining reactivity.[42,48]

If CT complexation in the α-mesityl ketones were leading to extra hydrogen transfer and biradical formation, a possibility that we discuss and discount above, our conclusion about geometric effects on k_H would still be valid, since it involves comparison of only α-mesityl ketones, all of which apparently undergo 50% or more CT quenching.

The very low quantum efficiency for δ-hydrogen abstraction by **12** is due to a great increase in the rates of competing reactions, since k_H is about the same as in **9**. The X-ray structure of **12** indicates that the mesityl group occupies the same position geometrically as in **9–11**; the calculations agree, although a conformation with the mesityl group eclipsing the carbonyl may be partially populated in solution. As indicated above, the lower k_H values for the cyano- and methoxy-substituted **12**'s are caused primarily by electronic, not conformational, changes.

Now we must explain the much larger decrease in k_H for the α-tolyl ketones. The rate constant for γ-hydrogen abstraction in **7** is comparable to that in α-phenylvalerophenone and half the value for valerophenone itself; thus, the population of the most reactive conformation for γ-hydrogen abstraction is not much different from what it is in valerophenone. Therefore, the measured reactivities in both types of internal hydrogen abstraction by triplet **7** reflect the molecular mechanics prediction that the α-tolyl group is twisted away from the carbonyl into two similar G conformations. The syn conformer has a benzylic hydrogen within bonding distance of the carbonyl oxygen but at an angle ω of 65°. The anti conformer has the methyl group twisted far away from the carbonyl, so it must be completely unreactive. The factor of 50 decrease in reactivity therefore reflects two factors: the reactive syn conformation is only partially populated and it suffers from poor orbital orientation. The higher k_H values for the mesityl ketones (as discussed above) and the 2.5 ppm chemical shift of the methyl protons in **5** (discussed above) cause us to infer a high anti/syn ratio for the α-tolyl ketones as the major cause of the low k_H value. The MMX calculations listed in Table VIII suggest only a 3.4 kcal/mol barrier for rotation to an E isomer that lies 1.8 kcal/mol above the G form. Consequently, we cannot rule out the possibility that some of the hydrogen abstraction by **5** and **7** arises from low equilibrium populations of E conformers. However, rotation around bond b raises the energy of **5E** much more than that of **4E** without greatly decreasing ω, so **5E** is probably appreciably less reactive than **4E**. In any event, the low reactivity is caused by very low populations of reactive conformations. The syn G geometry presumably has similar reactivity to that of **9**, so the anti/syn ratio may be as high as 16:1.

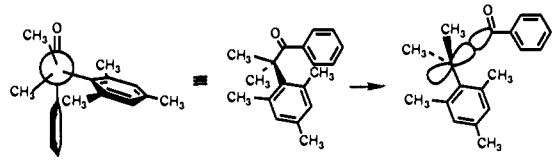
The lack of measurable δ-hydrogen abstraction and the high yield of α-cleavage from **6** indicates a maximum k_δ of $\sim 2 \times 10^6$ s^{-1}, similar to the measured values for **5** and **7**. The NMR line broadening confirms the molecular mechanics prediction that the tolyl group occupies essentially the same position as in the G orientations of **5** and **7**.

Of the other ketones studied, only **13** undergoes measurable δ-hydrogen abstraction, with a rate constant closer to that in **9** than in **8**. Normally, *o*-methyl ketones have a long-lived anti triplet from which reactions other than rapid enolization can occur; but only one short-lived triplet is observed for **13**. MMX calculations suggest that the lowest energy conformer closely resembles that of **15**, with both aryl rings perpendicular to the carbonyl. A conformation suitable for δ-hydrogen abstraction lies about 1 kcal higher.

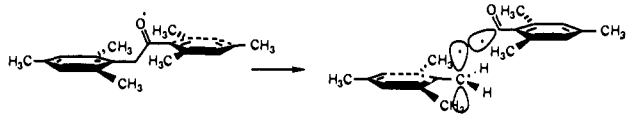
All of the ketones that undergo only radical cleavage also have greatly reduced k_H values; Table X lists estimated maximum values. The behavior of **15** is the most intriguing. It does not cyclize either to an indanol or to a benzocyclobutenol, a reaction which can have a large rate constant.[49] Its structure holds all of the *o*-methyls at least 3.1 Å away from the carbonyl oxygen. Slight twists around bonds a and b apparently allow hydrogen abstraction in **8**;[1] we doubt that they require so much energy in **15** as to be responsible for the lack of δ-hydrogen abstraction. Recently two examples have been reported of phenyl ketones whose triplets undergo hydrogen abstraction very sluggishly because their benzene rings are perpendicular to the carbonyl.[10,50] The lack of hydrogen abstraction by triplet **15** may be due to this as yet unexplained phenomenon; the high rate constant for α-cleavage certainly minimizes the efficiency of any competing hydrogen abstraction.

Structural Effects on α-Cleavage. Values of k_α for some comparable α-phenyl ketones are included in Table X for comparison. For **6**, **10**, and **14–16**, α-cleavage is the only reaction and k_α values must be nearly equal to $1/\tau$. The maximum quantum yields for thiol-trapped benzaldehyde are all in the range 0.31–0.38. These values are slightly lower than the 0.44 reported for simple α-phenylacetophenone but not as low as the 0.24 for α-(*p*-anisyl)-acetophenone.[27] After correction for radical recoupling, the measured benzaldehyde quantum yields represent 60–75% α-cleavage. The k_α values in the table are minimums.

There has been long-standing interest in the extent to which steric congestion drives radical cleavage reactions. In general, *o*-methyls on the α-aryl group do not cause k_α values to change much. Although **10** cleaves 3.5 times faster than does α-phenylisobutyrophenone, **6** cleaves only one-fourth as fast. The mesityl group in **10** has restricted rotational freedom, so that cleavage initially produces a nonconjugated cumyl radical. Therefore, **10** must derive most of its driving force for cleavage from steric congestion.



Ketone **15** undergoes only cleavage, despite looking relatively uncongested. Its two mesityl groups are parallel, such that their π systems are parallel to the C–C bond that is broken during cleavage. Consequently it has the ideal geometry for cleavage, forming two fully conjugated benzyl radicals. The 250-fold rate enhancement it shows over α-phenylacetophenone apparently consists mainly of the improved conjugation in the developing radicals.

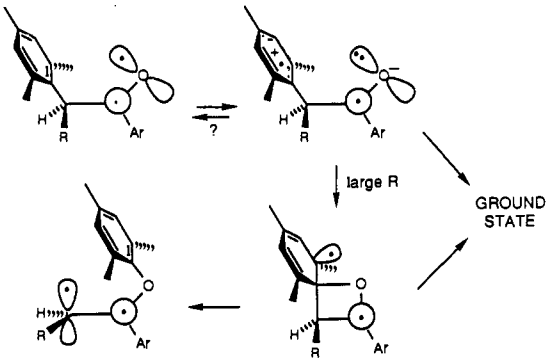


Ketone **16** is very similar to those studied by Hart. Like **15**, it has two cyclization possibilities but undergoes only cleavage extremely rapidly. Its X-ray structure was shown above. Rappoport has shown that once compounds become this congested they are forced into geometries with a good deal of built-in steric strain.[6] The best compromise for this molecule is a twist around bond b, with the α-phenyl group twisted 90° so as to minimize interaction with the α-mesityl's *o*-methyl groups. This geometry holds one mesityl group perpendicular to the bond being broken and another at a 45° angle. Therefore, the large cleavage rate constant is produced both by steric congestion and good resonance stabilization of the developing radicals. Interestingly, the α-mesityl group appears to be in a relatively good geometry for δ-hydrogen abstraction, but its rate is apparently overwhelmed by that for cleavage.

Mechanism for 1,3-Mesityl Migration. Previous to this work, only three highly congested ketones had been reported to undergo this rearrangement.[5,19] The fact that the reaction of **12** is quenched with the same efficiency as are cleavage and indanol formation demonstrates that it is a triplet reaction. The fact that the three

(48) Burke, S. D.; Silks, L. A.; Strickland, S. M. S. *Tetrahedron Lett.* **1988**, *29*, 2761.
(49) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259.
(50) Turro, N. J.; Gould, I. R.; Liu, J.; Jenks, W. S.; Staab, H.; Alt, R. *J. Am. Chem. Soc.* **1989**, *111*, 6378.

