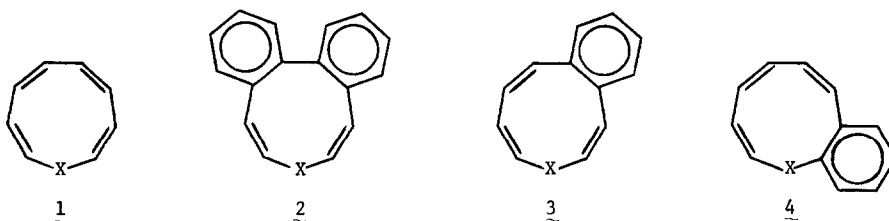


## THE 4,5-BENZAZONINE SYSTEM

A. G. Anastassiou, (Miss) E. Reichmanis and R. L. Elliott<sup>1</sup>Department of Chemistry  
Syracuse University  
Syracuse, New York 13210

(Received in USA 12 June 1973, received in UK for publication 7 August 1973)

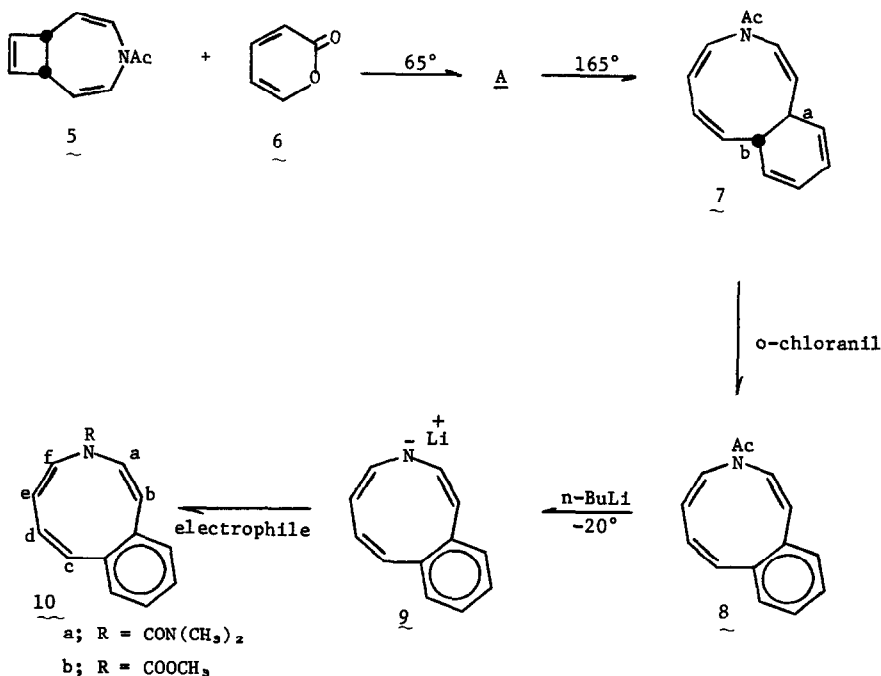
Whereas unsubstituted (1)<sup>2</sup> and dibenzo (2)<sup>3</sup> heteronins have been known for several years, their monobenzo variants (3 and 4) remained unknown. Obviously, these substances (3, 4) are ideally structured for purposes of direct comparison between heteronin and benzene in terms of  $\pi$ -electron delocalization. Presently, we describe the first synthetic entry into the general skeleton shown in 3 by an efficient three-step sequence designed on the basis of our recently reported<sup>4</sup> cycloadditive trapping of a cis,cis,trans,cis-azonine generated on thermal activation of azabicyclic 5.



X = heteroatom

Prolonged (ca. 40 hr.) exposure of 5<sup>5</sup> to  $\alpha$ -pyrone (6) at ca. 65° leads to a mixture of 1:1 cycloadducts, A (mp 113-128°; m/e 257)<sup>6</sup>, in ca. 75% yield. Vacuum thermolysis of A at 165° produces the novel azabicyclopentaene 7<sup>7</sup> [white crystals, mp 110.5-111.5°;  $\nu$  (KBr) prominent maxima at: 1650, 1300, 738 and 698 cm.<sup>-1</sup>,  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{14}}$  262 nm ( $\epsilon$  7930); nmr (60 MHz; C<sub>6</sub>D<sub>6</sub>)  $\tau$  3.19 (1H, d, J = 10 Hz), 4.0-4.7 (8H, m), 4.87 (1H, dd, J = 10 Hz, 5 Hz), 6.13 (1H, dd, H<sub>a</sub> or H<sub>b</sub>, J = 19 Hz, 9 Hz), 7.20 (1H, brd, H<sub>a</sub> or H<sub>b</sub>, J = 19 Hz), 8.11 (3H, s); m/e 213 (P<sup>+</sup>; 16.7%)] in ca. 80% yield after purification. The trans ring fusion depicted in 7 follows clearly, from the magnitude of J<sub>ab</sub> (19 Hz), while the assignment of a non-vicinal relationship between heteroatom and cross-link is made on the basis of (i) the appearance of the H<sub>a</sub> and H<sub>b</sub> resonances at relatively high field<sup>8</sup>, (ii) mechanistic analogy<sup>4</sup> and (iii) oxidative conversion of this substance into a 4,5-benzazonine ring frame (vide infra).

