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that the methoxy group resides within the calixarene cavity, as is shown in Figure 1, and the three remaining oxygen atoms act as an additional head group, binding with the contents of the hydrophilic layer. The ability of calix[4]arene to include guests is well-known.[11] Indeed, the classic picture of a calixarene host–guest complex is one in which a toluene molecule resides within the cavity.[12] The position of the methyl group of the methyl sulfate anion is raised slightly from the position adopted by the methyl group in the toluene inclusion complex. The Me···O(hydroxyl) separations are 4.15, 4.27, 4.57, and 5.03 Å. The main interactions that hold the MeOSO$_3^-$ into the cavity of the calix-[4]arenesulfonate anion are hydrogen bonds between oxygen atoms of the anions and two ammonium cations. The SO$_3^-$ group of the MeOSO$_3^-$ which effectively comprises the fifth head group of the anion is asymmetrically positioned with respect to the four SO$_3^-$ groups of the calixarene. The S···S(MeOSO$_3^-$) separations are 4.77, 5.41, 5.58, and 6.10 Å.

The overall structure is that of an inclusion complex in which ammonium cations, methyl sulfate anions, and water molecules are intercalated into the organic host structure. This is illustrated by the stereoview in Figure 2. The calix[4]arenesulfonate anions are arranged into bilayers that are oriented such that the –SO$_3$ head groups face the polar regions of the intercalated species.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (6 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Effects of Steric Congestion on Photochemistry: Enol Ether Formation from α-Mesityl Ketones

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Hart and Lin recently reported that 1,2,2-trimesitylethanone (**1**) undergoes very efficient, unquenchable photorearrangment to an enol ether.[1] This observation was astounding not so much because the rearrangement itself had only one precedent[2] but
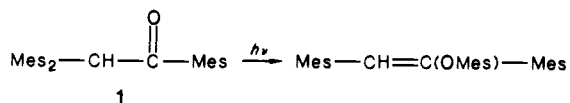
because neither indanol[3] nor benzocyclobutenol[4] formation competes, even though each reaction in monomesityl ketones involves intramolecular hydrogen abstraction with rate constants over 10^9 s^{-1}. We have now studied several α-mesityl ketones of intermediate steric congestion and find that the rearrangement represents an unprecedented n,π* triplet reaction. More importantly, bond rotations are so retarded and conformations are so changed by
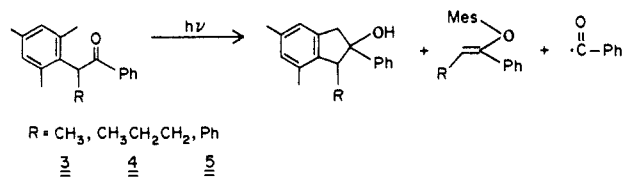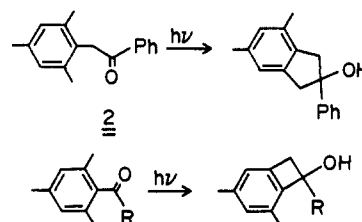
Scheme I

R = CH$_3$, CH$_3$CH$_2$CH$_2$, Ph
    3   4   5

Table I. Photoreactivity of Some α-Mesityl Ketones

ketone	$1/\tau^a$	Φ indanol	Φ ether	ArCHO^b	$k_{\delta\text{-H}}{}^a$	$k_{CT}{}^{a,c}$
1^d	>5		0.4		<1.	>5.
2^e	11	0.52	0	0	5.5	5.5
3	3.0	0.24	0.01	0.02	0.7	2.2
4	10.0	0.12	0.004		1.2	8.7
5	62	0.02	0.023	0.004	1.2	60
p-MeO-**5**	1.0	0.02	0.01		0.02	1.0

^{a}Units of 10^8 s^{-1} in benzene. ^{b}Trapped with 0.05 M thiol: ref 15. $^c k_{CT} = [1 - \Phi(\text{indanol}) - 2\Phi(\text{ArCHO})]/\tau$. ^{d}The reaction is not quenched by 10^{-2} diene: ref 1. ^{e}Reference 3.

α-substitution that rate constants for the various competing triplet reactions vary tremendously.

We have studied four α-mesityl ketones, whose reactions are summarized in Scheme I. Addition of either an alkyl or a phenyl group to the α-carbon causes a decrease in the quantum efficiency of indanol formation, which is 50% for α-mesitylacetophenone (**2**), and the appearance of radical cleavage products and the two enol ether stereoisomers, none of which were detected from **2**.[3] Interestingly, **4** undergoes Norrish type II elimination in only trace quantities. Product yields (both chemical and quantum) are quite low for **5**, which contains an α-phenyl group, although the only rearrangement products detected result from a mesityl migration. The enol ether Z/E ratios were all 1:1 at low conversion, as already observed for **1**.[1]

All product formation from all three ketones is quenched by added triplet quenchers such as 2,5-dimethyl-2,4-hexadiene or 1-methylnaphthalene. Stern–Volmer analysis of the quenching provided $k_q\tau$ values (in benzene) of 17 M^{-1} for **3**; 5 for **4**; 0.94 (indanol quenching) and 0.80 (enol ether quenching) for **5**; and 45 for the *p*-methoxy derivative of **5**. These data yield the $1/\tau$ values[5] listed in Table I. Flash spectroscopic analysis[6] indicates a triplet lifetime of 10 ns for *p*-MeO-**5** and verifies the value of k_q. These quenching results plus the comparable quantum yields for **5** and *p*-MeO-**5** establish that all three reactions occur from n,π* triplets. Since the n,π* triplet of *p*-MeO-**5** is only ~1% populated,[7] significant reaction from the π,π* lowest triplet would have increased the proportion of enol ether dramatically.[7,8]

