REACTION OF ISOQUINOLINIUM YLIDS WITH KETENETHIO-ACETALS

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Reaction of isoquinolinium ylides with ketenethioacetals gave isoquinolinium allylides, pyrrolo[2,1-a]isoquinolines, and imidazo[2,1-a]isoquinolines, in fairly good yield.

In our previous paper, we have reported that the reaction of ketenethioacetals, 1-[2,2-bis(methylthio)vinyl]pyridinium iodides, with the active methylene compounds gave pyridinium allylides in good yield.¹⁾ Here, we wish to report the main reactions of isoquinolinium ylides with the typical ketene-thioacetals.

The reaction of isoquinolinium salts (Ia, b, c) with ketenethioacetal, 2-cyano-3,3-bis(methylthio)acrylonitrile²⁾, in the presence of powdered potassium hydroxide in dimethyl sulfoxide at room temperature under stirring for 2 - 3 hr gave isoquinolinium allylides (IIIa, b, c) in good yields, respectively.

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This reaction also occurred in the presence of triethylamine as a base in ethanol under refluxing for 1 - 2 hr to form isoquinolinium allylides (IIIa, b) in 30 - 50% yield. These Nallylides were characterized by analytical and spectroscopic data. However, the reaction of Ia with 2,3-dicyano-3-methylthioacrylonitrile, which was prepared by the reaction of II with sodium cyanide in dimethyl sulfoxide³⁾, did not give an isoquinolinium allylide, but a cyclized and decyanated product, ethyl 1,2-dicyanothiopyrrolo[2,1-a]isoquinoline-3-carboxylate (IV) in 68% yield.



When Ia reacted with 1-nitro-2,2-bis(methylthio)ethyleme⁴⁾ . in the presence of potassium carbonate as a base in dimethylformamide on a boiling water bath, an isoquinolinium allylide system compound did not give but yellow needles of mp 121° in 45% yield. This compound was found to be ethyl 2-methylthiopyrrolo[2,1-a]isoquinoline-3-carboxylate (Va) which was identical with the authentic sample synthesized by the reaction of 3-ethoxycarbonyl-2-methylthiothiazolo[2,3-a]isoquinolinium sulfate with acetophenone.⁵⁾ Similarly, Ta and c reacted with 1-nitro-2,2-bis(methylthio)ethylene to form 3-substituted 2methylthiopyrrolo[2,1-a]isoquinolines (Vb, c), in 15% and 22% yield, respectively.



Next, under similar condition previously described, the reaction of Ia with N-bis(methylthio)methylene-p-toluenesulfonamide⁶⁾ gave colorless needles, mp 154°, in 78% yield. This compound was found to be a cyclized product, ethyl 2-methylthioimidazo[2,1-a]isoquinoline-3-carboxylate (VI) from micro analysis and spectral data. Although, N-bis(methylthio)-

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methylenecyanamide⁷⁾ reacted with Ia, b, c in a similar manner to form only isoquinolinium heteroallylides (VIIa, b, c) in good yields.



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