# The Synthesis and Reactions of
3-Hydroxy- and 3-Benzenesulfonyloxyalloxazine (1)

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The novel base-induced conversions of 3-benzene-sulfonyloxylumazine to s-triazolo[4,3-a]pyrazine derivatives (2), prompted us to investigate a series of related reactions for 3-benzenesulfonyloxyalloxazine, 1a. This sulfonate, 1a, was synthesized in two different ways from 2,3-quinoxalinedicarboxylic acid, 2 (X = Y = CO_2H). We found that the most convenient route was from the corresponding ester, 2a, via the hydroxamate 2b, and its one-pot rearrangement with benzenesulfonyl chloride to furnish 1a.
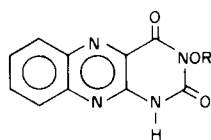

1a, R = $SO_2C_6H_5$
b, R = H
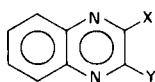
2a, X = Y = CO_2CH_3
b, X = Y = $CONHO^-Na^+$
c, X = CO_2H, Y = CONHOH

As anticipated, the reaction with sodium methoxide in methanol degraded 1a to the ester 3a, which was hydrolyzed to the corresponding acid, 3b. Decarboxylation of 3b provided 3c which was identical to an authentic sample (4). Thus, the overall sequence, 1a → 3c, paralled the one starting from lumazine derivatives (2).
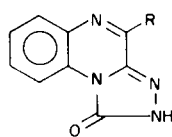
3a, R = CO_2CH_3
b, R = CO_2H
c, R = H
d, R = CONHCH₃
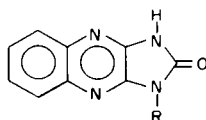
4a, R = H
b, R = $CON(C_4H_9-n)_2$

However, some of the reactions of 1a differed to those reported for condensed aromatic N-sulfonyloxyuracils. We had not encountered any particular difficulty in hydrolyzing this type of sulfonate to the corresponding N-hydroxy derivatives (2,3). For example, the closest analog to 1a, viz., 3-benzenesulfonyloxylumazine, was hydrolyzed in several minutes by boiling 10% aqueous

sodium hydroxide solution to furnish 3-hydroxylumazine in 44% yield (5).

Attempts to hydrolyze 1a under a variety of conditions using either dilute aqueous sodium hydroxide or carbonate solution for short periods failed to produce 1b. Rather than being hydrolyzed, 1a rearranged under the influence of hydroxide ion and provided the acid, 3b. This unexpected development can only be explained if hydroxide ion attacks the C-4 carbonyl group to commence the degradative ring-opening by the mechanism postulated previously (2). The fact that hydroxide ion attacks that CO group, in preference to the sulfonate sulfur atom, or the acidic NH points to the extremely high electrophilicity of the C-4 carbon atom in 1a. Apparently, the electron-attracting nature of the quinoxaline ring imparts unusually high electrophilicity to the carbon of the C=O group at 4 in 1a, which results in such facile covalent bond formation.

This additional electrophilicity manifests itself in another degradative ring opening for 1a. It was found that 40% aqueous methylamine rearranged 1a to the amide, 3d, quantitatively. The structure of 3d was established on the basis of an analysis of spectral characteristics, particularly its uv spectrum, which was almost identical to that of 3a.

It had been shown that aqueous 20% ammonia or 40% methylamine (5 minutes at 95°) attacked the sulfur atom of the sulfonate group in 3-benzenesulfonyloxy-2,4-quinazolinedione and displaced 3-hydroxy-2,4-quinazolinedione (72%) (12). In order to ascertain if a bulky amine might encounter sufficient steric hindrance during an attack at the CO group at C-4 to prevent the rearrangement of 1a to 3, di-n-butylamine was reacted with 1a. It was hoped that if this amine failed to attack the CO group, it might attack the sulfonate group and release 1b. However, this bulky amine neither attacked the sulfonate, nor the C=O group, but neutralized the N-H proton which induced a Lossen rearrangement (3) to form 4b. The carbamate, 4b, was hydrolyzed to the known imidazo-quinoxaline, 4a. The reaction resembles the one in which the anion is formed from the neutralization of the N-H

group, followed by ring opening and subsequent rearrangement to a bis-isocyanate.

