[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

Azabenzazulenes. III.[1] 1-Azanaphth[1,2-*b*]azulene

CHESTER W. MUTH AND EDWARD S. HANRAHAN[2]

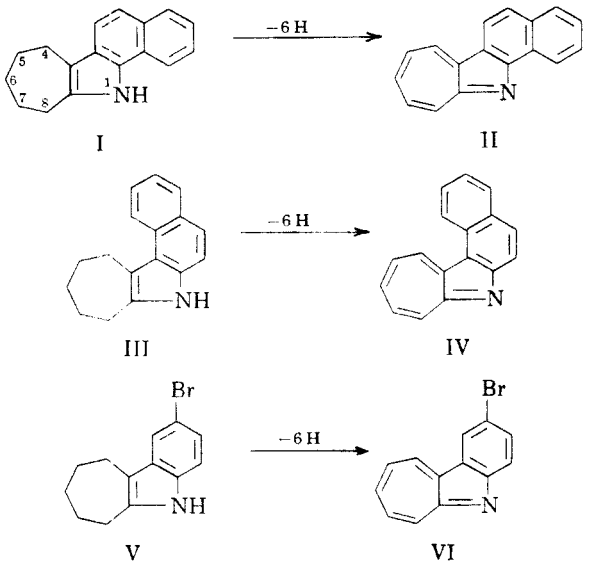
Received August 2, 1957

The foregoing azanaphthazulene as well as 1-azanaphth[2,1-*b*]azulene[3,4] has been prepared by the dehydrogenation of the appropriate indole.

It is desirable to study modifications of azulene since it is a chromophore the number of which is extremely limited. The list of reported azazulenes[4,5] is small.

1-Azanaphth[1,2-*b*]azulene (II) has been prepared from 1,4,5,6,7,8-hexahydro-1-azanaphth[1,-2-*b*]azulene (I) by both catalytic and chloranil dehydrogenations. Also, 1-azanaphth[2,1-*b*]azulene (IV) has been prepared from 1,4,5,6,7,8-hexahydro-1-azanaphth[2,1-*b*]azulene (III) by the catalytic method by us and by the chloranil method of Treibs *et al.*[3] We were not able to convert III to IV with chloranil in boiling xylene; Treibs[3,4] has not reported the solvent used in converting III to IV. We observed that boiling *n*-amyl alcohol was a better solvent than boiling xylene for converting I to II. For the preparation of II, the chloranil method is superior to the catalytic method.

Attempts to dehydrogenate 1,4,5,6,7,8-hexahydro-1-aza-(4′-bromo)benz[*b*]azulene (V) by either the chloranil or catalytic methods yielded little if any VI. The compound corresponding to V without bromine has been dehydrogenated by both the catalytic[6] and chloranil[7a,b] methods.

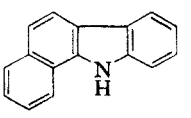


I II III IV V VI

The structure proofs for II and IV are based on elemental analyses, visible, ultraviolet, and infrared spectra, and hydrogenations to the indole precursors, I and III, respectively. Also, for II and IV the methiodides were prepared and found to have satisfactory elemental analysis. For IV the proper neutral equivalent was found and the perchlorate formed during the neutral equivalent determination gave the proper elemental analyses.

It is to be noted that the structures of II and IV are dependent on the structures of indoles I and III, respectively. Indoles I and III were made in one-step processes in glacial acetic acid from cycloheptanone and 1- and 2-naphthylhydrazine hydrochlorides, respectively. Indolization with 1-naphthylhydrazine might occur at the 2-position or a six-membered ring would form if attack were made at the 8-position. Since the ultraviolet spectrum of I is different from those of III and V which are similar there was some doubt as to which structure to assign to I. Also, indolization with 2-naphthylhydrazine might occur at the 1- or 3-positions.

