45. On Hinopurpurins, the Rearrangement Products of Azohinokitiols (I).¹⁾

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One of the authors (Nozoe)^{2a)} previously assumed an unsaturated, seven-membered quinone-like structure (A) for the hinopurpurins (which he first called iso- or β -azohinokitiol), the rearrangement products of azohinokitiols. By later studies, it had become clear that the azo group in azohinokitiols, contrary to the case of halogenohinokitiols, is in the para position, and based on the facts that the azotropolones, which do not possess the isopropyl group in the meta position, do not undergo this rearrangement, that the light-colored leuco compounds obtained by catalytic reduction of hinopurpurins swiftly regain the original compounds by autoxidation in air, and that aromatic amines are invariably liberated in a small quantity by the rearrangement of azohinokitiols to hinopurpurins, he corrected the structure of hinopurpurins as in (B). No conclusive evidence has been obtained for this structure as yet.

By studies made in the present laboratory later, it had been confirmed that the azo compounds of m-methyl- and m-ethyl-tropolones⁴⁾, and azo compounds of α -thujaplicin⁵⁾ which is the o-isomer of hinokitiol, do not undergo this rearrangement. It had also been found that m-tert.-butyltropolone⁶⁾, due to its large steric hindrance, does not submit even to azo coupling. It is worthy of notice, therefore, that this hinopurpurin-type rearrangement is a reaction peculiar to azo compounds of hinokitiol, i.e. m-isopropyltropolone.

During the course of experiments to reexamine the structure of hinopurpurins, the present authors obtained a few observations which are described in this paper.

In order to determine the p-tropoquinonoid nucleus ^{2b)3)} assumed for hinopurpurin structure, o-phenylenediamine was applied on p-toluidido-hinopurpurin³⁾ (I) (B : X = CH₃), m.p. 244°, but only the unchanged original compound was recovered. However, heating (I) on a water-bath for 30 minutes to one hour with the calculated amount of hydroxylamine hydrochloride easily yielded a dioxime (II) (C : X = CH₃) as orange yellow, prismatic needles, m.p. 219° (Anal. Calcd. for C₁₇H₂₀O₂N₄ : N, 17.39. Found : N, 17.77). Recrystallization of (II) from glacial acetic acid gave purplish brown needles, m.p. 219° (Anal. Calcd. for C₁₇H₂₀O₂N₄ · CH₃CO₂H : N, 15.04. Found : N, 15.30). This easily liberates acetic acid at 140–150° and regains (II). Recrystallization from ethanol containing hydrochloric acid gives black needles, m.p. 204° (decomp.) (Anal. Calcd. for C₁₇H₂₀O₂N₄ · HCl : N, 16.06. Found : N, 16.31). (II) easily yields complex salts with various metals. Ni complex : Black, m.p. > 330° ; Cu complex : Black, m.p. > 330° ; Fe complex : Black, m.p. > 330° ; Zn complex : Reddish purple, m.p. 212–213°.

In exactly the same manner, p-bromoanilidohinopurpurin³⁾ (III) (B : X = Br), m.p. 236° (decomp.), also yields a dioxime (IV) (C : X = Br) of orange prismatic needles, m.p. 219° (Anal. Calcd. for C₁₆H₁₇O₂N₄Br : N, 14.85. Found : N, 15.03). (IV) also yields various metallic inner complex salts.

Only p-nitroanilidohinopurpurin³⁾ (V) (B : X = NO₂) yields a mono-oxime (VI) of reddish purple powder, m.p. > 350°, which is almost insoluble in various solvents, but is soluble in alkalis (Anal. Calcd. for C₁₆H₁₆O₂N₃ : N, 17.06. Found : N, 16.81).

From the above results, it seems almost doubtless that hinopurpurin possesses an o-diketone linkage, and that it contains a tropoquinonoid structure as shown by (B).

(I) remains entirely unchanged when heated to 100° with conc. hydrochloric acid but if heated to 150°, it yields p-toluidine (confirmed as a p-acetotoluidide). p-Toluidine is also liberated when (I) is dry distilled with soda lime or zinc dust. This makes it almost certain that (I) possesses a p-toluidine residue as shown in (B).

In order to confirm the imido and secondary amino groups in (B), acetylation, nitrosation, methiodination, and formation of ammonia by conc. sulfuric acid or conc. alkalis were attempted but all failed to give any positive result.

Application of one molecular equivalent of bromine on anilido-hinopurpurin³⁾ (VII) (B : X = H), m.p. 148°, yields a dibromide (VIII) as golden yellow scales with a metallic luster, m.p. 249–250° (Anal. Calcd. for C₁₆H₁₄O₂N₂Br₂ : C, 45.11 ; H, 3.31. Found : C, 46.10 ; H, 3.26).

Similar bromination of (I) also yields a monobromide (IX) of golden yellow scaly crystals of metallic luster, m.p. 222–223° (Anal. Calcd. for $C_{17}H_{17}O_2N_2Br$: Br, 22.12. Found: Br, 21.79). (IX) is not identical with p-toluidido-o'-bromohinopurpurin¹⁾ (X), m.p. 225°, their mixed m.p. being 207–210°. It is, therefore, assumed that the positions of the bromine atoms in (VIII) are at ortho and para and that of (IX) is at an ortho position to nitrogen in the benzene ring.

Treatment of (VII) in conc. sulfuric acid with a calculated amount of conc. nitric acid yields a mononitro compound (XI) as brownish purple needle microcrystals, m.p. > 330°. [Anal. Calcd. for $C_{16}H_{15}O_3N_3$: N, 13.41. Found: N, 12.99]. Use of an excess of conc. nitric acid gives a dinitro compound (XII) as dark brown needles, m.p. 246° (decomp.) (Anal. Calcd. for $C_{16}H_{14}O_6N_4$: N, 15.64. Found: N, 15.35). (I) also gives a dinitro compound²⁾ (XIII) of reddish orange prisms, m.p. 204° (decomp.), by an excess of conc. nitric acid (Anal. calcd. for $C_{17}H_{16}O_6N_4$: N, 15.05. Found: N, 15.32). In these nitration products, the nitro groups are assumed to be at similar positions to bromine atoms in (VIII) and (IX).

These experimental results can generally be explained by the structural formula as assumed in (B) but detailed confirmation must await further study. It is of course possible that (B) and (C) exist in tautomeric forms, respectively.

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