Scheme IV



competing reactions of **12** maintain similar rate-constant decreases when para substituents force a π,π^* lowest triplet indicates that all three reactions arise from the same n,π^* triplet.[9,11,51] Either a single n,π^* conformer undergoes all three reactions or the three reactions arise from different conformers that are in rapid equilibrium. Since, as discussed above, the α,α-diaryl ketones show lower rotational barriers than do the α-aryl-α-alkyl ketones, it is more likely that different conformers may react in **12** than in **9–11**.

No mechanism has been demonstrated for this rearrangement. Given its n,π^* triplet origin, we suspect some form of biradical process. The reaction obviously demands steric congestion at the α-carbon. The low overall reaction quantum yields that accompany this rearrangement indicate that the process that initiates it is both rapid and inefficient. Therefore, we have associated the reaction with the CT quenching that we have suggested for ketones with electron-rich α-aryl groups.[1,2] Scheme IV depicts the postulated mechanism, which is similar to one suggested by Hart[5] that did not include any prior charge transfer.

The key features of the mechanism are charge donation from an α-aryl group to the half-empty carbonyl n orbital. In the absence of significant steric congestion, this process merely produces quenching. The driving force for actual bonding of the ring to oxygen is attributed to increased steric congestion; such bonding pulls the mesityl group away from the center of congestion. The resulting 1,4-biradical has its two half-occupied p orbitals orthogonal to each other, so that cleavage of either middle bond looks stereoelectronically disfavored. However, the nearly 1:1 initial Z/E enol ether ratio for all three **12**'s strongly suggests that the rearrangement is a rare adiabatic triplet reaction, producing the triplet enol ether. Both Hart[5] and we have shown that the steady-state Z/E ratios are far from unity. The collapse of twisted triplet alkenes generally gives Z/E ratios close to unity.[52] There are no stereoelectronic restrictions on the biradical in Scheme IV cleaving to the twisted enol ether triplet. MMX calculations indicate that **12** and its enol ether photorearrangement product have the same energy within 2 kcal/mol. Given the low triplet energy of twisted stilbenes,[53] the overall conversion of triplet ketone to triplet enol ether (which is a stilbene) must therefore be decidedly exothermic.

The structure of ketone **17** was shown above; unlike our ketones, its mesityl groups undergo free rotation.[6] Its geometry should allow fairly rapid δ-hydrogen abstraction, but efficient rearrangement is the sole reaction.[5] Its geometry is very similar to that of **16**, which undergoes only cleavage. Both have an α-mesityl ring oriented for maximal overlap with the carbonyl n orbital. The lack of rearrangement in the less congested **16** may reveal a reversible CT interaction, with the actual aryl–oxygen bonding being rate determining, and it certainly accentuates how much enol ether formation depends on steric congestion.

The specificity of mesityl rather than phenyl migration in **12** undoubtedly reflects primarily the greater donor ability of the former and the greater relief of steric strain achieved when it moves away from the α-carbon. It is not clear what the exact effect of geometry is on the rearrangement. It would seem that a perpendicular eclipsing mesityl as in **8** would be the best geometry for the CT mechanism. Certainly all of the ketones with such a structure show internal quenching rate constants of at least 5×10^8 s^{-1}. The more sterically congested ones show larger rate constants. Ketones **9–11**, which have their α-mesityl groups strongly twisted, undergo slightly slower internal quenching but do give rearrangement. It may be that π overlap with the n orbital shows an angular dependence similar to that shown by hydrogen transfer or even draws the triplet state into an E geometry. In the case of **12**, an equilibrium mixture of two similar energy conformations, with the α-mesityl nearly eclipsing the carbonyl in one, probably explains the fast CT quenching and the single triplet lifetime for all reactions.

Biradical Behavior. The simple α-arylacetophenones form 1,5-biradicals that cyclize with very high efficiency.[1] The 1,5-biradicals from these more congested ketones cyclize much less efficiently. Thus pyridine, the strongest Lewis base used to maximize cyclization yields, enhances the quantum yield for **8** by only 20%, whereas aprotic Lewis bases enhance indanol quantum yields from **9**, **11**, and **12** by factors of 1.5 to 3. Several other biradicals also show large variations in partitioning as a function of solvation.[54] The null effect of α-deuteration on product quantum yields for **12** indicates that the biradical does not disproportionate to enol to any appreciable extent.[1] Apparently the bulkier biradicals encounter steric barriers to cyclization such that disproportionation back to ketone competes effectively as long as the hydroxy group is not hydrogen bonded to the solvent.[1] The fact that most of these ketones cyclize in the solid state indicates that the biradicals, once formed, can readily reach the geometry needed for final cyclization. Thus it is unlikely that the lack of indanol formation from **15** can be ascribed to an inability of the biradical to cyclize; if it had been formed, it should have cyclized.

α-Substituents on the ketone increase the steric energy of the indanol products. The 1-methyl group preferentially assumes the pseudo-equatorial position in the Z indanols formed from **5** and **7** as well as from α-(*o*-ethylphenyl)acetophenone (**19**).[1] Such a geometry in the indanols formed from **9–12** creates strong steric interference between the 1-substituent and the *o*-methyl group. The fact that **9** produces 17% of the (E)-indanol, while **5** produces only the Z, demonstrates that the extra methyl group can affect the conformational preferences of the 1,5-biradicals as well. We do not know why none of the E isomers were found from **11** and **12**. The quantum yield of indanol from **12** is low enough that a small amount of the E isomer may have been missed. The fact that the cyclization quantum yield of **11** is only half that of **9** indicates that the propyl group in **11** impedes cyclization more than does the methyl group in **9**.

These 1,5-biradicals show diastereoselectivity that is determined by different types of preexisting steric interactions. In the biradical from **19**, interactions of the methyl and phenyl groups with the rest of the molecule produce a dominant biradical conformation that cyclizes to the (Z)-indanol.[1,55] Scheme V compares the biradicals from **5** (X = H) and **9** (X = CH_3, *p*-CH_3 omitted) and assumes a basic conformational preference similar to that for the biradical from **19**. Because of the G reactant conformation, the biradical is formed in nearly the exo,syn geometry, from which cyclization produces the Z product. However, such biradicals normally prefer to be in endo geometries, and (E)-indanol would be formed from endo,syn. However, both forms are more stable anti when X = H. Consequently the biradical from **5** presumably cyclizes entirely from the endo,anti geometry. When X = CH_3, more of the endo,syn and exo,anti forms are populated to minimize steric interactions of the phenyl or *o*-methyl groups, respectively,

(51) Such substitution affects molecular geometry by changing the coplanarity of the benzoyl group, so relative rate constants may vary somewhat: Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.

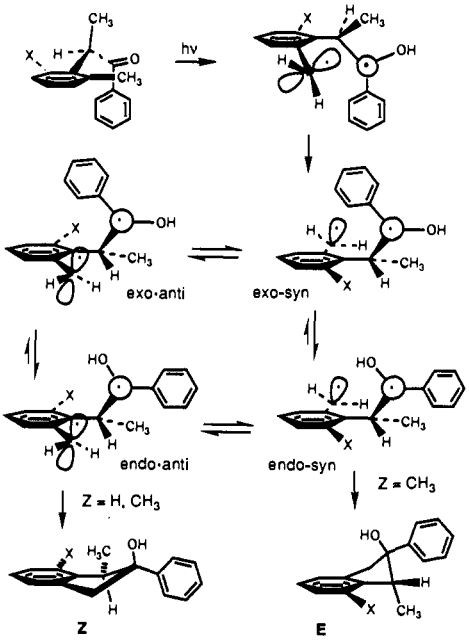
(52) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197.

(53) Tuqiang, N.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

(54) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

(55) Wagner, P. J.; Park, B.-S. *Tetrahedron Lett.* **1991**, *32*, 165.

Scheme V



with the α-methyl group. These results strengthen our belief that biradicals do not cyclize blindly after intersystem crossing and that normal steric effects control biradical partitioning even though intersystem crossing remains lifetime-determining.[1] We presume that these 1,5-biradicals have lifetimes of at least 20–50 ns like their less congested analogues;[1] we could not directly detect the biradicals by flash kinetics because of intense interference by the enol ether fluorescence.

