

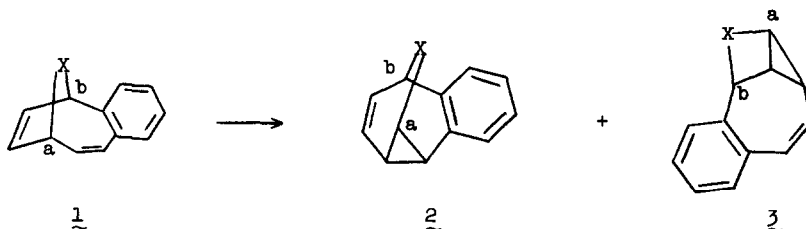
THE INFLUENCE OF THE AMIDE FUNCTION ON EXCITED STATE FREE VALENCE. THE DI- $\pi$ -METHANE  
 PHOTOREARRANGEMENT OF 5,6-BENZO-2-AZABICYCLO[2.2.2]OCTA-5,7-DIEN-3-ONES<sup>1</sup>

Leo A. Paquette and Robert H. Meisinger

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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During our recent examination of the mechanistic details by which 1a and 1b are transformed photochemically (acetone sensitization) to 2 and 3,<sup>2</sup> we noted the particularly intriguing fact that 1a afforded principally 2a while 1b gave rise chiefly to 3b. Since ap-

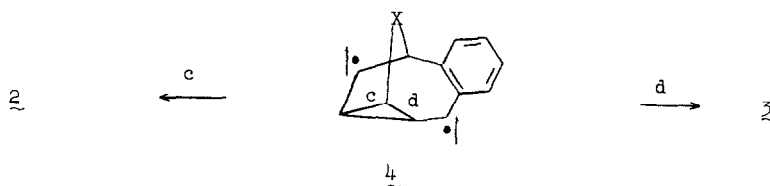


1a, C<sub>a</sub>-N=C(OCH<sub>3</sub>)-C<sub>b</sub>\*

1b, C<sub>a</sub>-NH-C(O)-C<sub>b</sub>\*

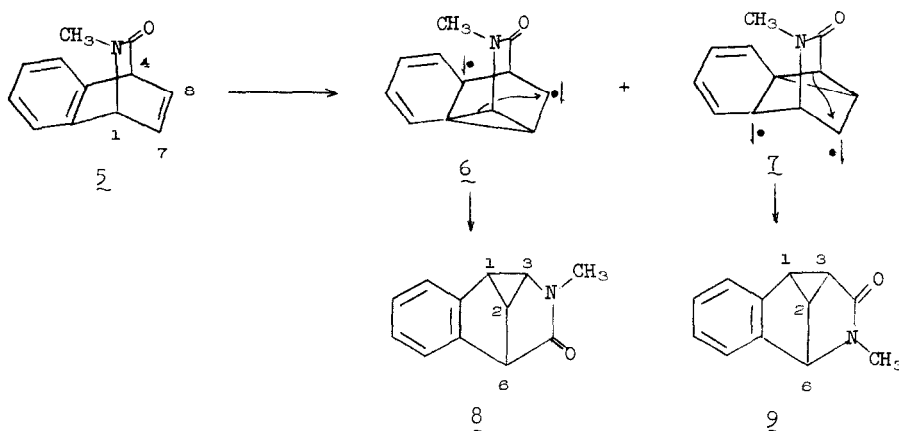
\*subscripts a and b serve only the purpose of bridge labelling and do not identify the individual carbon atoms.

propriate deuterium labelling studies revealed that the di- $\pi$ -methane mechanism<sup>3</sup> with initial vinyl-vinyl bonding was followed in both cases,<sup>2a</sup> the structural make-up of the heteroatomic bridge was clearly controlling the preference for scission of bonds c and d in intermediate 4. This remarkable selectivity was rationalized in terms of a possible charge-transfer interaction of the carbonyl group in the lactam with the non-benzylic radical center. In order to determine if such impressive control of excited state free valence by a lactam carbonyl function was a general phenomenon, we have investigated the photorearrangement of several 5,6-benzo-2-azabicyclo[2.2.2]octa-5,7-dien-3-ones. This system was selected since it combined ready accessibility with the requirement that the di- $\pi$ -methane rearrangement, if operational, proceed by benzo-vinyl bonding and thus have energy requirements quite different



from those involved in the transformations of 1.

Irradiation of dilute acetone solutions of 5<sup>4</sup> afforded in high yield (92% isolated) the isomeric dihydrobenzazasemibullvalones 8 (25%) and 9 (75%). The structures of 8 [ $\nu_{\text{max}}^{\text{Nujol}}$  1685  $\text{cm}^{-1}$ ;  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  7.08-7.58 (m, 4, aryl), 3.93 (d,  $J = 6.0$  Hz,  $\text{H}_E$ ), 3.53 (dd,  $J = 5.0$  and 7.5 Hz,  $\text{H}_D$ ), 3.12 (m,  $\text{H}_F$ ), 2.81 (m,  $\text{H}_1$ ), and 2.70 (s,  $-\text{CH}_3$ )] and 9 [ $\nu_{\text{max}}^{\text{Nujol}}$  1680  $\text{cm}^{-1}$ ;  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  7.08-7.64 (m, 4, aryl), 4.63 (d,  $J = 6.0$  Hz,  $\text{H}_E$ ), 3.38 (dq,  $J = 6.5$  and 6.0 Hz,  $\text{H}_D$ ), 2.93 (dd,  $J = 6.5$  and 8.0 Hz,  $\text{H}_F$ ), 2.60 (m,  $\text{H}_1$ ), and 2.53 (s,  $-\text{CH}_3$ )] follow unequivocally from their respective spectral properties. In particular,  $\text{H}_D$  in 8 and  $\text{H}_E$  in 9 are, as expected, downfield shifted by 0.60-0.70  $\delta$  relative to their  $\alpha$ -carbonyl counterparts in 2 and 8, respectively (assignments derived from double resonance studies). A priori, the triplet state of 5 can reasonably rearrange to 8 and 9 via either the ( $2\sigma + 2\pi$ ) intramolecular cycloaddition pathway<sup>2c</sup> or the di- $\pi$ -methane route. Although several benzobicyclooctadiene derivatives undergo photoisomerization by the latter mechanism, benzobicyclooctadienones, the only other carbonyl compounds to be examined to date, seemingly rearrange by 1,2-acyl