The structures of I and III were confirmed by the very close similarity of their spectra (Table I) with those of 1,2-benzo-5,6,7,8-tetrahydrocarbazole[8] (VII) and 3,4-benzo-5,6,7,8-tetrahydrocarbazole[8] (VIII), respectively. Compound VIII was made from cyclohexanone and 1-naphthylhydrazine and compound VIII was made from cyclohexanone and 2-naphthylhydrazine. The structure proof for VII[8] has been based on its dehydrogenation to 1,2-benzocarbazole (IX) which was prepared by Kym.[9] Kym's structure proof for IX, although



IX

(1) Paper II, C. W. Muth, W. L. Sung, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 3393 (1955).

(2) We wish to thank the Research Corporation for its support of this work. Abstracted in part from the M.S. thesis of Edward S. Hanrahan presented at West Virginia University, 1956. Presented in part before the West Virginia Academy of Science, Keyser, W. Va., April 1957.

(3) W. Treibs, W. Kirchof, W. Ziegenbein, and H. Piffko, *Angew. Chem.*, **65**, 542 (1953).

(4) W. Treibs, W. Kirchof, and W. Ziegenbein, *Fortschritte der Chemischen Forschung*, Springer, Berlin, 1955, p. 401.

(5) C. W. Muth, D. O. Steiniger, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 1006 (1955).

(6) A. G. Anderson and J. Tazuma, *J. Am. Chem. Soc.*, **74**, 3455 (1952).

(7a) W. Treibs, R. Steinert, and W. Kirchof, *Ann.*, **581**, 54 (1953). (b) D. Lloyd, *Chem. & Ind. (London)*, 921 (1953).

(8) W. Borsche, *Ann.*, **359**, 49 (1908).

(9) O. Kym, *Ber.*, **23**, 2458 (1890).

his structure was found to be correct, was not convincing. For that reason, carbazole IX was prepared by an unambiguous route: the dehydrogenation of 1,2-benzo-3,4-dihydrocarbazole (X).[10] Carbazole IX so prepared is identical with the product obtained by the dehydrogenation of 1,2-benzo-5,6,-7,8-tetrahydrocarbazole (VII) as shown by mixed melting point, elemental analysis, infrared and ultraviolet spectra. *Therefore the previously assigned structure for VII has been confirmed, the structure of I is proved, and as a result the structure of II is also established.* The structure for hydrocarbazole VIII was firmly established by Huisgen,[11] consequently the structure for III and IV are correct.

The broad maximum in the visible absorption spectrum, which is typical of azabenzazulenes, is at longer wave lengths for II and IV than for 1-azabenz[*b*]azulene,[6] 1-azadibenz[*bf*]azulene[5] or 1-azadibenz[*bh*]azulene.[5,7a] Inspection of the spectra of II and IV (Table I) shows that II is absorbing less in the violet and more in the red region than is IV. This is in agreement with the purple color of II and the more reddish color of IV.

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA DATA[a]

Compound	Wave Length in mμ (Log ε)
I	Min. 240 (3.80), shoulder 260–265 (4.56), max. 270 (4.85), shoulder 285–295 (4.0), min. 330 (3.08), max. 335 (3.17), min. 347 (2.68), max. 350 (2.88).
VII	Min. 241 (4.01), shoulder 258–266 (4.48), max. 270 (4.78), shoulder 285–295 (3.9), min. 328 (3.21), max. 332 (3.27), min. 345 (2.91).
III	Max. 229 (4.47), min. 241 (4.36), max. 251 (4.40), min. 256 (4.34), max. 258 (4.36), min. 264 (4.20), max. 268 (4.26), min. 277 (3.26), max. 314 (4.01), min. 318 (3.99), max. 321 (4.04), min. 326 (4.00), max. 329 (4.02), min. 333 (3.91), max. 336 (4.04).
VIII	Max. 230 (4.48), min. 245 (4.38), max. 248 (4.40), min. 254 (4.36), max. 256 (4.38), min. 262 (4.25), max. 266 (4.34), min. 275 (3.46), max. 312 (4.02), min. 317 (3.96), max. 320 (4.01), min. 325 (3.93), max. 335 (3.99).
V	Max. 235 (4.24), min. 255 (3.24), max. 290 (3.80).
II	Min. 238 (4.01), max. 258 (4.26), min. 280 (4.15), max. 315 (4.67), min. 320 (4.65), max. 328 (4.68), min. 335 (4.45), max. 342 (4.55), min. 355 (3.98), max. 358 (3.99), min. 365 (3.87), max. 377 (3.96), min. 382 (3.89), max. 388 (3.99), min. 400 (3.00), max. 404 (ε 1890), min. 430 (ε 88), max. 560 (ε 748), min. 590 (ε 625), max. 610 (ε 638).
IV	Min. 243 (3.96), max. 275 (4.22), min. 278 (4.20), max. 301 (4.50), min. 310 (4.41), max. 324 (4.48), min. 330 (4.45), max. 342 (4.50), min. 368 (3.74), max. 380 (3.91), min. 390 (3.65), max. 395 (3.92), min. 404 (3.58), max. 415 (ε 10,825), min. 450 (ε 113), max. 540 (ε 414).