Summary. These α-substituted α-arylacetophenone derivatives all appear to be so sterically crowded that their excited triplet reactivities are limited by their ground-state conformational preferences. Bond rotations are slower than triplet decay. For all aryl groups studied (phenyl, *o*-tolyl, and mesityl), the favored ground-state conformation G has the α-aryl group rotated some 120° relative to the eclipsed conformation E that prevails in α-arylacetophenones, in which the α-aryl group eclipses the carbonyl group. Rate constants for triplet δ-hydrogen abstraction differ for E and G conformations in a way that is consistent with a $\cos^2$ dependence on the angle ω; the angles Δ and θ do not appear to be as important as the distance between H and O. Several of the ketones are held in particularly good geometries for α-cleavage to conjugated benzylic radicals; rate constants for cleavage are thus high and are further enhanced by steric congestion. A few of the most congested ketones rearrange to enol ethers by a 1,3-mesityl migration to oxygen. A CT process abetted by relief of steric strain is suggested. All of these competing triplet reactions occur from the n,π* triplet level.

Experimental Section

Chemicals. All solvents were reagent grade materials purified as follows. Benzene and hexane were 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. 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. *n*-Dodecanethiol was distilled at reduced pressure.

Analyses. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-250 FT spectrometer, always in $CDCl_3$ solvent, 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 and 3400 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 Starting Ketones. All new compounds were analyzed by X-ray crystallography or by high-resolution MS on a JEOL HX-110 instrument by FAB with 6 keV xenon excitation of samples in nitrobenzyl alcohol matrices. They were purified to >99% as determined from their clear NMR spectra and by GC analysis.

α-Phenyl ketones were prepared by adding Grignard reagents to methylenedeoxybenzoin, which was prepared and reacted as described by Fiesselmann and Ribka.[56]

α-Phenylbutyrophenone was recrystallized from 10:1 hexane/benzene, mp 56–57 °C: IR (CCl_4) 1686, 1599, 1448, 1213 cm^{-1}; ^{1}H NMR δ 0.85 (t, J = 7.4 Hz, 3 H), 1.81, 2.15 (AB quar of quint, J = 7.4, 7.2 Hz, 2 H), 4.39 (t, J = 7.25 Hz, 1 H), 7.15–7.17 (m, 1 H), 7.21–7.26 (m, 4 H), 7.34 (td, J = 7.4, 1.4 Hz, 2 H), 7.41 (tt, J = 7.4, 1.4 Hz, 1 H), 7.91 (dd, J = 7.1, 1.4 Hz, 2 H); ^{13}C NMR δ 12.3, 27.1, 55.4, 126.9, 128.2, 128.5, 128.6, 128.8, 132.7, 137.0, 139.6, 200.1; MS m/z 224, 196, 165, 118, 105, 91, 77; (FAB) m/z 225.1279 (MH^+).

α-Phenyl-γ-methylvalerophenone was recrystallized from methanol and then hexane, mp 74.5–75.5 °C: IR (CCl_4) 2959, 1686, 1599, 1495, 1448, 1207; ^{1}H NMR δ 0.825, 0.88 (each d, J = 6.6 Hz, 3 H), 1.43 (non, J = 6.85 Hz, 1 H), 1.67, 2.01 (AB quar of t, J = 13.6, 7.4 Hz, 2 H), 4.61 (t, J = 7.4 Hz, 1 H), 7.13–7.15 (m, 1 H), 7.19–7.28 (m, 4 H), 7.33 (td, J = 7.4, 1.5 Hz, 2 H), 7.42 (tt, J = 7.4, 1.5 Hz, 1 H), 7.91 (dd, J = 7.0, 1.5 Hz, 2 H); ^{13}C NMR δ 22.0, 22.5, 25.35, 42.6, 50.6, 126.5, 127.8, 128.1, 128.2, 128.4, 132.4, 136.5, 139.4, 200.0; MS m/z 252, 237, 209, 196, 163, 147, 131, 105, 91, 77; (FAB) m/z 253.1592 (MH^+).

α-(*o*-Tolyl)propiophenone. A mixture of 0.048 mol of α-(*o*-tolyl)-acetophenone and a suspension of sodium hydride in mineral oil (0.047 mol) was refluxed in 160 mL of toluene for 1 h. Excess methyl iodide was added at room temperature: afer 12 h of refluxing, normal workup and distillation provided product, which was recrystallized from ethanol, mp 46.5–47.5 °C: IR (CCl_4) 3080–2860, 1693, 1603, 1498, 1453, 1335, 1230 cm^{-1}; ^{1}H NMR δ 1.48 (d, J = 7.3 Hz, 3 H, α-CH_3), 2.50 (s, 3 H, ArCH_3), 4.76 (quar, J = 7.3 Hz, 1 H, CH), 6.95–7.23 (m, 4 H, tolyl), 7.30–7.83 (t, t, d, 5 H, benzoyl); ^{13}C NMR δ 17.7, 19.2, 44.2, 126.4, 126.6, 128.1, 128.2, 130.7, 132.3, 134.2, 136.2, 136.6, 139.9, 200.4; MS m/z 224 (M^+), 119, 105 (base), 91, 77; (FAB) m/z 225.1279 (MH^+).

α-(*o*-Tolyl)valerophenone was prepared exactly as the analogous propiophenone with propyl bromide instead of methyl iodide. The liquid product was purified by chromatography on silica with 40% benzene in hexane as the eluent: IR (CCl_4) 3080–2875, 1690, 1603, 1495, 1455, 1252, 1230 cm^{-1}; ^{1}H NMR δ 0.94 (t, J = 7.7 Hz, 3 H, CH_2CH_3), 1.2–1.5 (m, 2 H, CH_2CH_3), 1.68 (ddt, J = 7.2, 5.3, 4.5 Hz, 1 H, $CHCH_2CH_2$), 2.20 (ddt, J = 8.0, 7.2, 4.5 Hz, 1 H, $CHCH_2CH_2$), 4.76 (dd, J = 8.0, 5.3 Hz, 1 H, CH), 7.05–7.20 (m, 4 H, tolyl), 7.3–7.5 (two t's, 3 H, phenyl), 7.84 (d, J = 7 Hz, 2 H, *o*-phenyl); ^{13}C NMR δ 14.0, 19.6, 21.0, 35.6, 49.2, 126.4, 126.6, 127.0, 128.0, 128.2, 130.7, 132.4, 134.7, 137.1, 138.4, 200.2; MS m/z 252 (M^+), 210, 147, 131, 117, 105 (base), 91, 77.

α-(*o*-Tolyl)isobutyrophenone was prepared by the methylation of α-(*o*-tolyl)propiophenone, as described in the preparation of α-(*o*-tolyl)-propiophenone itself. The liquid was purified by chromatography on silica with 20% benzene in hexane as the eluent: IR (CCl_4) 3080–2885, 1692, 1605, 1475, 1458, 1250, 1175 cm^{-1}; ^{1}H NMR δ 1.67 (s, 6 H, α-CH_3's) 2.07 (s, 3 H, ArCH_3), 7.03–7.2 (m, 4 H, tolyl), 7.3–7.82 (usual benzoyl); ^{13}C NMR δ 20.3, 27.5, 51.4, 124.4, 126.6, 126.8, 127.8, 129.1, 132.0, 132.1, 135.5, 135.9, 143.8, 203.9; MS m/z 238 (M^+), 223, 133, 115, 105 (base), 91, 77; (FAB) m/z 239.1436 (MH^+).

