volumes of methylene chloride, dried, and evaporated to dryness *in vacuo* to afford 37.55 g (86%) of a red-brown semisolid. Analysis by glpc on a 2% SE 30, 6-ft column starting at 100° and temperature programmed at 30°/min, showed that only *ca.* 2.6% of the starting material was present after stirring overnight at room temperature and that the ratio of 5-nitro(1)/4-nitro(2) was approximately 3.6:1. Only *ca.* 5% of volatile side products were detectable. The crude mixture was triturated with 150 ml of carbon tetrachloride and then filtered to leave, predominantly, 5.89 g of **2**, mp 80–125°. Recrystallization from methanol gave two fractions, 3.71 g (mp 133–136°) and 1.35 g (mp 125–132°).

Anal.[18] Calcd for $C_4H_4N_2O_2S$ (**2**): C, 33.32; H, 2.80; N, 19.43; S, 22.24. Found: C, 33.24; H, 2.97; N, 19.30; S, 22.10.

The carbon tetrachloride filtrate was evaporated to dryness *in vacuo*, the residue was redissolved in methylene chloride, the solution was decolorized with activated carbon and evaporated to dryness, and the solid was recrystallized from methanol to give 9 g of **1**, mp 70–72°. Subsequently, 11.98 g of lower melting fractions (mp 58–71°) were obtained by work-up of mother liquors. The combined isolated yield was 59.5%.

Anal.[18] Found for **1**: C, 33.37; H, 2.98; N, 19.54; S, 22.11.

Similarly, 2-methylthiazole hydrochloride afforded a 54% yield of mixed product but the 1:2 ratio was 2.8:1.

B. Mixed Acids.—To 7 ml of 20% fuming sulfuric acid at 20°, 1.7 g (93% pure by glpc, 1.6 mmol) of 2-methylthiazole was added and the mixture was heated to 100° before 2 g of potassium nitrate was gradually added. At the end of the addition the temperature was 170°, and, at this point, 1 ml of fuming nitric acid was added. The temperature was then kept at 180–197° for 18 hr. Glpc analysis (on a 6-ft, 10% SF 96 column[19]) of a 1-hr sample which had been basified, extracted, and dried over magnesium sulfate indicated a 1:2 ratio of 1:2; after 18 hr. Compound **2** was detected but **1** was no longer detectable. In a similar run using concentrated nitric acid instead of fuming nitric acid a 0.5-hr sample showed a 1:2 ratio of 5:4.

2-[2-(5-Nitro-2-thiazolyl)vinyl]pyridine (3). A. Condensation Method.—In 15 ml of 1-propanol containing 0.5 ml of piperidine, 2 g (14 mmol) of 2-methyl-5-nitrothiazole was refluxed with 3 g (28 mmol) of 2-pyridinecarboxaldehyde for 1 hr. The mixture was cooled and the solid was collected and washed with cold methanol to give 2.12 g (65%) of product, mp 179–181°. Recrystallization from methanol afforded yellow crystals: mp 181.5–183°; ir spectrum (Nujol), 3050, 1500, 1350, and 980 (*trans* H?) cm^{-1}. The AB quartet for the olefinic protons could not be resolved in deuterated chloroform on the Varian Model A-60 nmr instrument.

Anal. Calcd for $C_{10}H_7N_3SO_2$: C, 51.49; H, 3.03; N, 18.02; S, 13.75. Found: C, 51.22; H, 3.16; N, 17.97; S, 13.59.

