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The Preparation of 2-Oxo-1,2-dihydro-10a*H*-imidazo[1,2-*a*]-(1,2,5)-oxadiazo[3,4-*b*]indole from Isatin

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There are several studies in the literature concerned with isatin oximes. o-Cyanophenylisocyanate was obtained from isatin-β-oxime[1] by treating it with phosphorus pentachloride and also from *N*-asetylisatin dioxime.[2] Previous workers[3] have shown that the pyrolysis of isatin-β-oxime resulted in decomposition, yielding o-aminobenzonitrile.

In connection with our continuing interest in the reaction of isatin derivatives,[4] we have obtained a new tetracyclic compound from *N*-acetylisatin dioxime.

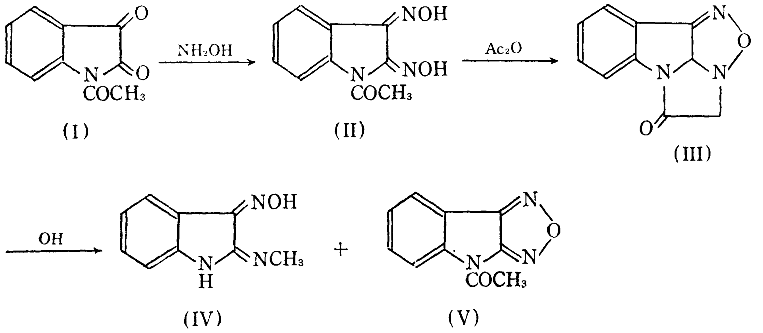
N-Acetylisatin dioxime (II), prepared from *N*-acetylisatin (I), was heated in acetic anhydride. A crystallizable compound, accompanied with uncontractable tars, was obtained in a low yield from the reaction mixture. Results of the elemental analysis and the mass spectra of the compound (III) supported the idea of the structure of $C_{10}H_7N_3O_2$ (*m/e* 201). The IR spectra (KBr) showed a C=O stretching frequency at 1810 cm^{-1}, but no NH or OH absorptions. The proton resonance (in DMSO-d_6) was observed at τ 1.7—2.4 (m, 4H), 5.92 (s, 1H), and 7.28 (s, 2H). Thus, the structure of III was established by these data to be the cyclized compound, 2-oxo-1,2-dihydro-10a*H*-imidazo[1,2-*a*]-(1,2,5)-oxadiazo[3,4-*b*]indole, which is a heterocycle with a new ring system.

The treatment of III with potassium hydroxide at room temperature afforded two crystalline compounds. The major product (IV) (45% yield) showed the NMR spectra (in DMSO-d_6) of methyl and oxime protons at τ 7.72 (s, 3H) and −0.18 (s, 1H) respectively, but no NH proton. However, the sharp absorption at 3340 cm^{-1} in the IR spectra (KBr) was apparently due to NH streching, along with the absorption at 3030—2700 cm^{-1} (OH) and 1635 cm^{-1} (C=N). The identification of IV as 3-hydroxyimino-2-methyliminoindoline was based on these data and the analytical value of $C_9H_9N_3O$ (*m/e* 175). IV must be a result of the scission of the imidazole skeleton of III, followed by decarboxylation.

The structure of the minor product (V) (8% yield) was established to be 4-acetyl-(1,2,5)-oxadiazo[3,4-*b*]indole, whose analogous compounds have not yet been synthesized, by the following data; NMR (in DMSO-d_6) τ 1.6—2.5 (m, 4H) and 7.28 (s, 3H); IR (KBr) 1800 cm^{-1} (C=O) 1640 cm^{-1} (C=N) and no NH or OH absorption; elemental analysis $C_{10}H_7N_3O_2$; mass spectral molecular ion at *m/e* 201.

Experimental

2-Oxo-1,2-dihydro-10a*H*-imidazo[1,2-*a*]-(1,2,5)-oxadiazo[3,4-*b*]indole (III). Two grams of *N*-acetylisatin dioxime were added to 20 m*l* of acetic anhydride,



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[1] W. Borsche and W. Sander, *Ber.*, **47**, 2815 (1914).

[2] E. Beckmann and E. Bark, *J. Prakt. Chem.*, [**2**] **105**, 227 (1923).

[3] a) W. Borsche, H. Weussmann and A. Fritzsche, *Ber.*, **57B**, 1149 (1924); b) G. Bargellini and C. J. Turi, *Gazz. Chim. Ital.*, **84**, 157 (1947); c) G. R. Bedford and M. W. Partridge, *J. Chem. Soc.*, **1959**, 1633.

[4] a) T. Sasaki and M. Takahashi, This Bulletin, **41**, 1967 (1968); b) T. Sasaki and M. Takahashi, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 899 (1968).

and the mixture was heated at 120°C for 1 hr. Then the solution was poured into 100 m*l* of water, and, after several hours, the aqueous solution was then washed with water, and, after the solvent had been removed, the residue was washed with a small amount of MeOH, giving white solids (31—10% yield). White needles, mp 233—234°C, after recrystallization from MeOH. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ(ε) 260 (7900), 274 (5900), 284 (5500), 316 (4700), 330 (4400).

Found: C, 59.66; H, 2.99; N, 20.71%. Calcd for $C_{10}H_7N_3O_2$: C, 59.73; H, 3.50; N, 20.90%.

3-Hydroxyimino-2-methyliminoindoline (IV) and 4-Acetyl-(1,2,5)-oxadiazo[3,4-*b*]indole (V). To a stirred solution of 20 m*l* of 5% KOH (H_2O : MeOH–1 : 1), 660 mg of III were added, after which the mixture was stirred for 2 hr at room temperature. Then the solution was neutralized with dilute HCl. After the solution which contained the resulting precipitate had been extracted with 50 m*l* of $CHCl_3$, the materials insoluble in both layers were gathered by filtration to give 262 mg of IV (45% yield), mp 198—201°C; white powder after recrystallization from MeOH. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (ε) 252 (57000), 261 (51000), 318 (26000).

Found: C, 61.72; H, 5.11; N, 23.72%. Calcd for $C_9H_9N_3O$: C, 61.75; H, 5.16; N, 24.00%.

The $CHCl_3$ solution was evaporated, and the crude residue was chromatographed on silica gel. Elution with $CHCl_3$ gave 56 mg of V (8% yield), mp 195—197°C, from MeOH. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε) 236 (17000), 244 (23000), 250 (19000), 294 (4700), 305 (4400), 320 (2900).

Found: C, 59.77; H, 3.64; N, 21.22%. Calcd for $C_{10}H_7N_3O_2$: C, 59.73; H, 3.50; N, 20.90%.

I wish to thank Professor Tadashi Sasaki for his valuable discussions and for the measurement of the NMR and mass spectra.