

RING EXPANSION REACTION OF 4-QUINAZOLINONES
TO 1,4-BENZODIAZEPINES

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During the course of study on the syntheses of 1-acyl, and 1-alkyl-3-aryl-4-oxo-1,2,3,4-tetrahydroquinazolines, we established simple methods for the preparations of 1,4-benzodiazepines by the ring expansion reactions of 4-quinazolinones. Treatment of 2-chloromethyl-3-aryl-4-oxo-1,2,3,4-tetrahydroquinazolines with sodium ethoxide in ethanol afforded 3-ethoxy-4-aryl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepin-5-ones in good yields. The mechanism of the reaction, which involves the formation of an intermediate, 4-phenyl-5-oxo-1,3,4,5-tetrahydro-2H-azirino-[1,2-a]quinazoline, and the subsequent ring cleavage of the aziridine moiety, was corroborated by the isolation of the intermediate. Reaction of 1-methyl-3-phenyl-4-oxo-3,4-dihydroquinazolinium bromide with diazomethane in ethanol gave 1-methyl-3-ethoxy-4-phenyl-5H-1,4-benzodiazepin-5-one in 68 % yield. The reaction may involve the intermediary formation of azirinoquinazolinium bromide. These reactions provided us with convenient methods for the syntheses of 1-acyl, and 1-alkyl-1,4-benzodiazepines.