Tetrahedron Letters No. 6, pp 523 - 526.
©Pergamon Press Ltd. 1979. Printed in Great Britain.
0040-4039/79/0201-0523$02.00/0

CONCERNING FACTORS WHICH CONTROL REGIOSELECTIVITY IN THE DI-π-METHANE PHOTOREARRANGEMENT OF 5,6-BENZOBICYCLO[2.2.2]OCTADIENES

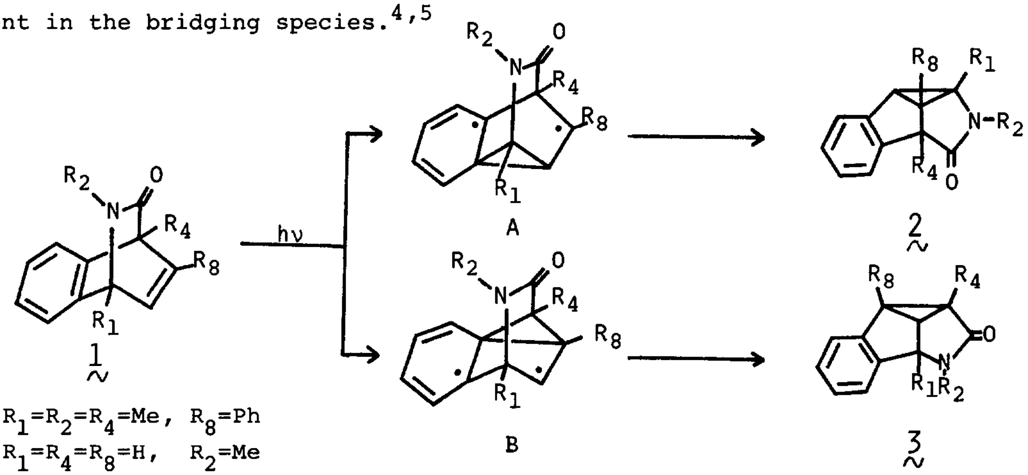
Masayuki Kuzuya*, Masanao Ishikawa, and Takachiyo Okuda
Gifu College of Pharmacy, 5-6-1, Mitahora-Higashi, Gifu, 502 Japan
and
Harold Hart
Department of Chemistry, Michigan State University, East Lansing,
Michigan, 48824, U.S.A.

The influence of substituents on the photochemistry on the 5,6-benzo-[2.2.2]octadiene ring system presents some interesting anomalies particularly regarding selectivity between the two products expected by di-π-methane rearrangement. Several reactions remain unexplained.[1]

To gain more insight into the factors which control this selectivity, we prepared and examined the photoisomerization of several derivatives of 5,6-benzo-2-azabicyclo[2.2.2]octa-7,8-dien-3-one. This series, several members of whcih initially studied in 1970 by Paquette and Meisinger,[1c] provides sufficient versatility to permit structural and electronic substituent effects to be probed. We described here a reversal of the previously observed regioselectivity through phenyl substitution, a novel structural limitation to this phenyl group effect, and a solvent effect on the regioselectivity.

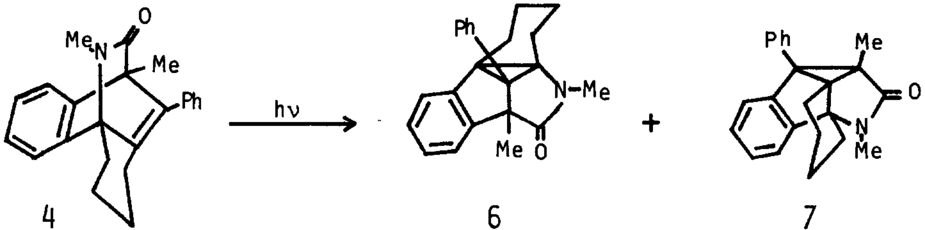
Irradiation of a nitrogen purged acetone solution of **1a**[2] (mp 118°) through a Pyrex filter with a high-pressure mercury lamp resulted in clean conversion to a single photoproduct **2a** (mp 202°). The structure of **2a** follows from its spectral properties.[3]

The special feature of this result is that the product arose exclusively from the bridging intermediate A, whereas the acetone-sensitized photoisomerization of **1b** and each of its four monomethyl derivatives gave predominantly product from intermediate B.[1c] The reversed regiospecifity of 1a can be easily rationalized in terms of greater delocalization of an odd electron by the phenyl substituent in the bridging species.[4,5]

