A NOVEL SYNTHESIS OF SUBSTITUTED INDOLES BY PHOTOCHEMICAL RING-CONTRACTION OF BENZ[d]-3,1-OXAZEPINES

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Quinoline 1-oxides upon photolysis (≳300 nm) in an aprotic solvent afforded the corresponding benz[d]-3,1-oxazepines in high yields (≳80%). While these oxazepines were believed to be stable for further photochemical reactions, we have found that 5-unsubstituted benz[d]-3,1-oxazepines and their 5-halogeno- or 5-carboxyl-derivatives afforded 3-formylindoles by photolysis (254 nm) in an appropriate condition. It is also found that the oxazepines having an alkyl or alkoxycarbonyl group at the 5-position gave the indoles having these substituents in their 3-position. It seems to be noteworthy that the oxazepines carrying a carboxyl or alkoxycarbonyl group at the 5-position were quite labile to ≥300 nm-rays and thus gave rise to these ring-contraction products from the corresponding N-oxides without isolating the corresponding oxazepines. The direct formation of indole derivatives was also possible from other quinoline 1-oxides if we irradiated them by 254 nm-rays from the beginning.

The intermediacy of 3H-indole species in these photochemical ring-contraction reactions of the oxazepines was demonstrated by an actual isolation of methyl 3-acetyl-2-phenyl-3H-indole-3-carboxylate by photolysis (254 nm) of methyl 3-methyl-2-phenylquinoline-4-carboxylate 1-oxide in acetonitrile. Furthermore, this 3H-indole afforded methyl 4- and 6-acetyl-2-phenylindole-3-carboxylates by irradiation with 254 nm-rays, and this provides the first example where a carbon unit in the 3-position of indole species rearranges to the 4- and 6-positions.

Since the syntheses of various quinoline 1-oxides are quite easy, the present results seem to open a new and convenient synthetic method of substituted indole derivatives from the N-oxides via the corresponding benz[d]-3,1-oxazepines.