Tetrahedron Letters,Vol.30,No.13,pp 1601-1604,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SURFACE VERSUS BULK REACTIVITY IN SOLID STATE ORGANIC CHEMISTRY

Phani Raj Pokkuluri, John R. Scheffer* and James Trotter*
Department of Chemistry, University of British Columbia
Vancouver, V6T 1Y6, Canada

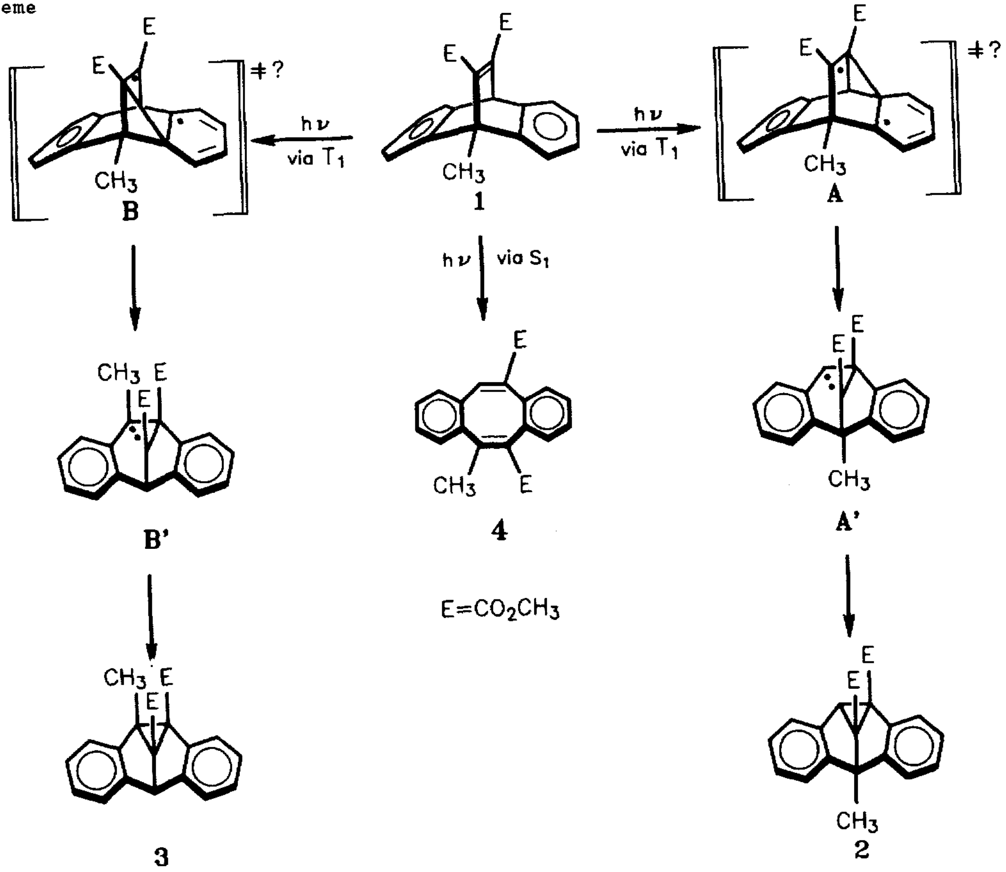
Abstract. Dibenzobarrelene derivative 1 exhibits different reactivity when photolyzed in the form of large single crystals, as a polycrystalline powder and in solution.

An organic molecule at the surface of a crystal finds itself in an environment that is quite different from that which is present in the bulk of the crystal. For example crystal symmetry is reduced at the surface and, with few exceptions, different faces of organic crystals expose different aspects of molecular anatomy to the external environment. It follows that chemical reactions that are sensitive to environmental factors may exhibit significantly different surface/bulk solid state reactivity. Surface reactivity is particularly likely for photoinduced reactions of crystals that absorb strongly at the photolysis wavelength, where a simple Beer-Lambert calculation reveals that most of the incident radiation will be absorbed near the surface. For this reason investigations of crystal photoreactivity should be conducted on samples of widely differing surface area, and where bulk reactivity is desired, photolysis wavelengths near the absorption tail should be used. In this communication we describe a photorearrangement whose regioselectivity changes considerably, not only in proceeding from the liquid to the crystalline phase, but also in going from the surface to the bulk of the crystal.

