THERMOLYSIS OF TRIAZOLOPYRIMIDINE N-YLIDES AND THEIR REACTIONS WITH ELECTROPHILIC REAGENTS

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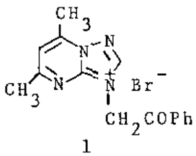
[1,2,4]Triazolo[1,5-a]pyrimidine derivatives were alkylated at N^3-position with alkyl halides in dry acetone. An iminium salt (1) thus synthesized was treated with triethylamine to form an ylide (2) in situ. Thermolysis of the ylide (2) gave a pyrimidine derivative (3) through N^1-N^8 bond cleavage. The compound (3) cyclized to the pyrimidinyl oxazoline (4) with triethylamine. Moreover this cyclic imino ether (4) underwent acid alcoholysis to give an imidazole derivative (5) and an acid hydrolysis to give a 2-oxazolone derivative (6).

Dimethyl fumarate, diphenylcyclopropenone, dimethyl acetylenedicarboxylate (DMAD) and methyl propiolate (MP) were used as electrophiles. In any case ordinary 1,3-dipolar cycloadition adducts were not obtained. For example the reaction of the ylide (2) with MP gave 1 : 2 adduct (7). The structure of 7 was confirmed by X-ray crystalloglaphy. A plausible mechanism of this novel transformation reaction is also discussed.



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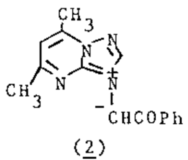

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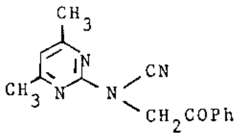

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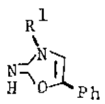

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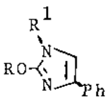

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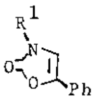

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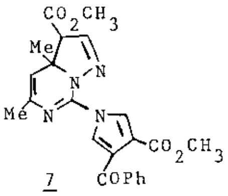

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R^1: 4,6-dimethyl-2-pyrimidinyl