The addition of one molecule of di-*n*-butylamine to this bis-isocyanate and ring closure finished the reaction to form **4b** (3). In summary, it appeared that at least 2 of the 3 types of reactions previously reported for *N*-sulfonyloxy system were observed for **1a**.

Since **1a** could not be converted to **1b**, alternate syntheses of **1b** were explored. One successful approach utilized the method of Kühle and Wegler (6) which involved the reaction of *N*-benzenesulfonyloxy-2,3-quinoxalinedicarboximide, **5c**, with hydroxylamine to produce **1b**. In order to prepare **5c**, 2,3-quinoxalinedicarboxylic acid derivatives had to be converted to the corresponding *N*-hydroxyimide, **5a**.
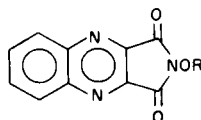
5a, R = H
b, R = COCH₃
c, R = SO₂C₆H₅

Several methods were developed. Unlike the reaction of phthalic anhydride with hydroxylamine in aqueous media to produce *N*-hydroxyphthalimide spontaneously and in excellent yield, (6), 2,3-quinoxalinedicarboxylic acid anhydride, **2**, (X, Y = CO-O-CO) opened by hydroxyl amine to furnish the carboxy-hydroxamic acid, **2c** (7). Cyclization of **2c** to **5a** was attempted. The reaction with refluxing thionyl chloride, a method which has been used by Hurd (7) in related reactions, proved not as effective in this quinoxaline system and gave a mixture of **5a** and the starting material, **2c**. It was found that the cyclization was effected best by phosphoryl chloride to produce **5a** in 71% yield. Acetic anhydride transformed **2c** to the corresponding acetate, **5b**, (84%) from which **5a** (84%) was released on subsequent treatment with hydroxylamine. When an aqueous solution of the bis-hydroxamate, **2b**, was acidified, **5a** was obtained (57%). It should be noted that when **5a** was permitted to stand in an aqueous acidic solution for an extended period of time, it was opened up to the starting carboxy-hydroxamic acid, **2c**. This relatively easy hydrolysis can also be related to its structure. This *N*-hydroxyimide system is attached to the quinoxaline system, or even better to the quinoxalinium cation in an acidic medium. This structural property would confer additional electrophilicity to the C=O groups of **5a**, compared to *N*-hydroxyphthalimide, and hence **5a** would be more prone to hydrolytic ring opening.

In view of its sensitivity to hydrolysis, the reaction of **5a** with benzenesulfonyl chloride was conducted in pyridine and **5c** was obtained in excellent yield. The reaction

of **5c** with hydroxylamine by Kühle and Wegler's method (6) produced 3-hydroxyalloxazine in 92% yield.

EXPERIMENTAL

M.p. apparati, spectrometers, tlc determinations have been described at the beginning of a previous Experimental Section (2).

3-Benzenesulfonyloxalloxazine.

Method A.

A solution of hydroxylammonium chloride (14.0 g., 0.2 mole) in absolute methanol (300 ml.) was neutralized by a solution of sodium methoxide in methanol (4.7 g. sodium in 100 ml.), and was filtered to remove sodium chloride. Methyl 2,3-quinoxalinedicarboxylate (8) (24.6 g., 0.1 mole) was added, in portions, over 10 minutes to this stirred solution of hydroxylamine at 25°, followed by an additional quantity of sodium methoxide (4.7 g., sodium in 100 ml. methanol) after 10 minutes. After the mixture was stirred for 2 hours at 25°, it was diluted with anhydrous ether (300 ml.) to insure precipitation of the orange bis-hydroxamate. The product (41 g.) was filtered, washed with ether and dried, *in vacuo*, at 25° over sulfuric acid and was used without further purification.

