Tetrahedron Letters,Vol.27,No.29,pp 3343-3344,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

MACROCYCLIC RING FORMATION IN MICELLES

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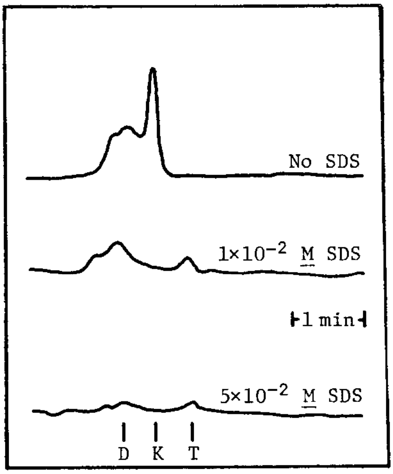
Abstract: *The influence SDS micelles exert on the course of the chemical reaction initiated by excimer laser photolysis of long-chain bis-dibenzylsulfone detergent molecules is evaluated. In the presence of SDS* $[2.12]_3$*-paracyclophane forms; in the absence of SDS it does not.*

The geodesic hypothesis of micelle structure predicts that the aggregation numbers and symmetries of micelles are related and that the internal arrangement of the detergent tails is a twisted one.[1] The latter prediction is a physical manifestation of "tensegrity".[2] It should therefore be possible to confer the twist on reagents dissolved in micelles and template appropriate chemical reactions by this means. In an attempt to test this hypothesis a special "guest detergent" (4) was synthesized which contains photolabile head groups that are compatible with sodium dodecylsulfate (SDS), which serves as the "host" micelle. These solutions (@ ~1.0×10^{-3} M) were irradiated at ambient temperature in a quartz cuvette by using an excimer laser at 248 nm, then extracted with CH_2Cl_2 to obtain the non-polar products, and analyzed by using size exclusion chromatography.[3] The results (Fig. 1) indicate that in addition to 1,12-*bis*-[4-hydroxymethylphenyl]-dodecane, which is formed in each of these experiments,[4] unknotted $[2.12]_3$-paracyclophane forms in the presence of SDS. In the absence of SDS the formation of this paracyclophane is suppressed and an as yet unidentified product[5] forms which does not correspond to any unknotted macrocycle prepared to date.[7] Efforts to prepare and isolate sufficient quantities of this material are in progress, but even at this stage in the investigation it is apparent that the SDS micelle facilitates the formation of the unknotted macrocycle. This observation raises questions concerning the validity of the geodesic hypothesis which can only be addressed experimentally. Experiments designed to further test the geodesic hypothesis and to evaluate the importance of various other factors including concentrations of host and guest detergents, temperature and ionic strength are in progress.

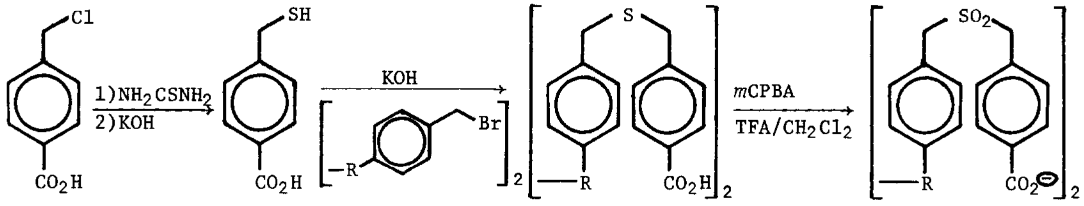
Figure 1



D = diol; K = unknown; T = trimer

The "guest" detergent was synthesized from available materials by a method analogous to that used previously to prepare macrocyclic sulfones. As shown in the Scheme, 4-chloromethylbenzoic acid was treated with one equivalent of thiourea in ethanol and hydrolyzed by standard procedures[8] to give the sulfhydrol compound which was isolated as a precipitate on acidic work-up and dried over $CaCl_2$ under N_2 in the dark at 4°C. The dried material was dissolved in ethanol containing 3 eq of KOH and treated with ½ eq of 1,12-*bis*-[4-bromomethylphenyl]-

Scheme

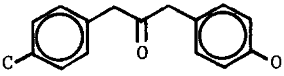


1 2 3 4

dodecane to give the nearly insoluble diacid 3 in 90% yield. Oxidation of this material by using *m*CPBA in 1:1 CH_2Cl_2/TFA gave the sulfone in quantitative yield. This material is so insoluble in most solvents that impurities may be removed by multiple washings with a variety of solvents. The solid thus obtained was treated with $NaHCO_3$ and sonicated for 1 hr. The remaining solid material proved to be slightly soluble in water and it was used in the laser photolysis without further purification.

Acknowledgement: We thank Dr. Alan Marshal and Mr. Ron Shomo for providing mass spectra of these compounds. We gratefully acknowledge financial support from Ohio University, Research Corporation, and the donors of the Petroleum Research Fund administered by the American Chemical Society, as well as the National Science Foundation.

References and Notes:

1. Butcher, J.A., Jr.; Lamb, G.W. *J. Am. Chem. Soc.* 1984, 106, 1217-1220.
2. Kenner, H. "Geodesic Math and How to Use It"; University of California Press: Berkeley and Los Angeles, 1976.
3. Zorbax SPM-60^R (DuPont), CH_2Cl_2 @ 0.7 mL/min. The diol elutes in 8 min; the trimer in 7 min.
4. 1,12-*bis*-[4-hydroxymethylphenyl]-dodecane is the only product formed during lamp photolysis. Presumably the sulfone cleaves from a zweiterionic singlet state which can react readily with water to yield the alcohol.
5. The unknown product does not correspond to any of the standard materials ([2.12], $[2.12]_2$, or $[2.12]_3$-paracyclophanes) synthesized to date.[6] It forms only during photolysis at high laser power. Based on its retention volume the unknown appears to be larger than $[2.12]_2$-paracyclophane and smaller than $[2.12]_3$-paracyclophane. TLC (silica) separates the unknown from the diol as a single spot with an R_F consistent with a hydrocarbon (i.e., similar to $[2.12]_3$-paracyclophane). Mass spectral analysis using laser volatilization techniques revealed a single mass fragment at a nominal mass = 256 amu. The unknotted trimer exhibits significant fragmentation under these conditions. Whether this will prove to be the knotted $[2.12]_3$-paracyclophane must await further analysis.
6. Laser photolysis of [NaO_2C  $O(CH_2)_6-]_2$ yields a product with a comparable SEC retention volume, but many other (recognizable) products also form. Butcher, J.A., Jr. and Lamb, G.W. (unpublished results).
7. [2.12]-, $[2.12]_2$-, $[2.12]_3$-, and $[2.12]_4$-paracyclophanes have been made. Likewise, 1,12-*bis*-[4-methylphenyl]-dodecane is known. None of these materials match the measured retention volume.
8. Speziale, A.J. *Org. Synth. Coll.* Vol. IV, pp. 401-403.

(Received in USA 19 March 1986)