Thermal Decomposition of 1,3-Dipolar Cycloadducts of Pyridazine N-Acetylimes and Tetrachlorocyclopropene

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Thermolysis of 6-acetyl-4b,5,5,5a-tetrachloro-4a,4b,5a,6-tetrahydro-5H-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 pyrazole N-acetylimes (1) undergo 1,3-dipolar cycloaddition with tetrachlorocyclopropene (2) to give 6-acetyl-4b,5,5,5a-tetrachloro-4a,4b,5a,6-tetrahydro-5H-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).

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

¹Dedicated 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-CH₃COCl]. The NMR spectrum of 6a showed a singlet at 6 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 LiAlH₄ and gave an alcohol (9) which had the melting points at 93° and 162° (double melting points). A reduction of 7a with Bu₃SnH gave a compound (10, mp 133.5°) which bears a methyl group. The mass spectrum of 10 showed a high fragment peak due to C₆H₆N₂ [[(10-CH₃CN)⁺, m/e: obs. 106.0533; calc. 106.0530] but not the peak due to C₅H₃N₂Cl [[(10-CH₃CN)⁺. 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).

Moreover, the aldehyde 7a was oxidized with AgNO₃-NaOH/H₂O to give a carboxylic acid (13), which was then dechlorinated by a catalytic reduction and methylated with diazomethane to give an ester 13a (mp 126°). The ester was identical with the authentic sample 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 have the structure of the pyrazolo[1,5-b]pyridazine 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 6a 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 2 and other compounds 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.
REFERENCES AND FOOTNOTES

3. The alcohol showed a single melting point at ca. 130° when the bath temperature was raised rapidly.
7. The ring structure of the pyrazolo[1,5-b]pyridazines and the positions of the substituents have been supported by UV, 1H- and 13C-NMR, and mass spectroscopies and chemical data, for all the compounds 6-14.

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