DERIVATIVES OF 1,2-DIHYDROPYRAZINO[3,2,1-jk]CARBAZOLE

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By the dehydration of derivatives of 1, 10-trimethylenepiperazino-[1,2-a]indole (I)[1] we have obtained a number of derivatives of a class of compounds not previously described in the literature—1,2-dihydropyrazino[3,2,1-jk]carbazoles—including the parent compound II.

Dehydrogenation was carried out by the brief heating of the trimethylenepiperazino[1,2-a]indole derivatives with a Raney nickel catalyst in an inert solvent (benzene, toluene, xylene) above 70° C. The yields of the 1,2-dihydropyrazino[3,2,1-jk]carbazole derivatives were close to quantitative.

The proposed method is a convenient preparative procedure for the synthesis of the previously inaccessible 1,2-dihydropyrazino[3,2,1-jk]-carbazoles.

The UV spectra of the compounds obtained (in methanol) are similar to those of other carbazole derivatives and have the following absorption maxima: λ_{max} 230, 255, 297, and 345-355 nm, log ϵ 4.59, 4.59, 3.97, and 3.73.

Hydrochloride of 1,2-dihydro-3H-pyrazino[3,2,1-jk]carbazole (II), white crystals, mp $154-155^{\circ}$ C (from a mixture of acetone and

methanol). Found, %: C 68.53, 68.69; H 5.48, 5.37; N 11.81; 11.63. Calculated for $C_{14}H_{13}N_2C1$, %: C 68.71; H 5.35; N 11.44.

Hydrochloride of 8-methyl-1,2-dihydro-3H-pyrazino[3,2,1-jk]-carbazole (III), white crystals with mp 167-168° C (from methanol). Found, %: C 69.86,69.72; H 5.78, 5.85; N 10.80, 10.65. Calculated for $C_{15}H_{13}N_2Cl$, %: C 69.58; H 5.84; N 10.82.

3-Methyl-1,2-dihydropyrazino[3,2,1-jk]carbazole (IV). White crystals with mp 114-115° C (from methanol). Found, %: C 81.18; 81.26; H 6.65, 6.48; N 12.68, 12.81. Calculated for $C_{15}H_{14}N_{2}$, %: C 81.00; H 6.34; N 12.60.

3,8-Dimethyl-1,2-dihydropyrazino[3,2,1-jk]carbazole (V). White crystals, mp 134-135° C (from acetone). Found, %: C 81.13; 81.33; H 6.75, 6.82; N 11.92, 11.64. Calculated for $C_{16}H_{16}N_2$, %: C 81.32; H 6.82; N 11.85.

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4-CHLOROBENZOPYRYLIUM AND 4-CHLOROFLAVYLIUM SALTS

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We have synthesized 4-chlorobenzopyrylium (I) and 4-chloroflavylium (II) salts in the form of their hexachloroantimonates for the first time by the reaction of 4, 4-dichlorochromene (III) [1] and 4, 4-dichloroflavene (IV) [2] with SbCl₅ in neutral solvents with yields of $\sim 90\%$.

Compounds I and II are yellow crystalline substances melting with decomposition above 250° C which are insoluble in benzene and dichloroethane. With p-nitroaniline, I and II give 4-p-nitrophenyl-iminochromene [1] and 4-p-nitrophenyliminoflavene [2], in the same

way as the corresponding dichlorides III and IV. The dichloride III is obtained more conveniently by the action of di(chloromethyl) ether, which is an effective halogen-transfer agent, on chromone.

- I. Found, %: Cl 49.51, 49.43. Calculated for $C_9H_6Cl_7OSb$, %: Cl 49.64%.
- II. Found, %: C1 42.75, 42.59. Calculated for $C_{15}H_{10}Cl_7OSb$, %: C1 43.08.

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