α-Mesitylpropiophenone. 2,4,6-Trimethylbenzyl chloride was heated overnight at 80 °C with an excess of sodium cyanide in DMSO. Normal workup provided crude α-mesitylacetonitrile. It was added to freshly prepared LDA in THF at −78 °C and then stirred at ambient temperature for 2 h. A slight excess of methyl iodide was added; the mixture was stirred for 2 h and then refluxed overnight. Workup provided crude α-mesitylpropionitrile. It was refluxed overnight with freshly prepared phenylmagnesium bromide in ether. Normal workup and chromatography on silica gel were followed with recrystallization from ethanol to give the pure ketone, mp 76.5–77.5 °C (lit.[29] 79.5–80 °C): IR (CCl_4) 3100–2890, 1693, 1602, 1488, 1455, 1325, 1230, 1187 cm^{-1}; ^{1}H NMR δ 1.48 (d, J = 7.3 Hz, 3 H, α-CH_3), 2.11 (s, 3 H, *p*-CH_3), 2.16 (s, 6 H, *o*-CH_3), 4.50 (quar, J = 7.3 Hz, 1 H. $CHCH_3$), 6.78 (s, 2 H, *m*-mesityl), 7.3–7.8 (usual benzoyl); ^{13}C NMR δ 15.0, 20.4, 20.6, 23.3, 45.7, 128.1, 130.2, 132.3, 135.3, 136.0, 136.7, 136.8, 202.3; MS m/z 252 (M^+), 147 (base), 105, 91, 77; (FAB) m/z 253.1592 (MH^+).

(56) Fiesselmann, H.; Ribka, J. *Chem. Ber.* **1956**, *89*, 27.

α-Mesitylvalerophenone. α-Mesitylvaleronitrile was prepared by alkylation of α-mesitylacetonitrile with propyl bromide, as described above for α-mesitylpropionitrile. This nitrile was reacted with phenylmagnesium bromide as described for the α-mesitylpropiophenone. The ketone was chromatographed on silica and then recrystallized from ethanol, mp 61.8–63.0 °C: IR (CCl_4) 3060–2875, 1689, 1602, 1485, 1453, 1253, 1215 cm^{-1}; ^1H NMR δ 0.97 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.30 (m, 1 H, $CHCH_2$), 1.57 (m, 2 H, $CH_2CH_2CH_3$), 2.19 (s, 3 H, p-CH_3), 2.28 (br s, 6 H, o-CH_3), 2.48 (m, 1 H, $CHCH_2$), 4.42 (dd, J_{AX} = 7.3 Hz, J_{AY} = 4.7 Hz, 1 H, $CHCH_2$), 6.78 (br s, 2 H, m-mesityl), 7.3–7.76 (usual benzoyl); ^{13}C NMR δ 14.4, 20.6, 20.8, 21.4, 32.7, 51.0, 128.0, 128.1, 130.3, 132.2, 135.8, 135.9, 137.6, 201.6; MS m/z 280 (M^+), 175, 133 (base), 105, 91, 77.

α-Mesitylisobutyrophenone. α-Mesitylpropionitrile was reacted with freshly prepared LDA in THF and then with methyl iodide as described above for α-mesitylpropionitrile. It was reacted with phenylmagnesium bromide in ether. Hydrolysis and workup provided the ketone, which was purified by chromatography on silica and recrystallization from ethanol, mp 64.5–66.0 °C: IR (CCl_4) 3070–2870, 1686, 1600, 1480, 1455, 1245, 1166 cm^{-1}; ^1H NMR δ 1.72 (s, 6 H, α-CH_3's), 2.23 (s, 3 H, p-CH_3), 2.30 (s, 6 H, o-CH_3), 6.77 (s, 2 H, m-mesityl), 7.3–7.74 (usual benzoyl); ^{13}C NMR δ 20.3, 23.6, 28.3, 53.3, 127.9, 129.4, 132.0, 132.1, 135.4, 135.6, 136.0, 139.4, 204.0; MS m/z 266 (M^+), 251, 236, 161 (base), 133, 121, 105, 91, 77; (FAB) m/z 267.1749 (MH^+).

α-Mesityl-α-phenylacetophenone was prepared by Friedel–Crafts alkylation of mesitylene with desyl chloride. A 2-fold excess of aluminum chloride and the desyl chloride were heated in mesitylene at 50 °C for 4 h. After workup, the ketone was recrystallized from ethanol, mp 112.5–113.5 °C (lit.[29] 113–114 °C): IR (CCl_4) 3090–2860, 1697, 1603, 1500, 1452, 1210 cm^{-1}; ^1H NMR δ 2.19 (s, 6 H, o-CH_3), 2.28 (s, 3 H, p-CH_3), 5.99 (s, 1 H, α-H), 6.89 (s, 2 H, m-mesityl), 7.03 (d, J = 7 Hz, 2 H, o-phenyl), 7.20 (t, J = 7 Hz, 1 H, p-phenyl), 7.32 (t, J = 7 Hz, 2 H, m-phenyl), 7.33 (t, J = 7 Hz, 2 H, m-benzoyl), 7.48 (t, J = 7 Hz, 1 H, p-benzoyl), 7.83 (d, J = 7 Hz, 2 H, o-benzoyl); ^{13}C NMR δ 20.6, 21.0, 56.6, 126.6, 128.0, 128.2, 128.6, 129.3, 130.2, 132.5, 133.2, 136.7, 136.8, 137.0, 137.1, 199.6; MS m/z 314 (M^+), 209 (base), 105, 91, 77.

α-Mesityl-α-phenyl-p-cyanoacetophenone. α-Phenylacetyl chloride was heated for 3 h at 60 °C with aluminum chloride in fluorobenzene. Workup provided crude α-phenyl-p-fluoroacetophenone. This was heated at 120 °C overnight with sodium cyanide in DMSO to prepare α-phenyl-p-cyanoacetophenone. This was dried and ground into a fine powder and chlorinated as described by Wyman and Kaufman.[57] It was added slowly to sulfuryl chloride and stirred for 5 h at ambient temperature. Addition of benzene and aqueous workup afforded crude α-chloro-α-phenyl-p-cyanoacetophenone, which contained 15% of the dichlorinated product (mass spectroscopy). It was reacted as such with mesitylene and aluminum chloride. Workup and recrystallization from ethanol/chloroform gave the desired ketone, mp 159.0–160.0 °C: IR (CCl_4) 3095–2870, 2230, 1700, 1614, 1502, 1456, 1298, 1210, 1010 cm^{-1}; ^1H NMR δ 2.17 (s, 6 H, o-CH_3), 2.28 (s, 3 H, p-CH_3), 5.90 (s, 1 H, α-H), 6.88 (s, 2 H, m-mesityl), 7.02 (d, J = 11 Hz, 2 H, o-phenyl), 7.25–7.36 (m, 3 H, phenyl), 7.63, 7.89 (AB quar, J = 12 Hz, 4 H, p-cyanobenzoyl); ^{13}C NMR δ 20.7, 21.0, 57.0, 115.7, 117.8, 127.0, 128.2, 128.6, 129.3, 130.5, 132.1, 135.8, 136.8, 137.3, 140.1, 198.6; MS m/z 339 (M^+), 209 (base), 130, 102, 91, 77.

α-Mesityl-α-phenyl-p-methoxyacetophenone. α-Mesityl-α-phenylacetic acid was prepared by heating mandelic acid in mesitylene with a 2-fold excess of stannic chloride for 2 h at 65–70 °C, followed by aqueous workup and recrystallization. The acid was heated with PCl_3 for 2 h at 70–80 °C to prepare the acid chloride. The acid chloride was heated with aluminum chloride in anisole at 75 °C for 3 h. Workup and column chromatography were followed by recrystallization from ethanol, mp 96.4–98.5 °C: IR (CCl_4) 3090–2840, 1690, 1600, 1514, 1460, 1313, 1265, 1216, 1175 cm^{-1}; ^1H NMR δ 2.18 (s, 6 H, o-CH_3), 2.27 (s, 3 H, p-CH_3), 3.80 (s, 3 H, OCH_3), 5.92 (s, 1 H, α-H), 6.82, 7.82 (AB quar, J = 7 Hz, 4 H, p-methoxybenzoyl), 6.85 (s, 2 H, m-mesityl), 7.02 (d, J = 7 Hz, 2 H, o-phenyl), 7.19–7.32 (m, 3 H, phenyl); ^{13}C NMR δ 20.7, 21.1, 55.1, 56.4, 113.4, 126.5, 128.0, 129.4, 130.1, 130.2, 130.5, 133.7, 136.6, 136.9, 137.4, 163.0, 198.2; MS m/z 344 (M^+), 209, 135 (base), 107, 91, 77; (FAB) m/z 345.1855 (MH^+).

