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5a-Azoniaacephenanthrylene Salts

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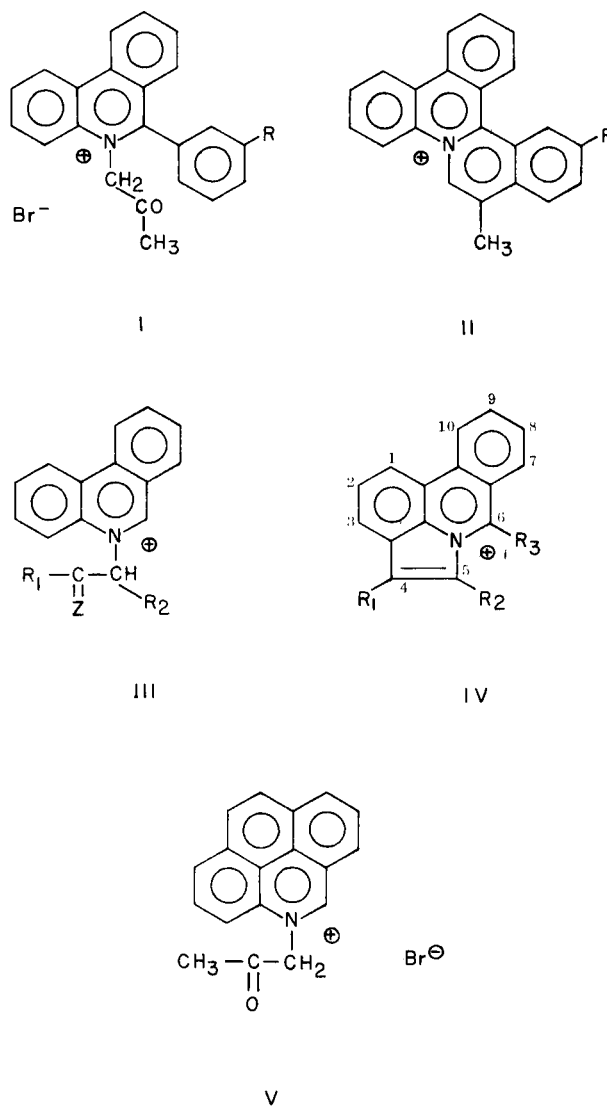
It has been reported previously (1) that 5-acetyl-6-phenylphenanthridinium bromide (I) could not be cyclized under conditions much more drastic than were employed in the cyclization of 1-acetyl-2-phenylpyridinium salts (2). Subsequently it was found (3) that 6-phenylphenanthridinium systems having an activating methoxyl on the phenyl group (I, R = OCH₃) will undergo cyclization to yield 11-methyldibenzo[a,c]phenanthridizinium salts (II, R = OCH₃).

We now wish to report that under very vigorous conditions, namely heating in polyphosphoric acid at 200-220° cyclization of the unsubstituted 5-acetyl-6-phenylphenanthridinium bromide (I) does occur, but the product is not the expected 11-methyldibenzo[a,c]phenanthridizinium salt (II). All available evidence indicates that cyclization has occurred in the adjacent 4-position of the phenanthridinium ring, affording (in small yield) 5a-azonia-4-methyl-6-phenylacephenanthrylene bromide (IV, R₁ = CH₃, R₃ = C₆H₅). The ultraviolet absorption spectrum of the new salt does not resemble that of known alkoxy-11-methyldibenzo[a,c]phenanthridizinium systems (3), or that of the related hydrocarbon (4), dibenzo[a,c]phenanthrene. Unfortunately, the related hydrocarbon system, 4,5-acephenanthrylene is unknown.

