

STUDIES ON QUINOLIZINES AND INDOLIZINES. IX.

REACTION OF α -BISMETHYLTHIOMETHYLENE-2-PYRIDINEACETONITRILES

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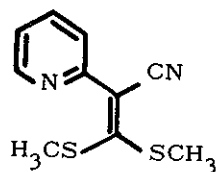
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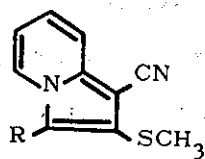
Bunkyo, Nagasaki 852

Reaction of α -(bismethylthio)methylene-2-pyridineacetonitrile and α -halo carbonyl compounds(ethyl bromoacetate, bromoacetone and α -bromoacetophenone) and ethyl γ -bromocrotonate using triethylamine afforded indolizine derivatives with the corresponding substituent in the 3-position(IIa,b,c,d). Similarly, reaction of dimethyl(2-pyridyl)dithiocarbimide(III) and halo carbonyl compounds afforded azaindolizine derivatives(IVa,b,c,d). Reaction of I and nitromethane using potassium carbonate afforded 1-cyano-2-methylthio-3-nitroindolizine (V).

Cycl[3,2,2]azine derivative(VII), dimethyl 1-cyano-2-methylthiocycl[3,2,2]azine-3,4-dicarboxylate, was synthesized by application of dimethyl acetylenedicarboxylate and indolizine derivative(VI), which was obtained by decarboxylation of IIa using sulfuric acid in the presence of palladium-on-charcoal catalyst.

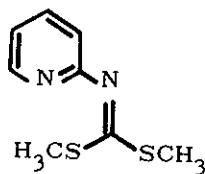


(I)

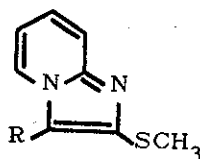


(IIa,b,c,d)

- (a) $R = \text{COOCH}_2\text{CH}_3$
- (b) $R = \text{COCH}_3$
- (c) $R = \text{COC}_6\text{H}_5$
- (d) $R = \text{CH}=\text{CH}-\text{COOCH}_2\text{CH}_3$



(III)



(IVa,b,c,d)

- (a) $R = \text{COOCH}_2\text{CH}_3$
- (b) $R = \text{COCH}_3$
- (c) $R = \text{COC}_6\text{H}_5$
- (d) $R = \text{CH}=\text{CH}-\text{COOCH}_2\text{CH}_3$

