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PHOTOCHEMISTRY OF NOVEL AZABICYCLIC COMPOUNDS; CONCERNING THE SITE- AND REGIO-SELECTIVITY OF DI-π-METHANE TRANSFORMATIONS OF 5,6-BENZO-2-AZABARRELENES

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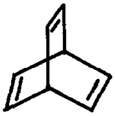
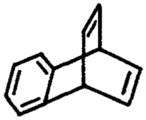
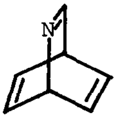
Abstract: Acetone sensitized irradiation of novel 5,6-benzo-2-azabarrelenols were performed to afford di-π-methane photoproducts whose structures and ratios depended on the structural features and substituents; the phenyl substituent at C-8 rendered the pronounced effect on the formation of novel "cross-bonding" product through the imino-ether bridge, and importance of the product forming step for the observed regioselectivity was pointed out.

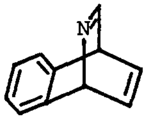
Direct comparisons of the relative photoreactivity of more than two competing pathways have been the subject of numerous investigations in photochemistry. There are a number of structural and electronic features of bicyclic "doubly connected" di-π-methane systems which make them mechanistically interesting. Among those, the studies on di-π-methane transformation of barrelenes and benzobarrelenes have produced a very detailed understanding of such photorearrangements.[1] However, no structurally related heterocyclic derivatives such as 2-azabarrelene, 5,6-benzo-2-azabarrelenes have yet been investigated to undergo an analogous rearrangement, although they have considerable interest from a theoretical and photochemical point of view.


barrelene


benzobarrelene



2-azabarrelene



5,6-benzo-2-azabarrelene

The regioselectivity induced by the strong directional effects of the polar substituents on the chromophore observed in the triplet-sensitized rearrangements of "doubly connected" di-π-methane systems such as benzonorbornadienes were nicely interpreted by the consideration of "LUMO" and/or "HOMO" polarization assuming that the triplet states mainly involve a configuration of the HOMO-LUMO transition.[2] And we have shown with some 5,6-benzo-2-azabicyclo[2.2.2]octadienones that it is also important to consider the product forming step for the observed regioselectivity.[3,4]

Our continuing interests in this area of photochemistry are now focused on the influence of structural and electronic substituent effect on the regioselectivity of di-π-methane transformation of aza-analog of benzobarrelenes.

We have recently reported that some N-unsubstituted pyridone derivatives have undergone Diels-Alder addition with benzyne to afford 5,6-benzo-2-aza-barrelenones,[5] which were converted to novel 5,6-benzo-2-azabarrelene derivatives (**1a**-**1e**) by treatment with trimethyloxonium tetrafluoroborate.[6,7]

We wish to report here the regiochemistry of the photorearranement observed with 5,6-benzo-2-azabarrelenols (**1a**-**1e**), and a novel cross-bonding product formation via the imino-ether bridge. And also we discuss an origin of the observed regioselectivity.

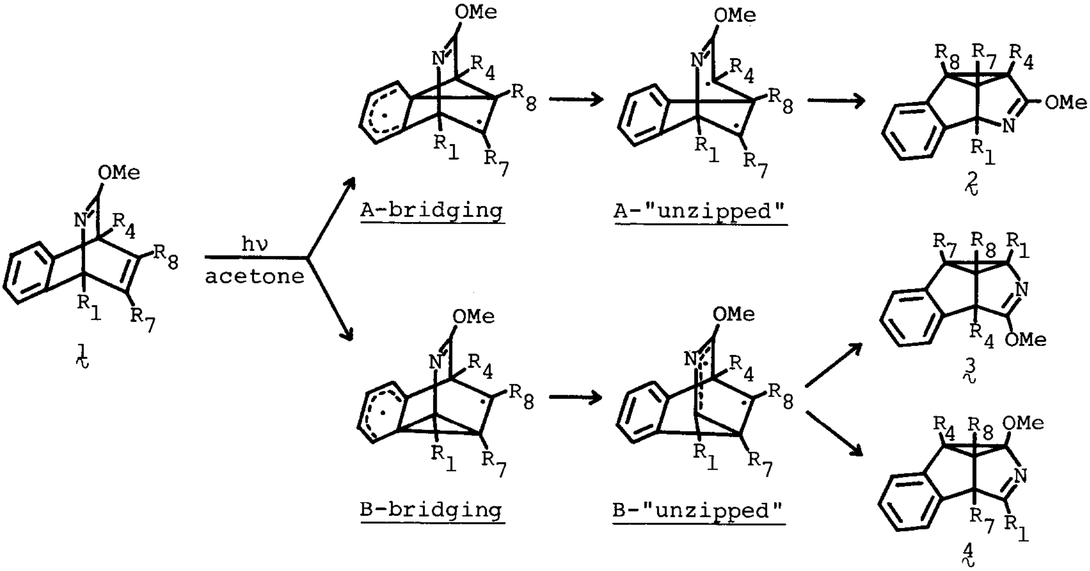


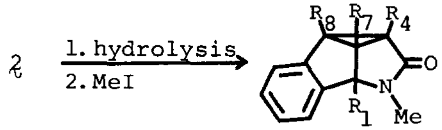
Table Product Distributions and Quantum Yield (Φ_{dis}) for Acetone-Sensitized Irradiation of **1a**-**1e**

