N,N-Dimethylaminoisocolchicide.—A solution of isocolchicine (200 mg., 0.5 mmole) in 8 ml. of 2.7 *M* methanolic dimethylamine in a sealed tube was placed in an oil-bath at 96°. After 1.5 minutes, the bath temperature was raised to 165° over an 8.5-minute period and, after an additional 4 minutes, the tube was removed. The residue from evaporation of the solvent was dissolved in 10 ml. of benzene and extracted with three 10-ml. portions of 1 *N* hydrochloric acid. Alkalization of the combined aqueous extracts to *p*H 11, extraction with benzene, and concentration of the dried benzene extracts gave a residue which was dissolved in ethyl acetate, filtered through a column of alumina (8 g., Merck) and crystallized from benzene after removal of the ethyl acetate. Dimethylaminoisocolchicide was thus obtained in 75% yield (154 mg.), m.p. 199–200°, $[\alpha]^{26}D$ −315 (*c* 0.31, ethanol).

Anal. Calcd. for $C_{23}H_{28}O_5N_2$: C, 67.0; H, 6.8; N, 6.8; OCH_3, 22.6; equiv. wt., 413. Found: C, 66.8; H, 6.8; N, 6.5; OCH_3, 22.5; equiv. wt., 419.

N-Methylaminoisocolchicide.—Isocolchicine was treated with methanolic methylamine in the same manner as described above for the dimethylamino compound, except that the only heating was at 100° for 24 hours. The methylaminoisocolchicide was isolated by the same procedure as was used with the dimethylamino compound, substituting ethyl acetate for benzene in the extractions. Sublimation at 220–230° (10 μ) of the crystals obtained from benzene gave 58% of material melting at 292–293°, $[\alpha]^{26}D$ −349 (*c* 1.05, ethanol) [reported[22] m.p. 272–275°, $[\alpha]^{27}D$ −357° (chloroform)].

(22) A. Uffer, *Helv. Chim. Acta*, **35**, 2135 (1952).

Anal. Calcd. for $C_{22}H_{26}N_2O_5$: C, 66.3; H, 6.6; N, 7.0. Found: C, 66.2; H, 6.5; N, 6.8.

Solvation Experiments.—From a solution of isocolchicine in chloroform, aliquots were removed at 6-, 20-, 50- and 100-minute intervals and concentrated *in vacuo* at room temperature. Final concentration was done at 0.3 mm. pressure and in each case the residue contained one mole of chloroform per mole of isocolchicine. The residue was then reconstituted in chloroform and the mutarotation followed as before, assuming that mutarotation stopped 0.5 minute after concentration began due to the rapid decrease in temperature and removal of solvent. In each case the sample resumed its place on the mutarotation curve as expected, allowing for the time of concentration (0.5 min.) and the time of reconstitution (1 to 4 min.).

Molecular Weight Determinations.—Bromoform was purified by washing with concd. sulfuric acid, water and satd. sodium carbonate. It was dried over potassium carbonate, filtered, distilled at reduced pressure, and stored at 0°; b.p. 53–54° (26 mm.), d^{20}_4 2.8875, d^{27}_4 2.8700.

A sample of isocolchicine (110.0 mg.) in bromoform (20.3 g., 7 ml.) was prepared at 15° and kept at this temperature except when melting point determinations were made. The initial determination, made 15 minutes after solution of the isocolchicine, showed a depression of 0.095° when compared to the pure solvent. The final determination, made after ten hours, showed a melting point lowering of 0.110°. Using 14.4 as the cryoscopic constant for bromoform, this leads to a molecular weight of 821 initially and 709 finally (mol. wt. of isocolchicine, 399.4).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

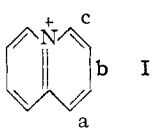
Aromatic Cyclodehydration. XXXI.[1] New Polycyclic Aromatic Systems Containing the Quinolizinium Nucleus

BY C. K. BRADSHER AND LEO E. BEAVERS[2,3]

