Tetrahedron Letters No. 43, pp 4121 - 4124. 0040-4039/78/1022-4121$02.00/0

1,3-Dipolar Cycloaddition of Pyridazinium N-Ylides with Perhalocycloalkenes

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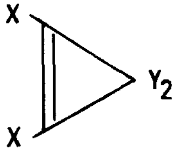
Cyclopropenes and their analogues have been well known to give the cycloadducts with linear 1,3-dipoles such as diazoalkanes$^{1,2)}$ and with cyclic 1,3-dipoles such as the sydnones$^{3)}$. On the other hand, the exocyclic 1,3-dipoles such as heteroaromatic N-ylides commonly cause nucleophilic reaction towards cyclopropenones and their analogues$^{4)}$, and little are known on the 1,3-dipolar cycloaddition of heteroaromatic N-ylides with cycloalkenes.

In this respect, Matsumoto _et al._$^{5)}$ and Kascheres _et al._$^{6)}$ reported that the 1,3-dipolar cycloaddition proceeded between cyclopropenones and pyridinium N-ylides, and that the tricyclic (primary) adducts are unstable, the bicyclic products being obtained as the result of ring openings of three membered rings of the primary adducts and eliminations of the neutral molecules.

We describe in this paper the cycloaddition of perhalocyclopropenes(_1_) and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene(_2_) with pyridazinium N-ylides (_3_) and the formation of the tricyclic (primary) adducts(_4_).



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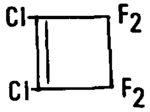

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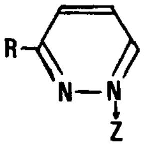

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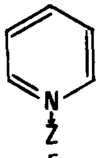

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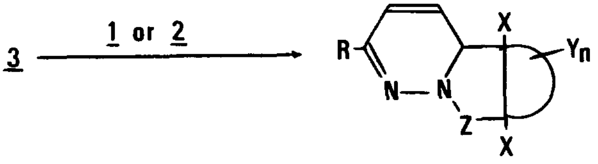

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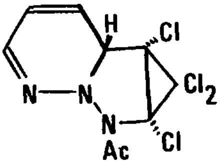

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Chart

Contrary to the expectation, the reaction of the pyridinium ylides(5, Z=NAc and O) and pyridazinium N-oxide(3, R=H, Z=O) with 1 or 2 did not afford the cycloadducts under the examined conditions.

However, when 3 were allowed to react with 1 or 2 under the conditions described in the table, the adducts were produced. The yields and the melting points of the products are collected in the table. The perhalocyclobutene(2) showed much lower reactivity compared to that of 1.

Table

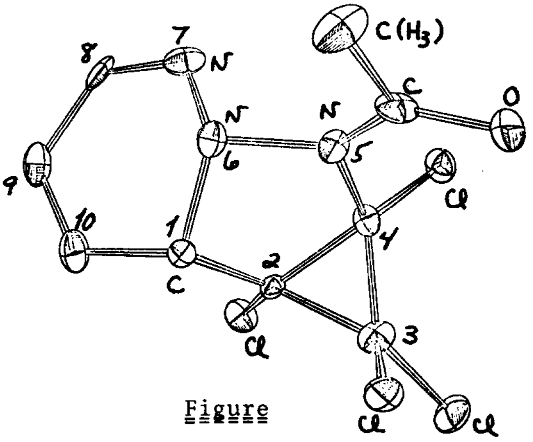
3	Z	R	1 or 2	Yields(%)	m.p.(°C)
a,	NCOMe	H	1a,a) X=Y=Cl	37	151.5(dec.)
b,	NCOMe	Ph	1a	38	162(dec.)
c,	NCOMe	OEt	1a	27	158(dec.)
d,	NCOPh	H	1ab)	19	150(dec.)
e,	NCO_2Et	H	1ac)	14	oil(unstable)
f,	NCO_2Et	Ph	1a	5	143.5(dec.)
g,	$C(CN)_2$	H	1ad)	67	98(dec.)
a			1b, X=Br, Y=F	44	143(dec.)
b			1b	34	142.5
a			1c, X=Y=Br	--e)	----
a			2f)	5	108
b			2	2	153(dec.)
d			2	--g)	----
e			2	2	oil(unstable)
f			2	1	glassy solid(unstable)
g			2	--g)	----