The longer triplet lifetime and lower indanol quantum yield from **3** relative to **2** together indicate that α-substitution lowers the rate constant for δ-hydrogen abstraction. The ^{1}H NMR spectra of ketones **3**, **4**, and **5** reveal highly restricted rotation about the α-carbon–mesitylene bond. In **3**, the signals for the ortho-methyls and the meta-protons are broad even at room temperature

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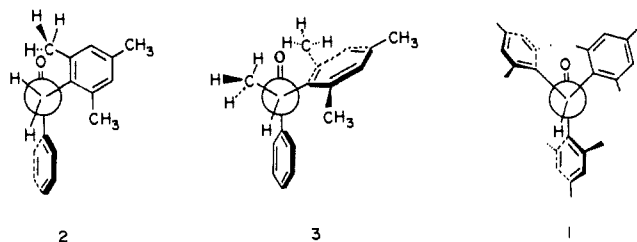
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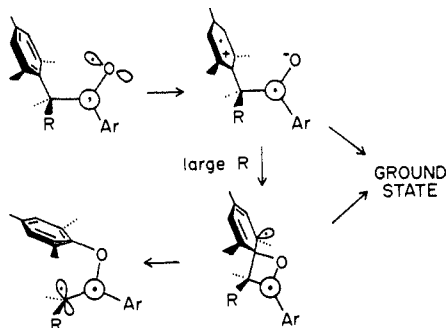
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Chart I

2   3   1

Scheme II

and coalesce at –38 °C; those for **5** coalesce below –80 °C. Line width analysis indicates a rotation rate of only 3000 s⁻¹ for **3** and **4** at room temperature. The two separate ortho-methyls show chemical shifts of 1.9 and 2.6 ppm. The α-alkyl group obviously hinders bond rotation and forces the mesitylene ring to twist such that one ortho-methyl is held in the shielding region of the carbonyl, where it is not well positioned for hydrogen abstraction.[9] Thus the measured rate constant for this process is depressed. Chart I shows what are deduced to be the preferred conformations for **2** and **3**, the former from MMPMI calculations and precedent[10] (and the observed high reactivity), the latter from calculations and the NMR changes. The current results provide a unique example of how photoreactivity can be dominated by ground-state conformational preferences whenever bond rotations are significantly slower than excited-state decay reactions.[11]

The significant drop in triplet lifetime of **5** relative to **3**, together with the low yield of radicals, suggests that the process that initiates rearrangement to enol ether is both rapid and inefficient. This inefficiency is apparent even in **2**, where added Lewis base raises the indanol quantum yield from 0.44 to only 0.50. The inefficiency does *not* involve enol formation, since α-deuteriation does not affect the quantum efficiency of indanol formation from **2** and no H–D exchange occurs between the ortho-methyls and the α-carbon. In contrast, α-(2,4,6-triisopropylphenyl)acetophenone-α-d₂, which forms enol in high yield,[12] forms indanol in twice the quantum efficiency of the fully protonated compound and recovered starting ketone shows extensive D incorporation at an ortho-isopropyl group and H-incorporation at the α-carbon.

It appears that α-mesityl groups interact with n,π* triplets in all the ketones studied; rate constants k_{CT} are included in Table I. We assume that the interaction is charge transfer in nature, as is alkylbenzene quenching of most triplet ketones,[13] and parallels the much faster quenching in β-phenyl ketones.[8b] Since mesitylene is a much better electron donor than is toluene, the effect does not show up in α-tolyl ketones.[3] The interaction leads to quenching in all cases but to enol ether only when the α-carbon is sufficiently crowded, as indicated in Scheme II. The preference for mesityl over phenyl migration in **5** probably reflects primarily a ground-state conformational preference[10,14] but would also be

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ensured by different donor abilities if free rotation occurred. The 1:1 *Z/E* enol ether ratios suggest that the rearrangement may represent a rare adiabatic triplet reaction. Certainly the near-orthogonal orientation of the half-occupied orbitals in the postulated biradical intermediate would more easily lead to triplet than to ground-state enol ether; and conversion of triplet ketone to triplet α-alkoxystyrene is exothermic.

The X-ray structure and NMR spectrum of **1**[14] (which gives only rearrangement) both indicate free rotation of both α-mesityl groups, with the preferred conformation shown in Chart I. This geometry should also allow fairly rapid δ-hydrogen abstraction. The fact that both indanol and enol ether arise from a triplet state of **5** with the same lifetime suggests that the competition between hydrogen abstraction and 1,3-shift may occur not in the triplet but in the CT complex, with the extent of steric congestion determining the partitioning. This question is under active investigation.

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Nucleophile-Promoted Electrophilic Cyclization Reactions of Alkynes

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The participation of alkynes as nucleophiles in polyene cyclizations is well documented[1] notably through the extensive investigations of the Johnson group.[1,2] In contrast, cyclization reactions of alkynes with weak electrophiles such as iminium ions have received less attention.[3,4] In this communication we report that simple alkynes, although immune to reaction with intramolecular iminium ions in non-nucleophilic environments, cyclize readily with these versatile electrophiles in the presence of added nucleophiles.[5] We also report experiments that demonstrate that alkynes, although intrinsically less reactive than alkenes toward iminium cations, are dramatically more reactive than comparably substituted alkenes in cyclizations conducted in the presence of strong external nucleophiles.

Attempted cyclizations of the formaldiminium ion derived from 4-hexynylamine **1a** (5 equiv of paraformaldehyde, 1 equiv of camphorsulfonic acid, CH₃CN, 100 °C, 1 h) provided, upon quenching with aqueous base, only unchanged **1a** and the symmetrical diaminomethane derived from condensation of 2 equiv

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