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# STUDIES ON KETENE AND ITS DERIVATIVES (LXIV)[1]

## REACTION OF DIKETENE WITH ACRIDINE N-OXIDE

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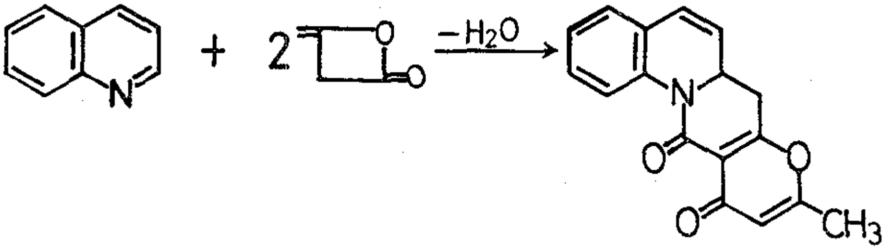
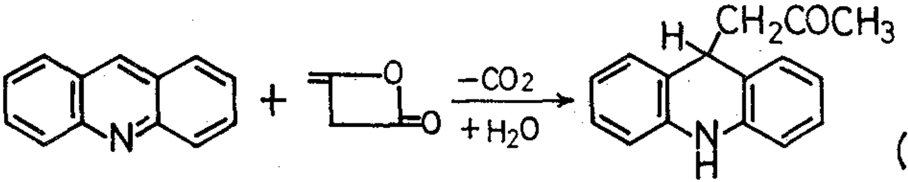
Acridine N-oxide reacts with diketene to give 9-acetonylacridine. A probable mechanism is discussed.

In the previous paper of this series, we have reported reaction of diketene with the C=N double bond in some aromatic heterocycles such as quinoline to give the Wollenberg type compound (1).[2]



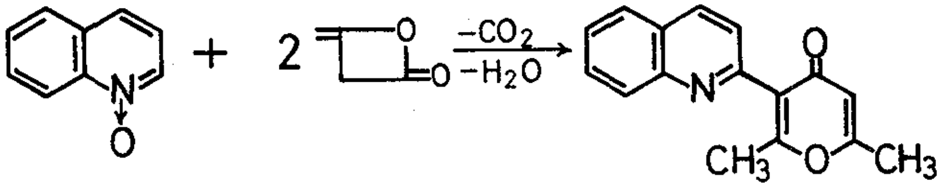
(1)

Also, we have reported that acridine, which has no hydrogen at α-position, underwent the reaction to give 9-acetonylacridane (2).[3]



(2)

On the other hand, quinoline N-oxide reacted with diketene to give 3-(2-quinolyl)-2,6-dimethyl-4-pyrone (3).[4)]



(3)

In the present paper we wish to report the reaction of diketene with acridine N-oxide to proceed in the same fashion as quinoline N-oxide to give 9-acetonylacridine (4).

A mixture of 500 mg of acridine N-oxide and 1 ml of diketene was stirred at room temperature. After five minutes, exothermic reaction with the evolution of carbon dioxide occured. Stirring for additional 15 minutes in the same condition, the mixture was condensed under reduced pressure. The oily residue was extracted with a mixture of petroleum benzin and ether (1:1). The extract was condensed in vacuo, and the crystalline residue was purified by recrystallization from anhydrous ether to give yellow needles of mp 142-143°, undepressed on admixture with an authentic sample (4) prepared according to the literature.[5)] Namely, acridine was allowed to react with acetone in sodium methoxide to give 9-acetonylacridane (2) which was then oxidized with chloranil in benzene to afford 9-acetonylacridine. Yield, 125 mg (21%). IR $_{max}^{CHCl_3}$ cm$^{-1}$: 2950, 1720(sh), 1710, 1625, 1610, 1554. Other data were reported in reference 3.