It should be noted that when absolute ethanol was substituted for methanol as the medium, a gelatinous pptte of the hydroxamate was obtained which defied filtration.

A stirred suspension of this powdered dry hydroxamate (41 g.) in 600 ml. THF was treated dropwise with a solution of benzenesulfonyl chloride (34 g.) in THF (100 ml.) over 1 hour at 5°. After 0.5 hour, sodium acetate (12 g.) was added. The mixture was stirred overnight (18 hours) at 25° and then filtered. The THF insoluble material was dried in air and suspended in water (600 ml.). The insoluble solid was washed with ethanol (50 ml.) and ether (100 ml.) to furnish **1a** (14.5 g., m.p. 284°, dec.).

The THF filtrate was evaporated to dryness *in vacuo*. The residue was partitioned between petroleum ether (b.p. 30-60°, 350 ml.) and water (350 ml.). The solid which was filtered, was washed with water, and then triturated with cold ethanol (10 ml.) to give more of **1a** (8.2 g.).

The combined yield of **1a** was 61% based on the starting ester. It was recrystallized by dissolving the crude product (5 g.) in 250 ml. of boiling *p*-dioxane, filtering and adding 400 ml. of boiling water to give yellow needles (4.6 g., 91% recovery) m.p. 290°, dec., ir (Nujol): 3240 (NH, broad), 1765, 1740 (C=O) cm⁻¹; pmr (DMSO): δ 7.60-8.40 (m); uv max (95% ethanol): nm (log ε), 214 (4.47), 244 (4.44), 254 sh (4.42), 324 (3.79); mass spectrum (70 eV) m/e (rel intensity): 320 (13), 230 (2), 214 (16), 212 (33), 198 (19), 185 (9), 184 (10), 171 (9), 170 (10), 158 (12), 156 (6), 143 (43), 141 (50), 116 (19), 104 (14), 102 (10), 94 (25), 90 (10), 89 (7), 86 (6), 78 (6), 77 (100), 76 (10), 75 (6), 73 (10), 70 (14).

Anal. Calcd. for C₁₆H₁₀N₄O₅S: N, 15.13. Found: N, 15.13.

Method B.

A suspension of **1b** (0.1 g.) in 10 ml. of pyridine was added 1 ml. of benzenesulfonyl chloride. A solution was formed immediately and the temperature rose to 70°. The hot solution was kept at 60-70° for 10 minutes and then poured into 150 ml. of ice water. After stirring for several minutes, the yellow precipitate was collected, washed with water and 95% ethanol to give **1a** (0.14 g.), 87%, m.p. 290°. Its uv and ir spectra were identical with the compound synthesized above.

4-Methoxycarbonyl-s-triazolo[4,3-a]quinoxalin-1(2H)one.

A stirred suspension of **1a** (1.85 g., 0.005 mole) in 75 ml. of boiling methanol was treated dropwise with a solution of sodium methoxide (0.115 g. sodium in 25 ml. of methanol) over 0.5 hour. After boiling 0.5 hour longer, the mixture was cooled to 5° (1 hour). The crystalline precipitate was collected, washed with methanol to give **3a** (1 g., 82%, m.p. 271-273°). The filtrate was evaporated to dryness and the residue was mixed with water (10 ml.) to yield an additional batch of **3a** (0.15 g., 13%). The product was recrystallized from water, (80% recovery) to furnish yellow plates, m.p. 273-275° dec.; ir (Nujol): 1715 cm^{-1} (C=O); pmr (DMSO-d_6): δ 4.00 (s, CH_3), 7.35-8.04 (3, m, H-5, H-6, H-7), 8.60-8.89 (m, H-8); uv max (95% ethanol): nm (log ϵ), 206 (4.23), 252 (4.20), 320 (3.52); mass spectrum (70 eV) m/e (rel intensity): 245 (13), 244 (100), 187 (5), 186 (46), 185 (7), 143 (6), 142 (12), 130 (30), 129 (9), 103 (12), 102 (14), 90 (10); tlc, methanol (R_f = 0.66).

