THERMAL DECOMPOSITION OF 1,3-DIPOLAR CYCLOADDUCTS OF PYRIDAZINE *N*-ACETYLIMINES AND TETRACHLOROCYCLOPROPENE[+]

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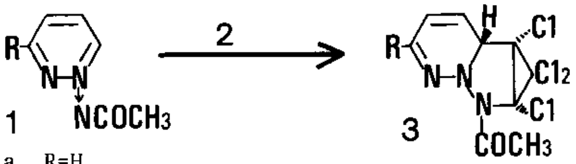
Thermolysis of 6-acetyl-4b,5,5,5a-tetrachloro-4a,4b,5a,6-tetrahydro-5*H*-cyclopropa[3,4]pyrazolo[1,5-*b*]pyridazines afforded 2-chloro-3-(dichloromethyl)pyrazolo[1,5-*b*]pyridazines which were converted to various types of pyrazolo[1,5-*b*]pyridazines.

In a previous paper,[1] we described that pyridazine *N*-acetylimines (**1**) undergo 1,3-dipolar cycloaddition with tetrachlorocyclopropene (**2**) to give 6-acetyl-4b,5,5,5a-tetrachloro-4a,4b,5a,6-tetrahydro-5*H*-cyclopropa[3,4]pyrazolo[1,5-*b*]-pyridazines (**3**, 5-acetyl-2,3,3,4-tetrachloro-5,6,7-triazatricyclo[4,1,0,0]-7,9-decadienes). The adducts contain [4,1,0,0] tricyclic systems, consequently, have strained three membered rings in the molecules, and the thermal behavior of these compounds is of interest.

Matsumoto *et al.*[2] reported that a compound (**4**) which contains a ring system similar to that in **3** was thermally transformed into a pyrrolo[1,5-*b*]pyridazine (**5**).



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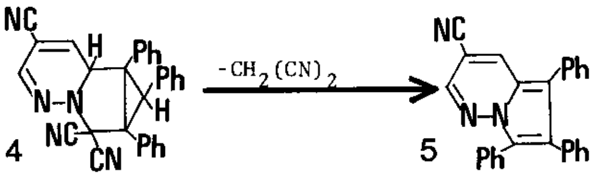
a, R=H
b, R=Ph
c, R=OEt

3



4

5

However, the described compounds **3** underwent a thermal transformation of a novel type. Thus, when the adduct **3a**(R=H) was refluxed in inert solvents such as

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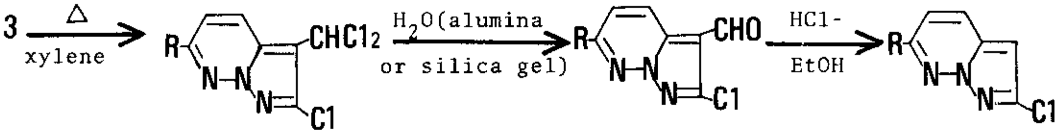
[+] Dedicated to Professor T. Kametani on the occasion of his retirement from Tohoku University.

xylene, it suffered a decomposition to give a product (6a, mp 123°) which has the composition of [3a-CH_3COCl]. The NMR spectrum of 6a showed a singlet at δ 6.98 which was assignable to the proton of a dichloromethyl group. The compound was quite unstable when it was subjected to a chromatographic purification using alumina or silica gel and resulted in ready conversion to an aldehyde (7a, mp 139.5°). On treating the aldehyde with alcoholic hydrochloric acid, it was deformylated to give a compound (8a, mp 88.5°). The aldehyde 7a was reduced with $LiAlH_4$ and gave an alcohol (9) which had the melting points at 93° and 162° (double melting points).[3] A reduction of 7a with Bu_3SnH gave a compound (10, mp 133.5°) which bears a methyl group. The mass spectrum of 10 showed a high fragment peak due to $C_6H_6N_2$ $[(10\text{-ClCN})]^{+\cdot}$, m/e: obs. 106.0533; calc. 106.0530] but not the peak due to $C_5H_3N_2Cl$ $[(10\text{-}CH_3CN)]^{+\cdot}$]. This observation suggests that the chlorine atom is bound to the carbon atom adjacent to a nitrogen atom in 10 (*i.e.*,the chlorine atom is located in the 2-position in the methylpyrazolo[1,5-*b*]pyridazine).