RECEIVED NOVEMBER 18, 1955

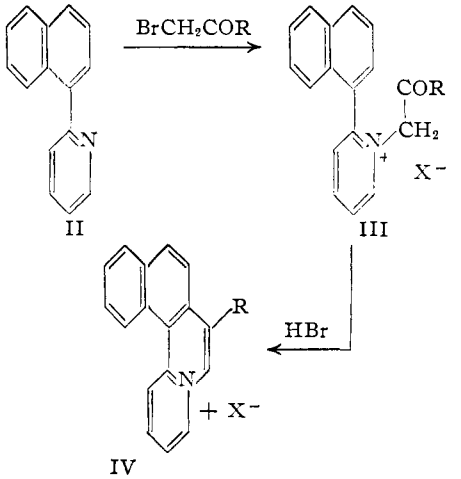
The two general methods described earlier for the synthesis of benzologs of the quinolizinium ion have both been applied to the preparation of some new tetra- and pentacyclic aromatic systems containing the quinolizinium nucleus. The systems include the naphtho[1,2-a]quinolizinium as well as the benzo[h]-, the benzo[j]- and the dibenzo[h,j]acridizinium ions.

Although it has been stated[4] that "the chemistry of polycyclic nitrogen heterocycles containing one hetero nitrogen atom has probably been the object of more intense investigation than any other single group in the broad field of heterocyclic chemistry," it was not until very recently that synthesis of the quinolizinium[5] ion I was first announced.[6] In the two most recent communications of this series, it was demonstrated how the methods of aromatic cyclodehydration could be extended to the synthesis of the first angular[7] (benzo[a]) and linear[1] (benzo[b]) benzologs of this aromatic nucleus. The present paper describes our effort to apply these two general methods to the synthesis of tetra- and pentacyclic aromatic systems containing the quinolizinium nucleus.



I

The literature lists no 2-(1-naphthyl)-pyridine (II), but our preparation, from 1-naphthyllithium and pyridine, afforded a picrate melting at a tem-



II III IV

(1) For the preceding communication of this series, see THIS JOURNAL, **77**, 4812 (1955).

(2) Public Health Service Research Fellow of the National Institutes of Health, 1952–1954.

(3) Taken in part from a thesis submitted by Leo E. Beavers in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

(4) R. C. Elderfield, "Heterocyclic Compounds," Vol. III, John Wiley and Sons, New York, N. Y., p. v.

(5) *Chemical Abstracts* nomenclature, *C. A.*, **46**, 13667 (1952).

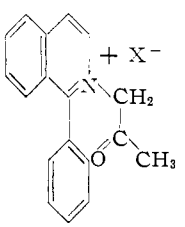
(6) V. Boekelheide and W. G. Gall, THIS JOURNAL, **76**, 1832 (1954).

(7) C. K. Bradsher and L. E. Beavers, *ibid.*, **77**, 453 (1955).

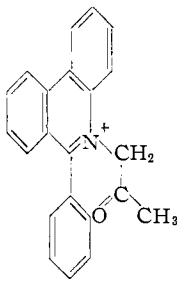
perature fairly close to that reported earlier[8] for the picrate of a (1-naphthyl)-pyridine of uncertain orientation.

Both bromoacetone (R = CH_3) and phenacyl bromide (R = C_6H_5) formed quaternary salts with II, and these salts III could be cyclized in boiling 48% hydrobromic acid to yield the expected 7-methyl- and 7-phenylnaphtho[1,2-a]-quinolizinium salts (IV, R = CH_3, C_6H_5). The over-all yields were 54 and 81.5%, respectively. As might be expected, these cyclizations involving condensation with the naphthalene ring were much more rapid than those observed earlier with the phenyl ring. For example, an 81.5% yield of 7-phenylnaphtho-[1,2-a]quinolizinium bromide was produced after a reaction time of 41 hours *versus* a 42% yield of 7-phenylbenzo[a]quinolizinium bromide[7] obtained after 14 days.

The cyclization of 1-phenyl-2-acetonylisoquinolinium bromide (V, X = Br) would be expected to give rise to dibenzo[a,h]quinolizinium salts isomeric with those obtained from III (R = CH_3).