The compound chosen for study was the crystalline Diels-Alder adduct 1 (Scheme) formed between 9-methylanthracene and dimethylacetylene dicarboxylate.[1] Previous workers had shown that acetone-sensitized photolysis of this material gives rise to the di-π-methane regioisomers 2 and 3 in a ratio of 65:35;[2] a later paper by different authors[3] reported a 71:29 ratio. Our analytical techniques (capillary gas chromatography, quantitative ^{1}H NMR) indicated a ratio of 76:24. What was not reported earlier is that direct irradiation of 1 leads to substantial amounts of the cyclooctatetraene derivative 4. In benzene the 2:3:4 ratio was 52:12:36 and in acetonitrile it was 55:15:30. The structure of photoproduct 4 was assigned on the basis of its spectral data. It seems likely, in analogy to the case of dibenzobarrelene itself,[4] that cyclooctatetraene 4 is formed through the singlet excited state of 1.

Iwamura et al.[3] analyzed the triplet state photochemistry of compound 1 in terms of the Zimmerman mechanism[5] for the di-π-methane rearrangement, which involves initial benzo-vinyl bridging to afford either biradical A or B.[6] It was suggested that biradical B (leading to minor photoproduct 3) was destabilized by the methyl group in the same way that electron-donating substituents at the 7-position shift the cycloheptatriene-norcaradiene equilibrium toward the cycloheptatriene tautomer. Steric factors undoubtedly disfavor biradical B as well. It was interesting to observe, therefore, that Pyrex-filtered irradiation of relatively large, carefully grown single crystals of dibenzobarrelene derivative

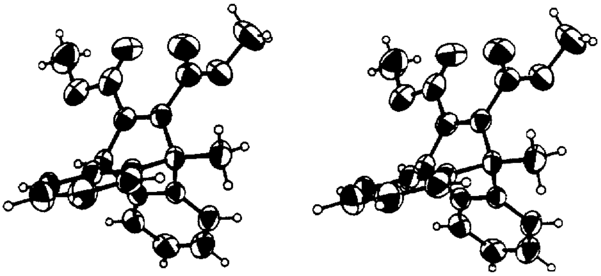
Scheme



1 affords regioisomer 3 as the major product;[7] the 2:3:4 ratio was 12:82:6. In order to assess the solid state photoreactivity more fully, the crystal and molecular structure of 1 was determined by X-ray diffraction methods.[8] This revealed that compound 1 crystallizes in a conformation (Figure 1) in which the π-system of the ester group adjacent to the bridgehead methyl group lies at right angles (88°) to the π-system of the carbon-carbon double bond, whereas the remote ester group is fully conjugated (2°). Presumably this conformation reflects an avoidance of eclipsing interactions between the adjacent methyl and ester groups, and molecular mechanics calculations confirm this conformation as lying near the energy minimum.

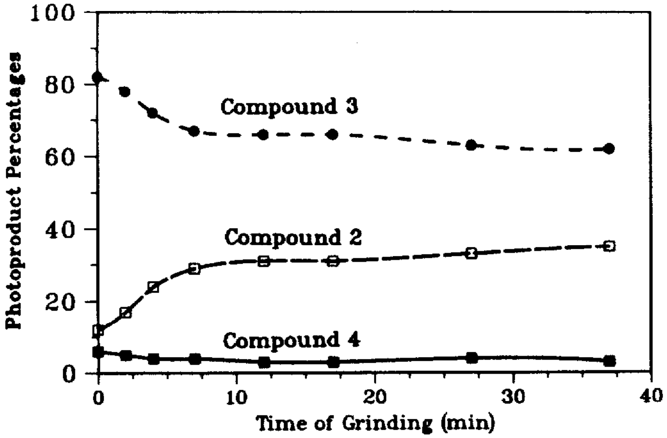
The finding that the two ester groups of crystalline 1 have dramatically different degrees of conjugation to the double bond between them provides a plausible explanation for the solid state regioselectivity. If this difference is maintained in biradicals **A** and **B**, then 3 should be formed preferentially as is observed experimentally.[9] We must point out, however, that such explanations do not appear to apply to mixed dibenzobarrelene-11,12-diesters that lack bridgehead substituents and as a result possess ester groups with less divergent degrees of conjugation.[10] In these cases it was the free space around the non-equivalent ester groups (the groups that move most during benzo-vinyl bridging) that was suggested to control regioselectivity. An analysis of the packing arrangement around the ester groups of **1** revealed that the conjugated ester is the freer of the two by a slight amount; this would tend to favor photoproduct **2** in the solid state. We tentatively conclude, however, that this effect is overridden in the present case by the conjugation effect. What _is_ clear is that the forces that determine regioselectivity in solution are quite different from those that control it in the solid state.

