

NEW COMPOUNDS

Derivatives of Diphenyl Sulfone

5-Nitro-2-(*p*-acetamidobenzenesulfonyl)-benzaldehyde.—Into a 500-ml. flask were placed 9.95 g. (0.05 mole) of *p*-acetamidobenzenesulfonic acid, 5.00 g. (0.05 mole) of potassium bicarbonate, 9.25 g. (0.05 mole) of 2-chloro-5-nitrobenzaldehyde, about 10 ml. of water and about 40 ml. of ethanol. All reactants went completely into solution after short boiling. Refluxing was continued for about 9.5 hours at which time a very voluminous precipitate suddenly appeared. This was collected and washed with alcohol and water. After air-drying overnight the light straw-colored crystals weighed 14.1 g. (81%) and melted at 191.2–192.2°.

Anal. Calcd. for $C_{15}H_{12}O_6N_2S$: S, 9.20. Found: S, 9.29.

Hydrolysis of the above acetamido compound in the usual way with hot dilute HCl afforded a yellow powder, **5-nitro-2-(*p*-aminobenzenesulfonyl)-benzaldehyde**, which did not melt up to 350°.

Anal. Calcd. for $C_{13}H_{10}O_5N_2S$: S, 10.47. Found: S, 10.66.

5-Nitro-2-(*p*-acetamidobenzenesulfonyl)-acetophenone.—A solution of 4.97 g. (0.025 mole) of acetamidobenzenesulfonic acid, 2.5 g. (0.025 mole) of potassium bicarbonate and 4.99 g. (0.025 mole) of 5-nitro-2-chloroacetophenone in 30 ml. of 65% ethanol was heated to the boiling point. The solution first became light green, then darker green and finally brownish. Although solid began to separate after half an hour, the refluxing was maintained for eighteen hours. The mixture was then cooled, the very light yellow colored solid collected, washed with cold alcohol and water and allowed to dry. The product amounted to 7.5 g. (81%) and melted at 274.2–275.6°.

Anal. Calcd. for $C_{18}H_{14}O_6N_2S$: S, 8.85. Found: S, 9.03.

Deacetylation of the amide by boiling with dilute hydrochloric acid solution gave the deep orange colored **5-nitro-2-(*p*-aminobenzenesulfonyl)-acetophenone**, melting at 224–227° (on the block, uncorrected).

Anal. Calcd. for $C_{14}H_{10}O_5N_2S$: S, 10.01. Found: S, 10.01.

8-Nitrothiazanthone-5-dioxide-2-carboxylic Acid.—A suspension of 6.1 g. (0.02 mole) of 2-methyl-7-nitrothiazanthone dioxide in 240 ml. of glacial acetic acid and 6 ml. of concd. sulfuric acid was refluxed a total of two hours with 8 g. (0.08 mole) of chromic anhydride which was added in 1-g. portions, allowing time enough between each portion for the solution to acquire a green color (about two minutes for each of the first four portions). The product was isolated by dilution of the reaction mixture with water and filtration. Dissolution in aqueous sodium bicarbonate solution, reprecipitation and finally recrystallization from 400 ml. of acetic acid afforded 5.7 g. (86%) of quite pure colorless acid melting at 286.7–288.3°. Another sample, prepared by the same procedure and melting at 288.2–289.8°, was analyzed.

Anal. Calcd. for $C_{14}H_7O_7NS$: neut. eq., 333.3. Found: neut. eq., 327.4, 334.7.

2-Nitro-8-chloroformylthiazanthone-5-dioxide.—One gram (0.003 mole) of the above acid was boiled for a few minutes in 10 ml. of chlorobenzene (in which it appeared to be insoluble) containing 0.7 g. (0.003 mole) of phosphorus pentachloride. As reaction occurred, the solid dissolved and on cooling there precipitated 0.8 g. of colorless acid chloride melting at 250.5–252.5°.

Anal. Calcd. for $C_{14}H_6O_6NClS$: Cl, 10.1. Found: Cl, 10.3.

One gram of the above acid chloride was converted to **2-nitrothiazanthone-dioxide-8-carboxamide** with aqueous

ammonia yielding 0.5 g. of material melting, after recrystallization from aqueous dioxane, at 303.5–306°.

Anal. Calcd. for $C_{14}H_8O_6N_2S$: S, 9.65. Found: S, 9.67.

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Anhydrous Bis-(acetylaceton)-dioxouranium¹

We first prepared the monohydrate of this compound as directed by Biltz and Clinch.² We then converted this to the anhydrous form by drying in a vacuum over phosphorus pentoxide for four hours at 110°. The loss for the monohydrate was: calcd. 0.37%; found 0.37%. The anhydrous compound was recrystallized from toluene in a dry ice-acetone-bath; yield 65%. The product varied in color from orange to yellow-orange as particle size decreased, being darker than the hydrate. It showed no melting point but decomposed at 230–235°. *Anal.* Calcd. for $UO_4C_{10}H_{14}$: U, 50.84. Found: U, 50.90.

The anhydrous compound was obtained directly by refluxing a mixture of 50 ml. of absolute alcohol and 20 g. of dry uranyl acetate with the slow addition of 20 g. of acetylaceton.³ After refluxing for one hour the solution was filtered and allowed to crystallize in a dry ice-acetone-bath with the constant exclusion of moisture. The crystals were washed with 10 ml. of chilled dry ether, and dried for four hours at 110° *in vacuo* over phosphorus pentoxide; yield 75%. The dried crystals were recrystallized from toluene in a dry ice-acetone-bath; yield 68%. *Anal.* Calcd. for $UO_4C_{10}H_{14}$: U, 50.84. Found: U, 50.80.

Bis-(acetylaceton)-dioxouranium was moderately soluble in the anhydrous solvents, benzene, acetone, toluene, carbon tetrachloride and absolute alcohol. The compound is extremely sensitive to moisture and should be stored in a vacuum desiccator over sulfuric acid.

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(2) Biltz and Clinch, *Z. anorg. Chem.*, **40**, 221 (1904).

(3) Acetylaceton was dried over sodium sulfate and distilled; fraction taken 138.0–138.8° at 750 mm.

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Sulfonamides in the Thiophene Series. I. Sulfonamides of 2-Chlorothiophene¹

The *N*-substituted sulfonamides of 2-chlorothiophene listed in Table I were prepared by adding 0.046 mole of the appropriate amine to 25 ml. of ether containing 2 g. (0.023 mole) of 5-chloro-2-thiophenesulfonyl chloride (prepared by the reaction of 2-chlorothiophene with chlorosulfonic acid at –5° for 1 hour).² After filtering the precipitate of amine hydrochloride, the ether solution was washed with dilute hydrochloric acid and allowed to evaporate. The residue was dissolved in Skellysolve A, treated with Norit A, filtered, and cooled to obtain the crystalline sulfonamide.

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(2) Steinkopf and Kohler, *Ann.*, **582**, 264 (1937).