V



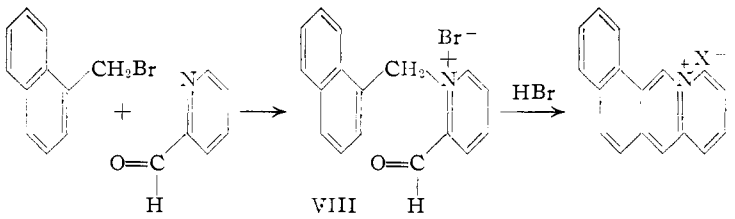
VI

It was actually found that V was extremely resistant to cyclization, the starting material being recovered after a ten-day reflux period with hydrobromic acid or three hours with concentrated sulfuric acid at 80°. Since V is a benzolog of the 1-acetonyl-2-phenylpyridinium salt which cyclized in 75% yield in 51 hours,[7] this unreactivity might appear surprising. It seems probable that in V the interference between the hydrogen atoms attached to the two *ortho* positions of the phenyl group with that at the 8-position of the isoquinoline ring impedes the attainment of the coplanarity necessary for cyclization.

If the inhibition of rotation does play a major role in the failure of V to undergo ring closure, it would be predicted that VI likewise would be difficult if not impossible to cyclize. Such was found to be the case, for when N-acetonyl-6-phenylphenanthridinium bromide (VI) was refluxed for 200 hours with hydrobromic acid, it was recovered unchanged.

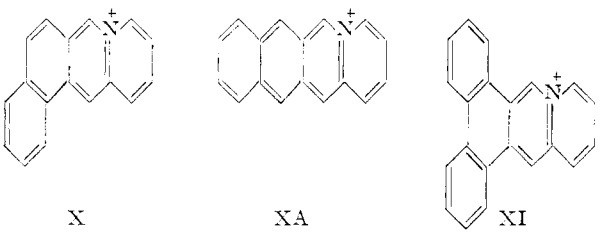
The remainder of the experiments to be described deal with the preparation of benzologs of the benzo-[b]quinolizinium or acridizinium[1] ion. The reaction of 1-bromomethylnaphthalene (VII) with pyridine-2-aldehyde yielded a quaternary salt VIII which cyclized under the usual conditions to produce a 52% yield of the new benzo[h]acridizinium bromide (IX).

(8) D. H. Hey and E. W. Walker, *J. Chem. Soc.*, 2213 (1948).



VII VIII (not isolated) IX

Similarly 2-bromomethylnaphthalene with pyridine-2-aldehyde afforded a salt which on cyclization gave rise to a canary-yellow salt to which we have assigned the structure of benzo[j]acridizinium bromide X rather than the alternate linear formula XA.



X XA XI

The structure X is suggested by analogy to the aromatic cyclodehydration of *o*-(2-naphthylmethyl)-acetophenone to yield 9-methyl-1,2-benzanthracene[9] as well as to the α cyclization of γ-2-naphthylbutyric acids.[10] However at least one case has been recorded where a cyclodehydration occurs preferentially in the β-position.[11] More direct evidence for the angular structure is provided by the ultraviolet absorption spectrum, through use of a crude application of the annulation principle developed by Clar[12] for aromatic hydrocarbons. The effect of linear annulation on the wave length of the ultimate absorption peak[13] as one goes from the quinolizinium (I) to the acridizinium ion is a relatively large increase, 765 Å. By comparison angular annulation of the acridizinium ion to yield the benzo[h]acridizinium salt results in a *decrease* of 50 Å. The ultimate absorption maximum shown by the benzoacridizinium salt obtained from 2-bromomethylnaphthalene is only 50 Å. greater than that for the acridizinium ion. This small increase is inconsistent with the assumption that linear annulation has occurred, and indicates that formula X is to be preferred.

Starting with 9-bromomethylphenanthrene, the pyridine-2-aldehyde method yielded dibenzo[h,j]-acridizinium bromide. Despite the presence of five aromatic rings, this substance was quite soluble in water.

(9) C. K. Bradsher, THIS JOURNAL, **62**, 1077 (1940).

(10) W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 123.

(11) W. Johnson and F. Mathews, THIS JOURNAL, **66**, 210 (1944).

(12) E. Clar, "Aromatische Kohlenwasserstoffe, Polycyclische Systeme," Edwards Brothers, Inc., Ann Arbor, Michigan, 1944, p. 20 ff.