Further, the compound 10 was catalytically hydrogenated to give the dechlorinated compound (11, mp 62.5°) which was unidentical with the known compound, 2-methylpyrazolo[1,5-*b*]pyridazine (12).[4]



a, R=H	6a, 50%$^{a,b)}$	7a, 73%$^{c)}$	8a, 71%$^{a)}$
b, R=Ph	b, 64	b, 62	b, 74%
c, R=OEt	c, 53	c, 86	c, 91

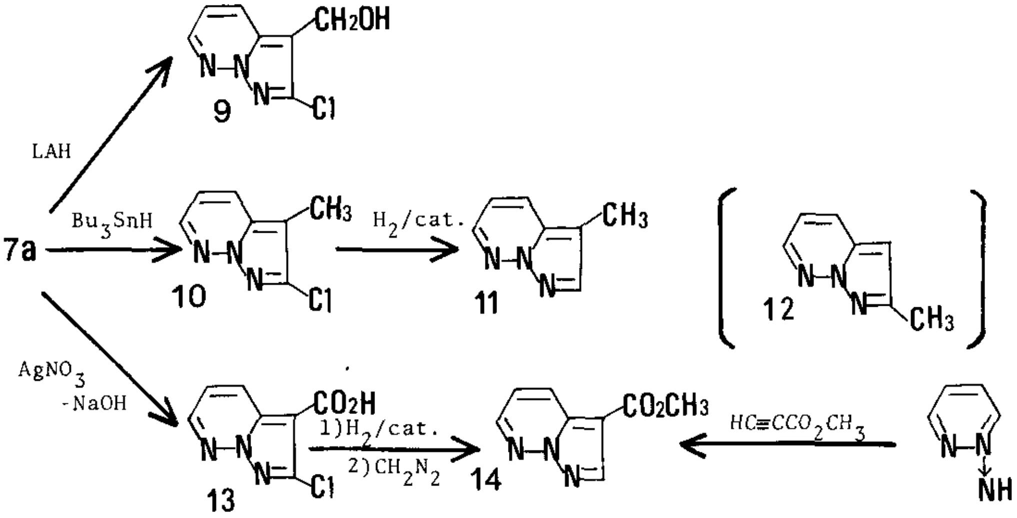
a) Isolation yields. b) The yields of 6 are low compared with those of 7 because of the instabilities and difficulties of the isolation of the former compounds. c) Isolation yields from 3.

Moreover, the aldehyde 7a was oxidized with $AgNO_3$-NaOH/H_2O[5] to give a carboxylic acid (13), which was then dechlorinated by a catalytic reduction and methylated with diazomethane to give an ester 14 (mp 126°). The ester was identical with the authentic sample[6] obtained from a 1,3-dipolar cycloaddition between pyridazine *N*-imine and methyl acetylenecarboxylate.

These data show that the carboxyl group of the acid 13 is situated in the 3-position, so that, the chlorine atom in the 2-position.

Thus, it became apparent that the decomposition products 6 have the structure of the pyrazolo[1,5-*b*]pyridazine[7] and the ring-attached chlorine atom and the dichloromethyl group of 6a are situated in the 2- and 3-positions respectively.

The similar treatments of the other adducts 3b and 3c, as were previously described, also gave the corresponding compounds 6, 7, 8 in the yields shown in the preceding scheme.



Although the question, whether the proton of the dichloromethyl group of 6 had been introduced intermolecularly (namely, the thermal conversion of 3 proceed *via* intermediary radicals) or the proton could be introduced intramolecularly (in this case, the conversion might proceed through a concerted mechanism) has been left unresolved from the present data, the cleaving manner of the exterior C-C bond is a particular one, compared to the results of the decomposition of 4[2] and other compounds[8] which contain similar three membered rings as in 3.

Additionally, it may be notable that the described bond-cleaving phase resembles that of the "normal" Reimer-Tiemann reaction.[9]

REFERENCES AND FOOTNOTES

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3. The alcohol showed a single melting point at ca. 130° when the bath temperature was raised rapidly.
4. K.Kasuga, M.Hirobe, and T.Okamoto, Yakugaku Zasshi, 94, 952 (1974).
5. For example, see J.C.Sheehan and C.A.Robinson, J.Amer.Chem.Soc., 73, 1207 (1951).
6. K.Kasuga, M.Hirobe, and T.Okamoto, Chem.Pharm.Bull., 22, 1814 (1974).
7. The ring structure of the pyrazolo[1,5-b]pyridazines and the positions of the substituents have been supported by UV, ^{1}H- and ^{13}C-NMR, and mass spectroscopies and chemical data, for all the compounds 6-11, 13, and 14.
8. For example, see H.M.Cohen, J.Heterocyclic Chem., 4, 130 (1967); A.Ellinger, Ber., 39, 2515 (1906); G.L.Closs and G.M.Schwartz, J.Org.Chem., 26, 2609 (1961); R.L.Jones and C.W.Rees. J.Chem.Soc., (C), 1969, 2249, and refs. cited therein.
9. For example, H.Wynberg, Chem.Rev., 60, 169 (1960).

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