α-Mesityl-α-phenyl-2,4,6-trimethylacetophenone. The α-mesityl-α-phenylacetyl chloride prepared as just described was refluxed with aluminum chloride for 2 h in a 1:2 mixture of mesitylene and carbon disulfide. Workup was followed by chromatography on silica and recrystallization from ethanol/chloroform, mp 161–162 °C; IR (CCl_4) 3090–2860, 1705, 1615, 1506, 1458, 1235, 1161 cm^{-1}; ^1H NMR δ 1.93 (s, 12 H, o-CH_3), 2.27 (s, 6 H, p-CH_3), 5.98 (s, α-H), 6.73 (s, 2 H, m-mesityl), 6.81 (s, 2 H, m-mesityl), 7.24–7.37 (m, 5 H, phenyl); ^{13}C NMR δ 18.4, 20.7, 20.9, 57.5, 126.1, 127.6, 128.2, 128.4, 129.3, 130.2, 133.7, 137.2, 138.2, 138.5, 139.4, 204.5; MS m/z 356 (M^+), 209, 147 (base), 119, 103, 91, 77; (FAB) m/z 347.2218 (MH^+).

α-Mesityl-2,4,6-trimethylacetophenone. α-Mesitylacetonitrile was hydrolyzed by heating with potassium hydroxide in ethylene glycol at 155 °C for 6 h. The cooled solution was acidified with hydrochloric acid; the resulting solid was washed and recrystallized from acetone. The acid chloride was prepared with PCl_3, followed by Friedel–Crafts acylation of mesitylene as described above for the α-phenyl compound. Workup and recrystallization from ethanol provided white crystals, mp 91.0–92.5 °C: IR (CCl_4) 3010–2870, 1710, 1620, 1490, 1455, 1262 cm^{-1}; ^1H NMR δ 2.16 (s, 6 H, o-CH_3), 2.20 (s, 6 H, o-CH_3), 2.25 (s, 3 H, p-CH_3), 2.27 (s, 3 H, p-CH_3), 4.07 (s, 2 H, CH_2), 6.81 (s, 2 H, m-mesityl), 6.86 (s, 2 H, m-mesityl); ^{13}C NMR δ 19.1, 20.4, 20.8, 20.9, 45.9, 127.4, 128.4, 129.0, 132.7, 136.4, 137.2, 138.2, 139.4, 206.1; MS m/z 280 (M^+), 147 (base) 133, 119, 91, 77.

α-Mesityl-o-methylacetophenone was prepared by refluxing o-tolylmagnesium bromide with α-mesitylacetonitrile in ether overnight. Hydrolysis and workup were followed with chromatography on silica and recrystallization from ethanol, mp 33.6–35 °C; IR (CCl_4) 3100–2865, 1692, 1615, 1485, 1458, 1320, 1218, 985 cm^{-1}; ^1H NMR δ 2.20 (s, 6 H, mesityl o-CH_3), 2.28 (s, 3 H, p-CH_3), 2.47 (s, 3 H, tolyl CH_3), 4.26 (s, 2 H, CH_2), 6.92 (s, 2 H, m-mesityl), 7.24–7.42 (m, 3 H, tolyl), 7.78 (d, 2 H, J = 7 Hz, o-tolyl); ^{13}C NMR δ 20.1, 20.8, 20.9, 42.3, 125.6, 127.8, 128.7, 129.2, 131.0, 131.8, 136.1, 136.6, 137.7, 138.3, 201.1; MS m/z 252 (M^+), 133, 119 (base), 105, 91, 77.

α-Phenyl-2,4,6-trimethylacetophenone was prepared by acylating mesitylene with α-phenylacetyl chloride in carbon disulfide with $AlCl_3$ catalyst. The product was purified by chromatography on silica and recrystallization from methanol at −30 °C: IR (CCl_4) 3085–2820, 1704, 1615, 1500, 1460, 1210, 1038 cm^{-1}; ^1H NMR δ 2.12 (s, 6 H, o-CH_3), 2.29 (s, 3 H, p-CH_3), 4.00 (s, 2 H, CH_2), 6.83 (s, 2 H, m-mesityl), 7.2–7.4 (m, 5 H, phenyl); ^{13}C NMR δ 19.0, 20.9, 51.6, 126.9, 128.3, 129.7, 132.6, 133.2, 138.3, 139.0, 207.2; MS m/z 238 (M^+), 147 (base), 119, 103, 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.[58] After workup, the ketones were recrystallized either from hexane or from ethanol-O-d_1. The percent deuterium incorporation was determined by comparison of mass spectra for the parent ions and for the M − 105 ions (loss of benzoyl).

α-(o-Tolyl)propiophenone-d_1 (2-d): ^1H NMR, the same as for **2** except that the peak at δ 1.48 (tol-CDCH_3) is a singlet; 96% d_1.

α-Mesitylacetophenone-d_2: ^1H NMR, same as for **6**[1] 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.

α-Mesityl-α-phenylacetophenone-d_1: ^1H NMR, same as for **8** except no peak at δ 5.99; 96% d_1.

Identification of Photoproducts. Typically, 0.3 g of ketone in 500 mL of cyclohexane or benzene was irradiated with a water-cooled, Pyrex-filtered 450-W Hanovia mercury arc lamp until all of the ketone had reacted. Products were separated either by preparative GC (SE-30 column) or by preparative TLC.

α-(o-Tolyl)-p-methoxyacetophenone gave only one product, 2-(p-methoxyphenyl)-2-indanol, mp 206–208 °C (recrystallized from hexane): IR (CCl_4) 3600, 3080–2840, 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 ($CDCl_3$) 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.

α-(o-Tolyl)propiophenone provided three products after GC separation. Benzaldehyde was identified by its retention time in both GC and HPLC analysis.

(Z)-1-Methyl-2-phenyl-2-indanol: IR (CCl_4) 3550, 3095–2860, 1608, 1480, 1455, 1183, 1080, 1020, 990 cm^{-1}; ^1H NMR δ 1.25 (d, J = 7.3 Hz, 3 H, CH_3), 1.94 (s, 1 H, OH), 3.17, 3.52 (AB quar, J = 16.6 Hz, 2 H, CH_2), 3.58 (quar, J = 7.3 Hz, 1 H, $CHCH_3$), 7.15–7.32 (m, 5 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 2 H); ^{13}C NMR δ 10.9, 49.3, 50.4, 85.4, 123.7, 124.8, 125.4, 126.9, 127.0, 128.1, 128.6, 140.1, 144.2, 145.1; MS m/z 224, 206, 119, 105 (base), 91, 77.

***d,l*-2,3-Bis(o-tolyl)butane**: ^1H NMR δ 0.98 (d, J = 7.7 Hz, 3 H, $CHCH_3$), 2.38 (s, 3 H, $ArCH_3$), 3.25 (m, 1 H, $CHCH_3$), 7.08–7.42 (m, 4 H); MS m/z 238, 202, 119 (base), 118, 105, 91, 77.

***meso*-2,3-Bis(o-tolyl)butane**: ^1H NMR δ 1.32 (d, J = 7.7 Hz, 3 H, $CHCH_3$), 2.15 (s, 3 H, $ArCH_3$), 3.28 (m, 1 H, $CHCH_3$), 6.92–7.30 (m,

(57) Wyman, D. P.; Kanfman, P. R. *J. Org. Chem.* **1964**, *29*, 1956.

(58) Mcwilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* **1978**, *100*, 6407.

4 H); MS *m/z* 228, 202, 119 (base), 105, 91, 77.

α-(*o*-Tolyl)valerophenone gave only three significant products at 40% conversion: α-(*o*-tolyl)acetophenone, 2-phenyl-2-indanol, and 1-propyl-2-phenyl-2-indanol. The latter was a minor product and only an NMR spectrum could be obtained. At 100% conversion, only the latter two were present. The first two were identified by comparison with separately prepared samples. Benzaldehyde could be detected by GC and HPLC analysis.

1-Propyl-2-phenyl-2-indanol: ^{1}H NMR δ 0.84 (t, *J* = 7.3 Hz, 3 H, propyl CH_3), 1.36 (sext, *J* = 7.3 Hz, 2 H, CH_2CH_3), 1.75 (m, 2 H, $CH_2CH_2CH_3$), 2.01 (s, 1 H, OH), 3.17, 3.44 (AB quar, *J* = 16.6 Hz, 2 H, ring CH_2), 3.58 (t, *J* = 6.7 Hz, 1 H, C*H*Pr), 7.24–7.63 (m, 9 H).