(13) While the last peak of high absorption (increasing wave length) in the spectra of naphthalene, anthracene and naphthacene has been designated by Clar as parts of the p-bands, we do not imply that the corresponding peaks in the system of quinolizinium benzologs necessarily correspond to analogous transitions.

Experimental[14]

2-(1-Naphthyl)-pyridine (II).—A lithium reagent was prepared from 52 g. of α-bromonaphthalene. The ethereal solution of the reagent was cooled thoroughly in an ice–salt-bath and a solution of 40 g. of anhydrous pyridine in 65 ml. of dry ether was added over the period of one hour. At the end of this period, the ice-bath was removed and the mixture allowed to stir for five hours. After addition of water the ethereal layer was separated, 40 ml. of nitrobenzene added and the solution dried over magnesium sulfate. The dried solution was distilled until the temperature of the vapor reached 150° after which it was refluxed for 1.5 hours. Addition of ether to the reaction mixture caused the separation of a small quantity of a precipitate which was removed by filtration and the filtrate extracted with 10% hydrochloric acid. The acid solution was washed with ether and then neutralized with concentrated ammonia. The dark oil which separated was taken up in ether and dried over potassium hydroxide. Upon evaporation of the ether and vacuum distillation of the residue, 17.9 g. (34%) of a yellow oil was obtained, b.p. 161–164° (1 mm.).

The amine was used in subsequent experiments without further purification and was not obtained in a state of analytical purity. A sample converted to the **picrate** by the action of alcoholic picric acid crystallized as yellow needles, m.p. 199.5°. The x-(1-naphthyl)-pyridine picrate of Hey and Walker[8] was reported to melt at 196° and may be identical with ours.

Anal. Calcd. for $C_{21}H_{14}N_4O_7$: C, 58.07; H, 3.25. Found[15]: C, 58.38; H, 3.07.

1-Acetonyl-2-(1-naphthyl)-pyridinium Picrate (III, R = CH_3; X = $(NO_2)_3C_6H_2O$).—One-half gram of 2-(1-naphthyl)-pyridine and one-half gram of bromoacetone were mixed and allowed to stand for five days. The resulting dark glass was dissolved in water, treated with Norite and filtered. Evaporation of the water at 80° *in vacuo* yielded the crude bromide which was converted to the picrate by addition of alcoholic picric acid. The picrate formed small yellow prisms from ethanol; m.p. 172–173°.

Anal. Calcd. for $C_{24}H_{18}N_4O_8$: C, 58.77; H, 3.70. Found: C, 58.80; H, 3.95.

7-Methylnaphtho[1,2-a]quinolizinium Bromide (IV, R = CH_3; X = Br).—The crude 1-acetonyl-2-(1-naphthyl)-pyridinium bromide prepared as described above from 0.5 g. of 2-(1-naphthyl)-pyridine was transferred to a 25-ml. flask with the aid of 15 ml. of 48% hydrobromic acid. The acid solution was heated to boiling and evaporated under a stream of nitrogen until 1 ml. had been removed. The resulting solution was refluxed for 7.5 hours, then transferred with water to a 125-ml. flask equipped with a capillary and spray trap, and evaporated at 80° under vacuum (aspirator) until only a solid residue remained. The residue was crystallized from ethanol as tiny, faintly yellow crystals, 0.42 g. (54%), which decomposed in a sealed capillary at about 347°. On recrystallization, the product showed no improvement in appearance or decomposition temperature.

Anal. Calcd. for $C_{18}H_{14}NBr \cdot 2H_2O$: C, 60.01; H, 5.04. Found: C, 60.57; H, 5.38.

The **perchlorate** was produced by reaction of an aqueous solution of the bromide with 3 *M* perchloric acid. From acetone it yields colorless prisms which have no melting point, but decompose slowly when heated above 340° (capillary); $\lambda_{max.}$ (log ε) 226 (4.57), 265.5 (4.21) and 355.8 mμ (3.97); $\lambda_{min.}$ 251.5 (4.14) and 302 mμ (3.52).

Anal. Calcd. for $C_{18}H_{14}NClO_4$: N, 4.08. Found: N, 4.02.

