

were recrystallized from a benzene-dioxane mixture, yielding 1.5 g (29 %) of 2-carboxy-3-thiopheneboronic acid, m.p. 159.5–162.5°C (decomp.). NMR (dimethyl sulphoxide): τ_5 2.22; τ_4 2.56; $\tau_{\text{COOH,B(OH)_2}}$ 1.98; J_{45} 5.0 c/s [Found: C 35.69; H 3.16. Calc. for $\text{C}_5\text{H}_5\text{BO}_4\text{S}$ (172.0): C 34.92; H 2.93].

3-Hydroxy-2-thiophenecarboxylic acid. 6 ml of 10 % hydrogen peroxide solution was added drop-wise to 1.48 g (0.0086 mole) of 2-carboxy-3-thiopheneboronic acid dissolved in 85.8 ml 0.1 N sodium hydroxide solution and stirred for 3 h at 36°C. After cooling, ether and 10 ml of 1 N hydrochloric acid were added. The aqueous layer was extracted three times with ether. The combined ether extracts were dried over magnesium sulphate and the ether was removed *in vacuo* under nitrogen yielding 0.77 g (62 %) of crude 3-hydroxy-2-thiophenecarboxylic acid, which was sublimed *in vacuo*, m.p. 102–110°, literature value² m.p. 108°. NMR (acetone): τ_4 3.25; τ_5 2.38; $\tau_{\text{OH,COOH}}$ 1.85; J_{45} 5.6 c/s.

3-Hydroxy-2-thiophenealdehyde. 30 ml of 10% hydrogen peroxide solution was added dropwise with stirring during 15 min to a suspension of 3.12 g (0.020 mole) of 2-formyl-3-thiopheneboronic acid² in 100 ml of ether. The mixture was refluxed for 3.5 h, the ether phase was washed four times with 20 ml of water and dried with MgSO_4 . Removal of the ether *in vacuo* left 1.39 g (54 %) of a dark-brown crystalline residue which was sublimed *in vacuo* (10 mm Hg, 60°C), yielding colourless crystals, m.p. 88–89.5°C. NMR (acetone): τ_5 2.21; τ_4 3.18; τ_{CHO} 0.13; J_{45} 5.2 c/s; $J_{\text{CHO-5}}$ 0.8 c/s. [Found: C 47.08; H 3.20; S 24.57. Calc. for $\text{C}_5\text{H}_4\text{O}_2\text{S}$ (128.2): C 46.86; H 3.15; S 25.02].

3-Hydroxy-4-thiophenealdehyde. 4-Formyl-3-thiopheneboronic acid² was treated with hydrogen peroxide and worked up as described above. However, as the product rapidly decomposed to a resin, when the ether was removed, its NMR-spectrum was run in a concentrated ether solution. NMR (ether): τ_2 3.66; τ_5 1.94; τ_{CHO} 0.14; J_{25} 4.0 c/s; $J_{\text{CHO-2}}$ 0.8 c/s.

NMR-spectra were obtained as described earlier.²

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Photochemical Studies

IV. Photochemical Reactions of 2-Methylquinoline N-oxide Hydrate

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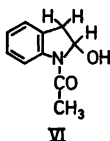
The recent report by Ishikawa, Yamada and Kaneko¹ on the photochemical transformation of 2-methylquinoline N-oxide (I) to a mixture of N-methylcarbo-styryl (II), 3-methylcarbo-styryl (III), N-acetylundole (IV), and 2-methylquinoline (V) in methanolic solution prompts us to report a novel type of photochemical reaction of 2-methylquinoline N-oxide.

In a typical run, 2-methylquinoline N-oxide dihydrate (5.0 g), dissolved in benzene (4.0 l), was irradiated (Hanovia 700 W, medium pressure mercury lamp, and Pyrex filter) for 15–20 h at ca. 20°.

Column chromatography on neutral aluminium oxide yielded as the first fraction an oil (0.86 g) which, by thin-layer chromatography, was shown to consist of largely 2-methylquinoline (V) with minor amounts of N-acetylundole (IV) and some other compounds which were not identified. Subsequent elution gave, as a second

fraction, a crystalline compound VI. M.p. 157–159°; (3.0 g, 66 %).^{*} (Found: C 67.75; H 6.24; N 8.05; M.w. (vapour pressure lowering in dioxane) 191. Calc. for C₁₀H₁₁NO₂: C 67.78; H 6.26; N 7.91; M.w. 177). Dipole moment in benzene, 3.25 D.

On the basis of its spectroscopic and chemical behaviour we assign VI the structure shown below *i.e.* *N*-acetyl-2-hydroxy-2,3-dihydroindole.



The UV-spectrum ($\lambda_{\text{max}}^{\text{EtOH}} = 247 \text{ m}\mu$, $\log \epsilon = 4.15$) was very similar to the UV-spectrum of 3,4-dihydrocarbostyryl.² The IR-spectrum (in KBr) showed an OH absorption at 3355 cm^{-1} and a C=O absorption at 1640 cm^{-1} . The aliphatic ring protons of VI appeared in the NMR-spectrum as an ABX system with a doublet at 4.16τ ($J_{\text{AX}} = 7 \text{ cps}$; $J_{\text{BX}} = 0$; 1H), a doublet of doublets at 6.62τ ($J_{\text{AX}} = 7 \text{ cps}$; $J_{\text{AB}} = 17 \text{ cps}$; 1H) and a doublet at 7.15τ ($J_{\text{AB}} = 17 \text{ cps}$; $J_{\text{BX}} = 0$; 1H). By irradiation at the center of the doublet at 4.16τ , while scanning the spectrum, the doublet of doublets coalesced to a doublet with $J = 17 \text{ cps}$. In the mass spectrum of VI the m/e 177 ion was absent. The mass spectrum of VI was very similar to that of *N*-acetylindole, showing the same pattern but with slightly different intensities (Table 1). This is probably due to loss of H₂O from the molecular ion of VI.

Table 1. Mass spectra. (Most abundant ions). Atlas CH₄. Electron energy 70 eV. Ion source temp. 250°. Vapor temp. 150°.

m/e	VI	<i>N</i> -acetyl-
	%	indole %
159	23	29
117	100	100
90	24	18
89	16	12
63	7	4
43	14	7

^{*} Yield of crystalline material varied much from run to run.

Compound VI was found to be very sensitive towards acids and bases. Acid hydrolysis yielded an oil which, by column chromatography, was separated into indole and *N*-acetylindole.^{*} When a solution of compound VI in *N* sodium hydroxide was refluxed, an oil separated which was found, by thin-layer chromatography, to consist of at least seven substances. Oxidation of VI with a dilute aqueous solution of potassium permanganate and sodium hydrogen carbonate yielded *o*-acetamidophenylacetic acid.^{*}

We have reinvestigated³ the photolysis of 2-methylquinoline *N*-oxide in aqueous solution at a very low concentration (*ca.* 10^{-3} M). Under these conditions we found, by thin-layer chromatography, that I was converted mainly to III and VI.

The effect of solvent and hydration on the photochemistry of quinoline *N*-oxides poses an interesting problem. In the literature, it has been reported that a seemingly similar effect exists for the photochemistry of quinoxaline *N,N*-dioxide,⁴ and it is known that the quantum yields in the photochemistry of some nitrones⁵ are dependent on the extent of hydrogen bonding. Additional work designed to clarify the preparative possibilities and the mechanistic problems of the photochemistry of quinoline *N*-oxides is in progress.

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^{*} The IR-spectra of these compounds were identical with the spectra of authentic samples.