HETEROCYCLES, Vol. 4, No. 5, 1976

REACTION OF ISOQUINOLINIUM YLIDS WITH KETENETHIOACETALS

Hiroshi Fujito, Yoshinori Tominaga, Yoshiro Matsuda,
and Goro Kobayashi*

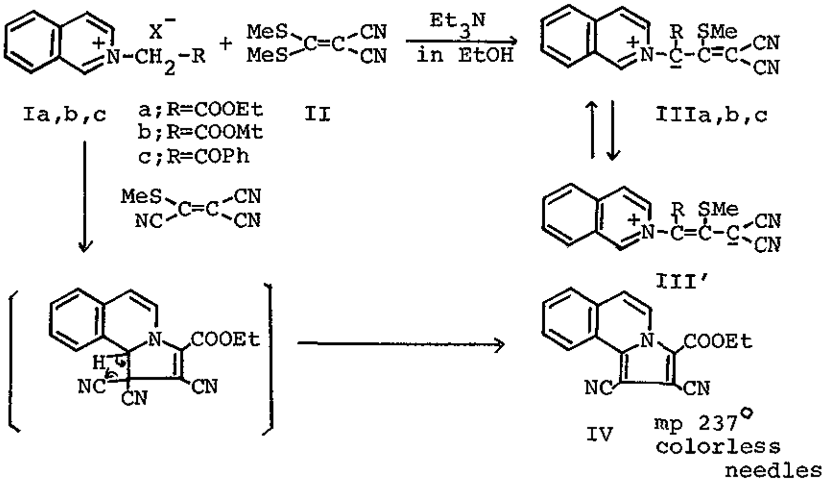
Faculty of Pharmaceutical Sciences, Nagasaki University
1-14 bunkyo-machi, Nagasaki 852, Japan

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 ketenethioacetals.

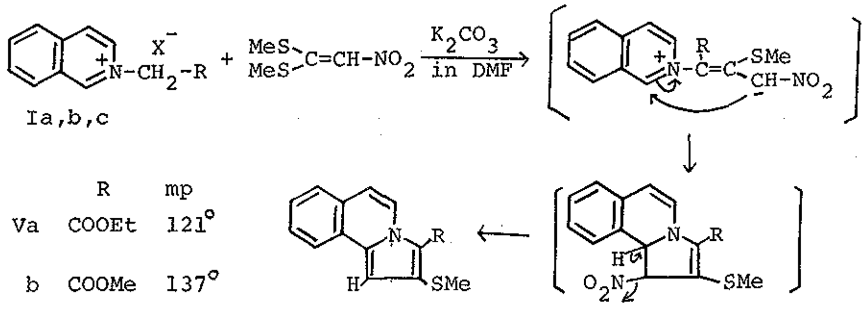
The reaction of isoquinolinium salts (Ia, b, c) with ketenethioacetal, 2-cyano-3,3-bis(methylthio)acrylonitrile2), in the presence of powdered potassium hydroxide in dimethyl sulfoxide at room temperature under stirring for 2 - 3 hr gave isoquinolinium allylides (IIIa, b, c) in good yields, respectively.

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 N-allylides 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 sulfoxide[3)], 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.



	R	Yield	mp	UVλ_{max}^{EtOH}nm(logε)	IR(KBr)cm^{-1}
IIIa	COOEt	62%	146°	232(4.50),364(4.15) 470(3.58)	1685(C=O) 2160,2170(CN)
b	COOMe	67%	197°	233(4.71),362(4.28) 465(3.79)	1670(C=O) 2140,2160(CN)
c	COPh	25%	250°	232(4.73),320(4.09) 407(4.24)	1630(C=O) 2180(CN)

When Ia reacted with 1-nitro-2,2-bis(methylthio)ethylene[4)] 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, Ia and c reacted with 1-nitro-2,2-bis(methylthio)ethylene to form 3-substituted 2-methylthiopyrrolo[2,1-a]isoquinolines (Vb, c), in 15% and 22% yield, respectively.



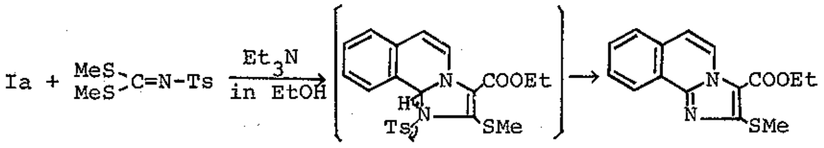
Ia,b,c

Va,b,c

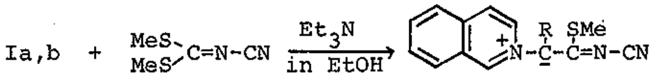
	R	mp
Va	COOEt	121°
b	COOMe	137°
c	COPh	140°

Next, under similar condition previously described, the reaction of Ia with N-bis(methylthio)methylene-p-toluenesulfonamide[6)] 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)-

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



VI colorless needles



VIIa,b

	R	Yield	mp	$UV\lambda_{max}^{EtOH}$nm(logε)	IR(KBr)cm^{-1}
VI		65%	154°	271(4.78),316(3.91)	1685(C=O)
VIIa	COOEt	92%	246°	233(4.75),268(4.13) 310(4.41),425(3.48)	1640(C=O) 2150(CN)
b	COOMe	48%	228°	233(4.73),267(4.15) 310(4.38)	1645(C=O) 2130(CN)

REFERENCES

1) Y.Tominaga, K.Mizuyama, Y. Miyake, H.Fujito, Y. Matsuda, and G. Kobayashi, *Heterocycles*, 1975, **3**, 793.

2) R. Gompper and W. Töpfel, *Chem. Ber.*, 1962, **95**, 2861, 2871.

3) Y. Tominaga, Y. Matsuda, and G. Kobayashi, *J. Pharm. Soc. Japan*, 1975, **95**, 378.

4) R. Gompper and H. Schefer, *Chem. Ber.*, 1967, **100**, 591.

5) K. Mizuyama, Y. Matsuo, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Heterocycles*, 1975, **3**, 533.

6) R. Kuwayama and S. Kataoka, *J. Pharm. Soc. Japan*, 1965, **85**, 391

7) A.Hantzsch and M. Wolvekamp, *Annalen* , 1964, **331**, 265.

Received, 24th January, 1976