The **picrate** was prepared in ethanol solution and recrystallized from acetone as tiny, yellow needles, m.p. 253.5–254° dec.

Anal. Calcd. for $C_{24}H_{16}N_4O_7$: C, 61.02; H, 3.41. Found: C, 60.84; H, 3.46.

1-Phenacyl-2-(1-naphthyl)-pyridinium Picrate (III, R = C_6H_5; X = $(NO_2)_3C_6H_2O$).—One gram of phenacyl bromide was added to 1 g. of 2-(1-naphthyl)-pyridine and warmed until the phenacyl bromide had melted. The mixture was allowed to stand for two months, yielding a hard amber-colored glass. The crude product was dissolved in water and extracted with ether to remove unreacted material and then concentrated at 80° under reduced pressure. The residue was dissolved in hot ethanol and treated with alcoholic picric acid to yield the picrate which crystallized from alcohol as slender yellow prisms, m.p. 160–161°.

Anal. Calcd. for $C_{29}H_{20}N_4O_8$: C, 63.04; H, 3.65. Found: C, 63.22; H, 3.80.

7-Phenylnaphtho[1,2-a]quinolizinium Bromide (IV, R = C_6H_5; X = Br).—A sample of crude 1-phenacyl-2-(1-naphthyl)-pyridinium bromide (III, R = C_6H_5; X = Br) prepared from 1 g. of 2-(1-naphthyl)-pyridine and purified as indicated above, was dissolved in 25 ml. of 48% hydrobromic acid and the cyclization procedure carried out as in the case of the methyl analog (III, R = CH_3; X = Br) except that refluxing under nitrogen was continued for 41 hours. After vacuum evaporation of nearly all of the hydrobromic acid, a brown oil remained which, upon addition of 10 ml. of water, scratching and cooling, crystallized. After standing overnight, the mixture afforded 1.53 g. (81.5%) of yellow-brown crystals, m.p. 273–275°. After recrystallization from alcohol, the product melted at 274–276° dec. The solid exhibits a yellow fluorescence under ultraviolet radiation and dilute solutions show a powerful yellow-green fluorescence under visible light.

Anal. Calcd. for $C_{23}H_{16}NBr$: C, 71.51; H, 4.18. Found: C, 71.44; H, 4.68.

The **perchlorate** prepared in the usual way was sparingly soluble in acetone from which it crystallized as microscopic orange-yellow needles, m.p. 267–268° dec.; $\lambda_{max.}$ (log ε), 261 (4.50), 289 (4.39), 338.5 (3.63), 355 (3.70) and 401 mμ (3.80); $\lambda_{min.}$, 241.5 (4.27), 282 (4.38), 330.5 (3.60), 345 (3.62), and 367 mμ (3.58).

Anal. Calcd. for $(C_{23}H_{16}NClO_4)_2 \cdot C_3H_6O$: C, 67.66; H, 4.40. Found: C, 67.77; H, 4.63.

The **picrate** prepared by adding alcoholic picric acid to a hot solution of the bromide was recrystallized from acetone as tiny golden flakes decomposing at about 227–228° with no clear indications of melting.

Anal. Calcd. for $C_{29}H_{18}N_4O_7$: C, 65.17; H, 3.39. Found: C, 65.16; H, 3.54.

1-Phenyl-2-acetonylisoquinolinium Bromide (V).—Five grams of 1-phenylisoquinoline, 5.0 g. of bromoacetone and 25 ml. of reagent grade acetone were placed in a flask equipped with a reflux condenser and brought to reflux. After five minutes, a crystalline solid started to form but refluxing was allowed to continue for 25 minutes longer and the mixture allowed to stand for two days. The solid was collected, washed with acetone and dried in a vacuum desiccator. The yield was 7.68 g. (92%) of faintly yellow prisms, m.p. 226–228° dec. The melting point was not improved by recrystallization from alcohol. The solid had a peach-colored fluorescence under ultraviolet light, while solutions had a blue fluorescence.

Anal. Calcd. for $C_{18}H_{16}NOBr$: C, 63.17; H, 4.71; N, 4.09. Found: C, 63.54; H, 4.75; N, 4.40.

