

CONTRASTING PHOTOCHEMICAL BRIDGING REGIOSELECTIVITY IN BRIDGEHEAD-  
SUBSTITUTED 9,10-ETHENO- VS. 9,10-(o-BENZENO)-9,10-DIHYDROANTHRACENES

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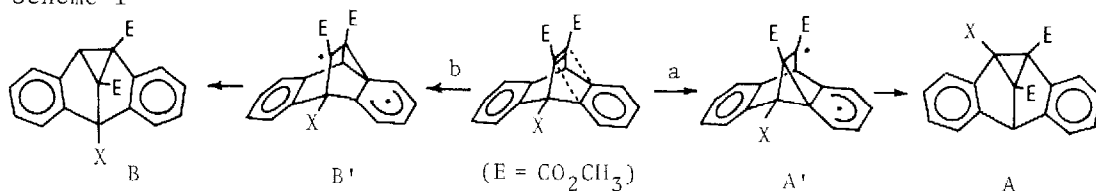
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Abstract: The two series of title compounds show contrasting bridging regio-  
selectivity with respect to the bridgehead substituents and are suggested to  
have different stages of the reactions which determine the ultimate pathway.

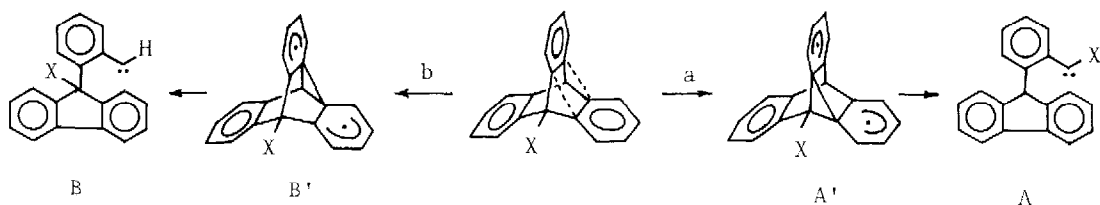
Whereas bridging regioselectivity with respect to different chromophores  
in photochemical di- $\pi$ -methane rearrangements is understood in terms of more  
favorable SO-LUMO interactions between the original  $\pi$ -moieties<sup>1</sup> and of  
stability of the radical centers of initial intermediate cyclopropyldicarbonyl  
diradicals,<sup>2</sup> little is known on controlling factors of the substituents at the  
"methane" position. Ciganek was the first to recognize the modest effect of  
the bridgehead methoxycarbonyl group.<sup>3</sup> Unfavorable (1 to 2) bridging at the  
end nearer to this group was interpreted as arising from a reluctance to have  
the electronegative group held by a bond which becomes heavy in s character.<sup>4</sup>  
The regioselective rearrangement of the bridgehead acetoxy- and hydroxy-  
dibenzobarrelene derivatives by alternative routes was explained in terms of  
the effect of hydrogen bonding and the electronegativity of the bridgehead  
substituents on the reaction profile.<sup>5</sup> In order to disclose the effect of a  
wider range of the substituents at the methane position on the bridging  
selectivity in di- $\pi$ -methane systems and to find some clues to mechanistic  
distinction of triptycene photorearrangements from those of the typical di- $\pi$ -  
methanes, we have undertaken a comparative study of the photoisomerization of  
a series of 9,10-etheno- and 9,10-(o-benzeno)-9,10-dihydroanthracenes with  
bridgehead substitution.

9-Substituted 9,10-etheno-9,10-dihydroanthracenes were prepared by the  
method of Diels and Alder.<sup>6</sup> In a typical run of uv-irradiation, an acetone  
solution (200 ml) of dimethyl 9,10-etheno-9,10-dihydro-9-methoxyanthracene-11,  
12-dicarboxylate (250 mg) was irradiated with an Ushio 450 W high pressure

Scheme 1



Scheme 2



mercury source through Pyrex filter in an immersion apparatus for 1.5 h at 10-15 °C while argon was passed through the solution. The resulting solution was concentrated under reduced pressure and the residue was purified by preparative tlc on silica gel to give 240 mg (96 %) of dimethyl 5-methoxydibenzotricyclo[3.3.0.0<sup>2,8</sup>]octa-3,6-diene-1,2-dicarboxylate as colorless needles (from THF-hexane, 1:5): mp 147-147.5 °C; <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 3.52(s, OCH<sub>3</sub>), 3.72(s, CO<sub>2</sub>CH<sub>3</sub>), 3.79(s, CO<sub>2</sub>CH<sub>3</sub>), 4.34(s, H-8), 7.0-7.4(m, aromatic 7H), and 7.5-7.8(m, aromatic 1H); IR (KBr discs) 1734, 1440, 1240 and 1217 cm<sup>-1</sup>.<sup>7</sup>

There are two possible termini capable of competitive vinyl-benzo bridging in the excited triplet states (path a and b in Scheme 1). Dibenzosemibullvalene A *via* path a can be distinguished from product B *via* path b based on the <sup>1</sup>H NMR chemical shifts;<sup>3,5</sup> the methine protons for A and B appear at δ 5.0-5.1 and 4.2-4.5, respectively. The bridging regioselectivity obtained from these product analyses is given in Table 1. The following trends are noted. There are the oxygen and bromine atoms which carry a lone pair of electrons and disfavor the bridging at the π-cnds near to these atoms. The carbonyl functions are moderately selective for b-bridging as already noted.<sup>3</sup> The effect of other π-accepting groups is apparently not consistent; bridging at the end of the phenyl substitution is accelerated whereas the nitro group is retarding. Simple alkyl groups favor b-bridging slightly but there appears to be a conspicuous steric inhibition of a-bridging in the case of the *tert*-butyl group.

