

SYNTHESIS OF FIVE MEMBERED HETEROCYCLES INVOLVING N AND O ATOMS VIA  
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O-Acylation of methyl nitroacetate with acetyl chloride in N,N-dimethylacetamide (DMA) gave 3,4-bis(methoxycarbonyl)furoxane(3). The formation of (3) shows that this acylation involves intermediate nitrile oxide(2) which would result from the fragmentation of initial formed mixed anhydride(1). Then, in O-acylation of nitroethane with acetyl chloride in the presence of dimethyl fumarate as a dipolarophile, 4,5-bis(methoxycarbonyl)-3-methylisoxazoline(5a) was resulted in 44% yield through 1,3-dipolar cycloaddition. Reaction condition of this synthetic method was examined. From these information we attempted to synthesize several five membered heterocycles in the presence of various dipolarophiles as follows: 1) Using ethylenic compounds such as methyl acrylate as dipolarophiles: Isoxazoline derivatives(5a-1) were synthesized in good yields. Using ethyl  $\beta$ -nitrocrotonate: 4-Ethoxycarbonyl-3,5-dimethyl-4-nitroisoxazoline(5m) was isolated. The isoxazoline (5m) converted to 4-ethoxycarbonyl-3,5-dimethylisoxazole(6j) rapidly. 2) Using acetylenic compounds such as dimethyl acetylenedicarboxylate: Isoxazole derivatives (6a-i) were resulted in good yields. 3) Using benzylideneaniline and propylidenebutylamine: Isoxazoline N-oxide derivatives(7a and 7b) which appear to be formed through Michael additional condensation were obtained from methyl nitroacetate and phenylnitromethane respectively. Using benzylidenealkylamines: 1,2,4-Oxadiazoline derivatives(8a-n) were resulted in considerable yields. 4) Using benzaldoxime: 3,5-Diphenyl-1,2,4-oxadiazole(9a) which appear to be formed through dehydration of initial formed cycloadduct were obtained. Using aromatic nitriles: 1,2,4-Oxadiazole derivatives(9a-1) were afforded. 5) Using some ketones which have an electronattractive group: 1,4,2-Dioxazole derivatives(10a-d) were synthesized.