migration.<sup>5</sup> The problem of elucidating the mechanism of this excited state transformation was resolved by examining the photorearrangement of the four possible monomethyl derivatives

of 5.<sup>4</sup> The results of these studies are summarized in Table I. Strikingly, it was found that no migration of either the acyl group or the nitrogen atom was occurring. In fact,

Table I. Product Distributions in the Acetone-Sensitized Photorearrangement of the 5,6-Benzo-2-azabicyclo[2.2.2]octa-5,7-dien-3-ones.

Substrate	Product Composition, % <sup>a</sup>	
	<u>8</u> <sup>b,c</sup>	<u>9</u> <sup>b,c</sup>
<u>5</u>	25	75
1-Methyl- <u>5</u>	3-Methyl- <u>8</u> , 18	6-Methyl- <u>9</u> , 82
4-Methyl- <u>5</u>	6-Methyl- <u>8</u> , 18	3-Methyl- <u>9</u> , 82
7-Methyl- <u>5</u>	1-Methyl- <u>8</u> , 9	2-Methyl- <u>9</u> , 91
8-Methyl- <u>5</u>	2-Methyl- <u>8</u> , 41	1-Methyl- <u>9</u> , 59

<sup>a</sup>Percentage values derived from calibrated vpc curves. <sup>b</sup>Satisfactory elemental analyses were obtained for all new compounds. <sup>c</sup>The nmr and infrared spectra of all photoproducts, to be detailed in our full paper, are in complete agreement with the structural assignments.

inspection of the methyl labelling patterns provides unquestionable proof that the dihydrobenzazasemibullvalones arise exclusively by way of the di- $\pi$ -methane route.

The product distribution resulting from the photoisomerization of 5 reveals that there exists a threefold preference for the formation of 9. Of the two initial bonding processes, therefore, that which gives rise to 7 affords rearranged lactam faster than that involving 6.<sup>6</sup> It is interesting and significant that the same trend is seen in the rearrangement of the four monomethyl derivatives. However, whereas positioning of methyl groups at C<sub>1</sub>, C<sub>4</sub>, and C<sub>7</sub> in 5 leads to an increase in the relative yield of the congeners of 9, introduction of an 8-methyl substituent results in an enhanced yield of 2-methyl 8. Clearly, the course of the photorearrangement is being controlled by localization of free valence as in 7 and the energy balance is not shifted in favor of 6 even in that example (8-methyl 5) which places a methyl group at the non-aryl odd-electron site in this latter intermediate. Steric effects are not considered to be of importance in these reactions since the peri CH<sub>2</sub>-H interactions involved at C<sub>1</sub> and C<sub>6</sub> in the methyl derivatives of 8 and 9 appear from molecular models to be entirely comparable.

The preferred benzo-vinyl bridging which leads to 7 can be understood on the following basis. As free-radical character begins to develop at C<sub>7</sub>, there is engendered direct

resonance interaction of this odd electron with the carbonyl group through the intermediacy of the cyclopropane ring. An analogous stabilizing effect is not available to 6. Yet we note that a significant amount of 6 must intervene in the photorearrangement of these heterobicyclics since it is the precursor of 8 (and its methyl homologs, Table I). This capability of 6 to compete successfully with 7 in a rearrangement process which is so susceptible to electronic effects<sup>7</sup> can be interpreted to mean that homoconjugative charge-transfer interaction of the free radical center with the proximate carbonyl group is decidedly energy releasing. Not expectedly, however, the stabilization to be gained from such an excited state situation does not exceed that achieved by the delocalized electronic arrangement found in 7.

Since compounds 1b and 4 are the only lactams whose di- $\pi$ -methane rearrangements have been examined in detail, the conclusions concerning particularly the long range charge-transfer effects of the carbonyl group must, of course, be considered tentative. Nevertheless, recognition of the existence of such energy minima along the potential energy surface now sets the stage for further studies designed to probe into the precise nature of the stabilizing effect.

#### References

1. Unsaturated Heterocyclic Systems. LXXII. For the previous paper in this series, see L. A. Paquette, S. Kirschner, and J. R. Malpass, J. Am. Chem. Soc., 92, in press.
2. (a) L. A. Paquette, J. R. Malpass, and G. R. Krow, J. Am. Chem. Soc., 92, in press.  
(b) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, ibid., 91, 5296 (1969);  
(c) L. A. Paquette and J. R. Malpass, ibid., 90, 7151 (1968).
3. H. E. Zimmerman and P. S. Mariano, ibid., 91, 1718 (1969) and appropriate references cited therein.
4. E. B. Sheinin, G. E. Wright, C. L. Bell, and L. Bauer, J. Heterocyclic Chem., 5, 859 (1968).
5. H. Hart and R. K. Murray, Jr., Tetrahedron Lett., 379 (1969). See also J. Ipaktschi, ibid., 215 (1969).
6. As the progress of each photochemical reaction was monitored (vpc analysis), the product ratio was shown not to be altered as a function of time, thereby ruling out later destruction or interconversion of one or the other photoisomer.
7. H. E. Zimmerman and C. O. Bender, J. Am. Chem. Soc., 91, 7516 (1969).