B. Meerwein Reaction.—To 450 ml of concentrated hydrochloric acid and 100 ml of water, 145 g (1 mol) of 2-amino-5-nitrothiazole was added and the slurry was cooled to about −70°. To this mixture, 69 g (1 mol) of sodium nitrite in 100 ml of water was introduced over a 0.5-hr period to give a pale green mixture. After an additional 10 min of stirring, 160 g (1.52 mol) of 2-vinylpyridine in 600 ml of acetone was added rapidly while the temperature was kept below −30°. Cupric chloride dihydrate (28 g) was then added and the mixture was stirred for 10 min before it was allowed to rise to room temperature. At −10° the green mixture became reddish and evolution of nitrogen was vigorous. After cessation of nitrogen evolution, the mixture was added to 500 ml of water. The mixture was neutralized with sodium bicarbonate, methylene chloride was added, the mixture was filtered, and the organic phase was separated. The aqueous layer was further extracted with methylene chloride, the combined organic phases were dried over magnesium sulfate and then evaporated to dryness *in vacuo* to give a viscous mixture. This was triturated with methanol and filtered to give 25.3 g of product, mp 179–182°. An additional 6 g of crude product was obtained from the methanol filtrate. Purification of products from chloroform and decolorization with activated carbon gave 25.43 g (10.5%) of yellow product, mp 180–183°, which was identical (infrared spectrum and melting point) with that obtained by the condensation reaction (*vide supra*).

(18) The analytical samples from earlier runs melted at 134–136° (hexane) for **2** and 70.5–72.5° (hexane) for **1**.

(19) The column temperature was set at 120° and then abruptly reset at 250° after 2-methylthiazole passed through the column in order to get well-defined, reproducible peaks.

Registry No.—2-Methylthiazole, 3581-87-1; **1**, 16243-71-3; **2**, 16243-72-4; **3**, 16243-73-5.

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The Revised Structure of the Condensation Product of N-(*p*-Methoxyphenyl)anthranilic Acid with Formamide

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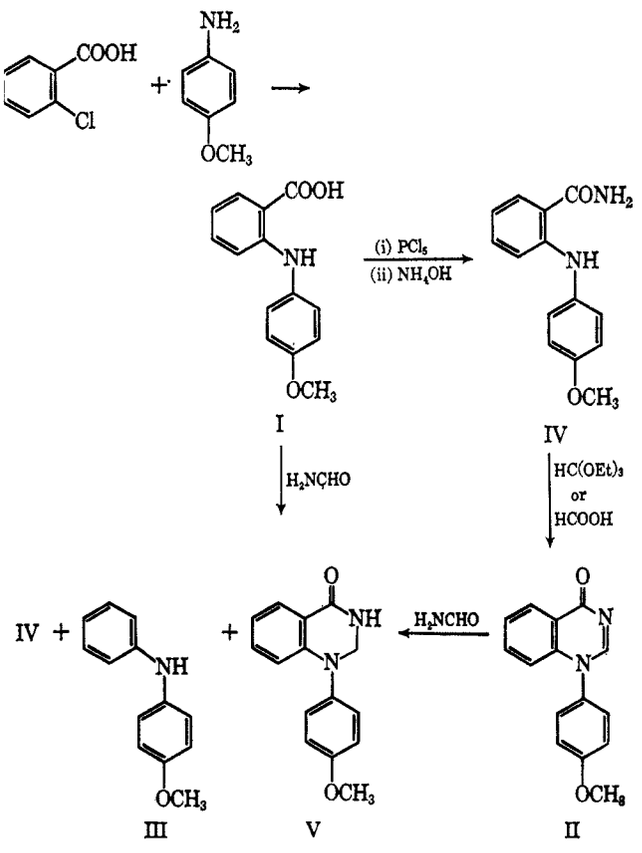
In an attempt to synthesize 1-aryl-1H-quinazolin-4-ones following the general route[1] to the synthesis of their 1-alkyl analogs, Mukherjee, *et al.*,[2] condensed N-(*p*-methoxyphenyl)anthranilic acid (I) with formamide and reported a product to which they assigned the structure II. The same experiment in our hands gave a mixture of three products (Chart I), *viz.*, 4-methoxydiphen-

CHART I



ylamine (III) and 2-(*p*-methoxyanilino)benzamide (IV) and a third one which was proven identical in all respects (melting point, mixture melting point, and uv, ir, and nmr spectra) with the compound believed to have