Anal. Calcd. for $C_{11}H_8N_4O_3$: N, 22.94. Found: N, 22.91.

4-Carboxy-s-triazolo[4,3-a]quinoxalin-1(2H)one.

A. From 3a.

A solution of **3a** (0.2 g.) in 10 ml. of 5% sodium hydroxide was heated on a steam bath for 10 minutes, and was then acidified with concentrated hydrochloric acid to pH 2. The precipitate was collected and dried at 25°, *in vacuo*, to afford **3b** (0.17 g., 91%, m.p. > 360°); ir (Nujol): 3300-2400 (COOH, broad), 1700 (C=O) cm^{-1}; pmr (DMSO): δ 7.35-8.04 (3, m, H-5, H-6, H-7), 8.60-8.89 (m, H-8), 13.32 (broad, CO_2H or NH, the other exchangeable proton could not be detected); it can not be recrystallized or dried at higher temperature as it caused decomposition of this labile acid.

Anal. Calcd. for $C_{10}H_6N_4O_3 \cdot 2H_2O$: N, 21.05. Found: N, 21.30.

B. From 1a.

A solution of **1a** (0.2 g.) in 2 ml. of hot DMF (95°) was added 5 ml. of 10% sodium hydroxide. The solution was heated at 95° (3 minutes), diluted with water (5 ml.) and then acidified (pH 1) with concentrated hydrochloric acid to yield **3b** (0.1 g., 83%), identical with sample isolated above.

A less pure product (**3b**, 0.11 g.) was isolated, if 10% sodium hydroxide or 10% sodium carbonate was used alone without DMF.

s-Triazolo[4,3-a]quinoxalin-1(2H)one.

A sample of **3b** was sublimed at 200° (0.01 Torr) to give **3** (quantitative), m.p. 293-295° (dec., rapid heating), lit. m.p. (11) 300°; ir (Nujol): 3300-2600 (NH, broad), 1725 (C=O) cm^{-1}; pmr (DMSO): δ 7.28-7.96 (3, m, H-5, H-6, H-7), 8.58-8.79 (m, H-8), 8.80 (s, H-4); mass spectrum (70 eV) m/e (rel intensity): 187 (11), 186 (100), 143 (11), 130 (39), 129 (15), 116 (15), 103 (15), 102 (18), 90 (5), 89 (6), 76 (9), 75 (10), 65 (6), 64 (5), 63 (8), 51 (7), 50 (5). Its ir and uv spectra were identical with an authentic sample kindly provided by Dr. K. Potts (4); tlc, methanol (R_f = 0.66).

The decarboxylation was also effected by heating **3b** in *dry* DMSO (0.5 hour) and the product was isolated by dilution with water.

4-(N-Methylcarboxamido)-s-triazolo[4,3-a]quinoxalin-1(2H)one.

A solution of **1a** (0.5 g.) in 10 ml. of 40% aqueous methylamine was heated at 95° for 5 minutes. After diluting with 20 ml. of water, this solution was acidified with concentrated hydro-

chloric acid to pH 2. There was obtained **3a** (0.33 g., quantitative), m.p. 305° (sealed tube), unchanged after recrystallization from 95% ethanol; ir (Nujol): 3350, 3125 (broad, NH), 1750, 1700 (C=O) cm^{-1}; pmr (DMSO-d_6): δ 8.85-8.60 (2, m, H-8 and one of the NH protons), 8.00-7.40 (3, m, H-5, H-6, H-7), 3.35 (broad, NH), 2.83 (d, CH_3, it changed to a singlet upon adding deuterium oxide, J = 5 Hz); uv max (95% ethanol): nm (log ϵ) 206 (4.18), 252 (4.18); mass spectrum (70 eV) m/e (rel intensity): 244 (13), 243 (85), 214 (10), 187 (20), 186 (100), 144 (6), 143 (21), 142 (11), 130 (13), 129 (10), 116 (11), 103 (11), 102 (12), 90 (12), 75 (5), 58 (15).

