

THE 1,3-DIPOLAR CYCLOADDITION OF SOME QUINOLINE N-OXIDES DERIVATIVES

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The 1,3-dipolar cycloaddition of some 3-substituted and 3,4-disubstituted quinoline N-oxides was examined in order to explore the effect of substituents on the reactivities of their N-oxide groups. It was first noticed that the reactivity was generally enhanced as compared with that of quinoline N-oxide itself. Further, the primary cycloadduct was found to undergo varied types of transformation depending upon the natures of substituents and 1,3-dipolarophile. Reactions of 3-bromo- (1), 3-bromo-4-nitro- (2), 3-bromo-4-methoxy-quinoline N-oxides (3) and others with phenyl isocyanate (A), enamines (B) and active acetylenes (C) are classified into six types, and the representative examples are shown below.

Type-I. The formation of primary cycloadduct: The reaction of 3 with methyl propiolate (C₁) and dimethyl acetylenedicarboxylate (C₂) gave primary adducts, 4a (33%) and 4b (22.5%). Type-II. The formation of 2-substituted product: Treatment of 3-piperidino-4-nitroquinoline N-oxide with A afforded 2-anilino-3-piperidino-4-nitroquinoline in 96% yield. Type-III. The formation of N-ylide (betaine): When a dioxane solution of 1 and C₂ was refluxed, product 5 was obtained in 66.5% yield. Type-IV. The formation of oxazolo[4,5-b]quinoline and furo[3,2-b]quinoline: Treatment of 1 and 3 with A afforded oxazolo-quinolines, 6a and 6b (10-15%). On the other hand, reactions of 2 with B smoothly occurred to give furo-quinolines 7 in good yields. Type-V. Reaction of 3-bromo- and 3-bromo-4-methoxy-quinoline N-oxides with enamines: Reactions of 1 and 3 with B gave not Type-IV compounds but instead 3-amino-2-substituted quinolines 8. Type-VI. The formation of 3-substituted product: Treatment of quinoline N-oxide with C₂ afforded a 3-substituted product 9.