Although details of the mechanism of the formation of 9-acetonylacridine is not clear at present, likely pathways are proposed as follows:

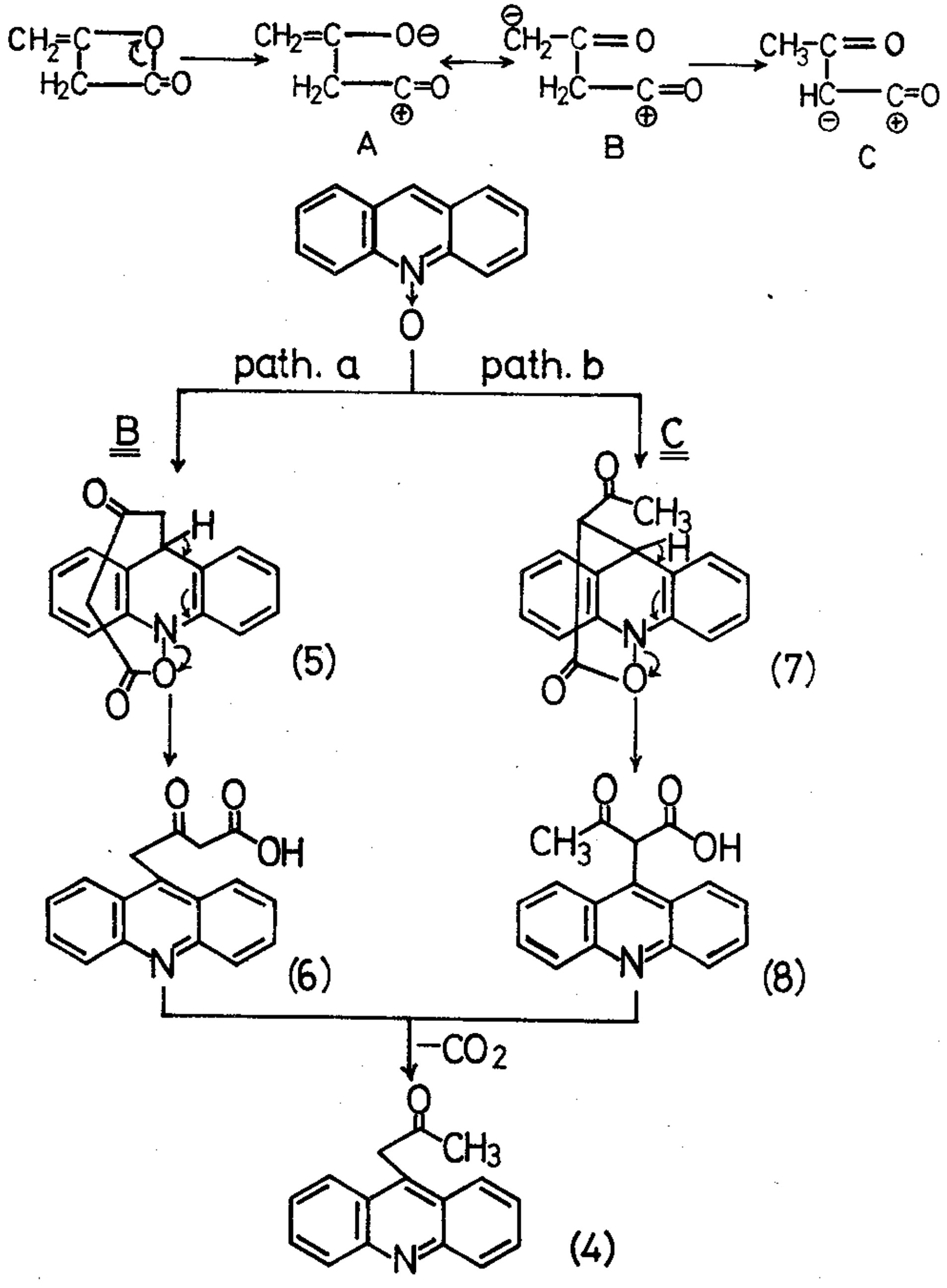


Chart 1

Among the ionic structures (A, B, and C), for convenience in symbolizing the reactivity of diketene in heterolytic addition reactions, two forms of **B** and **C** are supposed to be the participants in the reaction with acridine N-oxide. In this case two pathways **a** and **b** are suggested for the reaction mechanism as follows:

In pathway **a** addition of diketene, in **B** form, to 10-oxygen and 9-carbon of acridine N-oxide gives rise to debenzo-1-aza-2-oxabicyclo[5.2.2]undecane derivative (5) as an intermediate, which by prototropy can be converted to γ-(9-acridyl)acetoacetic acid (6), followed by decarboxylation to afford 9-acetonylacridine (4).

If addition reaction occurs through pathway **b**, involving **C** form of diketene, the intermediate should be dibenzo-1-aza-2-oxabicyclo-[3.2.2]nonane derivative (7), prototropy of which results in the formation of α-(9-acridyl)acetoacetic acid (8), followed by decarboxylation to give 4 as shown in chart 1.

REFERENCES

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