the singlet excited states (principally the $^1\Sigma^+$) drop in energy as the chain lengthens. It is noteworthy that the zfs are larger in the C_nO series than in the C_n series, as expected from the increased spin-orbit constant for O relative to C (150 versus 30 cm^{-1}).

$C_2O(^3\Sigma)$[3,4] and $C_3O(^1\Sigma)$[5] can form spontaneously in matrices from the ground-state reactants $C(^3P_{1/2})$, $C_2(^1\Sigma_g)$, and $CO(^1\Sigma)$; however, formation of C_4O and C_6O from $C_3(^1\Sigma_g)$ or $C_5(^1\Sigma)$ and $CO(^1\Sigma)$ is spin forbidden. This is circumvented by excitation of C_3 to the $^1\Pi_u$ state where it can react with CO

$$C_3(^1\Pi_u) + CO(^1\Sigma) \rightarrow C_4O(^1\Pi) \rightsquigarrow C_4O(X^3\Sigma)$$

A similar scheme can be devised for the formation of C_6O either via reaction of excited C_3 with $C_3O(X^1\Sigma)$ by these paths or possibly via excitation of C_5, whose absorption properties are unknown.

The observation of C_3O in interstellar space has been made possible by the efforts of R. D. Brown and his co-workers.[6,14] The proposed mechanisms for its formation[15,16] involve ion-molecule reactions so that it is improbable that the above mechanisms for the formation of C_4O and C_6O could apply there. However, these molecules will have large dipole moments,[17] and like the cyanopolyynes,[18] they should be readily detectable even if present in low concentrations.

Acknowledgment. This research was supported by the National Science Foundation Grant No. 85-14585.

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Intercalation of Cationic, Anionic, and Molecular Species by Organic Hosts. Preparation and Crystal Structure of $[NH_4]_6[calix[4]arenesulfonate][MeOSO_3]\cdot(H_2O)_2$

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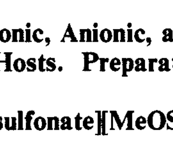
Received May 20, 1987

Much interest has recently been shown in the calixarenes (**1**)[1] and, more recently, in water-soluble members of this class of compounds (R = NO_2, SO_3H).[2] Calix[4]arenesulfonate (R =



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$-SO_3H$, R' = H, n = 4) is usually prepared as the sodium salt of the pentaanion[3,4] (i.e., the four sulfonate protons and a "superacidic" proton[5] from an -OH group are removed at the reaction pH). The salt crystallizes with 12 molecules of water per calixarene unit. Replacement of the sodium ions by use of the appropriate ammonium salt[6] leads to the related pentammonium calix[4]arenesulfonate, the structure of which is the subject of this contribution.[7]

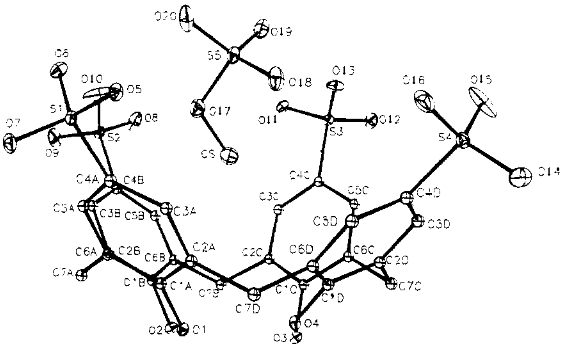

Figure 1. Inclusion of the methyl sulfate anion within the cavity of the calixarene anion.

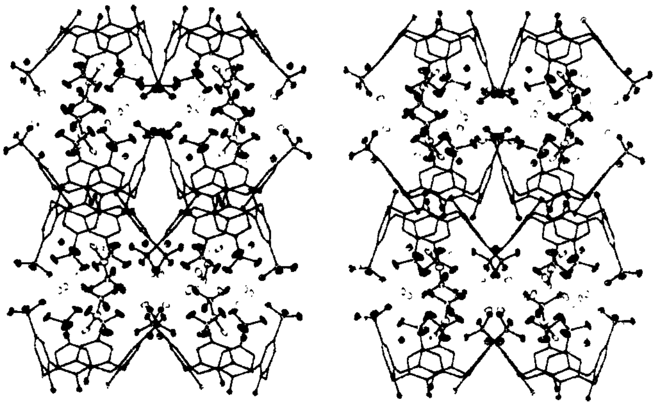

Figure 2. Stereoscopic view of the packing of the layers of calixarene anions and ammonium cations, methyl sulfate anions, and water molecules. Oxygen atoms are represented by dark circles.