These bridging regioselectivities would be interpreted in terms of the relative stability of the initially formed cyclopropyldicarbonyl diradicals A' and B'. As an example of the effect of a corner substituent on the strength of the opposite edge C-C bond in cyclopropanes one may cite the studies of the substituent effects at position 7 on the equilibrium between norcaradienes and

the corresponding tropilidenes. It is known experimentally as well as theoretically that  $\pi$ -electron acceptors, e.g., CN,  $\text{CO}_2\text{CH}_3$  and CHO, should stabilize the cyclopropane ring and thus favor the norcaradiene tautomer over cycloheptatriene, while  $\pi$ -electron donors, e.g.,  $\text{OCH}_3$ , should destabilize the cyclopropane ring and thus shift the equilibrium toward the tropilidene tautomer.<sup>8</sup> The preferred b-bridging observed as in Table 1 for the oxygen functions and bromine atom is thus accounted for. In order to explain the varied effects of the  $\pi$ -acceptors, the disfavoring effect of electronegativity of the substituents on residing at the bridging cyclopropane ring should be additionally taken into account. We point out that a rate of inhibition of ca. 150-fold relative to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene when the methane carbon bears two cyano groups instead of methyl has been interpreted in terms of the methane carbon becoming electron deficient as bridging occurs to form the  $\text{S}_1$  cyclopropyldicarbonyl diradical.<sup>9</sup> The phenyl group is least electronegative ( $\sigma_I = 0.10$ ) among the  $\pi$ -acceptors in Table 1 and therefore should be the only one  $\pi$ -acceptor which leads to a-bridging exclusively. As electronegativity increases as indicated by the Taft  $\sigma_I$  values of 0.34 and 0.35, the proportion of the a-bridging decreases to 29 and 12 % for the acetyl and formyl groups, respectively. The nitro group is most electronegative ( $\sigma_I = 0.70$ ) and path a is not observed any more.

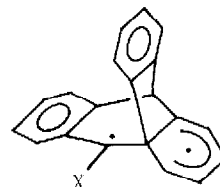
Table 1. Bridging Regioselectivity for Typical Di- $\pi$ -methane and Triptycene Photorearrangements

X	Ethenoanthracene		o Benzenoanthracene	
	path a	path b	path a	path b
$\text{OCH}_3$	0	100 %	100 <sup>10</sup>	0 %
OAc	0	100 <sup>5</sup>		
OCOPh	0	100	100 <sup>10</sup>	0
$\text{CH}_3$	29	71	21	79
$(\text{CH}_3)_2\text{CH}$	23	77		
$(\text{CH}_3)_3\text{C}$	0	100	0	100
Br	0	100	100	0
Ph	100	0	100	0
Ac	29	71	100 <sup>10</sup>	0
CHO	12	88	100	0
$\text{NO}_2$	0	100		

path b prevails and path a is rather an exception. The preference of path b for alkyl groups is probably due to steric inhibition of bridging as in the etheno-

Turning now to the bridging regioselectivity of the bridgehead-substituted 9,10-(o-benzo)-9,10-dihydroanthracenes, we note by locating the substituent in the photo-products due to carbene intermediates A and B<sup>11</sup> in Scheme 2 that, with the exception of alkyl groups, bridging takes place always at the end of the o-benzo moieties near to the substituents. The results are quite a contrast to the typical di- $\pi$ -methane rearrangement in the ethenoanthracenes in which

anthracenes. The predominant a-bridging irrespective of the other substituents suggests that the product developing step should not be associated with the initial bridging to form cyclopropyldicarbonyl diradicals A' and B' in the triptycenes but with a later stage on the excited state energy surface of the rearrangement. Since most of the substituents can stabilize the radical and carbenic centers when directly attached, either an alternative diradical C which may come later in the course of the rearrangement or a concerted cheletropic elimination of the monocentric diradicals is proposed as responsible for the product-forming step in the triptycene photorearrangement.



C

## REFERENCES AND NOTES

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- 11) The carbenes were mostly trapped externally with the methanol solvent to give the O-H insertion products. Some were characterized as the Wolff and the Wittig rearrangement products.<sup>7, 10</sup> 9-(o-Substituted phenyl)fluorenes from A showed a characteristic pair of 9-H due to rotational isomerism in the  $\delta$  5.0-5.5 region.

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