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SOLID STATE PHOTODIMERIZATION OF SURFACTANT ESTERS OF CINNAMIC ACID

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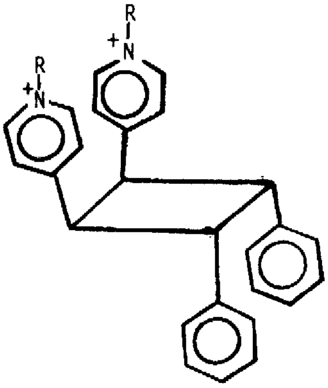
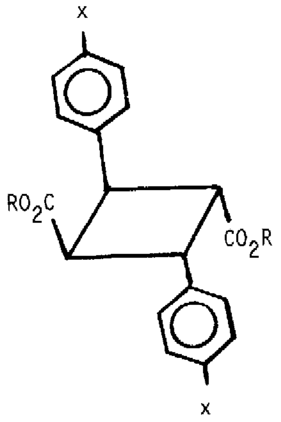
Numerous examples of solid state photodimerizations have been reported. Although many of these reactions are topochemically controlled and lead to a single dimeric product in high yield, the general synthetic utility of these reactions has been limited by the inability to manipulate and control crystal structures. The concept of "crystal engineering" has been advanced by Schmidt, Cohen and coworkers;[1] their approaches to controlling packing geometry have included introduction of a dichlorophenyl group into unsaturated systems and co-crystallization of mercuric chloride-organic mixtures. In the latter case, the packing of the mercuric chloride controls the type of lattice formed. In the course of our investigations of environmental and medium effects on photoreactions, we have investigated the photochemistry of several surfactant molecules. We were somewhat surprised to find that the p-chlorobenzenesulfonate salt of N-octadecyl-4-stilbazole undergoes clean solid state photodimerization to yield exclusively the syn-head-to-head dimer (1).[2] This is in contrast to the behavior of simple non-surfactant stilbazole salts and to that of other quaternary N-heteroaromatics which generally yield syn-head-to-tail dimers on irradiation in the solid state or in solution.[3-5]



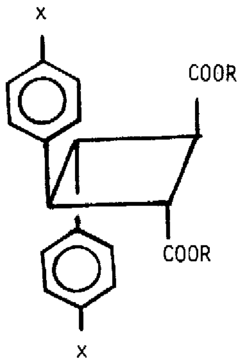
The possibility that hydrophobic-hydrophilic interaction may play a role in crystal packing of 1 led us to investigate the solid state photodimerization of other surfactant molecules. In this paper we report some results on the photodimerization of the octadecyl esters of trans-cinnamic acid and trans-p-chlorocinnamic acid which indicate that the hydrophobic group can play an important role in the solid state photochemistry of these compounds.

The octadecyl ester of trans-cinnamic acid (2)[6] forms monolayer films on water and otherwise exhibits surfactant properties. It was found that 2 could be crystallized from several solvents under a variety of conditions to yield three different crystal forms, A, B, and C. All three crystal forms melted at 48-50°; however, the forms were clearly different and could be distinguished on the basis of their x-ray powder patterns. Form A, which appeared to be the most prevalent form (formed by slow crystallization from alcohols or by concentrating solutions of 2 in hydrocarbon or chlorocarbon solvents), gave a dimer upon irradiation[7] which was identified by independent synthesis to be the dioctadecyl ester of α-truxillic acid (3).[6] Form B, which was obtained upon crystallization of 2 from ketonic solvents (acetone, methylethylketone) was found to be photostable. Form C, which could be most readily obtained by rapid cooling (dry ice - acetone) of ethanol solutions and appears to represent the kinetic crystal form, gave a different photodimer on irradiation which was identified by independent synthesis as the dioctadecyl ester of δ-truxinic acid (4).[6]



3 x = H

6 x = Cl



4 x = J

7 x = Cl

The octadecyl ester of trans-p-chlorocinnamic acid (5)[6] provided only two crystal types, both having mp 55.5-56.5°. Analogous to 2, recrystallization from acetone gave crystals which were photostable.[9] Crystals obtained from 5:1 ethanol:benzene photodimerized upon irradiation[9] to give a single dimer which was identified as the dioctadecyl ester of p,p'-dichloro-α-truxillic acid (6) by nmr.[12] No crystal form which produced 7 directly could be obtained.[14]

The photobehavior of 2 and 5 offers an interesting contrast to the solid state dimerizations of other cinnamic acid derivatives. The most stable (room temperature) crystal forms of the corresponding acids give different solid state dimers, *trans*-cinnamic acid yielding α-truxillic acid (syn-head-to-tail dimer) and trans-p-chlorocinnamic acid a dimer of the β-truxinic acid type (syn-head-to-head).[1] Although β-truxinic acid is also the primary photodimer of the metastable crystal form of trans-cinnamic acid, dimers of this type are not observed with either 2 or 5.

While it is possible that much more complicated intermolecular interactions influence the topochemical control observed, the fact that both 2 and 5 exhibit such similar photoreactivity, particularly with regard to formation of 3 and 6, indicates that the hydrophobic octadecyl portion exerts a significant orienting influence. The formation of 6 upon irradiation of 5 is potentially of synthetic significance since the truxillic structure was not obtained from the solid state irradiation of the corresponding acid.[15] Moreover, the formation of a single product with the δ-truxinate structure (4) is unprecedented for crystals of other cinnamic acid derivatives.[1,16,17] These results suggest that incorporation of surfactant orienting groups (preferably readily removable) into other photoreactive systems may add a new dimension to the synthetic utility of solid state photochemistry.

Acknowledgment

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References and Notes

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5. W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, and A. A. Lamola, Appl. Cpt., 11, 533 (1972).
6. Octadecyl esters were prepared by fusing the corresponding acid chloride (prepared from the acid and $SOCl_2$) with 1-octadecanol and recrystallization of the resultant

ester. α-Truxillic acid[7] and β-truxinic acid[8] were prepared by solid state photodimerization[9] of the appropriate crystal forms of *trans*-cinnamic acid. δ-Truxinic acid[10] and ε-truxillic acid[11] were prepared by the procedures of Stoermer. Spectral and analytical data were consistent with the structures.

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9. The solid (0.1-0.2 gm) was spread on a 7.5 cm watch glass and irradiated with light from a GE H100PFL44-4 reflector flood lamp filtered through Pyrex and 2 cm of H_2O at a distance of 7-8 cm. The temperature of the solid was maintained at 25-30°; typical irradiation times were 24-48 hrs. The dimeric products could be readily isolated by extracting with ether (acids) or hot ethanol (esters) to remove the residual monomer.

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12. *The nmr resonances for the cyclobutane protons of 3 and 6 were essentially equivalent,* as might be anticipated on the basis of nmr data for the photodimers of benzalacetone and p-chlorobenzalacetone.[13]

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14. Irradiation of 5 at higher temperatures (ca. 40°) led to rapid loss of crystallinity with subsequent formation of mixtures of 6 and 7. The nmr resonances for the cyclobutane protons of 7 were essentially equivalent to those for 4.

15. The truxillate structure can, however, also be obtained from solid state irradiation of p-chlorobenzalacetone and p-chlorobenzalacetophenone.[13]

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