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the formulation II. But on the basis of the mass spectrometrically derived molecular weight (M^+ 254), elemental analysis, and nmr proton count (14 H), the molecular formula of the compound had to be revised as $C_{15}H_{14}N_2O_2$, instead of $C_{15}H_{12}N_2O_2$ suggested by the previous workers.[2]

The uv spectrum of the compound [λ_{max}^{EtOH} 280 (log ϵ 3.99) and 342 mμ (log ϵ 3.71)] resembled that of 2-(*p*-methoxyanilino)benzamide rather than that of 1-phenyl-1H-quinazolin-4-one[3] and the ir spectrum showed a strong NH band at 3226 cm^{-1}. These observations and the fact that the nmr spectrum lacked the C-2 proton signal[3,4] of quinazolin-4-ones and instead exhibited a two-proton signal at δ 5.25, led us to propose the tetrahydro structure V. The mass spectrum of the compound which showed characteristic peaks at M − 29 and at *m/e* 210 and 182 presumably due to the sequential expulsion of the groups CH_2–NH, $-CH_3$, and C=O also provides tenuous support for the formulation V. The formation of V, instead of II seems to involve the reduction of II as the obligatory intermediate by hydride transfer from formamide molecules,[5] a contention which received experimental verification by the formation of V as the sole product on heating II (formed by condensation of 2-(*p*-methoxyanilino)benzamide with ethyl orthoformate) with formamide at 170–180°.

Experimental Section

The melting points were determined on the Kofler block and were uncorrected. The ultraviolet absorption spectra were measured in 95% ethanol (aldehyde free), the ir spectra were taken on a KBr disk unless otherwise stated. The analytical samples were dried at 80° over P_2O_5 for 24 hr *in vacuo*. Anhydrous sodium sulfate was used for drying organic solvents and for column chromatography; Brockmann alumina was used throughout.

N-(*p*-methoxyphenyl)anthranilic acid (I) was prepared by Ullmann condensation of *o*-chlorobenzoic acid with *p*-anisidine in presence of anhydrous potassium carbonate and activated copper powder. The product was crystallized from methanol as pale yellow needles: mp 182–183°, ν_{max} 3278, 2985, 2597, 1652, and 900 cm^{-1}; λ_{max}^{EtOH} 288 mμ (log ϵ 3.97) and 333 mμ (log ϵ 3.54); nmr ($CDCl_3$), δ 3.68 (s, 3 H), 6.02–7.28 (m, 8 H), 7.66 (d, 1 H, J = 6 cps) and 8.60 (NH, W_H = 12 cps).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.35; N, 5.76; O, 19.75. Found: C, 69.20; H, 5.27; N, 5.80; O, 19.89.

2-(*p*-Methoxyanilino)benzamide (IV) was synthesized according to the method of Blatter, *et al.*,[3] starting from I. The crude solid was crystallized from methanol as light yellow needles: mp 128–130°; ν_{max} 3508, 3322, and 1669 cm^{-1}; λ_{max}^{EtOH} 284 (log ϵ 3.97) and 342 mμ (log ϵ 3.61); nmr ($CDCl_3$), δ 3.82 (s, 3 H), 6.42 (NH_2, W_H = 20 cps), 6.56–7.60 (m, 8 H) and 9.5 (NH, W_H = 15 cps).

Anal. Calcd for $C_{14}H_{14}O_2N_2$: C, 69.42; H, 5.78; N, 11.56; O, 13.22. Found: M^+ 242; C, 69.61; H, 5.97; N, 11.58; O, 13.54.