Anal. Calcd. for $C_{11}H_9N_5O_2$: N, 28.79. Found: N, 28.84.

1-(N,N-Di-n-butylcarboxamido)imidazolo[4,5-b]quinoxaline.

A suspension of **1a** (1 g.) in 20 ml. of redistilled di-n-butylamine was refluxed for 0.5 hour. The solution was cooled to 5°. The salt of benzenesulfonic acid and di-n-butylamine was crystallized (0.85 g., m.p. 112-113°). It was filtered and identified as follows: ir (Nujol): 3150, 3080 cm^{-1}; pmr (deuteriochloroform): δ 8.05 (broad, 2, acidic protons), 8.00-7.69 (m, 2), 7.60-7.28 (m, 3), 3.10-2.66 (m, 4), 2.00-0.60 (m, 14).

The filtrates was evaporated to dryness, *in vacuo*. The oily residue was dissolved in 5 ml. of glacial acetic acid and 50 ml. of water was added. After keeping at 5° for 0.5 hour, the crude product **4b**, (0.9 g., 98%, m.p. 169-174°) was isolated. It was purified by dissolving the crude product (0.5 g.) in 15 ml. of 95% ethanol and filtered to remove insoluble substances. The clear solution was heated to boiling and 15 ml. of boiling water was added. The solution was cooled to 25° and pure **4b** separated as colorless needles in 80% recovery; m.p. 177-178°; ir (Nujol): 1760, 1695 (C=O) cm^{-1}; pmr (deuteriochloroform): δ 12.05 (broad, NH) 8.32-7.86 (2, m, H-5, H-8), 7.86-7.44 (s, m, H-6, H-7), 3.90-3.20 (4, m), 2.10-0.60 (14, m); uv max (95% ethanol): nm (log ϵ), 208 (4.54), 248 (4.28), 253 (4.29), 327 (4.08) 335 (4.07), 342 (4.11); mass spectrum (70 eV) m/e (rel intensity): 342 (5), 341 (17), 199 (8), 187 (11), 186 (22), 170 (6), 158 (7), 157 (10), 156 (74), 128 (20), 127 (13), 126 (10), 100 (23), 99 (8), 84 (23), 57 (100), 41 (18), 29 (14).

Anal. Calcd. for $C_{18}H_{23}N_5O_2$: C, 63.32; H, 6.79; N, 20.51. Found: C, 63.31; H, 6.79; N, 20.50.

A suspension of **4b** (0.2 g.) in 20 ml. of 10% sodium hydroxide was refluxed for 4 hours. The turbid solution was cooled, washed with ether (2 x 10 ml.) and acidified (pH 1) with concentrated hydrochloric acid to yield **4a** as a white amorphous powder (0.09 g., 100%), m.p. 450°, sublimation and darkening without melting, lit. m.p. (9) 447°, (10) 380°; ir (Nujol): 3300-2400 (broad, NH), 1740 (C=O) cm^{-1}; pmr (TFA): δ 8.33-7.90 (symmetric AA'BB' multiplet); uv max (95% ethanol): nm (log ϵ) 208 (4.70), 249 (4.26), 253 (4.25), 314 sh (3.99), 327 (4.18), 355 (4.13), 342 (4.15). The uv spectrum of a number of related compounds has been recorded and these compared well (9); mass spectrum (70 eV) m/e (rel intensity): 187 (10), 186 (100), 161 (13), 159 (9), 158 (24), 143 (7), 133 (6), 116 (12), 105 (9), 93 (6), 90 (9), 89 (6).

