Tetrahedron Letters, Vol. 34, No. 1, pp. 35-38, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

SUBSTITUENT EFFECTS ON THE DI-π-METHANE PHOTOREARRANGEMENT OF 9,10-ETHENOANTHRACENE DERIVATIVES

Graham Rattray, Jie Yang, Anna D. Gudmundsdottir and John R. Scheffer*

Department of Chemistry, University of British Columbia
Vancouver, B.C., Canada V6T 1Z1

Abstract. The photochemical result of placing electron-donating and electron-withdrawing substituents at the vinyl and aryl positions of the 9,10-ethenoanthracene nucleus is reported. The results are discussed in terms of the radical stabilizing and polar effects of the substituents on the biradical intermediates involved.

Studies of "dual-channel"[1] photorearrangements, i.e., photorearrangements that give a single product through two isoenergetic pathways in the absence of substituents, but which afford two different products when substituents are introduced, tell us a great deal about the stereoelectronic factors that govern the excited state behavior of organic molecules. The di-π-methane photorearrangment[2] has been particularly well studied from this point of view, with important contributions coming from Zimmerman and co-workers (acyclic di-π-methane systems),[2b] Paquette and co-workers, (benzonorbornadiene derivatives),[2c] Bender et al. (benzobarrelenes)[3] and Hemetsberger and Nobbe (benzonorbornadiene and dihydrobenzobarrelene derivatives).[4]

9,10-Ethenoanthracene, a four channel di-π-methane system, is especially attractive for substituent effect studies, since substituents can be introduced readily through well precedented Diels-Alder reaction chemistry. Advantage has been taken of this fact by Iwamura et al.[5] as well as Paddick et al.[6] to investigate the effect of bridgehead substituents on the photochemistry of this system, but very little is known concerning the effect of substituents located at vinyl or aryl positions. In this communication, we report some preliminary studies on the influence that vinyl and aryl substituents have on the photochemistry of the 9,10-ethenoanthracene system. We were particularly interested in preparing disubstituted compounds such as **1** in order to carry out intramolecular competition experiments between two different vinyl substituents. Such studies have not been reported previously for bicyclic di-π-methane systems.

Application of the Zimmerman mechanism[2a,b] to vinyl-substituted 9,10-ethenoanthracene derivative **1** leads to photoproducts **2** and **3**. Only two of the four possible pathways are shown, since involvement of the left-hand benzo ring leads to the enantiomers of **2** and **3**.

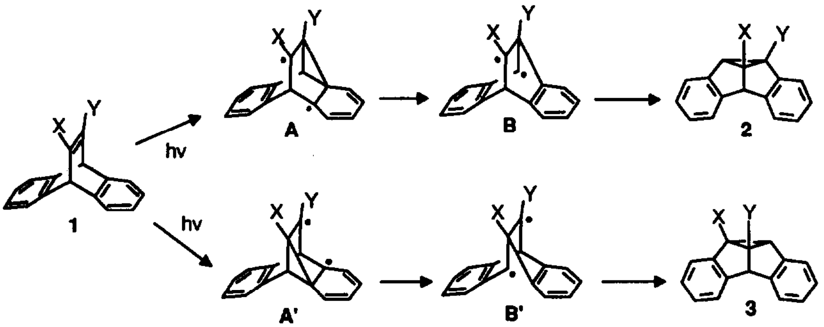


Table 1 summarizes the substituents **X** and **Y** studied along with the **2**:**3** ratio obtained as a result of photolysis in acetone at room temperature. Entry 1 is due to Ciganek,[7] but the remaining entries represent compounds prepared and photolyzed for the first time in our laboratory.[8]

Table 1. Compounds **1** Studied and **2**:**3** Photoproduct Ratios

Entry	X	Y	2:3 Ratio
1	H	COOMe	0:100
2	H	$CONH_2$	0:100
3	H	$CONMe_2$	0:100
4	$CONMe_2$	COOMe	3:97
5	CONHEt	COOMe	0:100
6	COONa	COOiPr	10:90
7	COOMe	CSOMe	0:100
8	COOMe	COSMe	0:100
9	CH_3	COOMe	0:100
10	COOMe	Ph	0:100

