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# THERMOLYSIS OF [1,2,4]TRIAZOLO[1,5-a]PYRIMIDINE N-YLIDES

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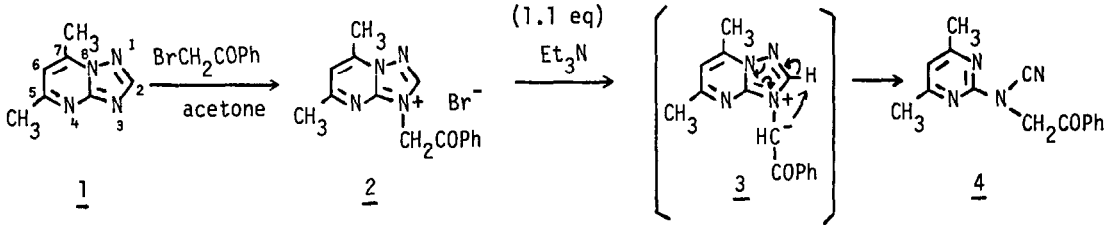
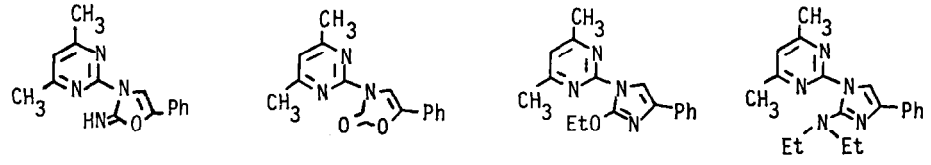
Abstract: 5,7-Dimethyl[1,2,4]triazolo[1,5-a]pyrimidinio-3-phenacylide (3) generated by the reaction of an iminium salt (2) with 1 eq. of triethylamine, underwent a new thermal ring cleavage of the triazole moiety to give the pyrimidine derivative. However reaction of 2 with 2 eq. of triethylamine afforded the 2-iminooxazoline derivative. The iminooxazoline reacted with nucleophiles such as alcohols or amines to give imidazoles.

Since [1,2,4]triazolo[1,5-a]pyrimidine skeleton has a bridgehead nitrogen, one can expect the new reactions different from those of the positional isomers of a nitrogen, adenine and guanine. We would like to report the thermolysis of 5,7-dimethyl[1,2,4]triazolo[1,5-a] pyrimidinio-3-phenacylide (3) and ring transformation reaction of a thermolysis product under acidic conditions. An iminium salt (2) which is a precursor of the ylide was prepared from 5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine (1)[1] and phenacyl bromide. Alkylation would occur at $N^3$- or $N^4$-position by reference to the known reactions.[2] The NMR spectrum of 2 showed a marked downfield shift of $C_2$-H ( $\delta$ 10.13 for 2 and $\delta$ 8.43 for 1 ). Therefore, it was determined that the $N^3$-position was alkylated.[3]

An ylide (3) was generated in situ from the iminium salt (2) and 1 eq. of triethylamine because the ylide (3) was unstable and could not be isolated. A solution of the ylide (3) in acetonitrile was refluxed for 0.5 h to give a pyrimidine derivative (4) in 35.0 % yield. The IR and NMR spectrum of 4 revealed the presence of a cyano, a phenacyl and the 4,6-dimethylpyrimidine groups.[4]




1 2 3 4




5 6 7 8

The triazole ring cleavage of [1,2,4]triazolo[1,5-a]pyrimidine has been reported in the glycosylation of N-trimethylsilyl-7-amino-5-chloro[1,2,4]triazolo[1,5-a]pyrimidine, but mechanism of the reaction has not been described.[5] Therefore, we attempted the thermal reaction of the iminium salt (2) in acetonitrile, but did not obtain the ring opening product (4). The thermal reaction of 2 with 1.1 eq. of triethylamine in acetonitrile was followed by the ESR measurement for elucidating the reaction mechanism. However, no radical was detected. Moreover 2-methyltriazolopyrimidinium salt having no $C_2$-H did not undergo the triazole ring cleavage. These facts supported that this reaction was initiated by the formation of ylide (3) and the thermolysis of the ylide (3) proceeded along the ionic abstraction of $C_2$-proton by the ylide carbanion followed by the $N^1$-$N^8$ bond cleavage to yield 4 .

On the other hand, when 2 was treated with 2.3 eq. of triethylamine, 2-iminooxazoline derivative (5)[4] was obtained in 64.4 % yield. This compoud 5 was also obtained from N-cyano-N-phenacylamino pyrimidine (4) by the treatment with 1.1 eq. of triethylamine in 72.5 % yield. This finding suggested that 4 formed from the ylide (3) was deprotonated by excess triethylamine to produce an enolate anion, which attacked at the carbon atom of the cyano group to cyclize into the oxazoline (5).

The 2-iminooxazoline (5) was converted to the 2-oxazolone derivative (6)[4] by acid hydrolysis in 69.7 % yield. The reaction of 5 with ethanol in the presence of p-toluenesulfonic acid gave imidazole derivative (7)[4] in 54.3 % yield. It has been known that treatment of oxazoles with ammonia ( or amines ) afforded imidazoles.[6] However it is interesting that 2-iminooxazoline (5) can be converted to imidazole derivatives without adding amines. This novel ring transposition reaction also occurred with diethylamine to yield 2-diethylamino imidazole derivative (8)[7] in 60.2 % yield.

Further studies are now under way on the reaction of this novel and reactive ylide with several electrophiles.

## References and Notes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3) $^1$H-NMR ($CDCl_3$, 60MHz) δ 10.13(s, 1H), 8.13-7.45(m,5H), 7.75(s, 1H), 6.60(s, 2H), 3.00(s, 3H), 2.75(s, 3H).

4) All of the products gave satisfactory elemental analysis and spectral data (IR, NMR, MS).

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7) MS (m/e): 321 ( $M^+$ ), $^1$H-NMR ($CDCl_3$, 60MHz) δ 7.93-7.24(m, 6H), 6.83(s, 1H), 3.30(q, 4H), 2.48(s, 6H), 1.18(t, 6H).


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