The **picrate** was prepared from the bromide in alcohol solution. Crystallization from alcohol gave yellow needles, m.p. 187–188.3° with some previous sintering.

Anal. Calcd. for $C_{24}H_{18}N_4O_8$: C, 58.77; H, 3.70; N, 11.43. Found: C, 58.45; H, 3.61; N, 11.65.

Attempts to cyclize the bromide by refluxing it in 48% hydrobromic acid for ten days led to recovery of the starting material (84%). Heating the bromide in concentrated sulfuric acid for three hours at 80° followed by dilution by addition to ice gave a solution from which perchloric acid precipitated the perchlorate of the starting material (90% yield).

N-Acetonyl-6-phenylphenanthridinium Bromide (VI).—Four and eight-tenths grams of 6-phenylphenanthridine[16] was dissolved in 15 ml. of dry acetone containing 10 g. of bromoacetone. Refluxing was continued until no further precipitation occurred (144 hours). A pale yellow solid decomposing at about 220° was obtained; yield 5.95 g. (81%). Two recrystallizations from alcohol did not alter the decomposition point.

(14) Except as noted, all melting points were taken on a Fisher–Johns apparatus and are uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol (1 cm. silica cells).

(15) Analyses by Micro-Tech Laboratories, Skokie, Illinois, and by Galbraith Laboratories, Knoxville, Tennessee.

(16) G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931).

Anal. Calcd. for $C_{22}H_{18}NOBr$: C, 67.35; H, 4.62; N, 3.57. Found: C, 67.28; H, 4.58; N, 3.86.

The **picrate** prepared from an alcoholic solution of the bromide in the usual way crystallized from ethanol as yellow rhombs, m.p. 218.5–219° dec.

Anal. Calcd. for $C_{28}H_{20}N_4O_8$: C, 62.22; H, 3.73. Found: C, 62.28; H, 3.79.

The bromide when refluxed in 48% hydrobromic acid for 200 hours gave back 78% of the starting material, decomposing at 220–222°.

Benzo[h]acridizinium Bromide.—Pyridine-2-aldehyde (1.0 g.) was mixed with 2.1 g. of α-bromomethylnaphthalene[17] (VII) and warmed until a homogeneous solution was obtained and then the mixture was allowed to stand for eight days. The hard brittle reddish glass dissolved with difficulty in hot alcohol and after concentrating the solution to a volume of 14 ml., it was cooled and scratched to induce crystallization. By repeated additions of ether to the solution, a total of 2.36 g. of small brown crystals was filtered off and dried in a vacuum desiccator. Recrystallization from ethanol gave 2.12 g. of brown crystals, m.p. 127.5–128° dec. A portion of this material (1.47 g.) was dissolved in 20 ml. of 48% hydrobromic acid and refluxed for three hours in a nitrogen atmosphere. Worked up in the usual way, 1.04 g. (52% over-all) of yellow needles crystallized from the alcohol solution, m.p. 308–309° dec., in a capillary, but did not melt at 310° on the Fisher–Johns block. The capillary melting point was not altered by further recrystallization.

Anal. Calcd. for $C_{17}H_{12}NBr \cdot H_2O$: C, 62.21; H, 4.30. Found: C, 61.57; H, 4.00.

The **perchlorate** prepared in the usual way crystallized from acetone as golden rhombs, m.p. 291–292° dec.; $\lambda_{max.}$ (log ε), 232.5 (4.54), 274 (4.58), 305 (4.33), 317 (4.39), 358 (3.93), 376 (4.22), and 395 mμ (4.34); $\lambda_{min.}$ 248 (4.04), 289.5 (4.20), 310 (4.28), 336.5 (3.64), 361 (3.92), and 384 mμ (4.03).

Anal. Calcd. for $C_{17}H_{12}NClO_4$: C, 61.92; H, 3.67. Found: C, 62.00; H, 3.88.

The **picrate** prepared as usual was very insoluble in alcohol. Crystallization from acetone gave minute yellow needles, m.p. 232° dec.

Anal. Calcd. for $C_{23}H_{14}N_4O_7$: C, 60.26; H, 3.08. Found: C, 60.65; H, 3.34.

