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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(3) H. M. Blatter, H. Lukaszewski, and G. deStevens, *J. Org. Chem.*, **30**, 1020 (1965).

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(6) R. Willstätter and H. Kubli, *Ber.*, **42**, 4135 (1909).

Benzyne Formation by Desulfamylation

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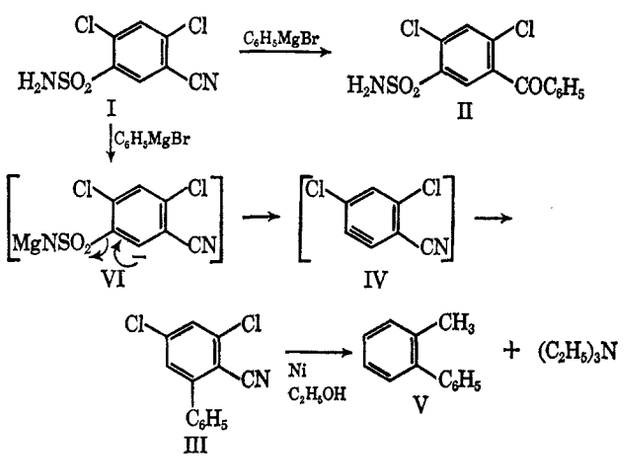
In a study of the chemistry of 2,4-dichloro-5-sulfamylbenzonitrile (I)[1] the reaction with an excess of phenylmagnesium bromide was carried out in anticipation that the product would be 2,4-dichloro-5-sulfamylbenzophenone. This product was formed in low yield, but the major product ($C_{13}H_7Cl_2N$) 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

(1) W. Siedel, K. Sturm, and W. Scheurich, *Ber.*, **99**, 345 (1966).

nickel desulfurizations of chlorosulfamylanthranilic acids.[2]

The loss of nitrogen could be rationalized by reduction of the nitrile to the primary amine followed by alkylation by ethanol and debenzylation all catalyzed by the Raney nickel.[3] This explanation is supported by isolation of triethylamine hydrochloride from this reaction.

The *cine* substitution found in the replacement reaction implicates the benzyne IV as an intermediate. The hydrogen on the phenyl flanked by the sulfamyl and cyano groups should be quite acidic, so the formation of the anion VI seems plausible. This could be converted into IV by loss of $MgNSO_2^-$. The addition of the phenyl *ortho* to the cyano seems contrary to the generalization that the reaction proceeds to place the negative charge adjacent to the most strongly electron-withdrawing group.[4] It is possible that phenylmagnesium bromide is complexed to the cyano group, and this directs phenylation to the adjacent carbon.



Experimental Section[5]

Reaction of Phenylmagnesium Bromide and 2,4-Dichloro-5-sulfamylbenzonitrile.—Phenylmagnesium bromide was prepared by the reaction of 12.16 g (0.5 g-atom) of magnesium and 78.5 g (0.5 mol) of bromobenzene in 225 ml of tetrahydrofuran. After addition of 25 g (0.1 mol) of 2,4-dichloro-5-sulfamylbenzonitrile dissolved in 100 ml of tetrahydrofuran the reaction mixture was stirred at 25° for 30 min and refluxed for 90 min. After chilling, ice–water (350 ml) and 12 *N* sulfuric acid (200 ml) were added and the resulting solution was extracted with ether. The ether was extracted with 10% sodium hydroxide and the organic phase was concentrated to give 15 g (60%) of **3,5-dichloro-2-biphenylcarbonitrile** (III). Recrystallization from an ethanol–water mixture gave white crystals, mp 149–150°.

Anal. Calcd for $C_{13}H_7Cl_2N$: C, 62.92; H, 2.84; N, 5.64. Found: C, 63.01; H, 3.04; N, 5.33.

Acidification of the basic ether extract with hydrochloric acid gave 4.0 g (12%) of **2,4-dichloro-5-sulfamylbenzophenone** (II). This was dissolved in dilute sodium hydroxide, treated with charcoal, and reprecipitated by addition of acid. Recrystallization from an ethyl acetate–hexane mixture gave white crystals, mp 200–201°.

