

Prototropic Control of the Di- π -methane Photorearrangement

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The state of protonation and hydrogen bonding in a monoester (**1**) of dibenzobarrelene-11,12-dicarboxylic acid (9,10-etheno-9,10-dihydroanthracene-11,12-dicarboxylic acid) controls the regioselectivity of its di- π -methane photorearrangement.

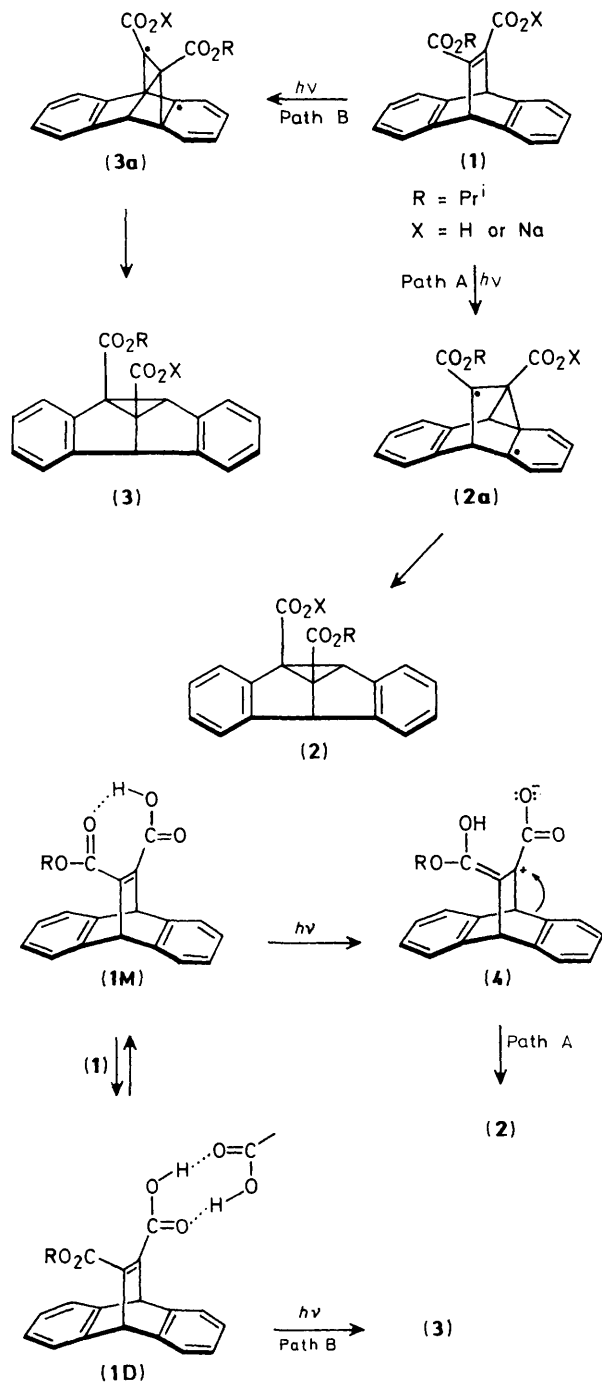
In the course of studying the regioselectivity of the di- π -methane photorearrangement of mixed diesters of dibenzobarrelene-11,12-dicarboxylic acid,¹ we had occasion to examine the photochemistry of the mixed acid-ester (**1**) (Scheme 1, X = H).[†] Irradiation of this material leads to di- π -methane regioisomers (**2**) and (**3**), and as summarised in Table 1, there was a marked variation in the (**2**):(**3**) photoproduct ratio as a function of reaction medium. The values ranged from 90:10 in aqueous sodium hydrogen carbonate solution to 5:95 in the solid state. Strikingly, the (**2**):(**3**) ratio in benzene decreased with increasing starting material concentration, but was independent of concentration in acetonitrile and t-butyl alcohol.

We interpret these results in terms of the effects of the

non-equivalent vinyl substituents on the relative stabilities of the biradical species (**2a**) and (**3a**) (Scheme 1) that are suggested as points on the excited hypersurface for the di- π -methane photorearrangement of dibenzobarrelenes.^{2,3} Turning first to the results in aqueous sodium hydrogen carbonate, the electronic properties of the CO₂⁻ group are very different from those of the CO₂R substituent. The latter is expected to be superior to the former for radical stabilisation,⁴ and this leads to the prediction that path A leading to photoproduct (**2**) should be preferred in basic solution. This is precisely the experimentally observed result.

The interpretation of the concentration-dependent results in benzene is based on the idea that at low concentrations compound (**1**) exists largely in the intramolecularly hydrogen bonded form (**1M**) shown in the Scheme 1, and that as the concentration is raised, *intermolecular* (dimeric) hydrogen bonding to form (**1D**) becomes increasingly important at the expense of (**1M**). Specific solvent effects on the u.v. absorp-

[†] Compound (**1**) was prepared by treatment of the corresponding anhydride (O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, 1931, **486**, 191) with Pr^tOH.



Scheme 1

tion and emission spectra as well as i.r. spectroscopic studies of (1) in benzene as a function of concentration strongly support this conclusion. Intramolecularly hydrogen bonded systems analogous to (1M) (e.g., potassium hydrogen maleate)⁵ are capable of excited state charge transfer interactions in which the proton is transferred from one oxygen to the other. Such a species (4) (Scheme 1) would present the conditions necessary for a regioselective, positive charge-initiated 1,2-aryl shift leading to (2) in analogy to the well studied ground state carbocationic rearrangement of dibenzobarrelenes.⁶ The dimeric species (1D), on the other hand, would face disruption of its hydrogen bonds were it to undergo

Table 1. Medium and concentration effects on photoproduct ratio.

Solvent	Conc./M	% (2) ^{a,b}	% (3) ^{a,b}
Aq. NaHCO ₃	0.01	90	10
Benzene	0.001	83	17
..	0.003	80	20
..	0.006	76	24
..	0.01	72	28
..	0.03	66	34
..	0.06	60	40
..	0.1	55	45
MeCN	c,d	50	50
Bu ^t OH	c	50	50
Solid state		5	95

^a The product percentages were obtained by g.c. analysis following esterification of the reaction mixtures with diazomethane. Both mixed diester photoproducts have had their structures established unambiguously by X-ray crystallography.¹ ^b The estimated error in the product percentages is 5%. ^c Product percentages constant within the limits of our detection at concentrations ranging from 0.1 to 0.001 M. ^d Work-up using oxalyl chloride followed by methanol indicates a ratio of 1:9,^{1c} which we now know does not reflect the true isomer ratio owing to the low yields obtained.

photorearrangement through pathway A. The vinyl substituent at the reaction site is required to undergo substantial displacement during vinyl-benzo bridging; in contrast, pathway B maintains hydrogen bonding at the CO₂H group, and as a result compound (3) becomes more prominent in the photoproduct mixture as the proportion of (1D) increases. This effect is likely to be operative in Bu^tOH and acetonitrile as well, but in these cases it is a solvent molecule rather than a second molecule of (1) that is the hydrogen bond participant. This is consistent with the lack of concentration dependence in the hydrogen bonding solvents. Finally, based on solid state i.r. spectroscopic measurements, we conclude that the hydrogen bonded dimer (1D) is the exclusive species present in the crystal. This explains the even higher proportion of photoproduct (3) formed in this medium. To date, attempts to verify the hydrogen bonding arrangement in the solid state by X-ray crystallography have been frustrated by poor crystal quality.

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