N-PYRYLATION OF HEXAHYDROCARBAZOLE

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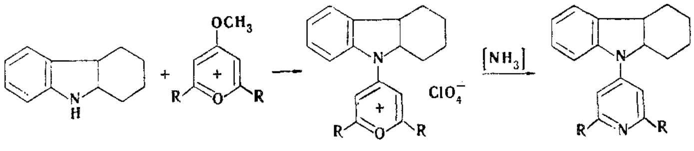
4-Methoxypyrylium salts react with hexahydrocarbazole to give 4-(9-hexahydrocarbazolyl)-pyrylium derivatives. The reaction of the latter with ammonia and hydrazine was investigated.

The reaction of pyrylium derivatives of carbazole with some nucleophilic reagents was used to obtain carbazoles containing other heterocyclic residues.

A 2,6-dimethyl-4-(9-hexahydrocarbazolyl)pyrylium salt (Ia) is formed when hexahydrocarbazole is refluxed with 2,6-dimethyl-4-methoxypyrylium perchlorate in methanol, while a 2,6-diphenyl-4-(9-hexahydrocarbazolyl)pyrylium salt (Ib) is formed with 2,6-diphenyl-4-methoxypyrylium perchlorate.* The structures proposed for Ia and Ib are confirmed by the presence in their IR spectra of intense bands at 1660, 1580 (pyrylium C=C bond [1]), and 1100 cm^{-1} (ClO_4^-). Under the influence of ammonium carbonate, they are converted to 2,6-dimethyl- (IIa) and 2,6-diphenyl-4-(9-hexahydrocarbazolyl)pyridine (IIb), respectively.

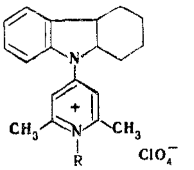


I a,b

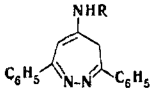
II a,b

I, II a $R=CH_3$; b $R=C_6H_5$

The differences in the nature of substituents R probably lead to different distributions of the positive charge in the pyrylium ring, as a result of which salts Ia and Ib react differently with hydrazine: 2,6-dimethyl derivative Ia is converted to 1-amino-2,6-dimethyl-4-(9-hexahydrocarbazolyl)pyridinium perchlorate (IIIa), while 2,6-diphenyl-substituted salt Ib gives 3,7-diphenyl-5-hydrazino-4H-1,2-diazepine (IVa). Intense absorption bands appear at 3380, 3290, and 3220 (NH_2 group), 1640 and 1520 (pyridinium cation), 1600 (benzene ring), and 1100 cm^{-1} (ClO_4^-) in the IR spectrum of IIIa, while there are bands at 3390, 3200, 1570 (MH_2 group), and 1635 cm^{-1} (C = N bond) in the spectrum of diazepine IVa. Maxima appear at 210, 256, and 300 nm in the UV spectrum of 1,2-diazepine IVa; this is characteristic for 4H-1,2-diazepines [2].



II a,b



IV a,c

a $R=NH_2$; b $R=C_6H_5CH{=}N-$;
c $R=p\text{-}NO_2{-}C_6H_4{=}N-$

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* This pyrylium salt was synthesized by S. V. Krivun.

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The presence of reactive amino groups in IIIa and IVa makes it possible to obtain from them products of condensation with aromatic aldehydes: IIIa reacts with benzaldehyde in refluxing acetic acid (but not in methanol) to give 1-benzylideneamino-2,6-dimethyl-4-(9-hexahydrocarbazolyl)pyridinium perchlorate (IIIb), while 5-hydrazino-1,2-diazepine IVa reacts with p-nitrobenzaldehyde in refluxing methanol to give a p-nitrobenzylidene derivative (IVc).

EXPERIMENTAL

The IR spectra of mineral oil suspensions were recorded with a UR-10 spectrometer. The UV spectra of methanol solutions were recorded with a Specord spectrophotometer. The melting points were determined with a Kofler block and were not corrected.