Benzo[j]acridizinium Bromide (X).—A solution of 0.50 g. of pyridine-2-aldehyde and 1.1 g. of 2-bromomethylnaphthalene[18] in 2 ml. of benzene was allowed to stand for three weeks. The benzene layer was decanted and the hard red glass which remained was dissolved in 21 ml. of warm 48% hydrobromic acid and refluxed for 3 hours under a nitrogen atmosphere. Worked up in the usual way, this yielded a dark gum which, on crystallization from 10 ml. of water, afforded 1.04 g. (72%) of tiny yellow crystals. The compound would not melt at 310° on the Fisher–Johns block, but melted with decomposition at 302–303° in a capillary. Recrystallization did not improve the melting point.

Anal. Calcd. for $C_{17}H_{12}NBr \cdot H_2O$: C, 62.21; H, 4.30. Found: C, 62.29; H, 4.70.

The **perchlorate** crystallized from acetone as tiny, faintly yellow needles, m.p. 268–270° (with considerable previous decomposition). A sample placed on the hot stage at 280° melted with decomposition in 20 seconds; $\lambda_{max.}$ (log ε) 227.5 (4.52), 276 (4.57), 321.5 (4.55), 364 (3.91), 384 (3.91), and 405.5 mμ (3.89); $\lambda_{min.}$ 245 (4.07), 292 (4.14), 358 (3.87), 374.5 (3.76) and 395 mμ (3.71).

Anal. Calcd. for $C_{17}H_{12}NClO_4$: N, 4.25. Found: N, 4.38.

The **picrate** prepared from a hot alcoholic solution of the bromide and alcoholic picric acid is very insoluble in acetone from which it crystallized as fibrous yellow needles, m.p. 259–260° dec.

Anal. Calcd. for $C_{23}H_{14}N_4O_7$: C, 60.26; H, 3.08. Found: C, 60.40; H, 3.23.

Dibenzo[h,j]acridizinium Bromide (XI).—One-half gram of pyridine-2-aldehyde and 1.0 g. of 9-bromomethylphenanthrene[19] were dissolved in 2 ml. of reagent grade acetone and allowed to stand for nine days. The acetone layer was decanted and the oily residue placed under vacuum to effect removal of most of the remaining acetone. The oily material solidified and was slurried with ether and collected. The solid was dissolved in 10 ml. of 48% hydrobromic acid and the solution washed with benzene to remove some oily material. The acid solution was next filtered through a sintered glass filter to remove some dark solid which was washed with 10 ml. of hydrobromic acid and then rejected. The combined acid solutions were boiled under a stream of nitrogen to remove any remaining benzene, then refluxed for two hours in a nitrogen atmosphere. The acid solution was diluted and filtered through Hyflo, then subjected to vacuum evaporation in the usual way. The residue crystallized from water (ice-bath) as small yellow needles decomposing at about 328° (capillary); yield 0.21 g. (24.5%).

Anal. Calcd. for $C_{21}H_{14}NBr \cdot {}^2/_3H_2O$: C, 67.75; H, 4.15. Found: C, 67.53; H, 4.25.

The **perchlorate** was difficultly soluble in acetone and crystallized as small pale yellow needles decomposing at about 327° (capillary); $\lambda_{max.}$ (log ε), 236 (4.50), 255 (4.45), 280 (4.45), 307 (4.61), 339 (4.09), 374 (4.03), and 394° mμ (4.10); $\lambda_{min.}$, 250 (4.42), 267 (4.37), 285.5 (4.39), 332.5 (4.06), 361.5 (3.86), and 383.5 mμ (3.94).

Anal. Calcd. for $C_{21}H_{14}NClO_4$: C, 66.41; H, 3.72. Found: C, 66.39; H, 3.72.

The **picrate** crystallized from acetone as fine yellow needles, m.p. 336° dec., in a capillary.

Anal. Calcd. for $C_{27}H_{16}N_4O_7$: C, 63.78; H, 3.17; N, 11.02. Found: C, 63.56; H, 2.89; N, 11.34.

DURHAM, N. C.

(17) By reduction of α-naphthoic acid with lithium aluminum hydride followed by treatment of the carbinol with phosphorus tribromide.

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