Compounds	R	Product ratio, % A-bridging **2**	 B-bridging **3**	 **4**	Φ_{dis}[a]
1a	$R_1=R_4=R_7=R_8=Me$	85	15	0	0.14
1b	$R_1=R_4=R_7=Me$, $R_8=Ph$	0	45	55	0.12
1c	$R_1 \sim R_7=-(CH_2)_4-$, $R_4=Me$, $R_8=Ph$	28	18	54	0.10
1d	$R_1 \sim R_7=-(CH_2)_3-$, $R_4=Me$, $R_8=Ph$	85	0	15	0.15
1e	$R_1=R_4=R_8=Me$, $R_7=Ph$	100	0	0	

a. Measured through 400 W High Pressure Mercury Lamp with the filter light (Toshiba UV-DS33 + 5% $NiSO_4$ solution) using a "merry-go-round" apparatus (Riko-Rotary RH-400), with 0.006 M Potassium Ferrioxalate solution as a chemical actinometer.

Nitrogen purged acetone solutions of **1a**-**1e** were irradiated through a pyrex filter with a 400 W high-pressure mercury lamp to result in the clean conversion to photoproducts whose structures and ratios depended on the structural features and substituent. The pathways undergone were illustrated stepwise, and the strong influence on products formation in these cases is summarized in Table.

The structures of photoproducts follow from spectral properties.[7] Further proof for structural assignments of **2** and **3** were provided by its hydrolysis followed by N-methylation to **5** and **6**, respectively, which were identified with those previously obtained from similar acetone-sensitized irradiations of 5,6-benzo-2-azabarrelenones.[3]



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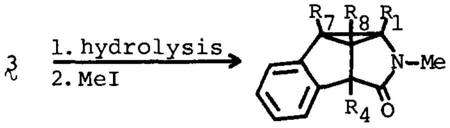

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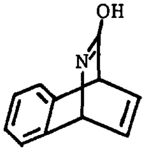
The special features of these results are following; despite <u>a priori</u> possibility, in a formal sense, of three types of bridging (benzo-imido, benzo-vinyl and imido-vinyl bridging), the only benzo-vinyl bridging was observed, demonstrating a strong sitespecificity. The compound (**1a**) showed a strong directional effect on the product composition of the observed di-π-methane transformation. This is obviously the consequence having induced by the imino-ether bridge which is not directly attached to the di-π-methane chromophore, and similar to that previously observed with 5,6-benzo-2-azabarrelenones.[3]

In the case of the compounds bearing the phenyl substituent at ethylenic moiety, the bridging regioselectivity is completely governed by such a substituent as in the case of **1b** and **1e**. However, a unique product (**4**), which is a novel cross-bonding product (azaallylic rearrangement) via the imino-ether bridge on the "B-unzipped species" was obtained in the case of the ones bearing the phenyl substituent at C-8 (**1b**-**1d**).

Another feature of interest is that introduction of the structural constraint into the bridgehead carbon of **1** by including it in another hydrocarbon ring, as in the case of **1c** and **1d**, resulted in lowering the ratio of the product formation arising from the B-bridging (**3** + **4**) as compared with that of **1b**, but the ratio of **4** to **3** was raised, and the only cross-bonding product (**4**) was formed from B-bridging species in **1d**. These results can be explained in terms of the combining factors of the rate retardation of collapse of the B-bridging species into the product and the localization of the free valence electron to the carbon bearing methoxy group on the imino-ether bridge of the "B-unzipped" species. The relative order of the quantum yield (Φ_{dis}), though only noticeably different, also supports these rationalizations.

The origin of the resioselectivity were also theoretically explored. We have preformed the excited state molecular orbital calculations of the fundamental ring systems, i.e. 5,6-benzo-2-azabarrelenol (**7**) and some other related compounds including 5,6-benzo-2-azabarrelenone (**8**) for comparison.



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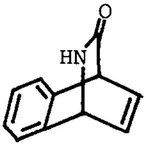

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Details will be presented later in a separate paper because of the space limitation. However, the sense of the results of **7** can be briefly mentioned here. The computed lowest excited triplet state (T_1), supported by the CNDO/S-CI method, which we believe is responsible for the di-π-methane transformation consisted of an admixture of many configurations, but little of the HOMO-LUMO transition. The coefficient distributions of all the molecualr orbitals responsible for the configuration interaction (CI) state of T_1 did indicate the rather local excitation on the ethylenic moiety (The triplet state calculation by the MINDO/3-UHF method also led to the same conclusions.), but did not show the clear molecular orbital polarization for the bridging to account for the regioselectivity observed with the one such as **1a**.

Based on these experimental findings and computed results, it seems most reasonable to consider that the observed regioselectivity can be determined by the rate of the product forming step in bicyclic systems such as those reported herein, where the stereoelectronic process involving attack of anti-lobe at the bridgehead carbon on the free valence electron at ethylenic moiety on the cyclopropyldicarbinyl diradical intermediate does occur.

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4. M.Kuzuya, E.Mano, M.Ishikawa, T.Okuda and H.Hart, Tetrahedron Lett., 1613 (1981)
5. M.Kuzuya, E.Mano, M.Adachi, A.Noguchi and T.Okuda, Chem. Lett., 475 (1982)
6. Experimental details for the preparation of these compounds will be reported in a full paper.
7. All new compounds reported herein gave a satisfactory elemental analyses, and full details of the spectral data will be given in a full paper.

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