a)The reaction was carried out in tetrahydrofuran under N_2 at room temperature, for 12hr, unless otherwise noted. b)In benzene at 55°C, for 10hr. c)In CH_2Cl_2 at room temperature, for 0.5hr. d)In tetrahydrofuran at room temperature, for 3 days. e)Only a tarry, hydrophilic product was obtained. f)Reflux in benzene, for all runs where 2 was used. g)The starting materials(3) were recovered in these cases.

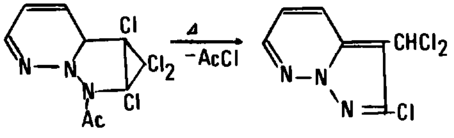
The adduct(6) obtained from the reaction of 3a with 1a showed the $\nu_{C=O}$ absorption at $1700cm^{-1}$(KBr) in the IR spectrum, whereas the starting material(3a) showed an absorption at $1570cm^{-1}$ due to the polarized C=O group. ^1H-NMR spectrum of 6 showed signals at δ 2.24(3H,s,Ac), 4.61(1H,dd,J=3.8 and 1.0Hz,1-H), 6.20(2H,m,9- and 10-H), and 7.08(1H,dd,J=3.8 and 3.5Hz,8-H).

These observations support that 6 has the structure of 5-acetyl-2,3,3,4-

tetrachloro-5,6,7-triazatricyclo[4,1,0,0]7,9-decadiene, i.e.,the primary 1,3-dipolar cycloadduct. Other products(4) obtained from the reactions of 3a-f with 1 and 2 also showed the similar patterns of $\nu_{C=O}$ absorptions as mentioned before. In the NMR spectra, all 4 showed the analogous features, especially the chemical shifts and the coupling constants of the signals due to the bridge-head protons were essentially identical. These data suggest that all the adducts obtained here have the same configuration with respect to the ring juncture. Additionally, the structure of 6 has been confirmed to be the exo form7) by single-crystal X-ray diffraction method. Crystal data: $C_9H_7N_3OCl_4$, colourless needles from Et_2O-hexane, orthorhombic, space group $P2_12_12_1$, a=10.99, b=12.37, c=9.22Å, Z=4. Intensity data were collected using Cu-K_α radiation on Phillips automatic four circle diffractometer, 659 independent reflection with $I>3\sigma(I)$ and $\theta<60°$ were used in the solution. The structure was solved by the direct method,8) and refined by block diagonal least square method to a final R-index of 0.067(figure).



Figure



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The compounds 5(Z=NAc and O) and 3(R=H,Z=O) did not give the expected adducts as mentioned before, and the reactions of these N-ylides with perhalocycloalkenes afforded hydrophilic products which are considered to be the quarternary salts which had been produced by the nucleophilic additions of N-ylides to perhalocycloalkenes(by means of their NMR spectra in D_2O). The reason of the differences in the reactivities among the investigated N-ylides have not been clear.

Finally, when 6 was heated in xylene at 150°C, 2-chloro-3-dichloromethyl-pyrazolo[1,5-b]pyridazine(7) was obtained[9], and this cleaving manner of the condensed three membered ring in the [4,1,0,0] tricyclic system is in contrast with that in the referential reactions where the cleavage had occurred at the interior C-C bond of the three membered ring of the adducts.[5,6]

References and Footnotes

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7)The endo structure could not be denied becouase there had been the possibility that the exo adduct could be unstable under these conditions.[1-3]

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9)The structure of 7 was determined by the identificatuon of 3-carbomthoxy-pyrazolo[1,5-b]pyridazine[10] which was derived from 7(4-steps).
The detailed procedures will be presented in the future paper.

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(Received in Japan 3 July 1978; received in UK for publication 4 September 1978)