In order to demonstrate that the cyclization did not involve the phenyl group at position 6, phenanthridine was quaternized affording salts from bromoacetone (III, R₁ = CH₃, Z = O), from chloroacetaldoxime (5) (III, Z = NOH) and from 3-bromo-2-butanone (III, R₁ = R₂ = CH₃, Z = O). Cyclization conditions were found for only the last of these, which fortunately afforded a 43% yield of 4,5-dimethyl-5a-azoniaacephenanthrylene (IV, R₁ = R₂ = CH₃).

The proton magnetic spectrum of the new salt (IV, R₁ = R₂ = CH₃) was measured in trifluoroacetic acid at 60 mc./sec. with tetramethylsilane as an external standard. Two singlets of equal area at τ 7.2 and τ 7.48 are assigned to the 5- and 4-methyl protons respectively, the 5-methyl being under greater influence of the positive nitrogen would be expected to be further down field. Similarly, a singlet at τ 0.12, down field from the other aromatic protons is assigned to the proton at position six, unique for its proximity to the positive charge. Complex multiplets centered at $\sim 1.25 \tau$ and $\sim 1.8 \tau$ had areas indicating 4 and 3 protons respectively, and probably represent protons 7,8,9,10 and 11,12,13 respectively. Furthermore, the ultraviolet spectra of IV (R₁ = R₂ = CH₃) and IV (R₁ = CH₃, R₃ = C₆H₅) were similar.

Attempts to extend the reaction to analogous systems were unsuccessful, 6-methylphenanthridine and acridine failed to quaternize with bromoacetone, while the quaternary salts from quinoline and 4-azapyrene (V) failed to afford any pure cyclization product. In the crude product obtained from 4-acetyl-4-azapyrene (V), a small amount of the expected cyclization product may have been present as evidenced by the ultraviolet absorption spectrum.



(R groups not otherwise indicated are assumed to be H)

EXPERIMENTAL

All analyses were carried out by Ing. A. Schoeller, Kronach, Germany. The melting points were determined in capillary tubes in a Mel Temp apparatus and are corrected. Ultraviolet absorption spectra were measured in 95% ethanol using 1 cm. quartz cells with a Cary Model 14 Spectrophotometer. The asterisk (*) is used to denote a shoulder.

4-Methyl-6-phenyl-5a-azoniaacephenanthrylene (IV, $R_1 = \text{CH}_3$, $R_3 = \text{C}_6\text{H}_5$) Perchlorate.

A mixture of 0.5 g. of 5-acetyl-6-phenylphenanthridinium bromide (I) (1) and 7.0 g. of polyphosphoric acid was heated at 200° for 6 hours. Ice water was added to dissolve the syrupy reaction mixture and the resulting solution filtered to remove a small amount of dark solid. The addition of perchloric acid precipitated a gummy orange material which could be crystallized from methanol (charcoal) as orange needles, m.p. 271-276°, yield 0.12 g. (29%). The infrared spectrum showed no carbonyl band and the compound exhibited fluorescence under ultraviolet light in ethanol. The pure substance melted at 290-292° with previous decomposition, λ max (log ϵ) 206 (4.58), 233 (4.34), 253* (4.15), 265 (3.99), 294* (3.60), 313* (3.79), 327 (4.08), and 340 μ (4.09).

Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{ClNO}_4$: C, 67.09; H, 4.10; N, 3.56. Found: C, 66.79; H, 3.99; N, 3.77.

5-(2-Oximidoethyl)phenanthridinium (III, Z = NOH) Chloride.

A mixture of 4.0 g. of phenanthridine and 2.8 g. of chloroacetaldoxime (5) in 10 ml. of tetramethylene sulfone was allowed to stand in a stoppered flask in the dark for 4 days. The precipitate was collected, washed with acetone, and crystallized from methanol, yield 6.0 g. (98%) m.p. 182-183°. Recrystallization afforded very pale yellow prisms, m.p. 183.5-184°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{ClNO}_2$: C, 66.18; H, 4.81; N, 10.29. Found: C, 65.80; H, 5.04; N, 10.46.