Overnight exposure of 7 to *o*-chloranil in benzene at ambient temperature affords benzazonine 8<sup>7</sup> [white crystals, mp 68–69°;  $\nu$  (KBr) prominent bands at: 1670, 1375, 1310, 790, 780, 758, 733, 712  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{14}}$  275 nm (sh) ( $\epsilon$  6300), 230 (14,900), nmr (60 MHz;  $\text{C}_6\text{D}_6$ )  $\tau$  2.8–3.3 (5H, m), 3.5–3.9 (2H, m), 4.0–4.4 (2H, m), 5.20 (1H, dd,  $J = 10$  Hz, 5 Hz), 8.25 (3H, s);  $m/e$  211 ( $\text{P}^+$ ; 10.5%)] in ca. 80% yield after purification. Further, on treatment with *n*-butyl lithium in THF at ca.  $-20^\circ$  acetamide 8 is converted to benzazonide 9 which, in turn, serves as a convenient source of other *N*-substituted benzazonines. Thus, in situ quenching of 9 with *N,N*-dimethylcarbamoyl chloride and methoxycarbonyl chloride yields benzazonines 10a [nmr (60 MHz;  $\text{C}_6\text{D}_6$ )  $\tau$  2.95 (4H, s), 3.70 (1H, d,  $H_c$ ,  $J_{cd} = 12$  Hz), 3.70 (2H, s,  $H_a + H_b$ ), 4.19 (1H, dd,  $H_d$ ,  $J_{dc} = 12$  Hz,  $J_{de} = 5.5$  Hz), 4.27 (1H, d,  $H_f$ ,  $J_{fe} = 10$  Hz), 5.32 (1H, dd,  $H_e$ ,  $J_{ef} = 10$  Hz,  $J_{ed} = 5.5$  Hz), 7.71 (6H, s)]<sup>9</sup> and 10b [nmr (60 MHz;  $\text{C}_6\text{D}_6$ )  $\tau$  2.93 (4H, s), 3.3–3.9 (4H, m), 4.11 (1H, dd,  $J = 12$  Hz, 4 Hz), 5.20 (1H, dd,  $J = 10$  Hz, 4 Hz), 6.63 (3H, s)] respectively.



It appears appropriate to conclude this report with a brief comment concerning the classification of the benzazonines described herein. On the basis of the preliminary information recorded

presently, this is best accomplished on comparison of the benzazonines with their classical polyenic counterpart 3,4-benzocyclonona-1,3,5,7-tetraene<sup>10</sup> in terms of the nmr chemical shift of H<sub>c</sub> (see 10) i.e., the proton which is least likely to be directly influenced by the nitrogen function of 10. We find this key proton to possess exactly the same chemical shift ( $\tau$  3.70 in C<sub>6</sub>D<sub>6</sub>) in 10a and 3,4-benzo CNT and are thus forced to the conclusion that 10a (and very probably 8 and 10b as well) does not sustain a ring current, i.e., that these substances are best classified as normal benzopolyenes. It remains to be seen of course whether or not parent 4,5-benzazonine and its salts e.g. 9, fit into the same category. We hope to answer this question in the near future.

Acknowledgment: We are grateful to the National Science Foundation (GP-38553X) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

#### REFERENCES AND REMARKS

- (1) NDEA Graduate Fellow, 1971-1974.
- (2) For a review on the subject see: A. G. Anastassiou, Accounts Chem. Res., 5, 281 (1972).
- (3) A. P. Bindra, J. A. Elix, P. J. Garratt and R. H. Mitchell, J. Amer. Chem. Soc., 90, 7372 (1968).
- (4) A. G. Anastassiou, R. L. Elliott, H. Wright and J. Clardy, J. Org. Chem., 38, 1959 (1973).
- (5) A. G. Anastassiou, S. W. Eachus, R. L. Elliott and E. Yakali, Chem. Commun., 531 (1972).
- (6) The presence in this cycloadduct(s) of a monocyclic C<sub>8</sub>H<sub>8</sub>NAc moiety is evidenced by the nmr spectrum the "aliphatic" region of which contains, besides the 3H methyl singlet, signals amounting to a total of three protons.
- (7) Correct elemental analysis was obtained for this substance.
- (8) Previous experience with related substances indicates that protons bound to tertiary centers directly linked to nitrogen resonate in the "olefinic" region of the nmr spectrum. See for example compounds 4a and 13 in reference (4).
- (9) The presence of a 2H singlet in the nmr spectrum of this unsymmetrical molecule is undoubtedly due to the accidental degeneracy of two 1H signals and necessitates that the protons in question be associated with an isolated ethylenic function. Clearly, this condition is met by 10 but not by its position isomer i.e., a 2,3-benzazonine.
- (10) A. G. Anastassiou, S. S. Libsch and R. C. Griffith, Tetrahedron Letters, in press.