Studies on Heteroaromaticity. XVII.[1] Photorearrangement of *N*-(2-Oxo-3-indolylidene)-aniline *N*-Oxides

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It is well known that the photochemical rearrangement of heterocyclic *N*-oxides is followed by ring-enlargement or -contraction,[2] but little has been reported on the similar reactions of exocyclic nitrones, though there are several papers published concerning their photochemical reactions.[3,4]

The present note deals with the experimental results of photochemical ring-enlargement of *N*-(2-oxo-3-indolylidene)-aniline *N*-oxide[5] (I), its 5,7-dibromo- (IV) and 5-nitro analog (VI), exocyclic ketonitrones of isatin and its analogs. The photochemical reactions of isatin itself[6] and isatin ylid[7] have been reported.

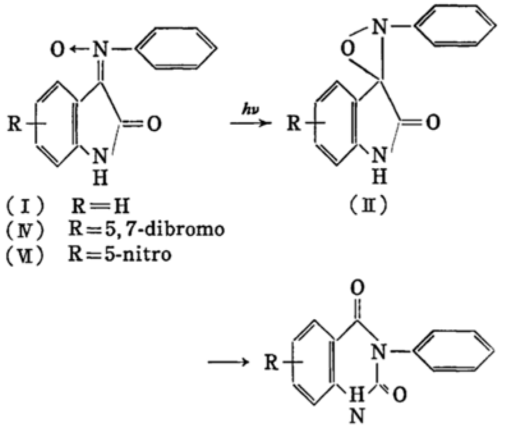
I was irradiated in tetrahydrofuran at room temperature with a 100 watt high pressure mercury lamp to afford III as colorless needles, which was identical with an authentic sample of 3-phenyl-2,4-(1*H*,3*H*)-quinazolinedione[8] in every respect.

Irradiation of some nitrones leads to the formation of the isomeric oxaziridines which are convertible to the corresponding amides[3] by further thermal or photochemical rearrangement and thermal rearrangement of some spiro-oxaziridines often gives the ring-enlarged lactams.[9] Considering above facts, it may be reasonably assumed that a spiro-type oxaziridine intermediate (II) might be involved in the present reaction, but several attempts to isolate II were unsuccessful.

Similar treatment of *N*-(5,7-dibromo-2-oxo-3-indolylidene)-aniline *N*-oxide (IV) afforded expected 6,8-dibromo-3-phenyl-2,4-(1*H*,3*H*)-quinazolinedione (V) in 13% yield, accompanied with III in 23% yield; other products were intractable tars.

It should be noteworthy that the formation of III from IV in this reaction has revealed occurrence of the photochemical elimination of two aromatic bromine atoms under the above reaction conditions; similar photochemical behaviors have been observed quite seldom,[10] except in some iodine-substituted aromatic compounds.[11]

Photolysis of *N*-(5-nitro-2-oxo-3-indolylidene)-aniline *N*-oxide (VI) only resulted in the formation of intractable tars under the same reaction conditions as described above.



(I) R=H
(IV) R=5,7-dibromo
(VI) R=5-nitro
(II)
(III) R=H
(V) R=6,8-dibromo

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[1] Part XVI of this series: T. Sasaki and T. Yoshioka, submitted to this Bulletin.

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Experimental[12]

Starting Materials. *N-(2-Oxo-3-indolylidene)-aniline N-Oxide (I).* This was prepared by the known method,[8] mp 218—220°C (decomp).

N-(5,7-Dibromo-2-oxy-3-indolylidene)-aniline N-Oxide (IV). To a solution of 2 g of 5,7-dibromoisatin[13] in 50 m*l* of ethanol was added 0.88 g of phenylhydroxylamine and the reaction mixture was refluxed on a water bath for 1 hr. After cooling, the precipitated crystals were collected and recrystallized from dioxane to afford 2.5 g (96%) of IV, mp 283—284°C.

Found: C, 42.62; H, 1.82; N, 7.27%. Calcd for $C_{14}H_8O_2N_2Br_2$: C, 42.44; H, 2.04; N, 7.07%.

N-(5-Nitro-2-oxo-3-indolylidene)-aniline N-Oxide (VI). This was prepared from 5-nitroisatin[14] and phenylhydroxylamine in the similar way as IV in 40% yield, mp 229—231°C.

Found: C, 59.60; H, 2.87; N, 14.92%. Calcd for $C_{14}H_9O_4N_3$: C, 59.38; H, 3.20; N, 14.84%.

Irradiation of I. A solution of 0.5 g of I in 80 m*l* of tetrahydrofuran was irradiated for 17 hr. After removing the solvent, the residue was treated with a small amount of ethanol and the insoluble products were recrystallized from ethanol to afford 0.255 g of white crystals, mp 287—289°C, which was identified to be III by infrared-spectroscopic comparison with a specimen prepared by the known method.[8]

Irradiation of IV. A solution of 0.5 g of IV in 100 m*l* of tetrahydrofuran was irradiated for 15 hr. After removing the solvent, the residual oil was dissolved in chloroform and chromatographed on a silica-gel column (17 g), using chloroform as an eluent. From the first fraction, 0.067 g (13%) of white needles, mp 238—241°C from methanol, was obtained; this was identified to be V from the elemental analysis and by comparison with a specimen prepared by the reported method[15] infrared-spectroscopically. From the second fraction, 0.13 g (23%) of III was isolated.

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[12] All melting points reported in this note were determined on a microhot stage and are not corrected. Microanalyses were carried out with a Yanagimoto C, H, N-Corder, MT-1 type.

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