RING CONTRACTION REACTION OF 1,3-OXAZIN-4-ONE DERIVATIVES

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The ring contraction reaction of 1,3-oxazin-4-one derivatives into 1,2,4-triazoles, pyrazoles, 1,2,4-oxadiazoles and isoxazoles was investigated.

Reaction of 2-aryl-6-methyl-4H-1,3-oxazin-4-one (1, aryl: C_6H_5, 2-pyridyl, 2-quinolyl) with hydrazines ($RNHNH_2$, R: H, CH_3, C_6H_5) exclusively brought about ring contraction into 5-acetonyl-3-aryl-1,2,4-triazole derivatives in satisfactory yields. Similar ring contraction took place when 2-alkyl-2-ethoxy-3,4-dihydro-6-methyl-2H-1,3-oxazin-4-one (2, alkyl: CH_3, C_2H_5, $C_6H_5CH_2$) was treated with $RNHNH_2$ giving 5-acetonyl-3-alkyl-1,2,4-triazole derivatives. In these reactions, use of hydroxylamine instead of $RNHNH_2$ led to the transformation of 1 and 2 into 5-acetonyl-2-aryl(or alkyl)-1,2,4-oxadiazole derivatives in good yields. The ring contraction reaction could be described to occur by an initial attack of the hydrazine or the hydroxylamine regioselectively on 2-position of the 1,3-oxazine ring.

On the other hand, treatment of 1 and 2 with hydrazine salts in place of hydrazine bases resulted in the formation of 3-acylamino-5-methylpyrazole derivatives. Similarly, reaciton of 1 and 2 with hydroxylamine hydrochloride yielded 3-acylamino-5-methylisoxazole derivatives in good yields. From the experimental finding, the ring contraction reaction into the pyrazole or the isoxazole could be concluded to proceed *via* 1,3-oxazinium salt as the intermediate, resulted from interaction between the 1,3-oxazine and the salt of hydrazine or hydroxylamine. Thus, the oxazinium salt undergoes the nucleophilic attack predominantly on the 6-position leading to the transformation into the pyrazole or the isoxazole.