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Conformational Control of Photoreactivity: Three α-Mesityl Ketones that Undergo Efficient Radical Cleavage

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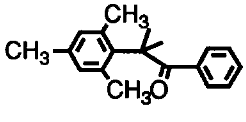
Abstract: *α-Mesitylisobutyropohenone, 1,2-dimesitylethanone, and 2-phenyl-1,2-dimesitylethanone all undergo only one photoreaction in solution, α-cleavage to acyl radicals. Quantum yields are all over 0.30 and triplet rate constants are* $\geq 5 \times 10^8$ s^{-1}*. In each case, bond rotations are so slow that reaction occurs from the preferred ground state geometries, which hold the molecules in conformations ideal for cleavage. The large cleavage rate constants reflect relief of steric strain as well as ideal orientation of π and σ orbitals.*

We reported several years ago that α-mesitylacetophenone undergoes highly efficient photocyclization to a 2-indanol *via* rapid triplet state δ-hydrogen abstraction.[1] Recently we have reported how α-alkyl substitution impedes hydrogen abstraction.[2,3] We now wish to describe three α-mesityl ketones that undergo *only* Norrish type I radical cleavage. They provide dramatic evidence that hindered rotations about acyclic single bonds can totally control photoreactivity. Moreover, their relatively fixed geometries provide unique information about the relative importance of steric congestion and "radical stability" in determining rate constants for α-cleavage reactions.



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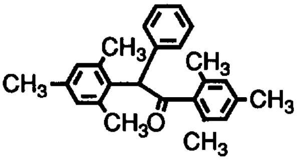

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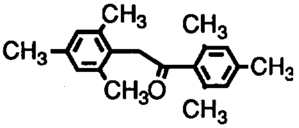


3

Irradiation of ketones **1**-**3** in benzene produces benzaldehyde and 2-mesitylpropene; mesitaldehyde and 1,2-diphenyl-1,2-dimesitylethane; and mesitaldehyde and 1,2-dimesitylethane, respectively. No other products were observed. Table 1 presents triplet lifetimes and maximum quantum yields for aldehyde formation for the three ketones. Degassed benzene solutions typically 0.04 M in ketone and 0.007 M in dodecanethiol were irradiated at 313 or 365 nm. Yields of aldehyde were determined by gas chromatography; actinometry was provided by parallel irradiation of valerophenone solutions.[4] Stern-Volmer analysis of quenching by either naphthalene or 2,5-dimethyl-2,4-hexadiene provided linear plots with

Table 1. Photokinetics in benzene for three α-mesityl ketones.radicals[6,7].

Ketone	Φ_α[a]	$k_q\tau$, M^{-1} [b]	k_α, 10^8 s^{-1} [c]
1	0.31	7.3 ± 1.3	7.0
2	0.33	0.6 ± 0.2	81.0
3	0.35	6.9 ± 0.8	7.3

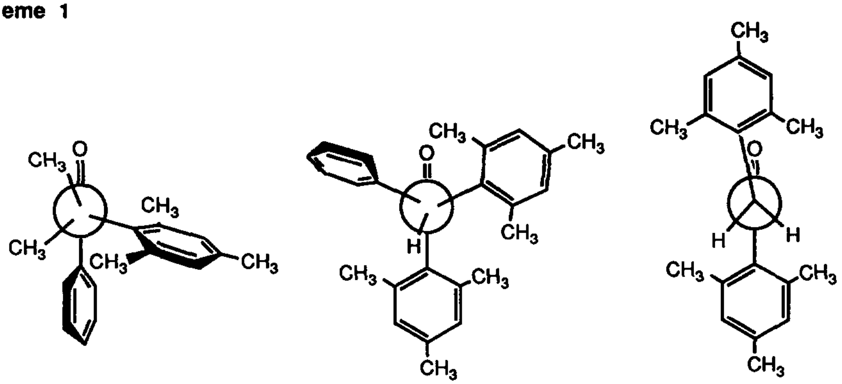
[a] aldehyde product, 313 nm, 0.007 M dodecanethiol. [b] 313 nm with 2,5-dimethyl-2,4-hexadiene, 365 nm with naphthalene. [c] $k_\alpha = 1/\tau$; $k_q = 5 \times 10^9$ M^{-1} s^{-1}

slopes equal to the $k_q\tau$ values listed in the table. We have already reported[2] that k_q values in these hindered ketones have the "normal[5]" diffusion-limited value of 5 x 10^9 M^{-1} s^{-1}. The thiol traps all free acyl radicals[6,7]. The >30% quantum yields of aldehyde from all three ketones indicate nearly quantitative radical formation, since ~50% in-cage recombination is expected.[6,7] Triplet lifetimes are determined primarily, if not entirely, by the cleavage rates, as indicated in the table.