Anal. Calcd. for $C_9H_6N_4O \cdot H_2O$: N, 27.44. Found: N, 27.15.

N-Hydroxy-2,3-quinoxalinedicarboximide.

3-Carboxy-2-quinoxalinecarbohydroxamic acid monohydrate **2c**, was the best starting material for the synthesis of **5a**.

This acid was prepared by a modification of the method of Hurd and Bethune (7). A solution of hydroxylammonium hydrochloride (8.35 g., 0.12 mole) in methanol (50 ml.) was neutralized by sodium methoxide solution (2.76 g. sodium in 100 ml. of

methanol). Sodium chloride was filtered off and 2,3-quinoxaline-dicarboxylic anhydride (8.2 g., 0.04 mole) was added to the filtrates over 10 minutes. It was stirred at 25° for 1.5 hour and the suspension was evaporated to dryness, *in vacuo*. The residue was dissolved in 50 ml. of water and acidified to pH 1 with concentrated hydrochloric acid to give the hydroxamic acid, **5a**, (8.7 g., 91%), m.p. 210°, lit. (7) m.p. for the monohydrate is reported, 213-216°.

1. Cyclization with Phosphoryl Chloride.

A suspension of finely powdered **2c** (4 g.) in 40 ml. of phosphoryl chloride was heated gently with swirling in a steam bath for 10 minutes. The suspension was evaporated to dryness, *in vacuo*, and the residue was triturated with 100 g. of ice. The pale yellow suspension was permitted to warm to 30° (ca. 0.5 hour) and the temperature was maintained below 30° by cooling in an ice-bath until no further heat was evolved, (ca. 10 minutes). The solid was collected, washed with water and dried to yield **5a**. It weighed 2.6 g. (71%), m.p. 285°. It gave no purple color with ferric chloride and was recrystallized from 95% ethanol as pale yellow needles, m.p. 285° dec.; ir (Nujol): 3300-2400 (broad, N-OH), 1800 (m), 1740 (s) (C=O) cm^{-1}; pmr (DMSO): δ 8.50-7.96 (symmetric AA'BB' multiplets); mass spectrum (70 eV) m/e (rel intensity): 216 (16), 215 (46), 200 (10), 199 (66), 157 (22), 156 (46), 143 (6), 130 (7), 129 (49), 128 (100), 116 (6), 102 (24), 101 (33), 78 (6), 77 (7), 76 (18), 74 (6).

Anal. Calcd. for $C_{10}H_5N_3O_3$: C, 55.82; H, 2.34; N, 19.53. Found: C, 55.67; H, 2.32; N, 19.70.

From the filtrates of this reaction at 25° for 1 day, some starting material, **2c** (0.7 g., 18%) was recovered. It should be noted that if **5a** is permitted to stand in acidic mother liquor for an extended period of time, lower yields of impure products were obtained. For example, after 18 hours at 25°, pure **2c**, was obtained.

2. From *N*-Acetoxy-2,3-quinoxalinedicarboximide.

A suspension of **2a** (4.7 g.) in 30 ml. of acetic anhydride was refluxed for 1 hour. After cooling at 0°, the collected precipitate was triturated with water to give **5b** (4.7 g., 84%), m.p. 262°; ir (Nujol) 1839 (m), 1800 (m), 1750 (s) (C=O) cm^{-1}; pmr (DMSO-d_6): δ 8.60-8.07 (4, symmetric AA'BB' multiplets, aromatic protons), 2.20 (s, CH_3). It was recrystallized from ethyl acetate.

Anal. Calcd. for $C_{12}H_7N_3O_4$: C, 56.04; H, 2.74. Found: C, 56.14; H, 2.76.

A sample of **5b** (1 g.) was added in portions over 10 minutes to a stirred aqueous 10% hydroxylamine solution. After acidifying to pH 2 with concentrated hydrochloric acid, crystalline **5a** (0.7 g., 84%) was obtained, m.p. 286°.