In general, the photochemical results are in accord with the idea put forward by Zimmerman[2b] that the radical terminii of the cyclopropyldicarbinyl diradicals (e.g., **A** and **A'**) become electron rich during the di-π-methane photorearrangement, and that as a result, both the polar nature as well as the radical-stabilizing ability of the substituents are important in determining regioselectivity. Consider, for example, entry 9. Here, the relative radical stabilizing abilities of the methyl and ester groups are probably about equal,[9] but photoproduct **3** is formed exclusively owing to the preference for the radical to be formed next to the electron-withdrawing ester group rather than the electron-donating methyl substituent. By way of contrast, in the case of ester versus phenyl (entry 10), the radical stabilizing ability of the latter substituent wins out. The competition between ester and amide is also interesting. Organic intuition tells us that, because of the strong resonance interaction between nitrogen and oxygen, amide groups should be poorer electron withdrawing substituents than esters, and probably poorer radical stabilizing groups as well.[9] The preferential formation of photoproduct **3** in these cases (entries 4 and 5) is consistent with this picture. An analogous argument can be used to rationalize the regioselectivity in the competition between ester and carboxylate anion (entry 6).[10] Finally, entries 7 and 8 deserve some comment. The observed regioselectivities indicate that there is a marked preference for the thioester substituents to occupy the electron rich radical terminii during photorearrangement. Such selectivity finds good analogy in the work of Wollowitz and Halpern, who showed that the COSEt group undergoes a 1,2-radical and a 1,2-anionic shift in preference to the COOEt substituent.[11]

Aryl substituent effects were briefly investigated in the 1,5-disubstituted dimethyl 9,10-ethenoanthracene-11,12-dicarboxylate system **4**. Photolysis of such compounds can lead to two possible regioisomeric di-π-methane products, **5** and **6**. The substituents studied and the **5**:**6** ratio obtained as a result of irradiation in acetone are shown in Table 2.[12]

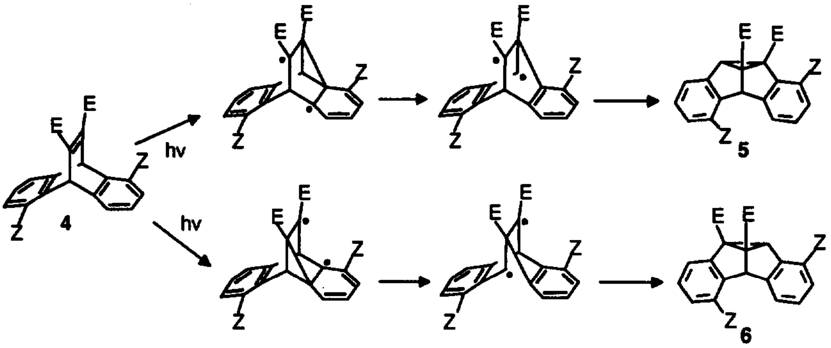


Table 2. Compounds **4** Studied and **5**:**6** Photoproduct Ratios (E = COOMe).

Entry	Z	**5**:**6** Ratio
1	CN	80:20
2	COOMe	35:65
3	Cl	38:62
4	OMe	86:14

The photochemical results summarized in Table 2 are reminiscent of the results obtained by Snow, Cottrell and Paquette with ortho-substituted benzonorbornadienes.[13] There, too, initial benzo-vinyl bridging occurred preferentially ortho to the cyano and methoxy substituents, and low regioselectivity was observed in the case of halogen (fluoro). Entry 2 is, however, anomalous in that one would expect COOMe and CN to exert similar effects. It may be that steric effects become important in the case of the bulkier carbomethoxy substituent. The biradical intermediates leading to photoproduct **5** are clearly more sterically hindered than those leading to **6**, and previous publications from our laboratory have documented the sensitivity of the di-π-methane photorearrangement to steric effects.[14]

Acknowledgment 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.