The first example, α-mesitylisobutyrophenone **1**, may not appear surprising. Triplet α-phenylisobutyrophenone **4** undergoes α-cleavage some 60 times faster than does triplet α-phenylacetophenone, which cleaves with a rate constant of only 2 x 10^6 s^{-1}.[8] The value of k_α for 1 is at least 5 x 10^8 s^{-1}, four times faster than for **4**, but still only equal to the rate for δ-hydrogen abstraction in α-mesitylacetophenone.[1,2] 1 undergoes only cleavage not just because δ-hydrogen abstraction is slowed, but because cleavage is enhanced. The cumyl radical formed from 1 does not enjoy much benzylic conjugation because of the o-methyls. That it is formed so rapidly attests to how relief of steric congestion can facilitate radical cleavage.[8] The ^{1}H-NMR signals for the α-methyls of 1 coalesce at 185° K and separate into two separate peaks at 175° K. Temperature dependent line-broadening measurements indicate a rate constant for rotation around the carbonyl–α-carbon bond of only 2 x 10^4 s^{-1} at room temperature, much slower than actual triplet decay. The preferred geometry calculated by MMPI methods agrees with the NMR evidence and is shown in Scheme 1. It explains the lack of δ-hydrogen abstraction from 1, since the mesitylene methyls are held in a poor position for reaction with the carbonyl[3,9] and the steric congestion forces reaction from an effectively frozen geometry.

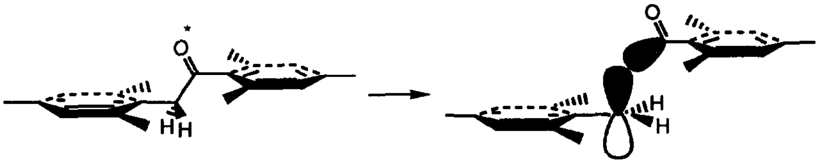
It may not appear surprising that **2** forms a diarylmethyl radical efficiently. However, **2** undergoes no benzocyclobutenol formation via γ-hydrogen abstraction, which is very rapid in acetylmesitylene[10]; and its isomer α,α-dimesitylacetophenone does not cleave but instead rearranges to an enol ether[11] MMX calculations and NMR spectra suggest the geometry in Scheme 1 from which a 1,3-mesityl shift would be slow, because the α-mesityl group is twisted so far from the carbonyl oxygen. δ-Hydrogen abstraction would have a rate constant of at least 10^8 s^{-1}.[3] The much higher rate constant for cleavage must reflect both relief of steric congestion and the fact that both mesityl groups are oriented so that the developing benzyl radicals are fully conjugated as they are formed.

Scheme 1



The behavior of 1,2-dimesitylethanone **3** is the most amazing. It appears relatively uncongested and capable of undergoing both δ-hydrogen abstraction from the α-mesityl group and γ-hydrogen abstraction from the other mesityl group[10]. Nonetheless, it does neither, instead forming only radicals, in high quantum efficiency. A k_α value near 10^9 s^{-1} is indicated by the kinetics data, 400 times larger than for α-phenylacetophenone.

We have measured the x-ray crystal structure of **3**, which is shown in Scheme 1. The two mesitylene rings are parallel to each other and perpendicular to the carbonyl.[12] That the acylmesitylene chromophore is highly twisted in solution is indicated by all spectroscopic information: a carbonyl stretch at 1710 cm^{-1}; a ^{13}C carbonyl resonance at 206 ppm;[13] and a L_a UV band at 218 nm instead of 240 nm.[14] The crystal geometry holds all of the methyl hydrogens too far from the carbonyl for hydrogen abstraction to compete with the rapid observed cleavage reaction. MMX calculations indicate that a 120° rotamer has the same energy. Both of these geometries hold the α-mesityl group in a perfect orientation to maximize benzylic conjugation in the developing radical. The non-crystal geometry also holds the mesityl group too far from the oxygen for a 1,3-transfer.[2] The molecule is not so congested as to have a lengthened (and weakened) carbonyl—α-carbon bond; it is 1.51 Å long, typical for sp^2-sp^3 C—C bonds. Therefore the high value of k_α appears to be mainly stereoelectronic in origin.



In summary, these three ketones further exemplify how steric congestion can limit individuals within a class of excited molecules to geometries suitable only for a single intrafunctional reaction, in this case α-cleavage, whereas freely rotating molecules of the same class undergo primarily bifunctional reactions, specifically hydrogen transfer. Moreover, the k_α values for the three ketones provide a unique comparison: **1**, driven primarily by steric crowding, and **3**, driven primarily by resonance stabilization of the developing radicals, cleave at much the same rate, while **2**, driven by both forces, cleaves ten times faster.

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