Figure 1. Stereodiagram of Solid State Conformation of Compound 1.



In some solid state photolyses, it was noted that finely divided, polycrystalline samples appeared to give regioselectivities different from those reported above. This was investigated by grinding crystals of diester **1** in a Fritsch Pulverisette apparatus and determining the photoproduct ratios as a function of grinding time. The results of these experiments, shown graphically in Figure 2, indicate that the **2**:**3**:**4** ratio levels off at approximately 35:62:3 after _ca_. 15 minutes of grinding. X-ray powder diffraction spectra taken at regular intervals showed that this change in regioselectivity was not the result of a phase change

Figure 2. Photoproduct Percentages versus Grinding Time.



upon grinding. Reducing particle size by grinding increases surface area, and we interpret the data as indicating a photochemical reaction occurring at the crystal surface with a regioselectivity intermediate between that of the bulk crystal and the liquid phase. This conclusion was reinforced by the following experiment: a large single crystal of 1 that had been irradiated to approximately 1% conversion was washed with three small portions of diethyl ether, in which the starting material is sparingly soluble and the photolysis mixture is moderately soluble. Gas chromatographic analysis of the first washing indicated a conversion of 30%; the second washing contained a photoproduct conversion of 7%, and the third washing 3%. It was also interesting to note that the product regioselectivity was higher in the bulk compared to that at the surface as indicated by the change in the 2:3 ratio with successive washings (18:64 to 10:79 to 6.5:87); a distinct yellow coloration of unknown origin which had developed in the crystal upon photolysis was also removed by the solvent washings.

Acknowledgement. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

1. O. Diels and K. Alder, Justus Liebigs Ann. Chem., **486**, 191 (1931).

2. R.G. Paddick, K.E. Richards and G.J. Wright, Aust. J. Chem., **29**, 1005 (1976).

3. M. Iwamura, H. Takuda and H. Iwamura, Tetrahedron Lett., 21, 4865 (1980).

4. (a) E. Ciganek, J. Am. Chem. Soc., **88**, 2882 (1966); (b) P.W. Rabideau, J.B. Hamilton and L. Friedman, ibid., 90, 4465 (1968); (c) W. Adam, O. De Lucchi, K. Peters, E-M. Peters and H.G. von Schnering, ibid., 104, 5747 (1982).

5. H.E. Zimmerman in "Molecular Rearrangements in Ground and Excited States," P. de Mayo, Ed., Academic, New York, 1980, Ch. 16.

6. We note that a question still remains as to the transition state versus intermediate nature of 1,4-biradical intermediates such as **A** and **B** in the di-π-methane photorearrangement. See W. Adam, M. Dorr, J. Kron and R.J. Rosenthal, J. Am. Chem. Soc., **109**, 7074 (1987) and references cited therein.

7. Compound 1 has $\epsilon = 450$ at 300 nm and $\epsilon = 25$ at 340 nm. Photolysis in the absorption tail (337 nm, nitrogen laser or uranium glass filter, ≈ 330 nm cutoff) gave barely detectable amounts of products even after prolonged irradiation times. As a result, a Pyrex filter was used in all photolyses.

8. Compound 1 crystallizes in space group $P\bar{1}$ with $a = 16.1642(15)$, $b = 14.7470(13)$, $c = 8.3073(6)$ Å; $\alpha = 90.855(69)$, $\beta = 112.821(56)$, $\gamma = 108.736(83)°$; $Z = 4$. Full details will be reported separately.

9. A good analogy is found in methyl dibenzobarrelene-11-carboxylate, which undergoes di-π-methane rearrangement exclusively at the unsubstituted vinyl carbon atom. See ref. 4a. Molecular mechanics calculations show that rotation about the vinyl carbon to ester carbon bond should be facile for compound 1 in solution, thus accounting for the absence of a conjugation effect in this medium.

10. J.R. Scheffer, J. Trotter, M. Garcia-Garibay and F. Wireko, Mol. Cryst. Liq. Cryst., **156**, 63 (1988).

(Received in USA 23 November 1988)