An attempt to cyclize this salt with 48% hydrobromic acid in a sealed tube at 220° resulted only in the formation of phenanthridine hydrobromide.

5-Acetylphenanthridinium (III, $R_1 = \text{CH}_3$, Z = O) Bromide.

By the general procedure 5.0 g. of phenanthridine and 6.0 g. of bromoacetone gave 7.5 g. (85%) of crude quaternary salt, m.p. 221.5-224.5°. Recrystallization from methanol afforded pale yellow prisms, m.p. 227-229° dec.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{BrNO} \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 59.09; H, 4.65; N, 4.31. Found: C, 58.94; H, 4.77; N, 4.42.

The perchlorate crystallized as colorless prisms, m.p. 237-238.5°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{ClNO}_5$: C, 57.25; H, 4.20; N, 4.17. Found: C, 57.36; H, 4.19; N, 4.26.

Attempted cyclization in polyphosphoric acid gave only a few milligrams of product which showed no carbonyl absorption in the infrared and showed approximately the expected spectrum in the ultraviolet, but could not be obtained in a state of analytical purity.

5-(1-Acetyl-ethyl)phenanthridinium III ($R_1 = R_2 = \text{CH}_3$, Z = O) Bromide.

A solution of 2.0 g. of phenanthridine and 2.5 g. of 3-bromo-2-butanone in 6 ml. of dry acetone was heated under reflux for 10 hours and allowed to stand overnight. Recrystallization from methanol-ethyl

acetate gave 1.5 g. (41%) of product m.p. 205° which showed a carbonyl absorption band in the infrared at 5.78 μ . The pure sample consisted of pale yellow prisms, m.p. 207-208°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{BrNO}$: C, 61.81; H, 4.88; N, 4.24. Found: C, 62.12; H, 5.18; N, 4.35.

The perchlorate was obtained as colorless prisms, m.p. 182-184° (previous softening).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{ClNO}_5$: C, 58.37; H, 4.61; N, 4.00. Found: C, 58.71; H, 4.72; N, 4.09.

4,5-Dimethyl-5a-azoniaacephenanthrylene (IV, $R_1 = R_2 = \text{CH}_3$), Perchlorate.

One-half gram of the quaternary bromide (III, $R_1 = R_2 = \text{CH}_3$, Z = O) was heated for 4 hours with stirring at 220° with 15 g. of polyphosphoric acid. The cooled mixture was diluted with ice water and the product precipitated as the perchlorate. The product, once crystallized from methanol (charcoal), showed no carbonyl band, yield 0.2 g. (43%), m.p. 286-288°. The pure product consisted of orange needles, m.p. 291° dec., λ max (log ϵ) 204 (4.59), 238 (4.19), 247 (4.17), 257 (4.21), 267 (4.18), 312* (4.14), 325 (4.08) and 334 μ (4.07).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{ClNO}_4$: C, 61.53; H, 4.25; N, 4.22. Found: C, 61.74; H, 4.55; N, 4.31.

The picrate crystallized from ethanol as orange-red prisms, m.p. 193.5-195.5° (previous softening).

Anal. Calcd. for $\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_7$: C, 60.00; H, 3.50; N, 12.17. Found: C, 60.10; H, 3.54; N, 12.08.

4-Acetyl-4-azapyrene Bromide (V).

The quaternization of 4-azapyrene with 1.0 g. of bromoacetone was carried out in refluxing acetone, yield 1.5 g. (90%). The analytical sample crystallized from methanol as golden yellow needles, dec. >215°.

An alcoholic solution of the product showed an intense yellow-green fluorescence.

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{BrNO}$: C, 63.53; H, 4.15; N, 4.12. Found: C, 63.30; H, 4.15; N, 4.20.

The perchlorate crystallized from methanol as golden yellow prisms, m.p. 286-288° dec.

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{ClNO}_5$: C, 60.09; H, 3.92; N, 3.89. Found: C, 60.20; H, 3.70; N, 3.99.

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