[a] All spectra were determined in cyclohexane with a Beckman quartz spectrophotometer, Model DU.

(10) E. Ghigi, *Gazz. chim. ital.*, **60**, 194 (1930); *Chem. Abstr.*, **24**, 3797 (1930).

(11) R. Huisgen, *Ann.*, **559**, 101 (1948).

EXPERIMENTAL[12]

1,4,5,6,7,8-Hexahydro-1-azanaphth[1,2-b]azulene (I). The method of Rogers and Corson[13] was used except the hydrazine hydrochloride was employed in place of the hydrazine. From 10.0 g. (0.051 mole) α-naphthylhydrazine hydrochloride (Eastman Kodak Co.) and 5.6 g. (0.050 mole) cycloheptanone (n_D^{25} 1.4595) in 37 g. of glacial acetic acid was obtained 8.65 g. of reddish-brown prisms, m.p. 143–146°. After recrystallization from 95% ethanol the yield was 6.02 g. of light red prisms, m.p. 145–148°. A portion of this material (4.55 g.) was twice chromatographed on alumina (45 × 150 mm. column). Chloroform was the solvent and developer; development was continued until a dark-brown zone neared the bottom of the column. The effluent on evaporation yielded 3.88 g. of light-brown prisms, m.p. 149–150°. Recrystallization of this material from 95% ethanol gave 3.07 g. (34%) of light-brown prisms, m.p. 152–153°. Absolute ethanol was used for crystallizing the analytical sample, m.p. 152–153°.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.8; H, 7.22; N, 6.01. Found: C, 86.7; H, 7.36; N, 5.96.

The ultraviolet spectrum for model compound, 1,2-benzo-5,6,7,8-tetrahydrocarbazole (VII)[14] was found to be almost superimposable on the spectrum of I except for a slight hypsochromic effect. The infrared spectrum was taken in chloroform and showed strong absorptions in μ at 2.9, 3.4, 7.2, 12.4, and 13.5. An absorption at 8.4 μ differentiated the spectrum of I from that of VII which had an absorption at 8.55 μ which I did not have.

1-Azanaphth[1,2-b]azulene (II). (*a*) *Palladium on charcoal dehydrogenation.* The apparatus, reagents, and technique for the dehydrogenation of 1,4,5,6,7,8-hexahydro-1-azanaphth-[1,2-*b*]azulene (I) to yield II were similar to those used by Anderson, *et al.*,[6,15] for the preparation of 1-azabenz[*b*]-azulene except that 1.5 g. of I was added to the dehydrogenation apparatus during 2 hr. The reaction temperature was 360–370°. The yield was 72 mg. (5%) of violet needles, m.p. 190–191°. A second run gave a 15% yield. The analytical sample was crystallized from benzene-petroleum ether mixture.

Anal. Calcd. for $C_{17}H_{11}N$: C, 89.0; H, 4.83; N, 6.11. Found: C, 89.0; H, 4.90; N, 6.17.

