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

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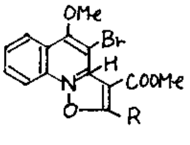
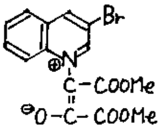
The 1,3-dipolar cycloaddition of some 3-substituted and 3,4-disubstituted quinoline N-oxides was examined in order to explore the effect of substituents on the reactivities of their N-oxide groups. It was first noticed that the reactivity was generally enhanced as compared with that of quinoline N-oxide 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 (**C_1**) and dimethyl acetylenedicarboxylate (**C_2**) 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 **C_2** 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 **C_2** afforded a 3-substituted product **9**.



4a : R=H
4b : R=COOMe



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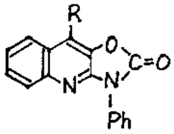
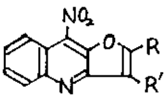
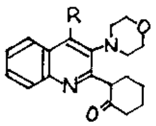


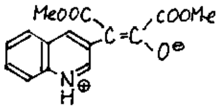
6a · R=H
6b : R=OMe



7
R,R'=H,Me,Et,$(CH_2)_4$



8
R=H,OMe



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