

REACTION OF PYRIDINIUM AND ISOQUINOLINIUM N-IMINES
WITH KETENETHIOACETALS

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

Faculty of Pharmaceutical Sciences, Nagasaki University

1-14 Bunkyo-machi, Nagasaki 852, Japan

Pyridinium and isoquinolinium N-vinylimine
and azaindolizine derivatives were synthesized
by a reaction of pyridinium and isoquinolinium
N-imine with ketenethioacetals.

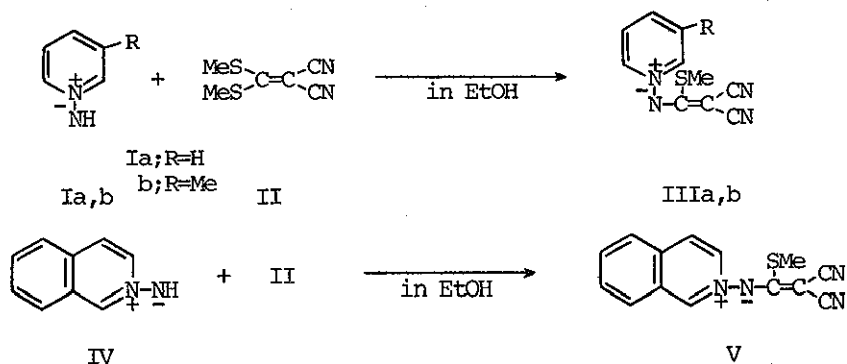
In a continuation of our previous studies, the authors
have reported that the reaction of pyridinium and iso-
quinolinium N-ylides with ketenethioacetals gave the
pyridinium and isoquinolinium allylides and indolizine
derivatives, respectively¹⁾.

In this paper, we wish to report the reaction of
pyridinium and isoquinolinium N-imines with the ketenethio-
acetals(II,VI,XI) to compare the reactivity of the related
N-ylides with the N-imines.

The reaction of pyridinium N-imines(Ia,b), prepared *in situ*
by a treatment of N-aminopyridinium chlorides with triethyl-
amine, with 2-cyano-3,3-bis(methylthio)acrylonitrile(II) in

ethanol under refluxing for 3 hr afforded the corresponding 2,2-dicyano-N-(1-pyridinio)vinylaminides²⁾ (IIIa,b) in 23% and 22% yield, which were characterized by analytical and spectroscopic data, respectively.

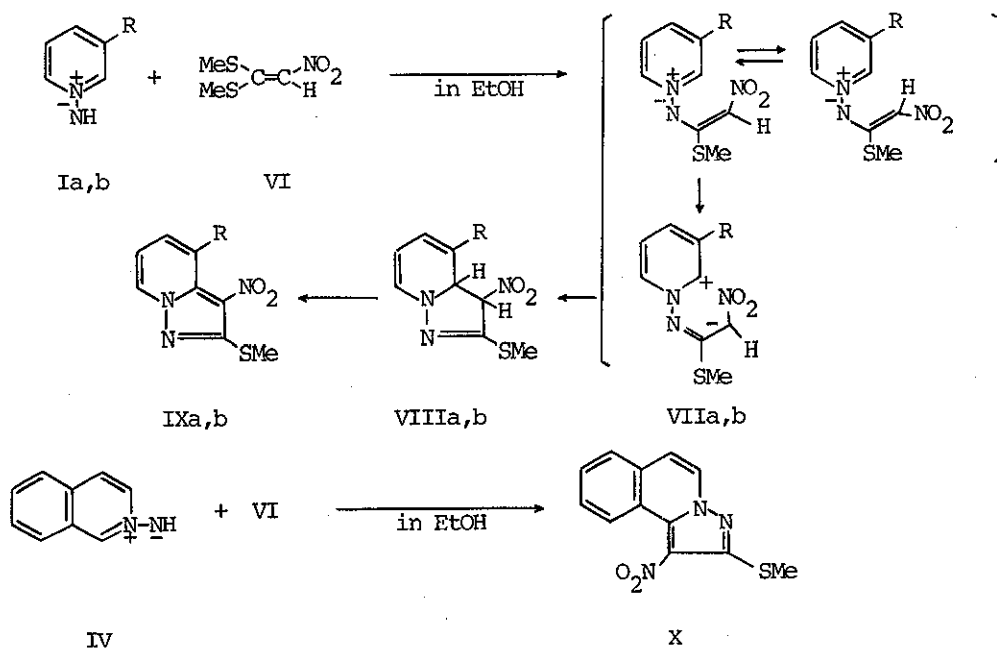
Similarly, 2,2-dicyano-N-(2-isoquinolinio)vinylaminide (V) was synthesized in 17% yield by the reaction of isoquinolinium N-imine (IV), prepared by the same way in case of pyridinium N-imine, with II under the same conditions.



