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APPARENT ANOMALOUS BEHAVIOR OF POLAR SUBSTITUENTS ON THE BENZENE RING IN THE REGIOSELECTIVITY OF DI-π-METHANE REARRANGEMENT OF 5,6-BENZO-2-AZABICYCLO[2.2.2]OCTADIENONES

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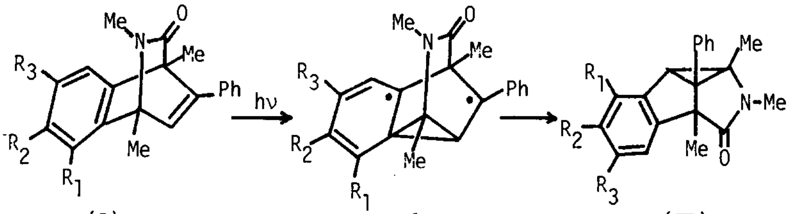
Summary: Polar substituent effects on the aromatic ring emerge in the regioselectivity of the di-π-methane rearrangement of the title compounds when they possess the structural feature of including the bridgehead carbon in a saturated ring; the importance of the environment at the bridgehead carbon is pointed out.

Photochemical investigation of systems containing more than one di-π-methane chromophore can provide much information about the physical and chemical properties of excited state molecules. Thus there is continued interest in the factors which control the regioselectivity of di-π-methane photorearrangements in bicyclic systems.

Recently, the triplet-sensitized di-π-methane rearrangements of benzonorbornadienes bearing polar substituents in the aromatic ring and/or vinyl moiety were reported.[1] The observed regioselectivity or regiospecificity induced by the strong directional effects of the polar substituents was ascribed to the excited state π-electron distribution, stressing the significance of "LUMO" (and/or "HOMO") polarization rather than that of the stabilities of the bridged species, which was emphasized in earlier reports.[2] And we have also shown previously with some 5,6-benzo-2-azabicyclo[2.2.2]octadienones that a variety of factors can be operative for determining the regioselectivity of this type.[3]

We wish to report here a direct comparison of the magnitude of the effect exerted by polar aromatic ring substituents (-OMe and -CN) with that of other effects previously observed[3] in acetone-sensitized photorearrangements of two series of 5,6-benzo-2-azabicyclo[2.2.2]octadienones, (I) and (II), and to show that the polar substituent does not affect the product composition in the case of (I), whereas such substituents at the same position do exert an strong influence on the product distribution in the case of (II).

Acetone-sensitized irradiations of (I_{b-e})[4,5] (400W High Pressure Mercury Lamp, Pyrex filter) for 2 hours led to isolation of a single photoproduct in nearly quantitative yield, arising from the bridging intermediate A, irrespective of the nature and location of the polar substituent. The structures of each photoproduct follow from spectral properties.[5] The assignment of each photoproduct to that from A bridging is based on the comparison of its ^1H NMR spectrum with that of (I_a).[3]



(I) A (III)

Ia: $R_1=R_2=R_3=H$

Ib: $R_1=CN$, $R_2=R_3=H$

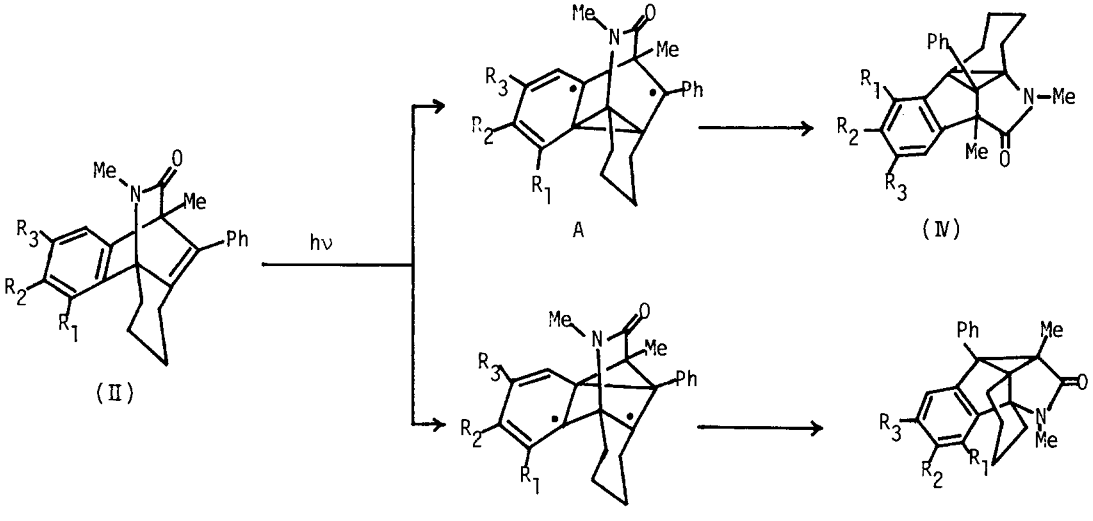
Ic: $R_1=R_3=H$, $R_2=CN$

Id: $R_1=OMe$, $R_2=R_3=H$

Ie: $R_1=R_2=H$, $R_3=OMe$

This result indicates that the phenyl substituent on the vinyl moiety plays a stronger directional role in controlling the regioselectivity than do the various aryl substituents. This role can be rationalized in terms of the "heavy localization of the excited triplet state"[6] on the site of styrene chromophore. This can be easily recognized by qualitative comparison of the triplet energy of styrene (E_T=61.7 Kcal/mol)[7] with that of anisole (E_T=80.8 Kcal/mol)[8] or benzonitrile (E_T=76.8 Kcal/mol)[9]. Furthermore, it is abundantly clear that the HOMO-LUMO configuration is in the main responsible for the lowest excited triplet state of these aromatic molecules. Thus the initial bridging occurs at the carbon remote from phenyl substitution on the styrene, this carbon having the larger orbital coefficient in view of the "LUMO" (and "HOMO") polarization of excited state styrene.