Hydrogenation of the foregoing product in absolute ethanol with 45 p.s.i. of hydrogen in the presence of platinum oxide immediately produced a colorless solution which yielded a substance which was proved to be I by mixed melting point and ultraviolet spectrum.

The methiodide derivative was prepared in benzene from 45 mg. of II and an excess of methyl iodide. The solution was warmed and shaken intermittently for 15 min. and then allowed to stand at room temperature for several days. The yield was 70 mg. (93%) of dark red flakes, m.p. 303–304° (corr.).

Anal. Calcd. for $C_{18}H_{14}NI$: C, 58.2; H, 3.80; N, 3.77. Found: C, 58.4; H, 3.99; N, 3.89.

(*b*) *Chloranil dehydrogenation.* Hexahydronaphthazulene (I) (1.18 g. 0.0051 mole) was dissolved in 25 ml. of boiling *n*-amyl alcohol. As 3.83 g. (0.0156 mole) of recrystallized chloranil was added in portions during 45 min. the solution became blue immediately and as more chloranil was added the solution became a dark reddish-brown color with suspended solid which caused bumping. An additional 15 ml. of amyl alcohol was added in an unsuccessful effort to pre-

(12) All temperatures are uncorrected unless otherwise indicated. All elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn.

(13) C. U. Rogers and R. B. Corson, *J. Am. Chem. Soc.*, **69**, 2910 (1947).

(14) We wish to thank Mr. Raymond Clutter for preparing this compound and recording its ultraviolet spectrum.

(15) A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

vent bumping. The total heating time was 1 hr. The reaction mixture was made homogeneous by adding methylene chloride and then the basic fraction was isolated as described;[7a] yield 190 mg. (18%) of violet needles, m.p. 189–191°, which did not require chromatography or recrystallization for purification. This product was the same as the one obtained by *method a* as shown by mixed melting point, ultraviolet, and visible spectra.

When a run lasting 2.5 hr. was made in boiling xylene, the yield of II after chromatography and recrystallization from benzene-petroleum ether mixture was about 3%.

1,4,5,6,7,8-Hexahydro-1-azanaphth[2,1-b]azulene (III). The procedure, reagents, and quantities were the same as for the preparation of I except that 2-naphthylhydrazine hydrochloride (Eastman Kodak Co.) was used in place of the 1-isomer. The yield of light-brown needles, m.p. 114–115°, once recrystallized from 95% ethanol was 9.70 g. (83%). The analytical sample was crystallized from absolute ethanol.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.8; H, 7.22; N, 6.01. Found: C, 86.8; H, 7.57; N, 5.71.

The ultraviolet spectrum of model indole 3,4-benzo-5,6,7,8-tetrahydrocarbazole[14] (VIII) was found to be very similar to that for III except for a slight hypsochromic shift. The infrared spectrum in chloroform was very similar to the infrared spectra for I and VIII. The spectrum for III showed slight maxima at 8.45 and 9.24 μ which were not present for VIII and the latter showed maxima at 7.92, 9.09, and 11.22 μ which were not in the spectrum for III.

1-Azanaphth[2,1-b]azulene (IV). Hexahydronaphthazulene (III) (1.70 g., 0.007 mole) was dehydrogenated by the same technique as was used for the preparation of II by *method a*. Methylene chloride was used to collect the reaction mixture as well as the solvent and developer in the chromatography. The yield of raspberry-red needles, m.p. 201–202°, (lit.[4] m.p. 201°) obtained by crystallization from benzene was 228 mg. (7%).

Anal. Calcd. for $C_{17}H_{11}N$: C, 89.0; H, 4.83; N, 6.11; neut. equiv., 229.3. Found: C, 89.6; H, 4.46; N, 5.83; neut. equiv., 228.9.

As the neutral equivalent was taken with perchloric acid in glacial acetic acid a reddish-orange flocculent solid, m.p. 282–283° (corr.) (73%) formed.