3. From Disodium 2,3-Quinoxaline-bishydroxamate.

A solution of **2b** in water (50 ml.) was acidified with concentrated hydrochloric acid to pH 1 at 5°. After 2 hours at 25° the precipitate was collected, washed with ice water to afford **5a** (4.4 g., 57%, based on the ester used), m.p. 280°.

The filtrates was acidified further by passing hydrogen chloride gas until no more precipitate formed. The product (2.3 g., m.p. 210°, 30%) showed a reddish violet color with ferric chloride reagent and was shown to be **5c**, by comparing its ir, mixed m.p. with the authentic sample prepared before. It can be cyclized to **5a** as described above.

3-Benzenesulfonyloxy-2,3-quinoxalinedicarboximide.

A solution of **5a** (2 g.) in 80 ml. of pyridine was reacted with 12 ml. of benzenesulfonyl chloride. The temperature rose to

70° immediately and this solution was maintained at 60-70° for 2 minutes. It was then cooled to 25° and poured into 200 g. of ice in 300 ml. water. The suspension was stirred for several minutes, the precipitate was collected and washed with water, 95% ethanol to afford **5c** (2.9 g., 88%), m.p. 229-230°. The crude product was used for the next step, but it can be recrystallized from ethyl acetate, m.p. 233-234°; ir (Nujol): 1815 (w), 1790 (w), 1754 (s) (C=O) cm^{-1}; pmr (DMSO): δ 8.50-7.25 (m); mass spectrum (70 eV) m/e (rel intensity): 355 (2), 275 (3), 200 (10), 199 (75), 157 (6), 156 (51), 151 (10), 129 (10), 128 (100), 102 (5), 101 (25), 77 (13), 76 (11), 75 (10).

Anal. Calcd. for $C_{16}H_9N_3O_5S$: N, 11.83. Found: N, 11.85.

3-Hydroxyalloxazine.

A sample of **5c** (1 g.) was added in several portions over 10 minutes to a stirred 10% aqueous hydroxylamine solution (25 ml. prepared by neutralizing a solution of 5.2 g. of hydroxyl-ammonium hydrochloride in 25 ml. of water with about 3 g. of sodium hydroxide, with cooling in an ice bath, to pH 9). The suspension was stirred for 0.5 hour at 25° and then acidified to pH 2 with concentrated hydrochloric acid. After cooling at 0° for several minutes, the solid was collected, washed with water to yield **1b** (0.6 g., 92%); m.p. 350° (open tube, sublimation occurred without melting) or 365° dec. (sealed tube); ir (Nujol): 3150 (broad, OH and NH) 1750, 1680 (C=O) cm^{-1}; pmr (DMSO) δ 10.90, 9.40 (broad, exchangeable with deuterium oxide, NH and OH protons), 8.33-7.67 (4, m, aromatic protons); recrystal-mass spectrum (70 eV) m/e (rel intensity): 231 (16), 230 (100), 214 (9), 200 (5), 198 (24), 172 (26), 171 (21), 170 (80), 144 (15), 143 (40), 142 (8), 129 (18), 117 (9), 116 (35), 102 (35), 90 (26), 89 (15), 76 (13), 75 (16); uv max (95% ethanol); nm (log ε) 212 (4.47), 243 (4.48) 252 (4.47), 324 (3.88). (4.47), 243 (4.48) 252 (4.47), 324 (3.88).

Anal. Calcd. for $C_{10}H_6N_4O_3$: C, 52.18; H, 2.63; N, 24.34. Found: C, 52.25; H, 2.73; N, 24.42.

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(12) 3-Benzenesulfonyloxy-2,4-quinazolinedione when reacted with either 20% ammonium hydroxide solution or 40% methyl-amine, as described for the synthesis of **3d** (See Experimental Section), gave after acidification, 3-hydroxy-2,4-quinazolinedione.