α-(*o*-Tolyl)isobutyrophenone was irradiated in the presence of 0.01 M dodecanethiol. Two major products were collected by GC and identified as benzaldehyde and a mixture of *o*-cymene and 2-(*o*-tolyl)propene by comparison with authentic materials.

***o*-Cymene**: ^{1}H NMR δ 1.23 (d, *J* = 7.3 Hz, 6 H), 2.34 (s, 3 H), 3.14 (sept, *J* = 7.3 Hz, 1 H), 7.12–7.18 (m, 4 H).

2-(*o*-Tolyl)propene: ^{1}H NMR δ 2.02 (t, *J* = 0.7 Hz, 3 H, $=CCH_3$), 2.32 (s, 3 H, $ArCH_3$) 4.74, 5.20 (each br s, 1 H, $=CH_2$), 7.1–7.2.

α-Mesitylpropiophenone provided three products after GC collection. Benzaldehyde was identified by GC and HPLC.

(*Z*)-1,5,7-Trimethyl-2-phenyl-2-indanol: IR (CCl_4) 3600, 3095–2880, 1610, 1480, 1450, 1380, 1072, 1035; ^{1}H NMR δ 1.25 (d, *J* = 8.5 Hz, 3 H, $CHCH_3$), 2.02 (s, 1 H, OH), 2.30 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 3.28, 3.36 (AB quar, *J* = 18.6 Hz, 2 H, CH_2), 3.51 (quar, *J* = 8.5 Hz, 1 H, C*H*CH_3), 6.87 (s, 1 H), 6.93 (s, 1 H), 7.25–7.50 (m, 5 H); ^{13}C NMR δ 13.5, 19.1, 21.1, 47.8, 49.8, 83.9, 122.8, 125.8, 126.8, 129.7, 133.9, 136.6, 140.1, 41.0, 146.9; MS *m/z* 252, 234, 219, 203, 149, 147, 105 (base), 77.

(*E*)-1,5,7-Trimethyl-2-phenyl-2-indanol: ^{1}H NMR δ 0.74 (d, *J* = 8.1 Hz, 3 H), 2.21 (s, 1 H, OH), 2.32 (s, 3 H), 2.37 (s, 3 H), 3.03, 3.88 (AB quar, *J* = 18.6 Hz, 2 H), 3.95 (quar, *J* = 8.1 Hz, 1 H), 7.03–7.43 (m, 7 H). This spectrum was derived from a mixture of the two diastereomers.

(*Z*)-1-Mesitoxy-1-phenylpropene: ^{1}H NMR δ 1.52 (d, *J* = 8.1 Hz, 3 H, $CHCH_3$), 2.18 (s, 3 H, *p*-CH_3), 2.24 (s, 6 H, *o*-CH_3), 5.19 (quar, *J* = 8.1 Hz, 1 H, C*H*CH_3), 6.74 (s, 2 H), 7.30–7.50 (m, 3 H), 7.65 (d, 2 H).

(*E*)-1-Mesitoxy-1-phenylpropene: ^{1}H NMR δ 1.64 (d, *J* = 8.1 Hz, 1 H), 2.22 (s, 6 H), 2.31 (s, 3 H), 4.38 (quar, *J* = 8.1 Hz, 1 H), 6.90 (s, 2 H), 7.3–7.66 (m, 5 H).

These NMR spectra were derived from a 1:4 *Z*/*E* mixture. The following data are for the mixture: IR ($CDCl_3$) 1660, 1480, 1440, 1360, 1210, 1150, 1080, 1065, 900 cm^{-1}; MS *m/z* 252, 223, 147, 136 (base), 121, 117, 115, 105, 91, 77.

α-Mesitylvalerophenone provided the indanol as the only major product. Benzaldehyde was identified by GC and HPLC. 1-Mesitoxy-1-phenylpropene was identified by GC–MS. A small amount of 4,6-dimethyl-2-phenyl-2-indanol was also detected by GC. This product is the cyclization product of the type II product, α-mesitylacetophenone.

(*Z*)-5,7-Dimethyl-1-propyl-2-phenyl-2-indanol: IR (CCl_4) 3600, 3090–2875, 1065, 1040 cm^{-1}; ^{1}H NMR δ 0.93 (t, *J* = 6.5 Hz, 3 H, propyl CH_3), 1.46 (sext, *J* = 6.5 Hz, 2 H, CH_2CH_3), 1.64, 1.98 (each m, 1 H, $CH_2CH_2CH_3$), 2.07 (s, 1 H, OH), 2.22 (s, 3 H, $ArCH_3$), 2.29 (s, 3 H, $ArCH_3$), 3.25, 3.40 (AB quar, *J* = 16.6 Hz, 2 H, ring CH_2), 3.31 (dd, *J* ≈ 4 Hz, 1 H, C*H*Pr), 6.81 (br s, 2 H), 7.13–7.30 (m, 3 H), 7.37 (d, 2 H); ^{13}C NMR δ 14.5, 18.9, 21.0, 21.4, 32.5, 47.5, 54.0, 83.4, 122.2, 124.7, 126.5, 127.9, 129.2, 133.3, 136.1, 140.0, 141.4, 149.1; MS *m/z* 280, 262, 233, 175, 159, 146, 133, 119, 105 (base), 91, 77.

1-Mesitoxy-1-phenylpentene: MS *m/z* 280, 223, 136, 121, 117, 115, 91, 67.

α-Mesitylbutyrophenone provided two major products by GC collection, benzaldehyde and 2-mesitylpropene.

2-Mesitylpropene: ^{1}H NMR δ 1.97 (s, 3 H, $=CCH_3$), 2.27 (s, 6 H, *o*-mesityl), 2.33 (s, 3 H, *p*-mesityl), 4.78, 5.29 (AB quar, *J* = 2.1 Hz, 2 H, $=CH_2$), 6.90 (s, 2 H, ArH).

α-Mesityl-α-phenylacetophenone gave three products, together with benzaldehyde, which was identified as usual.

(*Z*)-5,7-Dimethyl-1,2-diphenyl-2-indanol: IR ($CDCl_3$) 3560, 3090–2860, 1608, 1500, 1455, 1180, 1060; ^{1}H NMR δ 1.75 (s, 1 H, OH), 1.83 (s, 3 H, $ArCH_3$), 2.37 (s, 3 H, $ArCH_3$), 3.37, 3.50 (AB quar, *J* = 16.8 Hz, 2 H, ring CH_2), 4.66 (s, 1 H, C*H*Ph), 6.86 (s, 1 H), 6.99 (s, 1 H), 6.99 (m, 2 H), 7.30 (m, 6 H), 7.43 (d, 2 H); ^{13}C NMR δ 19.3, 21.3, 48.7, 63.2, 83.1, 122.5, 124.9, 126.8, 127.4, 128.1, 128.7, 129.5, 129.7, 134.8, 137.5, 137.6, 138.6, 141.9, 147.8; MS *m/z* 314, 296, 209, 105 (base), 77.

(*E*)-1-Mesitoxy-1,2-diphenylethene: IR ($CDCl_3$) 3070–2860, 1608, 1500, 1455, 1180, 1060; ^{1}H NMR δ 2.29 (s, 6 H, *o*-mesityl), 2.32 (2, 3 H, *p*-mesityl), 5.43 (s, 1 H, vinyl), 6.90 (s, 2 H), 7.05 (m, 3 H), 7.32–7.38 (m, 5 H), 7.58 (m, 2 H); MS *m/z* 314, 223, 209, 179, 178 (base), 136.

(*Z*)-1-Mesitoxy-1,2-diphenylethene: mp 97.5–99 °C (recrystallized from hexane); IR (CCl_4) 3080–2860, 1640, 1605, 1480, 1445, 1290, 1210, 1148, 1060, 1025; ^{1}H NMR δ 2.28 (s, 3 H, *p*-mesityl), 2.56 (s, 6 H, *o*-mesityl), 5.97 (s, 1 H, vinyl), 6.68 (s, 2 H) 7.2–7.4 (m, 8 H), 7.80 (d, 2 H); ^{13}C NMR δ 17.1, 20.5, 111.3, 126.3, 127.1, 127.9, 128.2, 128.3, 128.8, 129.7, 132.8, 136.2, 136.6, 150.3, 153.6; MS *m/z* 314, 223, 209, 179, 178, 136 (base), 121, 105.

