

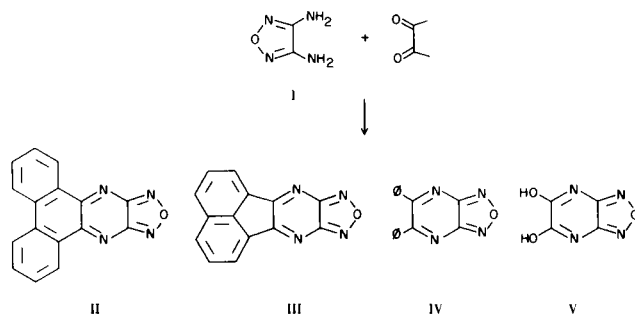
Studies in the Chemistry of 1,2,5-Oxadiazole. I.
Synthesis of Some Furazanopyrazines from 3,4-Diamino-1,2,5-oxadiazole

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The chemistry of derivatives of 1,2,5-oxadiazole (furan) was investigated some time ago in our laboratory (1) and recently, a further study of this subject was undertaken. The products of the condensation of 1,2,5-oxadiazole with some benzenoid rings have been known for a long time and pharmacological activity has been detected in some of their derivatives (1,2). Few compounds are known in which the furazan ring is condensed with other heterocyclic rings (3), and no furazanopyrazine rings have been described in the literature. The recent synthesis (4) of 3,4-diaminofurazan (I) provides an interesting intermediate for the preparation of such compounds.

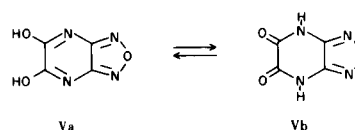
Compound I was found to condense with various α -diketones to form the corresponding furazano[3,4-*b*]pyrazines. Dibenzo[*f,h*]furazano[3,4-*b*]quinoxaline (II),



acenaphtho[1,2-*e*]furazano[3,4-*b*]pyrazine (III), and 5,6-diphenylfurazano[3,4-*b*]pyrazine (IV) were obtained by refluxing equimolar amounts of I and the appropriate α -diketone in acetic acid solution. Under somewhat different reaction conditions, I condensed with oxalic acid to produce 5,6-dihydroxyfurazano[3,4-*b*]pyrazine (V).

Compounds II, III, and IV are coloured and the electronic spectra show absorptions in the UV region and in the blue end of the visible region (see Experimental). IR spectra of these compounds show typical bands of ring stretching vibrations in the 6.15-7.00 μ region, a strong absorption near 9.8 μ and in the 12.8-14.4 μ region, typical bands of CH wagging vibrations. All the spectra were recorded in halocarbon. Compound V is colourless and absorbs only in the UV region. This absorption is

red shifted and intensified upon basification of the solution. The IR spectrum (in halocarbon) shows a complex pattern of peaks in the range 3.09-3.50 μ which would be due to either OH (Va) or NH (Vb) bands. Strong



absorptions are also present near 5.90 μ (C=O str.), near 6.25 μ (ring str.), near 7.45 μ (probably due to C-O str.) and near 9.85 μ .

The pharmacological study of the compounds is in progress.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin Elmer model 257 spectrophotometer; UV spectra were recorded using a Perkin Elmer model 350 spectrophotometer. All melting points are uncorrected.

Dibenzo[*f,h*]furazano[3,4-*b*]quinoxaline (II)

Compound I (0.300 g.) was heated with an equimolar amount of 9,10-phenanthraquinone in acetic acid solution for 5 hours. The crude product which separated upon cooling to room temperature was collected by filtration and upon crystallization from benzene or toluene gave orange-red needles (60%), m.p. 272-273° dec. UV λ max (dioxane) 377 (log ϵ , 4.12) 299 (log ϵ , 4.28) 289 (log ϵ , 4.12) 272 (log ϵ , 4.29) 265 (log ϵ , 4.31) 238 m μ (log ϵ , 4.78); IR 6.27, 6.79, 6.95, 9.86, 13.03 μ .

Anal. Calcd. for C₁₆H₈N₄O: C, 70.58; H, 2.96; N, 20.58. Found: C, 70.66; H, 2.97; N, 20.71.

Acenaphtho[1,2-*e*]furazano[3,4-*b*]pyrazine (III)

Compound III was prepared as above from I (0.300 g.) and an equimolar amount of acenaphthoquinone (3 hours) to give III as yellow-orange needles (xylene) (80%), m.p. 322-324° dec. UV λ max (dioxane) 370 (log ϵ , 3.15) 304 (log ϵ , 4.61) 294 (log ϵ , 4.54) 233 m μ (log ϵ , 4.77); IR 6.21, 6.54, 6.75, 6.95, 7.05, 9.78, 12.82 μ .

Anal. Calcd. for C₁₄H₆N₄O: C, 68.29; H, 2.46; N, 22.75. Found: C, 68.23; H, 2.22; N, 22.72.

5,6-Diphenylfurazano[3,4-*b*]pyrazine (IV)

Compound IV was prepared as above from I (0.300 g.) and an equimolar amount of benzil (5 hours) to give a yellow micro-

crystalline material (ethanol) (35%), m.p. 195-196°. UV λ max (ethanol) 354 (log ϵ , 3.93) 250 m μ sh (log ϵ , 3.88); IR 6.27, 6.48, 6.72, 6.97, 9.75, 12.87 μ .

Anal. Calcd. for C₁₆H₁₀N₄O: C, 70.07; H, 3.67; N, 20.43.
Found: C, 70.17; H, 3.52; N, 20.29.

5,6-Dihydroxyfurazano[3,4-*b*]pyrazine (V).

Compound I (0.300 g.) and 0.400 g. of oxalic acid dihydrate were gently refluxed for 1 hour in dilute aqueous hydrochloric acid (3 cc.). Upon cooling the solution to room temperature, a product separated which was dissolved in 2% sodium bicarbonate. Upon addition of acetic acid to the filtered solution, colourless crystals formed and were recovered. The crude material crystallized from water as needles (30%), m.p. 306-310° dec. after drying over phosphorus pentoxide. UV λ max (ethanol) 269 m μ (log ϵ , 4.06); IR 3.09-3.50, 5.90 (C=O), 6.25, 7.45, 9.85 μ .

Anal. Calcd. for C₄H₂N₄O₃: C, 31.18; H, 1.31; N, 36.36.
Found: C, 31.49; H, 1.23; N, 36.22.

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