Anal. Calcd. for $C_{17}H_{12}O_4NCl$: C, 61.9; H, 3.67; N, 4.25. Found: C, 62.3; H, 3.81; N, 4.27.

The methiodide derivative for IV, m.p. 329–331° (corr.), (63%) was prepared as was the methiodide for II.

Anal. Calcd. for $C_{18}H_{14}NI$: C, 58.2; H, 3.80; N, 3.77. Found: C, 58.1; H, 3.80; N, 3.59.

Hydrogenation of IV, under conditions similar to those used for II, produced III as shown by mixed melting point and ultraviolet spectra.

1,2-Benzocarbazole (IX). The chloranil method of Barclay and Campbell[16] was used for the dehydrogenation of both 1,2-benzo-5,6,7,8-tetrahydrocarbazole (VII) and 1,2-benzo-3,4-dihydrocarbazole (X).[10,17] The desired product (IX) was readily obtained from the latter but with much difficulty from the former. From VII the product was purified by chromatography (alumina), sublimation, and finally by crystallization from benzene. The white purified products were identical as shown by mixed melting point, ultraviolet, and infrared spectra. The authentic material, m.p. 229–230° (corr.), (lit.[9] 225°) obrained from X had a slightly more narrow melting range than the other product.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.4; H, 5.10; N, 6.45. Found: C, 88.3; H, 5.19; N, 6.34.

MORGANTOWN, W. VA.

(16) B. M. Barclay and N. Campbell, *J. Chem. Soc.*, 530 (1945).

(17) We wish to thank Mr. Edward A. Pacofsky for the preparation of this compound and Mr. Paul Brown for its dehydrogenation as well as the infrared spectra for this paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Halopropargyl Alcohols and Ethers[1]

LEWIS F. HATCH, WILLIAM E. BLANKENSTEIN, AND SHIH HSI CHU

Received July 8, 1957

The following compounds have been prepared and characterized: 2,3-dibromo-2-propen-1-ol, 3-bromo-3-chloro-2-propen-1-ol, 1,1-dibromo-3-ethoxy-1-propene, 1,1-dibromo-3-phenoxy-1-propene, 1-bromo-1-chloro-3-ethoxy-1-propene, 1-bromo-1-chloro-1-propene, 1,3-dibromo-1-chloro-1-propene, 3-bromo-2-propyn-1-ol, 3-chloro-2-propyn-1-ol, 1-bromo-3-ethoxy-1-propyne, 1-bromo-3-phenoxy-1-propyne, 1-chloro-3-ethoxy-1-propyne. The stereochemistry of the addition of bromine to *cis*- and *trans*-1-chloro-1-propene followed by dehydrohalogenation is discussed.

There are only fragmentary reports in the literature on the preparation of halopropargyl alcohols. Lespieau[2] prepared 3-bromo-2-propyn-1-ol by the hydrolysis of the corresponding acetate which in turn was formed by the reaction between 1,3-dibromopropyne and potassium acetate. The yields were very low and the alcohol was impure. 3-Bromo-2-propyn-1-ol has now been prepared by the dehydrobromination of 2,3-dibromo-2-propen-1-ol by potassium amide in liquid ammonia and by the dehydrobromination of 3,3-dibromo-2-propen-1-ol using potassium hydroxide in glycerol.

2,3-Dibromo-2-propen-1-ol was prepared by the addition of bromine to propargyl alcohol in carbon tetrachloride. Apparently only one geometrical isomer was formed and it is assumed to have the *trans* (Br,Br) configuration formed by *trans* addition of the bromine to the triple bond. Several attempts were made to dehydrobrominate this alcohol using alcoholic potassium hydroxide. The yield of 3-bromo-2-propyn-1-ol was very low because of the multiplicity of by-products. The follow-

(1) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-430. Reproduction in whole or in part is permitted for any purpose of the United States Government. This research was also supported in part by grants from the Robert A. Welch Foundation and the Research Corp.

(2) R. Lespieau, *Ann. chim.*, (7)11, 232 (1897).