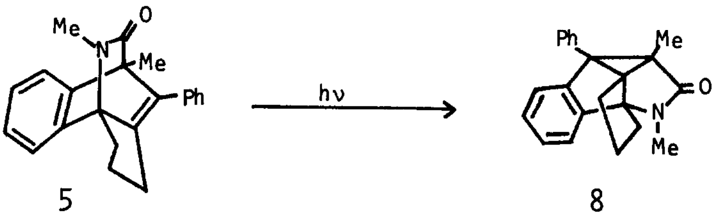


a, $R_1=R_2=R_4=Me$, $R_8=Ph$
b, $R_1=R_4=R_8=H$, $R_2=Me$
c, $R_1=R_4=R_8=H$, $R_2=CH_2Ph$

If the selectivity between the two photoproducts depended only upon the stability of the odd electron, compounds 4 and 5 might also have been expected to be regiospecific through the same type of intermediate A. In fact, however, similar irradiation of 4 provided a mixture of 6 (mp 135°) and 7 (mp 185°) in the ratio of 45:55.[7]



Similar photoisomerization of 5, in which the methylene bridge is shortened by one carbon atom, gave only a single photoproduct 8 (mp 172°), arising from the bridging intermediate B.



5 8

It thus appears that the selectivity between the two types of photoproducts is influenced by the structural feature of including the bridgehead carbon in another ring, which may retard cyclopropane ring-formation or ring-opening via intermediate A.

Likewise, the polarity of the amido function connected to the bridgehead carbon might be responsible for the preferential formation of **3** in the photoisomerization of **1b**, observed by Paquette and Meisinger,[1c] since odd electron stability on the two bridging intermediates is essentially identical (secondary vs secondary). To determine whether or not such a factor might be operative, we examined the photolyses of **1b** and of the N-benzyl derivative **1c** in various polar media, in which the polarity of the amido function would be enhanced.[8] The results of these photolyses are summarized in Table I.[9] It was found that there does exist a tendency toward the regiospecific formation of **3** in more polar media.

Table I

Substrate	Solvent	Product Ratio %[7]	
		2	**3**
1b	acetone	25	75[1c]
	30% aq. acetone	10	90
	70% AcOH-acetone	0	100
1c	acetone	18	82
	30% aq. acetone	7	93
	70% AcOH-acetone	0	100

Our results indicate that a variety of factors in addition to those previously considered contribute to the regioselectivity of these photoisomerizations, and also that it is important to consider the environment of the bridgehead carbon, i.e. the central carbon of di-π-methane moiety.

REFERENCES AND FOOTNOTES

1. a) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 2882 (1966); b) H. Hart and R. K. Murray, Jr., *ibid.*, **91**, 2183 (1969); c) L. A. Paquette and R. H. Meisinger, *Tetrahedron Lett.*, 1479 (1970); d) I. Murata and Y. Sugihara, *ibid.*, 3785 (1972); e) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **95**, 4592 (1973).

2. All new compounds reported here gave satisfactory elementary analyses.
3. Nmr($CDCl_3$): δ 1.30 (3H, s, α-carbonyl methyl), 1.45 (3H, s, cyclopropyl methyl), 2.70 (3H, s, N-methyl), 2.93 (1H, s, cyclopropyl proton), 7.02-7.45 (10H, m, aromatic). Ir(KBr): 1683 cm^{-1} (>N-CO). The nmr spectra of all photoproducts are consistent with the structural assignments as shown. Full details of the spectral data will be given in the full paper.
4. Indeed, a trend toward product from B is seen even with methyl substitution at C_8.[1c]
5. Alternatively, one may be able to compare the energy difference between the two types of the bridging species, A and B, qualitatively by comparing the energy of trans-stilbene triplet (E_T=50.0 Kcal/mole) for A with that of 1,1-diphenylethylene triplet(E_T=61.8 Kcal/mole) for B.[6]
6. For a thorough review of the di-π-methane rearrangement, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, Chem. Rev., **73**, 531 (1973).
7. The ratio based on the analysis of vpc peaks of the reaction mixture.
8. In fact, the downfield shift induced by adding an acid (TFA) was greater for the proton at C-1 than the proton at C-4, indicating that the C-1 bridgehead carbon becomes more electron deficient than that at C-4.
9. Photoproducts **2** and **3** were quite stable in acid for prolonged periods, thus eliminating any selective decomposition or interconversion between the two.

(Received in Japan 4 November 1978)