1,3-DIPOLAR CYCLOADDITION OF PYRIDAZINIUM *N*-YLIDES WITH PERHALOCYCLOALKENES AND THERMAL DECOMPOSITION OF THE ADDUCTS

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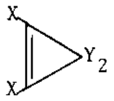
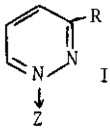
Reaction of perhalocyclopropenes (Ia and Ib) with pyridazinium *N*-ylides (IIa-g) yielded 1,3-dipolar cycloadducts (V) while the combination of Ia and pyridinium *N*-ylides (III) afforded only the quarternary salts. The reaction of a perhalocyclobutene (IV) with II also yielded the corresponding adducts.

The stereochemistry (regarding the ring juncture) of the adduct Va obtained from Ia and IIa was confirmed to be the exo form by means of its single-crystal X-ray diffraction analysis. The stereochemistry of the other adducts was assumed to be the same ring juncture by NMR etc.

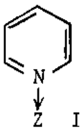
Thermolysis of V in xylene gave 2-chloro-3-dichloromethylpyrazolo[1,5-*b*]pyridazine (VI) which was introduced into various types of pyrazolo[1,5-*b*]pyridazines (VII-XIII). It was indicated that the hydrogen atom of $CHCl_2$ group in the compound VI was introduced through intermolecular transfer.



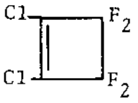
Ia, X=Y=Cl
b, X=Br; Y=F



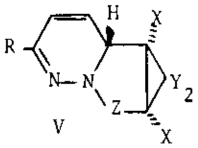
IIa, R=H; Z=NCOMe
b, R=Ph; Z=NCOMe
c, R=OEt; Z=NCOMe
d, R=H; Z=NCOPh
e, R=H; Z=NCO_2Et
f, R=Ph; Z=NCO_2Et
g, R=H; Z=$C(CN)_2$



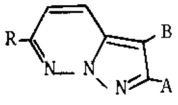
IIIa, Z=NCOMe
b, Z=O



IV



V



VI, A=Cl; B=$CHCl_2$
VII, A=Cl; B=CHO
VIII, A=Cl; B=CH_2OH
IX, A=Cl; B=CH_3
X, A=H; B=CH_3
XI, A=Cl; B=CO_2H
XII, A=H; B=CO_2CH_3
XIII, A=Cl, B=H