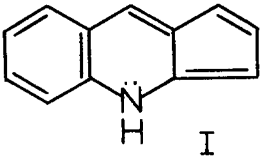
Tetrahedron Letters No. 10, pp 953 - 956, 1972. Pergamon Press. Printed in Great Britain.

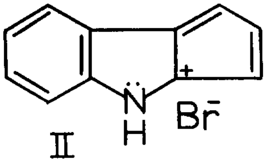
RE-INVESTIGATION OF THE REPORTED SYNTHESIS OF BENZ[b]AZAPENTALENIUM SALTS: ACTION OF BROMINE ON 2,3-DIHYDROCYCLOPENT[b]INDOLE[1]

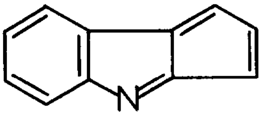
John J. Eisch and Tonson Abraham
Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. 20017

(Received in USA 25 January 1972; received in UK for publication 3 February 1972)

In pursuit of our interest in non-pyridinoid, aza-aromatic heterocycles we have recently synthesized the parent benzo[b]pyrindine[2,3], a highly reactive tautomeric mixture containing ca. 0.1% of the 4-H tautomer (I). For this reason our attention was drawn to a report[4] on the


I


II

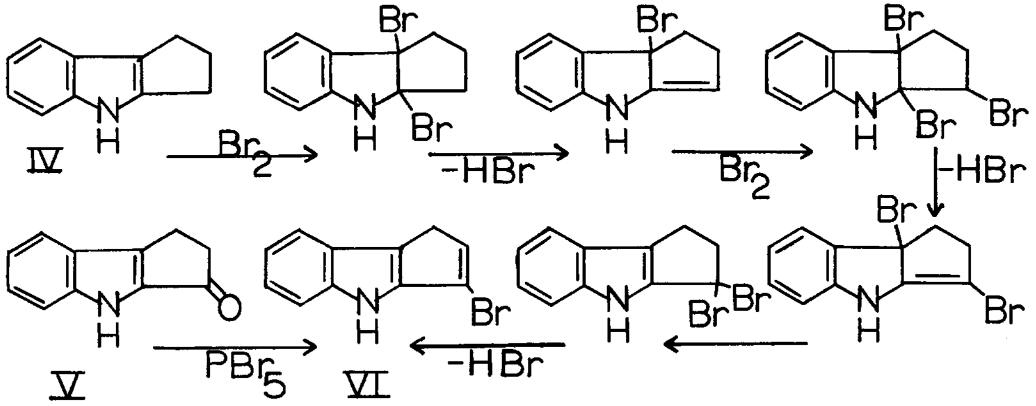

III

synthesis of a similar system, the purportedly stable hydrobromide salt of the benz[b,1]azapentalene nucleus (II). The claim was arresting that such a pseudo- or anti-aromatic[5] pi-electron system as II was so readily obtained from 2,3-dihydrocyclopent[b]indole (IV) and bromine. Equally surprising was the conclusion that benz[b,1]azapentalene itself (III) could be generated from II in basic solution and subsequently be reconverted into II. Accordingly, we were prompted to re-investigate these claims for the synthesis of II and III. On the basis of further spectral data we now wish to report an entirely different interpretation of the previous[4] observations.

In strict conformity with the experimental details for the previous work[6], we treated IV with two molar equivalents of bromine in carbon tetrachloride and then maintained the resulting purple suspension at the reflux temperature, until no more hydrogen bromide was evolved. The isolated, deep-violet solid II was obtained in 98% yield. Its infrared spectrum (dispersion in mineral oil) displayed prominent bands at 2.9-3.2 (N-H, hydrogen-bonded), 6.3 (aromatic C=C) 7.0 (strong), 7.6, 8.3, 8.5, 8.7, 9.2, 11.9 and 13.1-13.5 μ; the nmr spectrum (δ-scale; solution in DMSO-d_6) showed broad, poorly resolved absorptions at 1.0-2.5, 5.4 (HBr eliminated from II) and 7.0 p.p.m. In agreement with the previous report[4], a purple solution of II in ethanol or in DMSO promptly lost its color when treated with gaseous ammonia and a brown precipitate of III was formed. Treatment of III with hydrobromic acid immediately regenerated the purple solid II.