Anal. Calcd for $C_{13}H_9Cl_2NO_3S$: C, 47.29; H, 2.75; N, 4.24. Found: C, 47.56; H, 2.73; N, 4.28.

Dehalogenation of 3,5-Dichloro-2-biphenylcarbonitrile.—A mixture of 500 mg of 3,5-dichloro-2-biphenylcarbonitrile and a teaspoon of activated Raney nickel in 60 ml of ethanol was refluxed for 2.5 hr. The nickel was then removed by filtration and the volatile solvents were evaporated under vacuum. Addition of ether to the oily residue caused the separation of a white solid which was collected by filtration and identified by its nmr and infrared spectra as triethylamine hydrochloride. Evaporation of the ether gave an oil which on thin-layer chromatography (silica gel G, $CHCl_3$ development) showed a major spot (at highest R_f) and three traces. Chromatography on silica gel developing with chloroform gave four drops of the major product free of contamination. This was distilled in a small alembic (pot temperature 110°, 15 mm) to give a few drops of a colorless oil. The infrared and nmr spectra were identical with those of authentic 2-methylbiphenyl and very different than that of 3-methylbiphenyl.

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.20. Found: C, 92.93, 92.69; H, 7.27, 7.18.

Registry No.—Benzyne, 462-80-6; II, 16355-12-7; III, 16355-13-8; V, 643-58-3.

(2) J. Weinstock and N. C. F. Yim, unpublished results.

(3) For precedents for the last two steps, see G. R. Pettit and E. E. van Tamelin, *Org. Reactions*, **12**, 356 (1961).

(4) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

(5) We wish to thank Miss M. Carroll and her staff for microanalytical data and Mr. R. J. Warren for nmr spectral data. Infrared spectra were determined on a Perkin-Elmer Infracord spectrometer and nmr spectra were obtained on a Varian A-60 spectrometer.

The Chemistry of 3-Oxo-2-phenylindolenine[1]

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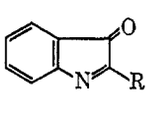
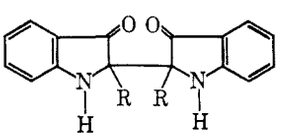
Recently Hassner and Haddadin[2] have shown that 17-keto steroids react with *o*-nitrobenzaldehyde to produce an exocyclic unsaturated indoxyl, which was postulated to have arisen from a 3-oxoindolenine of type **1a**, by a tautomeric shift. Little is known about endocyclic unsaturated indoxyls **1**. Although several workers have claimed to have isolated 3-oxoindolenines, these structures have either been shown to be erroneous, *e.g.*, the compounds are dimers of type **2**, or are subject to debate in the literature.[3-7]



1a, R = C_6H_5
b, Ia·HCl



2a, R = CH_3
b, R = C_6H_5

We decided to investigate the chemistry of 3-oxoindolenines and chose the 2-phenyl derivative because it could not undergo isomerization to an exocyclic unsaturated isomer. 3-Oxo-2-phenylindolenine (**1a**) was first described by Baeyer as an unstable red solid melting at 102°.[8] This compound was reported to readily react with base or acid and to dimerize on heating in benzene. That such endocyclic unsaturated indoxyls might be unstable and isomerize to an exocyclic unsaturated indoxyl or dimerize is not surprising; they contain a

(1) Stereochemistry. XXXIV. Nitro Compounds. VII. For paper XXXIII, see F. Fowler and A. Hassner, *J. Amer. Chem. Soc.*, **80**, 2875 (1968).

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(4) A. Hassner and M. Haddadin, *J. Org. Chem.*, **28**, 224 (1963).

(5) D. A. Jones, Ph.D. Thesis, University of Minnesota, Minneapolis, Minn., 1961 discussed several reactions in which 3-oxoindolenines have been postulated as intermediates but in no case have they been isolated.

(6) R. K. Callow and E. Hope, *J. Chem. Soc.*, 1191 (1929).

(7) R. Pummerer, *Chem. Ber.*, **44**, 338, 810 (1911).

(8) A. Baeyer, *ibid.*, **45**, 2157 (1912); L. Kalb and J. Bayer, *ibid.*, **45**, 2150 (1912).