α-Mesityl-α-phenyl-*p*-methoxyacetophenone gave three products isolated by preparative TLC, listed in order of their R_f values. *p*-Methoxybenzaldehyde was also detected by GC and HPLC.

(*E*)-1-Mesitoxy-1-(*p*-methoxyphenyl)-2-phenylethene: IR ($CDCl_3$) 3050–2870, 1710, 1640, 1610, 1515, 1480, 1380, 1250, 1210, 1175, 1150, 1090, 1060, 1040 cm^{-1}; ^{1}H NMR δ 2.28 (s, 6 H, *o*-mesityl), 2.34 (s, 3 H, *p*-mesityl), 3.86 (s, 3 H, OCH_3), 5.47 (s, 1 H, vinyl), 6.87, 7.54 (AB quar, *J* = 8 Hz, 4 H), 6.95 (s, 2 H), 6.95–7.14 (m, 5 H); MS *m/z* 344, 135 (base), 77.

(*Z*)-1-Mesitoxy-1-(*p*-methoxyphenyl)-2-phenylethene: mp 95.5–97.5 °C (recrystallized from methanol); IR ($CDCl_3$) 3040–2850, 1710, 1640, 1610, 1520, 1480, 1380, 1255, 1215, 1180, 1100, 1040 cm^{-1}; ^{1}H NMR δ 2.19 (s, 3 H, *p*-mesityl), 2.28 (s, 6 H, *o*-mesityl), 3.78 (s, 3 H, OCH_3), 5.91 (s, 1 H, vinyl), 6.71 (s, 2 H), 6.75, 7.29 (AB quar, *J* = 8 Hz, 2 H), 7.18–7.38 (m, 3 H), 7.81 (d, 2 H); MS *m/z* 344, 135 (base), 107, 77.

(*Z*)-5,7-Dimethyl-1-phenyl-2-(*p*-methoxyphenyl)-2-indanol: IR ($CDCl_3$) 3560, 3070–2845, 1610, 1510, 1450, 1300, 1250, 1180, 1035, 840 cm^{-1}; ^{1}H NMR δ 1.73 (s, 1 H, OH), 1.85 (s, 3 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 3.36, 3.48 (AB quar, *J* = 16.8 Hz, 2 H, ring CH_2), 3.82 (s, 3 H, OCH_3), 4.63 (s, 1 H, C*H*Ph), 6.85, 7.39 (AB quar, *J* = 8.5 Hz, 4 H), 7.01 (br s, 2 H), 7.30 (br s, 5 H); ^{13}C NMR δ 19.2, 21.2, 48.6, 55.2, 63.1, 82.9, 113.4, 122.5, 126.1, 127.3, 128.6, 129.5, 129.6, 134.7, 137.4, 137.7, 138.7, 140.0, 141.9, 158.5; MS *m/z* 344, 253, 209, 135, 105, 91, 69, 43 (base).

α-Mesityl-α-phenyl-*p*-cyanoacetophenone produced the same three types of major product, with *p*-cyanobenzaldehyde as a minor propduct.

(*E*)-1-Mesitoxy-1-(*p*-cyanophenyl)-2-phenylethene: IR ($CHCl_3$) 3090–2860, 2225, 1635, 1610, 1475, 1200, 1137, 840 cm^{-1}; ^{1}H NMR δ 2.19 (s, 6 H, *o*-mesityl), 2.25 (s, 3 H, *p*-mesityl), 5.51 (s, 1 H, vinyl), 6.88 (s, 1 H), 7.02 (s, 1 H), 6.84 (m, 3 H), 7.05 (d, 2 H), 7.55, 7.63 (AB quar, *J* = 7.5 Hz, 4 H); ^{13}C NMR δ 16.2, 20.8, 104.6, 112.3, 118.6, 126.3, 129.0, 129.3, 129.7, 129.9, 130.5, 132.0, 134.8, 135.6, 140.0, 148.1, 152.0; MS *m/z* 339, 248, 223, 209, 204, 203, 147, 136 (base), 105, 91, 77.

(*Z*)-1-Mesitoxy-1-(*p*-cyanophenyl)-2-phenylethene: mp 173–175 °C (recrystallized from methanol) IR ($CHCl_3$) 3060–2840, 2220, 1620, 1475, 1205, 1138, 890 cm^{-1}; ^{1}H NMR δ 2.16 (s, 3 H, *p*-mesityl), 2.23 (s, 6 H, *o*-mesityl), 6.04 (s, 1 H, vinyl), 6.69 (s, 2 H), 7.26–7.36 (m, 3 H), 7.44, 7.50 (AB quar, 4 H), 7.78 (d, 2 H); ^{13}C NMR δ 17.0, 20.4, 111.6, 113.7, 118.5, 127.2, 127.4, 128.5, 129.1, 130.0, 131.8, 132.6, 133.4, 135.4, 142.1, 149.8, 152.8; MS *m/z* 339, 248, 209, 204, 203, 136 (base), 135, 121, 105, 91, 77.

(*Z*)-5,7-Dimethyl-1-phenyl-2-(*p*-cyanophenyl)-2-indanol: mp 168.7–170 °C (recrystallized from methanol); IR ($CHCl_3$) 3525, 3090–2860, 2225, 1610, 1495, 1456, 1250, 1090, 850 cm^{-1}; ^{1}H NMR δ 1.88 (s, 1 H, OH), 1.85 (s, 3 H, $ArCH_3$), 2.37 (s, 3 H, $ArCH_3$), 3.38, 3.44 (AB quar, *J* = 16.8 Hz, 2 H, ring CH_2), 4.53 (s, 1 H, C*H*Ph), 6.88 (s, 1 H), 7.00 (s, 1 H), 6.88 (m, 2 H), 7.30 (m, 3 H), 7.54, 7.60 (AB quar, *J* = 7.5 Hz, 4 H); ^{13}C NMR δ 19.0, 21.2, 48.5, 63.0, 82.7, 110.6, 118.9, 122.4, 125.6, 127.8, 128.9, 129.3, 130.0, 132.0, 134.8, 136.8, 137.8, 138.1, 141.1, 153.5; MS *m/z* 339, 209, 195, 179, 178, 165, 130, 105, 102, 91, 69, 57, 43 (base).

α-Mesityl-α-phenyl-2,4,6-trimethylacetophenone produced two major diastereomeric products, which were isolated as a mixture by TLC. They were identified as the dimesityldiphenylethanes by comparison with literature data.[59] Mesitaldehyde was identified by GC and HPLC.

1,2-Dimesityl-1,2-diphenylethane (mixed *meso* and *d,l*): MS *m/z* 418, 417, 416, 356, 298, 209 (base), 179, 147; ^{1}H NMR δ (isomer 1) 2.07 (s, 6 H, $ArCH_3$), 2.12 (s, 6 H, $ArCH_3$), 2.22 (s, 6 H, $ArCH_3$), 5.46 (s, 2 H, CH), 6.55–7.09 (m, 14 H), δ (isomer 2) 2.10 (s, 6 H), 2.21 (s, 6 H), 2.31 (s, 6 H), 5.48 (s, 2 H), 6.72–7.24 (m, 14 H).

α-Mesityl-2,4,6-trimethylacetophenone produced primarily dimesitylethane, isolated by GC. Mesitaldehyde was identified by GC and HPLC.

1,2-Dimesitylethane: ^{1}H NMR δ 2.27 (s, 3 H, *p*-mesityl), 2.37 (s, 6 H, *o*-mesityl), 2.79 (s, 4 H, CH_2), 6.87 (s, 4 H, aryl); MS *m/z* 266, 189, 149, 133 (base), 117, 115, 105, 91.

α-Mesityl-*o*-methylacetophenone produced two products that were isolated by GC. One, 1,2-dimesitylethane, was identical to that described in the last paragraph. Tolualdehyde was identified by GC and HPLC.

(59) Luh, T. Y.; Lee, K. S.; Tam, S. W. J. *Organomet. Chem.* **1981**, *219*, 345.

The indanol dehydrated much more readily than any of the other indanol photoproducts.

