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CYCLIZATION OF 2-(1-ALKYLTHIO-2,2-DICYANOETHENYL)PYRROLES

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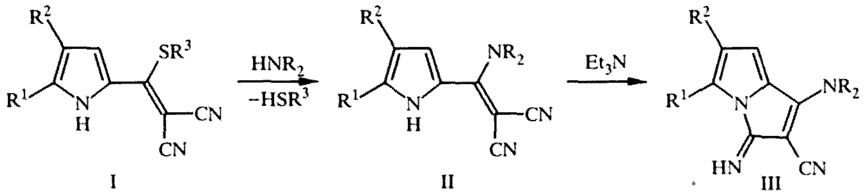
It has been reported [1] that condensation of 2-(1-methylthio-2,2-dicyanoethenyl)pyrrole (I) with secondary amines gave the corresponding 2-(1-amino-2,2-dicyanoethenyl)pyrroles (II) which cyclized to 1-amino-2-cyano-3-imino-3H-pyrrolizines (III) on heating in the presence of a tertiary amine:

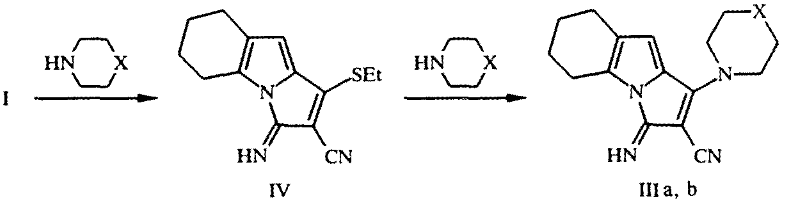


$R^1 = R^2 = H$, $R^3 = Me$, $NR_2 =$ piperidino, morpholino, pyrrolidino

According to Tominaga et al. [1], compound II was isolated and characterized but compound III was used for further reactions without isolation. We have compared the spectroscopic characteristics of compound II with literature data for aminovinylpyrroles [2] and for the analogous aminopyrrolizines III [2] and have found that the authors [1] had prepared the aminopyrrolizines III even at the step in which the vinyl derivatives react with amines avoiding the formation of the aminovinylpyrroles II.

Our results from the study of the reaction of 2-(1-ethylthio-2,2-dicyanoethenyl)4,5,6,7-tetrahydroindole (I, $R^1-R^2 = (CH_2)_4$, $R^3 = Et$) with piperidine and morpholine confirm this conclusion.

The first step of the reaction has been clearly shown (TLC, ^1H NMR) to be cyclization of the initial pyrrole I ($R^1-R^2 = (CH_2)_4$, $R^3 = Et$) to 1-ethylthio-2-cyano-3-imino-4,5,6,7-tetrahydrocyclohexa[*c*]-3H-pyrrolizine (IV), while the second step is the replacement of the alkylthio group by the secondary amine in the cyclic compound produced.



IIIa X = CH₂, IIIb X = O

Confirmation is provided by direct synthesis of the aminopyrrolizine III from the ethylthio derivative IV by treatment with a secondary amine.

1-Piperidino-2-cyano-3-imino-4,5,6,7-tetrahydrocyclohexa[*c*]-3H-pyrrolizine (IIIa) was obtained in 86% yield from 2-(1-ethylthio-2,2-dicyanoethenyl)-4,5,6,7-tetrahydroindole (I) and piperidine in methanol (boiling, 4 h). M.p. 141-142°C. ^1H NMR spectrum ($CDCL_3$): 6.19 (1 H, s, 3-H), 3.80 (4 H, s, 2-H and 6-H of piperidino ring), 1.75 (10 H, m, 3-, 4-, and 5-H of piperidine ring, hydrogens of the cyclohexane ring), 2.49 and 2.86 ppm (4 H, m, protons of the cyclohexane ring).

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1-Morpholino-2-cyano-3-imino-4,5,6,7-tetrahydrocyclohexa[*c*]-3H-pyrrolizine (IIIb) was obtained in 89% yield from pyrrole (I) and morpholine in methanol (boiling, 4 h). M.p. 160-161°C. ^{1}H NMR spectrum ($CDCl_3$): 6.17 (1 H, s, 3-H), 3.85 (8 H, s, $(CH_2\text{-}CH_2)_2O$), 2.84, 2.46, 1.78 ppm (8 H, m, cyclohexane ring).

In addition pyrrolizine IIIb was obtained from 1-ethylthio-2-cyano-3-imino-4,5,6,7-tetrahydrocyclohexa[*c*]-3H-pyrrolizine (IV) and morpholine in methanol (boiling, 4 h) in 94% yield.

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2. K. Hartke and S. Radua, Ann., No. 11, 2110 (1974).