References and Footnotes

1. L.A. Paquette, A. Varadarajan and L.D. Burke, J. Am. Chem. Soc., **108**, 8032 (1986).

2. For reviews of the di-π-methane photorearrangement, see (a) H.E. Zimmerman in "Rearrangements in Ground and Excited States," P. de Mayo, Ed., Academic Press, New York, 1980, Vol. 3, p. 131; (b) H.E. Zimmerman in "Organic Photochemistry," A. Padwa, Ed., Marcel Dekker, New York, 1991, Vol. 11, p. 1; (c) O. de Lucchi and W. Adam in "Comprehensive Organic Synthesis," B.M. Trost, I. Fleming and L.A. Paquette, Eds., Pergamon Press, Oxford, 1991, Vol. 5, p. 193.

3. (a) C.O. Bender, D.W. Brooks, W. Cheng, D. Dolman, S.F. O'Shea and S.S. Shugarman, Can. J. Chem.,**56**, 3027 (1979); (b) C.O. Bender, D.L. Bengtson, D. Dolman, C.E.L. Herle and S.F. O'Shea, Can. J. Chem., **60**, 1942 (1982); (c) C.O. Bender, I.M. Cassis, D. Dolman, L.D. Heerze and F.L. Schultz, Can. J. Chem., **62**, 2769 (1984).

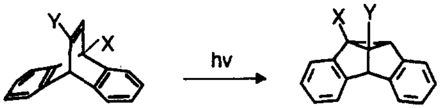
4. H. Hemetsberger and M. Nobbe, Tetrahedron, **44**, 67 (1988).

5. M. Iwamura, H. Tukada and H. Iwamura, Tetrahedron Lett., **21**, 4865 (1980).

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

7. E. Ciganek, J. Am. Chem. Soc., **88**, 2882 (1966).

8. The 9,10-ethenoanthracenes in Table 1 are either known materials [entry 9: W.R. Vaugham and K.M. Milton, J. Am. Chem. Soc., **74**, 5623 (1952); entry 10: H. Hart, D.L. Dean and D.N. Buchanan, J. Am. Chem. Soc., **95**, 6294 (1973)] or were prepared by standard functional group transformations of methyl 9,10-ethenoanthracene-11-carboxylate (reference 7) or dimethyl 9,10-ethenoanthracene-11,12-dicarboxylate (O. Diels and K. Alder, Liebigs Ann. Chem., **486**, 191 (1931). The reactants as well as the photoproducts all exhibited spectroscopic and analytical data fully in accord with their assigned structures. The assignment of regiochemistry to the photoproducts is based on their 400 MHz NMR spectra (all), X-ray crystallography (entries 7-10) and independent synthesis (entry 4). The independent synthesis utilized the regioselective di-π-methane photorearrrangement shown below.



9. F.G. Bordwell and T-Y. Lynch, J. Am. Chem. Soc., **111**, 7558 (1989).

10. Entry 6 is taken from M.A. Garcia-Garibay, J.R. Scheffer and D.G. Watson, J. Org. Chem., **57**, 241 (1992).

11. S. Wollowitz and J. Halpern, J. Am. Chem. Soc., **106**, 8319 (1984).

12. The 9,10-ethenoanthracene derivatives of Table 2 were prepared by Diels-Alder addition of dimethyl acetylenedicarboxylate to the corresponding 1,5-disbustituted anthracenes. The photoproducts **5** and **6** were differentiated by NOE experiments and, in the case of photoproduct **5**, entry 3, an X-ray crystal structure.

13. R.A. Snow, D.M. Cottrell and L.A. Paquette, J. Am. Chem. Soc., **99**, 3734 (1977).

14. (a) J. Chen, P.R. Pokkuluri, J.R. Scheffer and J. Trotter, Tetrahedron Lett., **33**, 1535 (1992); (b) R. Jones, J.R. Scheffer, J. Trotter and M. Yap, Tetrahedron Lett., accompanying paper, this issue.

(Received *in USA 17 August 1992; accepted 30 September 1992)*