3,5-Dimethyl-2-(*o*-tolyl)-2-indanol: IR (CCl_4) 3600, 3060–2860, 1615, 1482, 1452, 1220, 1048 cm^{-1}; ^1H NMR δ 2.26 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 2.52 (s, 3 H, *o*-CH_3), 3.22, 3.45 (AB quar, J = 16.5 Hz, 2 H, one ring CH_2), 3.27, 3.58 (AB quar, J = 16.5 Hz, 2 H, other CH_2), 6.84 (s, 1 H), 6.92 (s, 1 H), 7.19 (br s, 3 H), 7.57 (d, 1 H); ^{13}C NMR δ 19.0, 21.2, 21.7, 46.5, 48.2, 83.6, 122.9, 125.6, 125.8, 127.3, 128.5, 129.1, 132.3, 133.9, 136.3, 136.6, 140.6, 143.1; MS *m/z* 252, 234 (base), 219, 204, 203, 202, 133, 119.

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 in the indanol and the δ 4.32 α-methylene signal of the ketone (^1H NMR). Integration of the δ 6.13 vinyl signal of enol product and the same 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 spectrum of a separately irradiated sample was recorded on a Bruker WH-180 spectrometer with a 10-mm broad band 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 the indanol product and to the tertiary benzylic isopropyl proton in starting ketone and/or enol.

Similar irradiation of samples of α-(*o*-tolyl)propiophenone-d_1, α-mesitylacetophenone-d_2, and α-mesityl-α-phenylacetophenone-d_1 showed no incorporation of ^1H at the α-carbon of unreacted starting ketone, as determined by the absence of any ^1H NMR signals at δ 4.26, 4.30, and 5.99, respectively, at total conversion to indanols of 20–35%.

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[60] immersed in a room temperature water bath. A water-cooled Hanovia 450-W medium-pressure mercury arc lamp 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 are 0.33[7] and 0.016,[15] respectively.

Irradiations in the solid state were performed in two ways. In one, the ketones were dissolved in a minimum of methylene chloride and transferred onto 1 × 2.5 cm glass plates. These were allowed to air dry to powders and were then further dried under vacuum. They were placed in 13 × 100 Pyrex tubes that were sealed with rubber septa. They were irradiated as usual on a merry-go-round apparatus while being purged with argon.

Actual crystals also were irradiated directly. They were placed in tubes whose bottoms had been stretched into 2.5-cm lengths only a few millimeters wide. These were irradiated in a merry-go-round as for the powder samples.

Dynamic NMR measurements were performed at low temperatures on the Bruker 250-MHz spectrometer. Line widths were measured manually: for α-(*o*-tolyl)isobutyrophenone, the α-methyl signal; for α-mesitylpropiophenone and -valerophenone, the *o*-methyl signals; for α-mesityl-α-phenylacetophenone, the *m*-mesityl proton signal; for α-mesityl-isobutyrophenone, the α-methyl and *o*-methyl signals. Results are listed in Table V.

Molecular mechanics calculations were performed in two ways. Structural imput was generated by MIO and submitted to MMPMI for calculation on an IBM XT with an EGA and a 4027 emulator. The output was resubmitted to MMPMI for a second calculation. This was done first with a dihedral drive controlling the α-carbon–CO bond rotation; this rotation was then fixed at minimum energy conformations, and a second dihedral angle drive was applied to rotation of the α-aryl group. The resulting energy-minimized structures were used as input for a final calculation without a dihedral angle drive. MMX calculations were performed in a similar fashion with PCModel on a Macintosh II. All of the software was obtained from Serena Software, Bloomington, IN.

X-ray Crystallography. Samples of α-mesityl-2,4,6-trimethylacetophenone, α-mesitylvalerophenone, and α-mesityl-α-phenylacetophenone were allowed to crystallize from ethanol over several days. Data collection was performed with Mo Kα radiation (λ = 0.71073) on a Nicolet P3F diffractometer. Structures were solved by direct methods, the results of which are presented in the supplementary material.

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Registry No. 1, 16282-16-9; **2-*d***, 136667-07-7; **3**, 20736-42-9; **5**, 53423-27-1; **6**, 136667-03-3; **7**, 136667-02-2; **9**, 84839-90-7; **10**, 129526-16-5; **11**, 112247-46-8; **12**, 16282-17-0; **12**-CN, 136667-04-4; **12**-OMe, 136667-05-5; **12-*d***, 136667-10-2; **13**, 136667-06-6; **14**, 1889-72-1; **15**, 5796-78-1; **16**, 77787-77-0; α-mesitylacetophenone-d_2, 136667-08-8; α-(2,4,6-triisopropylphenyl)acetophenone-d_2, 136667-09-9; α-(*o*-tolyl)acetophenone, 5033-67-0; propyl bromide, 106-94-5; 2,4,6-trimethylbenzyl chloride, 1585-16-6; α-mesitylacetonitrile, 34688-71-6; α-mesitylpropionitrile, 136667-11-3; α-mesitylvaleronitrile, 136667-12-4; mesitylene, 108-67-8; desyl chloride, 447-31-4; α-phenylacetyl chloride, 103-80-0; fluorobenzene, 462-06-6; α-phenyl-*p*-fluoroacetophenone, 347-84-2; α-phenyl-*p*-cyanoacetophenone, 60694-99-7; α-chloro-α-phenyl-*p*-cyanoacetophenone, 136667-13-5; α,α-dichloro-α-phenyl-*p*-cyanoacetophenone, 136667-14-6; α-mesityl-α-phenylacetic acid, 3901-04-0; α-mesityl-α-phenylacetyl chloride, 97799-60-5; mandelic acid, 90-64-2; α-mesitylacetyl chloride, 52629-46-6; 2-(*p*-methoxyphenyl)-2-indanol, 136667-15-7; (*Z*)-1-methyl-2-phenyl-2-indanol, 128517-15-7; *d,l*-2,3-bis(*o*-tolyl)butane, 136667-16-8; *meso*-2,3-bis(*o*-tolyl)butane, 136667-17-9; *o*-cymene, 527-84-4; 2-(*o*-tolyl)propene, 7399-49-7; (*Z*)-1,5,7-trimethyl-2-phenyl-2-indanol, 128517-16-8; (*E*)-1,5,7-trimethyl-2-phenyl-2-indanol, 136667-18-0; (*Z*)-1-mesitoxy-1-phenylpropene, 136667-19-1; (*E*)-1-mesitoxy-1-phenylpropene, 136667-20-4; (*Z*)-5,7-dimethyl-1-propyl-2-phenyl-2-indanol, 128545-14-2; 1-mesitoxy-1-phenylpentene, 128517-20-4; 2-mesitylpropene, 14679-13-1; (*Z*)-5,7-dimethyl-1,2-diphenyl-2-indanol, 128517-17-9; (*E*)-1-mesitoxy-1,2-diphenylethene, 136667-21-5; (*Z*)-1-mesitoxy-1,2-diphenylethene, 136667-22-6; (*E*)-1-mesitoxy-1-(*p*-methoxyphenyl)-2-phenylethene, 136667-23-7; (*Z*)-1-mesitoxy-1-(*p*-methoxyphenyl)-2-phenylethene, 136667-24-8; (*Z*)-5,7-dimethyl-1-phenyl-2-(*p*-methoxyphenyl)-2-indanol, 136667-25-9; (*E*)-1-mesitoxy-1-(*p*-cyanophenyl)-2-phenylethene, 136667-26-0; (*Z*)-1-mesitoxy-1-(*p*-cyanophenyl)-2-phenylethene, 136667-27-1; (*Z*)-5,7-dimethyl-1-phenyl-2-(*p*-cyanophenyl)-2-indanol, 136667-28-2; *meso*-1,2-dimesityl-1,2-diphenylethane, 80351-66-2; *d,l*-1,2-dimesityl-1,2-diphenylethene, 81667-60-9; 1,2-dimesitylethane, 4674-23-1; 3,5-dimethyl-2-(*o*-tolyl)-2-indanol, 136667-29-3.

Supplementary Material Available: Tables of crystal data, bond distances and angles, torsion angles, positional parameters, temperature factors, and thermal vibration amplitudes (45 pages). Ordering information is given on any current masthead page.

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