Although the elemental analytical data and the "molecular weight" in DMSO found for II are in approximate agreement with the empirical formula[6], $C_{11}H_8BrN$, other observations made by us conflict decisively with assigning structure II to the purple solid and structure III to the brown solid subsequently obtained by ammonia treatment. First of all, dissolving the purple solid in ethanol or in DMSO and adding silver nitrate solution lead to no precipitate of silver bromide at room temperature; this fact excludes a structure such as II having anionic bromine. Secondly, both the purple solid and the halogen-free brown base displayed saturated C-H absorptions (1.0-2.5 ppm) in their respective nmr spectra. Thirdly, the infrared spectrum of the thoroughly dried, halogen-free, brown solid exhibits a strong, broad N-H band at 3.0 μ and a strong band in the 6.1 μ region where enamines absorb[7]. Fourthly, the mass spectra both of the purple solid and of the halogen-free brown solid offer convincing evidence for their high molecular-weight character. Each has mass peaks corresponding to dimers and to trimers of the cyclopent[b]indole system (M.W. 155); in addition, aside from very intense mass peaks for the purple solid at 80 and 82 (loss of HBr), both mass spectra are very similar in their peaks and relative intensities. Purple solid (70 eV, probe at 180°; peak intensity relative to 156 as base peak): 152 (5); 153 (16); 154 (63); 155 (61); 156 (100); 157 (87); 158 (16); 233 (8); 234 (10); 235 (21); 236 (10); 237 (13); 305 (10); 306 (24); 307 (18); 308 (18); 309 (13); 310 (13); 462, 463, 464, 465, 466, 467 and 468 (all with intensity of *ca*. 1-2); and peaks in the 540-560 region. Halogen-free, brown solid (70 eV, probe at 180°; peak intensity relative to 156 as base peak): 152 (11); 153 (33); 154 (83); 155 (83); 156 (100); 157 (83); 158 (33); 233 (11); 234 (16); 235 (28); 236 (16); 237 (11); 305 (16); 306 (45); 307 (33); 308 (33); 309 (33); 310 (22); 462, 463, 464, 465, 466, 467 and 468 (all with intensity of *ca*. 2); and peaks in the 540-560 region. From the mass spectral results it is clear that these two solids, purported to be II and III, respectively, are at least dimers and trimers of the cyclopent[b]indole systems and, in all likelihood, are polymers. If the purple solid did have structure II, then the observed, mass spectral loss of HBr should lead to a prominent peak at 153; such is not the case. Again, if the brown solid did have structure III, the same peak would be expected to be prominent.

Clearly, therefore, the action of bromine on IV has led to the polymerization of the cyclopent[b]indole system. A further observation points to the likely pathway of this polymerization: when the 3-keto derivative V[8] was treated with phosphorus pentabromide, a violet-colored solid was formed that possessed spectral properties identical with those of the purple solid obtained from IV and bromine. Consequently, we are led to formulate both reactions as leading to 3-bromocyclopent[b]indole (VI), which then undergoes polymerization to the purple solid:



$$\begin{array}{ccccc} \mathrm{VI} & \xrightarrow{H^+} & \text{Polymer VII} & \underset{H^+}{\overset{\text{Base}}{\rightleftarrows}} & \text{Polymer VIII} \\ & & \text{purple solid} & & \text{halogen-free brown solid} \end{array}$$

The nature of polymer VII would presumably resemble that of polymers formed by the Lewis-catalyzed polymerizations of substituted indenes[9]. From the ability of VII to be dehydrobrominated with ammonia or with hot alcoholic silver nitrate solution to yield VIII, one can deduce that the bromine in VII is attached to a carbon atom in the C_5 ring[10].

From our re-investigation it can be concluded that the products isolated by Paul and Weise cannot possess structures II and III, respectively, but must rather be formulated as oligomers or polymers of the indole system. As a consequence, the synthesis of the unsubstituted benzazapentalene nucleus still remains to be achieved.

ACKNOWLEDGMENT

The authors gratefully acknowledge the research support of the Public Health Service through Grant CA-10743. Furthermore, Dr. Heinz Paul of the Chemistry Department, Humboldt University, Berlin, German Democratic Republic, was most generous in providing us with experimental details given in the Diplomarbeit of A. Weise, 1962. Finally, we are deeply indebted to Dr. Henry Fales of the National Institutes of Health, Bethesda, Maryland, for the mass spectral data.

REFERENCES AND FOOTNOTES

1. Part III of the series: "Studies in Non-Pyridinoid Aza-Aromatic Systems". II: J. J. Eisch and F. J. Gadek, J. Org. Chem., 36, 3376 (1971).
2. J. J. Eisch and F. J. Gadek, J. Org. Chem., 36, 2065 (1971).
3. J. J. Eisch and F. J. Gadek, J. Org. Chem., 36, 3376 (1971).
4. H. Paul and A. Weise, Tetrahedron Letters, 163 (1963).
5. R. Breslow, J. Brown and J. J. Gajewski, J. Amer. Chem. Soc., 89, 4383 (1967).
6. A. Weise, Diplomarbeit, Humboldt University, pp. 32, 54 (1962).
7. H. Ahlbrecht and F. Kröhnke, Justus Liebigs Ann. Chem., 717, 96 (1968).
8. J. Elks, D. F. Elliott and B. A. Hems, J. Chem. Soc., 624 (1944).
9. Cf, the work of E. Maréchal; leading reference: P. Caillaud, J.-M. Huet and E. Maréchal, Bull. Soc. Chim. France, 1473 (1970).
10. Similar to the behavior of IV, 2,3-dihydrocyclopenta[b]quinoline undergoes substitution with two molar equivalents of bromine in a sodium acetate-acetic acid medium to yield the labile 3,3-dibromo-2,3-dihydrocyclopenta[b]quinoline. Upon heating, the latter loses hydrogen bromide and changes to an infusible, apparently polymeric, black solid that shows prominent mass spectral peaks at 488, 490, 492, corresponding to $C_{24}H_{14}N_2Br_2$ (J. J. Eisch and K. C. Fichter, unpublished studies).