1-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydroquinazolin-4-one (V).—Compound I was heated with 3–4 equiv of formamide in a sealed tube at 150–160° for 4 hr following exactly the method reported by Mukherjee, *et al.*[2] The residue was chromatographed. 4-Methoxydiphenylamine (III), obtained from the earlier fractions of the petroleum ether (60–80°) eluate, crystallized from petroleum ether as white needles (32% yield), mp 104–105° (lit.[6] mp 105°). Later fractions of the petroleum ether eluate furnished pale yellow needles (22% yield), mp 130° from benzene, and it was found to be identical in all respects (melting point, mixture melting point, and uv, ir, and nmr spectra) with IV. The major product (V), obtained from the chloroform eluate, crystallized from methanol as white rods (30% yield): mp 186°; ν_{max} 3226, 1681, and 1628 cm^{-1}; nmr ($CDCl_3$), δ 4.11 (s, 3 H), 5.25 (d, 2 H, J = 3 cps), 6.88–7.78 (7 H), 8.00 (NH, W_H = 15 cps) and 8.33 (d, 1 H, J_1 = 8 cps, J_2 = 2 cps).

Anal. Calcd for $C_{15}H_{14}O_2N_2$: C, 70.86; H, 5.51; N, 11.02; O, 12.59. Found: M^+ 254; C, 70.27; H, 5.73; N, 10.91; O, 12.82.

1-(*p*-Methoxyphenyl)-1H-quinazolin-4-one (II). A.—A mixture of 2-(*p*-methoxyanilino)benzamide (0.5 g) and ethyl orthoformate (5 ml) in diethylene glycol (5 ml) was heated at 120° for 15 hr. Excess of ethyl orthoformate was removed under reduced pressure and the residue was taken in chloroform and extracted with 5 *N* HCl. Acid extract was basified with ammonia and extracted with ether. Ether extract was washed, dried, and distilled. The residue was crystallized from acetone as white granules (0.3 g): mp 186–188°; ν_{max} 1642 and 1589 cm^{-1}; λ_{max}^{EtOH} 235 mμ (log ϵ 4.47), 280 (3.88), 304 (4.08) and 314 (4.0); nmr ($CDCl_3$), δ 3.96 (s, 3 H), 7.20 (d, 2 H, J = 9 cps), 7.36 (m, 3 H), 7.49 (d, 2 H, J = 9.0 cps), 8.33 (s, 1 H), and 8.38 (doublet of doublets, J_1 = 8.5 cps, J_2 = 2 cps).

Anal. Calcd for $C_{15}H_{12}O_2N_2$: C, 71.42; H, 4.76; N, 11.11; O, 12.69. Found: M^+ 252; C, 71.29; H, 4.88; N, 11.34; O, 12.99.

B.—A solution of IV (0.5 g) in formic acid (10 ml) was heated in a sealed tube at 110–120° for 24 hr. Excess formic acid was removed under reduced pressure and worked up as before. The crude product was chromatographed. The solid, obtained from the benzene–chloroform (1:1) eluate, crystallized from acetone as white granules (0.07 g), mp 186–188°. It was found to be identical in all respects (melting point, mixture melting point, tlc, and uv, ir, and nmr spectra) with II.

Conversion of II into V.—Compound II was heated with 6–8 equiv of formamide at 170–180° for 5 hr. Excess formamide was removed under reduced pressure and the residue was crystallized from methanol into white rods (92% yield), mp 186°. It was found to be identical with V in all respects (melting point, mixture melting point, tlc, and uv, ir, and nmr spectra).

Registry No.—I, 13501-67-2; II, 16328-59-9; IV, 16328-60-2; V, 16328-61-3.

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Benzyne Formation by Desulfamylation

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In a study of the chemistry of 2,4-dichloro-5-sulfamylbenzonitrile (I)[1] the reaction with an excess of phenylmagnesium bromide was carried out in anticipation that the product would be 2,4-dichloro-5-sulfamylbenzophenone. This product was formed in low yield, but the major product ($C_{13}H_7Cl_2N$) was shown to be 3,5-dichloro-2-biphenylcarbonitrile (III) by conversion into 2-methylbiphenyl (V) with Raney nickel. We were led to try this reaction because we had previously observed dehalogenation accompanying Raney

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