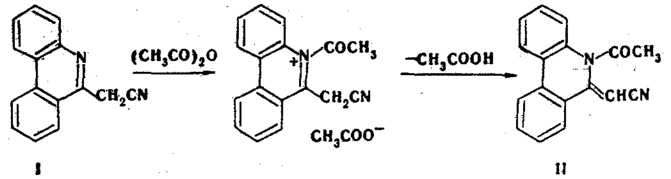
# REACTION OF 6-(CYANOMETHYL)PHENANTHRIDINE WITH ACYLATING AGENTS

E. V. Grishina, É. R. Zakhs,
and V. P. Martynova

UDC 547.836.3:542.951

We have established that on being heated in acetic anhydride 6-(cyanomethyl)phenanthridine (I) forms a neutral compound (II) differing sharply from phenanthridine derivatives by the intense splitting of the absorption band at about 400 nm. On the basis of a determination of its composition and molecular weight, and also from its IR and PMR spectra, compound (II) must be assigned the structure of 5-acetyl-6-cyanomethyl dihydrophenanthridine. The acid hydrolysis of compound (II) gives a high yield of 6-methylphenanthridine, compound (I) being detected chromatographically as an intermediate compound. Compound (II) is apparently formed by the splitting off of a proton from the cyanomethyl group of the phenanthridinium salt formed initially.



Compound (II) is relatively inert: it does not change at room temperature under the action of 2 N alkali, does not add hydrogen under normal conditions in the presence of Raney nickel, and does not react on being heated with benzaldehyde and its derivatives. However, on being heated with p-dimethylaminobenzaldehyde in acetic acid it is converted into 6-(α-cyano-p-dimethylaminostyryl)phenanthridine [1]. A compound analogous to (II) is formed by the reaction of compound (I) with benzoyl chloride.

5-Acetyl-6-cyanomethylene-5,6-dihydrophenanthridine (II). A mixture of 0.2 g of compound (I) and 6 ml of acetic anhydride was boiled for 4 h, and after cooling 0.15 g of (II) was filtered off and was crystallized from benzene (1:40). Yellow needles with mp 214-215°C. In $CDCl_3$, $\delta$ 2.55 ppm ($COCH_3$, singlet). IR spectrum (KBr), $cm^{-1}$*: 2180, 1630, 1600, 1585, 1530, 1500, 1480, 1405, 1360, 1280, 1225, 1170, 1140, 985, 950, 935, 765, 750, 710. In ethanol $\lambda_{max}$, nm (log $\varepsilon$): 241 (4.54), 255 (4.32, shoulder), 272 (4.18), 293 (3.95), 320 (3.70), 335 (3.70), 387 (4.29), 408 (4.32). Found: C 78.7; H 4.9; N 11.1%; mol. wt. 273 (reverse ebullioscopy in chloroform). $C_{17}H_{12}N_2O$. Calculated: C 78.5; H 4.6; N 10.8%; mol. wt. 260. For hydrolysis, 0.1 g of compound (II) was heated in 6 ml of 30% $H_2SO_4$ at 140°C for 8 h, and the mixture was neutralized and extracted with benzene to give 0.06 g (84%) of 6-methylphenanthridine, identical with an authentic sample.

5-Benzoyl-6-cyanomethyl-5,6-dihydrophenanthridine. A mixture of 0.25 g of compound (I) and 5 ml of benzoyl chloride was heated at 140°C for 2 h and was then evaporated in vacuum to 2 ml, poured into water, and neutralized with sodium carbonate. This gave 0.26 g of yellow crystals with mp 254°C (from ethanol). In ethanol, $\lambda_{max}$, nm (log $\varepsilon$): 248 (4.65), 272 (4.25), 295 (4.18), 325 (3.84), 340 (3.82), 395 (4.44), 415 (4.52). IR spectrum (KBr), $cm^{-1}$: 2184, 1630, 1600, 1565, 1535, 1500, 1480, 1440, 1410, 1360, 1340, 1315, 1260, 1230, 1170, 1000, 925, 755, 740, 718, 698. Found: N 8.8%; mol. wt. 316. $C_{22}H_{14}N_2O$. Calculated: N 8.7%; mol. wt. 322.

---

*The strongest absorption bands are underlined.

Lensovet Leningrad Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 138-139, January, 1974. Original article submitted July 13, 1973.