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REACTION OF PYRIDINIUM AND ISOQUINOLINIUM N-IMINES WITH KETENETHIOACETALS

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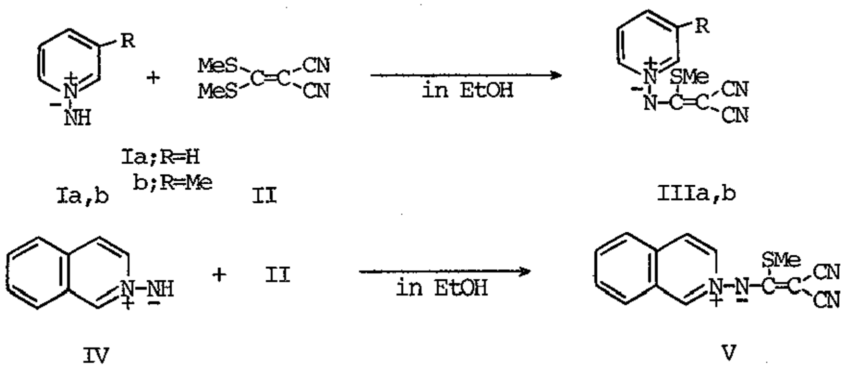
Pyridinium and isoquinolinium N-vinylimine and azaindolizine derivatives were synthesized by a reaction of pyridinium and isoquinolinium N-imine with ketenethioacetals.

In a continuation of our previous studies, the authors have reported that the reaction of pyridinium and isoquinolinium 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 ketenethioacetals(II,VI,XI) to compare the reactivity of the related N-ylides with the N-imines.

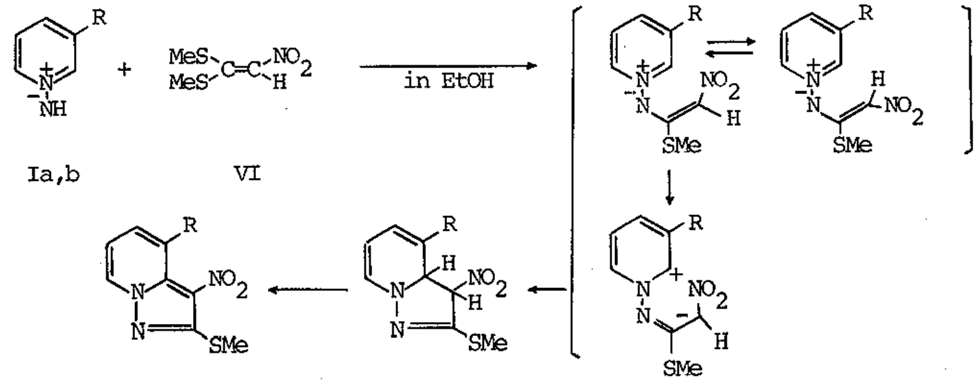
The reaction of pyridinium N-imines(Ia,b), prepared *in situ* by a treatment of N-aminopyridinium chlorides with triethylamine, with 2-cyano-3,3-bis(methylthio)acrylonitrile(II) in ethanol under refluxing for 3 hr afforded the corresponding 2,2-dicyano-N-(1-pyridinio)vinylaminides[2] (IIIa,b) in 23% 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.



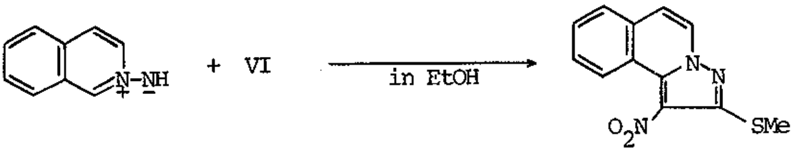
	R	mp	UVλ_{max}^{EtOH}nm(logε)	IR(KBr)cm^{-1}	appearance
IIIa	H	176°	247(4.17),279(4.17) 380(3.23)	2150,2180(CN)	pale yellow prisms
b	Me	164°	247(4.19),275(4.22) 378(3.28)	2165,2190(CN)	colorless needles
V		182°	222(4.23),249(4.31) 278(3.94),402(3.19)	2150,2180(CN)	yellow prisms

When 2,2-bis(metylthio)-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-nitropyrazolo[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).



Ia,b VI

IXa,b VIIIa,b VIIa,b



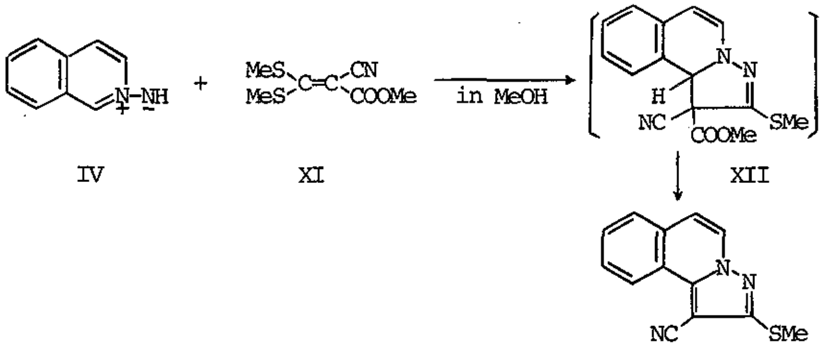
IV X

	R	mp	UVλ_{max}^{EtOH}nm(logε)	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 similer 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.



IV XI XII XIII

	mp	UVλ_{max}^{EtOH}nm(logε)	IR(KBr)cm^{-1}	appearance
XIII	186-90°	268(4.50),328(3.75) 343(3.75)	2200(CN)	yellow needles

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