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SYNTHESES OF HETEROCYCLIC COMPOUNDS VIA INTRAMOLECULAR BENZYNE REACTION AND PHOTOLYSIS OF N-SUBSTITUTED ENAMINONES

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Intramolecular arylations of a series of haloenaminones, prepared by reaction of appropriate primary amines with cyclic β-diketones, via benzyne reaction and photolysis were examined. Upon treatment of the N-phenyl enaminones with bromines at the 2' position with phenyllithium and diethylamine, halogen-metal exchange was preferentially occurred to give the corresponding dehalogenated products. When the N-phenyl enaminone with a bromine at the 3' position was treated with phenyllithium and piperidine, amination reaction proceeded via benzyne formation to give the 3'-piperidino derivative. Upon similar treatment with lithium diethylamide, the N-benzyl enaminones underwent intramolecular C-arylation via benzyne intermediates to give the 3,4-dihydro and 3,4,5,6-tetrahydro derivatives of 1(2H)-phenanthridone. In the competing formation between five- and seven-membered rings of the benzyne cyclization using the N-phenethyl analogs as substrates, N-arylation leading to five-membered ring predominantly occurred to give the indolines rather than the azepine ring formation.

When these haloenaminones were irradiated, homolytic N-arylation smoothly proceeded to yield the corresponding five- to seven-membered heterocyclic compounds.

In order to extend the synthetic utility of these cyclization reactions, 1,2,3,3a,4,5-hexahydro-1-(2-halogeno-4,5-methylenedioxybenzyl)indol-6-ones (1a and 1b) were treated with lithium diethylamide to give 3,3a,4,5,6,7-hexahydro-9,10-methylenedioxypyrrolo[3,2,1-de]phenanthridin-1(2H)-one (2). Air oxidation of 2 provided 3,3a,4,5-tetrahydro-9,10-methylenedioxypyrrolo[3,2,1-de]phenanthridine-1,7(2H)-dione (3) which have been appreciated as a key intermediate to α-anhydrodihydrocaranine and γ-lycorane. Compound 3 was also obtained by irradiation of haloenaminones 1a and 1b. Reduction of 2 with lithium aluminum hydride afforded (±)-α-dihydrocaranone and (±)-1-epi-γ-dihydrocaranine.