2,6-Dimethyl-4-(9-hexahydrocarbazolyl)pyrylium Perchlorate (Ia). Equimolar amounts of 2,6-dimethyl-4-methoxypyrylium perchlorate and hexahydrocarbazole were refluxed in a small volume of methanol for 10 min, and the mixture was then concentrated to half its original volume and allowed to stand for crystallization. A product with mp 159° was obtained in 56% yield. Found: C 60.3; H 5.7; Cl 8.9; N 3.9%. $C_{19}H_{22}ClNO_5$. Calculated: C 60.2; H 5.8; Cl 9.2; N 3.7%.

2,6-Diphenyl-4-(9-hexahydrocarbazolyl)pyrylium Perchlorate (Ib). This compound [mp 255° (from acetonitrile)] was similarly obtained in 70% yield from 2,6-diphenyl-4-methoxypyrylium perchlorate. Found: C 68.8; H 4.8; Cl 7.0%. $C_{29}H_{26}ClNO_5$. Calculated: C 69.1; H 5.1; Cl 7.1%.

2,6-Dimethyl-4-(9-hexahydrocarbazolyl)pyridine (IIa). Salt Ia was refluxed in methanol with excess ammonium carbonate for 30 min. The mixture was then cooled and poured into water, and the precipitate was removed by filtration to give a product with mp 102° (from methanol) in 44% yield. Found: C 82.6; H 8.2; N 10.0%. $C_{19}H_{22}N_2$. Calculated: C 82.0; H 7.9; N 10.1%. λ_{max}, nm (log ε): 207 (4.31), 238 (3.98), 339 (4.32).

2,6-Diphenyl-4-(9-hexahydrocarbazolyl)pyridine (IIb). This compound was similarly obtained from Ib in 54% yield and had mp 172°. Found: C 86.0; H 6.4; N 7.2%. $C_{29}H_{26}N_2$. Calculated: C 86.6; H 6.5; N 7.0%. λ_{max}, nm (log ε): 210 (4.43), 235 (4.20), 327 (3.09).

1-Amino-2,6-dimethyl-4-(9-hexahydrocarbazolyl)pyridinium Perchlorate (IIIa). Compound Ia was refluxed with excess hydrazine hydrate in a small volume of methanol for 10 min. The product crystallized when the mixture was cooled and was removed by filtration to give a material (100%) with mp 196°. Found: C 57.8; H 6.0; N 10.8%. $C_{19}H_{24}ClN_3O_4$. Calculated: C 58.1; H 5.6; N 10.9%.

3,7-Diphenyl-5-hydrazino-4H-1,2-diazepine (IVa). Salt Ib was refluxed with excess hydrazine hydrate in a small volume of methanol for 5 min, after which a few drops of water were added to the reaction mixture, and the mixture was cooled. The resulting precipitate was removed by filtration to give a substance with mp 168° in 100% yield. Found: C 74.3; H 5.2; N 20.2%. $C_{17}H_{16}N_4$. Calculated: C 73.9; H 5.7; N 20.3%. λ_{max}, nm (log ε): 210 (4.28), 256 (4.02), 300 (3.41).

1-Benzylideneamino-2,6-dimethyl-4-(9-hexahydrocarbazolyl)pyridinium Perchlorate (IIIb). Pyridinium salt IIIa was refluxed for 3 h with excess benzaldehyde in a small volume of acetic acid. The mixture was cooled and treated with ether to precipitate a material with mp 235° in 83% yield. Found: N 8.6%. $C_{26}H_{28}ClN_3O_4$. Calculated: N 8.7%.

3,7-Diphenyl-5-(p-nitrobenzylidenehydrazino)-4H-1,2-diazepine (IVc). This compound was obtained by refluxing IVa with p-nitrobenzaldehyde in methanol for 1 h. It crystallized readily on cooling of the reaction mixture to give a product with mp 192° in 100% yield. Found: C 70.3; 70.9; H 4.6; 4.7; N 17.2%. $C_{24}H_{19}N_5O_2$. Calculated: C 70.4; H 4.6; N 17.1%. IR spectrum: 1620, 1600, 1520 cm^{-1}.

LITERATURE CITED

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2. O. Buchardt, Ch. L. Pedersen, U. Svanholm, A. M. Duffield, and A. T. Balaban, Acta Chem. Scand., 23, 3125 (1969).