The gross structures adopted by the sodium and ammonium species are quite similar, consisting of bilayers of calixarenes alternating with layers composed of ammonium ions and water molecules. The cations and water molecules are responsible for both the inter- and intra-linking of the layers via hydrogen bonds.[8] The composition of the polar layer, however, changes from four sodium ions and eleven water molecules in the sodium salt to five ammonium ions, one water molecule, and a methyl sulfate anion in the ammonium salt.[9,10] The methyl sulfate is oriented such

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(6) A suspension of calix[4]arene (5.0 g) in concentrated H_2SO_4 (50 mL) was heated at 70 °C during 4 h. The solution was filtered and the solid extracted with water (500 mL). This solution was neutralized to pH 7 with $BaCO_3$ and filtered. The filtrate was reduced in volume to ca. 50 mL and $(NH_4)_2CO_3$ was added until the pH was in the range 9-10. The resultant solution was left to slowly evaporate, yielding large, colorless crystals of $[NH_4]_6[calix[4]arenesulfonate][MeOSO_3]\cdot(H_2O)_2$.

(7) The title compound has six ammonium ions, five formally associated with the calixarene anion and one with the methyl sulfate anion. The space group is the monoclinic $C2/c$ with a = 22.164 (5) Å, b = 25.945 (6) Å, c = 17.772 (7) Å, β = 124.71 (4)°, and D_c = 1.28 g cm^{-3} for Z = 8. The cations and anions possess no crystallographically imposed symmetry. Least-squares refinement based on 3590 observed reflections led to a final R value of 0.054. The sulfur, oxygen, and nitrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on a difference Fourier map or placed in calculated positions, but they were not refined. The details of data collection and refinement are given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(8) Both of the structures are quite similar to those found in clays such as montmorillonite: Mason, B.; Berry, L. G. *Elements of Mineralogy*; Freeman: San Francisco, 1968.

(9) One ammonium ion and one water molecule reside between calixarene anions within the calixarene bilayer. The methyl sulfate anion results from dehydration of methanol contained within the lattice of the parent calix[4]arene by H_2SO_4: $CH_3OH + H_2SO_4 \rightarrow CH_3OSO_3H + H_2O$.

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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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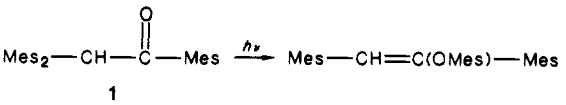
Received March 16, 1987

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



$$Mes_2—CH—\overset{O}{\overset{\|}{C}}—Mes \xrightarrow{h\nu} Mes—CH{=}C(OMes)—Mes$$

1

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

Scheme I

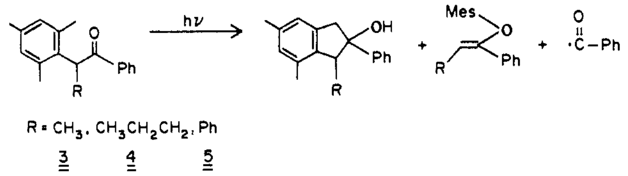
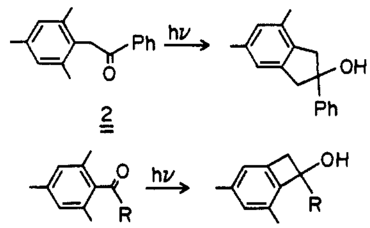


Table I. Photoreactivity of Some α-Mesityl Ketones

ketone	$1/\tau^a$	Φ indanol	Φ ether	Φ ArCHO[b]	$k_{\delta-H}{}^a$	$k_{CT}{}^{a,c}$
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.



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 ^1H 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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