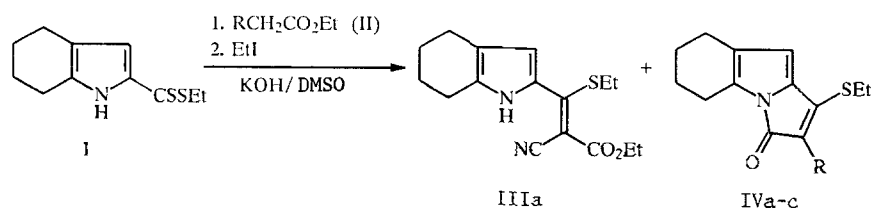


SYNTHESIS OF 1-ALKYLTHIO-3H-INDOLIZIN-3-ONES

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We have recently found that 2-(1-alkylthio-2-cyanoethenyl)pyrroles are formed in the reaction of ethyl pyrrole-2-dithiocarboxylates of the I type with malonodinitrile and cyanoacetamide in the KOH—DMSO system with subsequent alkylation [1].

In attempting to extend this reaction to methylene-active compounds II with an ester grouping we observed that the principal (R = CH) or only pathway in this case is the formation of 1-ethylthio-3H-indolizin-3-ones IVa-c.



Thus 2-(1-ethylthio-2-cyano-2-ethoxycarbonyl)pyrrole (IIIa, 29% yield, mp 95-96°C) and 4,5,6,7-tetrahydro-1-ethylthio-2-cyano-3H-indolizin-3-one (IVa, 61% yield, mp 163-164°C) were obtained when pyrrole I was heated with the cyanoacetate in the KOH—DMSO system with the subsequent addition of ethyl iodide.

Indolizines IVb (62% yield, mp 142-143°C) and IVc (75% yield, mp 105-106°C), respectively, are formed selectively in the reaction of pyrrole I with acetoacetic and malonic esters.

The structures of the synthesized compounds were confirmed by IR and ¹H and ¹³C NMR spectroscopy. Thus the absorption bands at 3255 cm⁻¹ (pyrrole ring NH) and 1673 cm⁻¹ (ν_{CO} of an ester grouping) disappear in the IR spectra of indolizin-3-ones IVa-c, and an absorption band corresponding to the vibrations of a carbonyl group appears at 1720 cm⁻¹.

In addition to signals of an ethylthio group (1.40 and 3.07 ppm), signals of a cyclohexane ring (1.73 and 2.73 ppm) and of a pyrrole proton (singlet, 6.22 ppm) are present in the PMR spectra (CDCl₃, δ, ppm) of IVa-c. Signals of a carboxyethyl group are absent in the spectra of IVa, b. Signals of an ethylthio group (14.36 and 27.26 ppm), of a pyrrole skeleton at 118.32-135.82 ppm, of a carbonyl group (163.37 ppm), and of a pyrrolizine ring [C₍₁₎ at 160.51 ppm and C₍₂₎ at 91.94-108.52 ppm] are present in the ¹³C NMR spectra (CDCl₃, δ, ppm).

The results of elementary analysis of IIIa and IVa-c were in agreement with the calculated values.

REFERENCES

1. B. A. Trofimov, L. N. Sobenina, A. I. Mikhaleva, M. P. Sergeeva, M. V. Sigalov, and N. I. Golovanova, *Zh. Org. Khim.* (in press).