	R	mp	UV λ_{max} ^{EtOH}	$\epsilon_{\text{m}}(\log \epsilon)$	IR(KBr) cm^{-1}	appearance
IIIa	H	176°	247(4.17), 279(4.17) 380(3.23)		2150, 2180 (CN)	pale yellow prisms
b	Me	164°	247(4.19), 275(4.22) 378(3.28)		2165, 2190 (CN)	colorless needles
V		182°	222(4.23), 249(4.31) 278(3.94), 402(3.19)		2150, 2180 (CN)	yellow prisms

When 2,2-bis(methylthio)-1-nitroethylene (VI) was used instead of II, a reaction of Ia with VI under the same conditions did not give a pyridinium N-vinylimine but afforded 2-methylthio-1-nitropyrazolo[1,5-a]pyridine (IXa) as yellow needles, mp 224-6°, in 41% yield. Product IXa was

obtained by intermolecular 1,5-dipolcyclization of intermediate IVa, followed by dehydrogenation. 8-Methyl-2-methylthio-1-nitropyrrazolo[1,5-a]pyridine (IXb) was also obtained by the reaction of Ib with VI in 58% yield. The structural assignments of IXa,b rest upon analytical and spectral data. The NMR spectrum of IXb showed the three protons of 5-position at 8.63 ppm (1H,d,J=7Hz), 6-position at 7.23 ppm (1H,t,J=7Hz) and 7-position at 7.65 ppm (1H,d,J=7Hz).

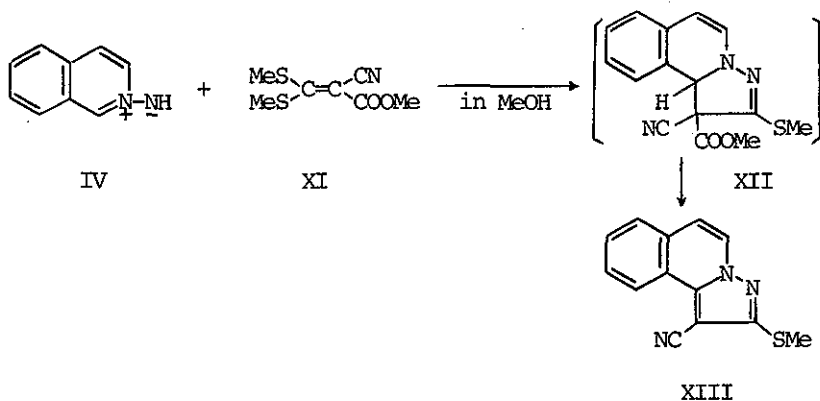


	R	mp	UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ)	IR (KBr) cm^{-1}	appearance
IXa	H	224-6°	244 (4.54), 365 (4.24)	1530 (NO ₂)	pale yellow needles
b	Me	204-6°	246 (4.52), 274 (3.80) 374 (4.08)	1365, 1505 (NO ₂)	pale yellow needles
X		226-7°	217, 232, 262, 286, 307 370*	1520 (NO ₂)	yellow needles

* Concentration is unknown because of insufficient solubility.

In the same manner, 2-methylthio-1-nitropyrazolo[2,3-a]-isoquinoline(X) was obtained by the reaction of IV with VI in 78% yield.

The reaction of isoquinolinium N-imine(IV) with methyl 2-cyano-3,3-bis(methylthio)acrylate(XI) under the similar conditions was also carried out to afford 2-methylthio-1-nitropyrazolo[2,3-a]isoquinoline(XIII) via XII, in 29% yield, but 2-methylthio-1-methoxycarbonylpyrazolo[2,3-a]isoquinoline was not obtained. The analytical and spectral data supported the structure XIII.



mp	UV $\lambda_{\text{max}}^{\text{EtOH}}$	nm(log ϵ)	IR(KBr) cm $^{-1}$	appearance
XIII 186-90°	268(4.50)	328(3.75)	2200(CN)	yellow needles
	343(3.75)			

REFERENCES

- 1) H.Fujito, Y.Tominaga, Y.Matsuda and G.Kobayashi, Heterocycles, 1976, 4, 939.
- 2) a; T.Sasaki, K.Kanematsu, A.Takehi and G.Ito, Tetrahedron, 1972, 28, 4947. b; Y.Tamura, Y.Miki, Y.Sumida and M.Ikeda, J.C.S. Perkin I, 1973, 2580.

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