On the other hand, similar irradiation of (II_{b-e}) afforded product whose structure depended on nature and location of the polar substituent, in accord with "LUMO" polarization.[10] The strong influence on product formation in these cases is shown in Table I. For ortho-substituted cases, regiospecific ortho bridging was observed regardless of electronic character, and for the meta-acceptor- and meta-donor-substituted cases, the net effect is a preference for para bridging and meta bridging, respectively. The behavior of these polar substituents is similar to that observed with the benzonorbornadienes.[1]



A (IV) (II) B (V)

Table I. Product Distributions for Acetone-Sensitized Irradiation of (II)

Compd	R	Product Ratio, % IV	V
IIa	$R_1=R_2=R_3=H$	45	55
IIb	$R_1=CN$, $R_2=R_3=H$	100	0
IIc	$R_1=R_3=H$, $R_2=CN$	20	80
IId	$R_1=OMe$, $R_2=R_3=H$	100	0
IIe	$R_1=R_2=H$, $R_3=OMe$	30	70

These results indicate that the [1,7] annelated six-membered ring hardly exerts any influence on the polar substituent effect, although it nearly neutralizes the directional effect of the phenyl group in (I). This result seems difficult to explain by simple molecular orbital considerations, since the orbitals involved in the initial bridging are essentially identical in the two cases, (I) and (II). To obtain further information on this point, we have measured the quantum efficiency (Φ_{dis}) of (I) and (II).[11] As is shown in Table II, introduction of a polar substituent to the aromatic ring exerts little influence on the quantum efficiencies, although the quantum yields of (II) have been noticeably reduced by [1,7] annelation.

Table II. Quantum Yields (Φ_{dis}) for Acetone-Sensitized Irradiation

Compd	Φ_{dis}	Compd	Φ_{dis}
Ia	0.18	IIa	0.10
Ib	0.18	IIb	0.12
Ic	0.17	IIc	0.12
Id	0.19	IId	0.07
Ie	0.16	IIe	0.09

That the observed directional effects of the polar substituents are similar to those in benzonorbornadiene derivatives[1] indicates that the [1,7] annelated six-membered ring does not appreciably retard the bridging rate, since the bridging step is totally responsible for regiospecificity of this type. Yet somewhat lower quantum efficiencies have been observed in (II).[13] Accordingly, we are inclined to consider the possibility that the product-forming step from the bridged species may be affecting rate in this case, although the current view is that the rate-determining step is the bridging stage in most di-π-methane rearrangements. Further elaborations on these points are in progress.

REFERENCES AND FOOTNOTES

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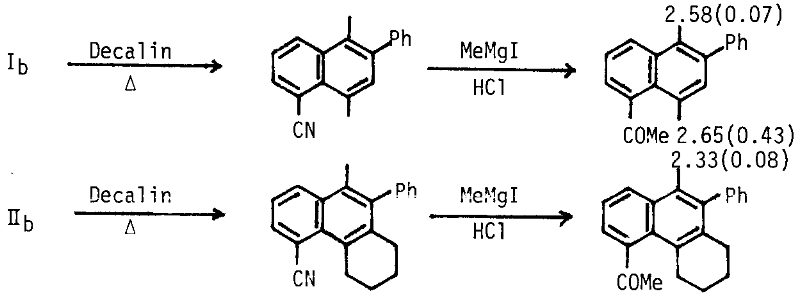
2. R.C.Hahn and R.P.Johnson, *J. Am. Chem. Soc.*, **97**, 212 (1975) and references cited therein. For a thorough review, see S.S.Hixon, P.S.Mariano and H.E.Zimmerman, *Chem. Rev.*, **73**, 531 (1973)
3. M.Kuzuya, M.Ishikawa, T.Okuda and H.Hart, *Tetrahedron Lett.*, 523 (1979)
4. Experimental details for the preparation of these compounds will be reported in a full paper. Precise location of the polar substituents, however, is essential to the discussions to be described, and has been determined as follows: Heating of (I) and (II) [except for (Ic) and (IIc), which were solved by direct examination of Eu shift slope of the aromatic protons] in decalin for 2 hours eliminated the amido bridging to give the naphthalene derivatives. The CN substituents were further converted to COMe group. Examination of Eu shift slope (number in parenthesis) relative to OMe or COMe on the resulting naphthalene derivatives unambiguously establishes the location of the polar substituents as shown.

   For example:



5. All new compounds reported herein gave a satisfactory elemental analyses.
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7. D.F.Evans, *J. Chem. Soc.*, 2753 (1959)
8. S.L.Murov, Ph.D. Thesis, Univ. of Chicago (1966)
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10. Although, in the case of (IIc) and (IIe), the two products were inseparable on several vpc columns, analysis of the crude reaction mixture by 'H NMR showed the product composition as shown in Table I.
11. Quantum yields were measured through 400W High Pressure Mercury Lamp with the filter light (Toshiba UV-D33S filter and 5% $NiSO_4$ solution) using a "merry-go-round" apparatus (Riko-Rotary RH 400), and potassium ferrioxalate actinometry[12] was used.
12. C.G.Hatchard and C.A.Parker, *Proc, R. Soc. London, Ser. A.* **235**, 518 (1956)
13. Although it has been noted that "quantum yields should not be taken too seriously in correlating photochemical reactivity with structural feature"[14], lowering the quantum efficiency necessitates that the triplet energy decay of (II) other than the rate leading to the product should be greater than that of (I), since the bridging chromophores are essentially identical.
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