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Photochemical Reactions on Heterocyclic Compounds. 1. Nitration of Quinoline 1-Oxide with Nitrosyl Chloride and *n*-Butyl Nitrite

Quite few papers concerning free radical reactions on heterocyclic systems has been appeared in literature.[1] We planned to progress free radical reactions in more wide range of heterocyclic systems. Recently, we have reported[2] that 2-phenyl-4-nitroquinoline 1-oxide was obtained by the thermal reaction of 4-nitroquinoline 1-oxide and benzoyl peroxide, indicating the radical active position on 4-nitroquinoline 1-oxide was 2. Also it is well known fact that cyclohexane react with nitrosylchloride under influence of actinic radiation to produce cyclohexanone oxime.[3] On the basis of above two radical reactions, we attempted to synthesize 2-nitroquionoline 1-oxide. But 3-nitroquinoline 1-oxide was obtained instead of expected 2-nitroquinoline 1-oxide. The present communication deals with nitration of quinoline 1-oxide with nitrosyl chloride and *n*-butyl nitrite.

1) Nitration of Quinoline 1-Oxide with Nitrosyl Chloride

On visible rays irradiation in benzene solution at 80° for 2 hours, quinoline 1-oxide reacted with nitrosyl chloride and gave a yellow crystalline, m.p. 190~191° in yield of of 26%. It was identified as 3-nitroquinoline 1-oxide by infrared spectrum and mixed melting point with an authentic sample.[4] On the same reaction in the dark room at 80° for 2 hours, 3-nitroquinoline 1-oxide was obtained in yield of |17.9%. The yield of 3-nitroquinoline 1-oxide under various conditions are shown in Table I.

TABLE I.

Temp. (°C)	Mole ratios quinoline 1-oxide : NOCl	Yield of 3-nitroquinoline 1-oxide (%) visible rays	dark room
25	1 : 2	14.6	9.9
25	1 : 6	17.3	10.7
50	1 : 2	14.1	8.7
80	1 : 6	26.0	17.9

From the result that this reaction was accelerated by visible rays irradiation, it is proved that this nitration proceed through free radical mechanism. Two possible mechanisms for this reaction are shown in Chart 1.

According to the mechanism (B) in which NO radical attacks directly against quinoline 1-oxide, the product may be 2-nitroquinoline 1-oxide. But from the fact that 3-nitroquinoline 1-oxide was obtained, it is asumed that this reaction proceed through mechanism (A).

2) Nitration of Quinoline 1-Oxide with *n*-Butyl Nitrite

On visible rays irradiation in benzene solution at 80° for 2 hours, quinoline 1-oxide reacted with *n*-butyl nitrite to give a yellow crystalline, m.p. 190~191°, in poor yields, but in the dark room the reaction proceeded fairly good yields. It was identified

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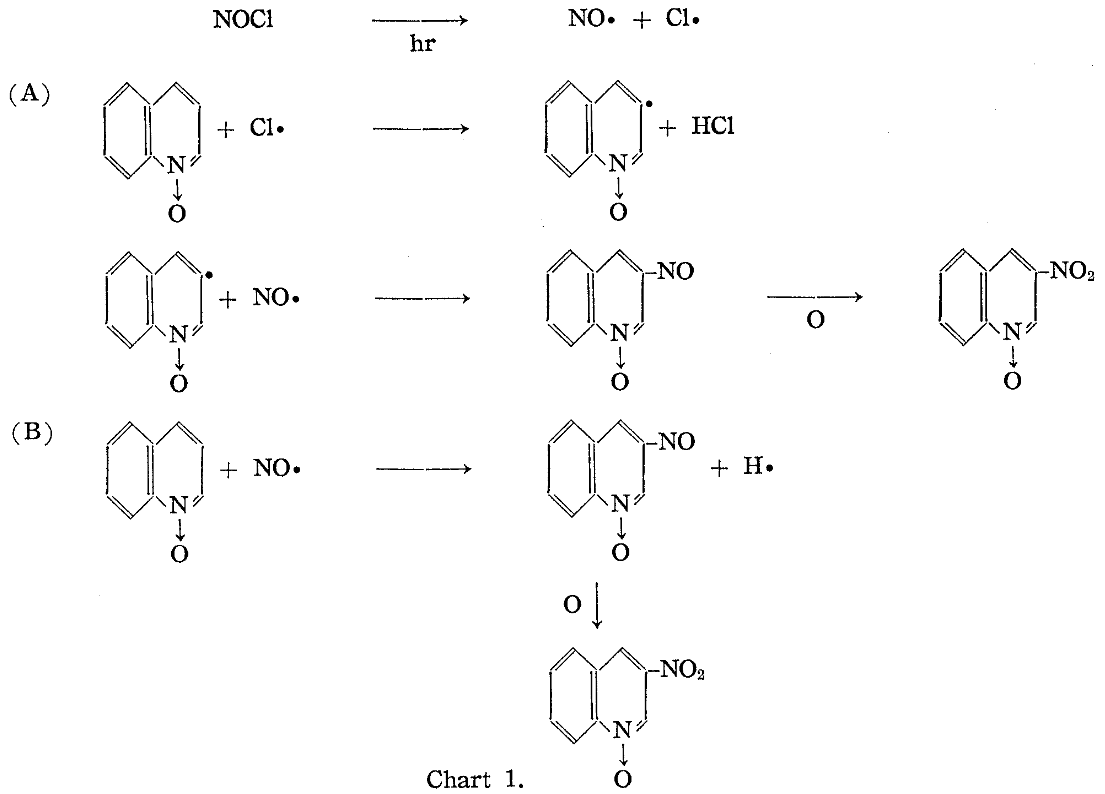

Chart 1.

Table II.

Temp. (C°)	Time (hr.)	Mole ratios quinoline 1-oxide : n-BuONO	Yield of 3-nitroquinoline 1-oxide (%) visible rays	dark room
25	2	1 : 2	0.7	1.7
80	2	1 : 4	1.7	9.0
25	35 days	1 : 4	—	10.7

as 3-nitroquinoline 1-oxide in comparison with an authentic sample. The yield of 3-nitroquinoline 1-oxide under various conditions are shown in Table II.

As shown in the above table, the yield of 3-nitroquinoline 1-oxide was diminished by visible rays irradiation, suggesting NO radical produced reacts rather fast with carbon in n-butyl nitrite than quinoline nucleus. This reaction may also be proceeded in free radical mechanism as the former.

Investigations for the scope and further classification of the free radical reactions on quinoline 1-oxide and 4-nitroquinoline 1-oxide being carried on by us.

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