NUCLEOPHILIC MOBILITY OF A BROMINE ATOM IN 1,6-DIBROMO-5,10-DIMETHYL-4,9-DIAZAPYRENE

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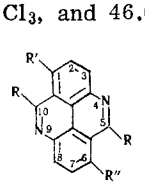
Unsuccessful attempts to nitrate and aminate 4,9-diazapyrene (I) [1] show the greatly reduced π-electronic density on the carbon atoms of its molecule. It may be expected that an electron-accepting substitutent introduced by a roundabout way into the benzene nucleus of the molecule of I would possess nucleophilic mobility. To test this hypothesis, we have synthesized 1,6-dibromo-5,10-dimethyl-4,9-diazapyrene (II) and have studied its reaction with piperidine. This gave 6-bromo-5,10-dimethyl-1-piperidino-4,9-diazapyrene (III).

1,6-Dibromo-5,10-dimethyl-4,9-diazapyrene (II). A mixture of 21.8 g (0.05 mole) of 2,2'-diacetamido-5,5'-dibromobiphenyl [2], 217 g (1.6 mole) of $AlCl_3$, and 46.6 g (0.8 mole) of NaCl was heated at 250° C for 8 hr.



I R = R' = R'' = H;
II R = CH_3, R' = R'' = Br;
III R = CH_3, R' = $N(C_5H_{10})$, R'' = Br

The reaction mixture was poured onto ice and made alkaline, the precipitate was separated off, and extraction with dichloroethane was carried out. Yield 1.6 g (8%), pale yellow needles. Decomp. p. 275–277° C (from dichloroethane). Found, %: Br 40.8; N 7.2. Calculated for $C_{16}H_{10}Br_2N_2$, %: Br 41; N 7.2. UV spectrum in dichloroethane): λ_{max} (nm) (log ε): 270 (4.16); 280 (4.25); 308 (3.54); 3.15 (3.74); 332 (4.01); 348 (4.16); 368 (4.05); 338 (4.22); 4.12 (3.06). IR spectrum (in KBr): 3050 cm^{-1}, 2950 cm^{-1} (in the form of a shoulder). PMR spectrum (in CF_3COOH, standard TMS): δ_{CH_3} = 4 ppm; δ_{CH} = 9.05 ppm.

6-Bromo-5,10-dimethyl-1-piperidino-4,9-diazapyrene (III). A mixture of 0.1 g of II and 10 ml of piperidine was heated in a sealed tube at 180° C for 5 hr. The reaction mixture was poured into water and the bright yellow precipitate was separated off; decomp. p. 175–178° C (from ethanol). Found, %: N 11.2; calculated for $C_{21}H_{20}BrN_3$, %: N 11.0. Chromatography on Al_2O_3 (ether–benzene, 1 : 1), R_f 0.8. IR spectrum (in dichloroethane): λ_{max} (nm) (log ε): 265 (4.08); 278 (4.10); 310 (3.87); 330 (3.81); 365 (3.83); 368 (3.85); 388 (2.90); 410 (3.92); 470 (3.33). IR spectrum (in KBr), cm^{-1}, 3100, 2900, 2800. The UV spectrum were taken on an SF-4 instrument, the IR spectra on an IKS-22 instrument, and the PMR spectra on a JMN (40 MHz) spectrometer.

REFERENCES

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