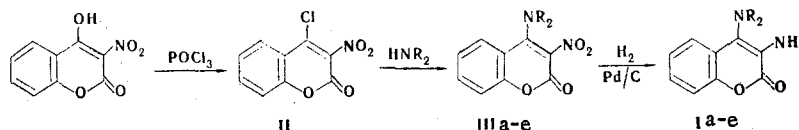


SYNTHESIS OF 3,4-DIAMINOCOUMARINS

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The previously unknown 3,4-diaminocoumarins (I) have been synthesized via the scheme



The replacement of the chlorine in II by an amino group proceeds very readily in inert solvents of the absolute benzene type. Compound III was hydrogenated in alcohol on 10% Pd/C under the usual conditions.

Compound II had mp 162-163° (dec.). Found: C 47.9; H 1.9; Cl 15.5; N 6.2%. $C_9H_4ClNO_4$. Calculated: C 47.9; H 1.8; Cl 15.7; N 6.2%. Compound IIIa ($NR_2 = NH_2$) had mp 273-275°. Found: C 52.5; H 2.9; N 13.7%. $C_9H_6N_2O_4$. Calculated: C 52.4; H 2.9; N 13.6%. Compound IIIb ($NR_2 =$ piperidino) had mp 146-147°. Found: C 61.3; H 5.1; N 10.2%. $C_{14}H_{14}N_2O_4$. Calculated: C 61.3; H 5.1; N 10.2%. Compound Ia ($NR_2 = NH_2$) had mp 201-205° (dec.). Found: C 61.7; H 4.6; N 15.7%. $C_9H_8N_2O_2$. Calculated: C 61.4; H 4.6; N 15.9%. Compound Ib ($NR_2 =$ piperidino) had mp 121-122°. Found: C 68.8; H 6.4; N 11.5%. $C_{14}H_{16}N_2O_2$. Calculated: C 68.8; H 6.6; N 11.5%.

Compounds I and III with $NR_2 = HNC_4H_9$, HNC_6H_5 , and $N(C_2H_5)_2$ were also obtained. According to the PMR spectra, III with a monoalkylamino group exists in the enamine form. It should be expected that I will have the properties of coumarin and 4-aminocoumarins, which contain a β -vinylcarbonyl fragment, and of 3-aminocoumarins, in which the aminovinyl and α -aminocarbonyl groupings can be isolated.

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