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*-acetamidobenzenesulfinic 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 acetamidobenzenesulfinic 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 $C_{16}H_{14}O_6N_2S$: 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-Nitrothiaxanthone-5-dioxide-2-carboxylic Acid.—A suspension of 6.1 g. (0.02 mole) of 2-methyl-7-nitrothiaxanthone 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-chloroformylthiaxanthone-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-nitrothiaxanthone-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-(acetylacetono)-dioxouranium[1]

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 acetylacetone.[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-(acetylacetono)-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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[1] This investigation was performed under the sponsorship of a Frederick Gardner Cottrell grant from the Research Corporation.

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

[3] Acetylacetone 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-Chlorothiophene[1]

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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[1] This work was carried out under a grant-in-aid from The Research Corporation.

[2] Steinkopf and Kohler, *Ann.*, **532**, 264 (1937).

TABLE I

Compound	M. p.,[a] °C.	Yield, %	Formula	N analyses,[b] % Calcd.	Found
5-Chloro-2-thiophenesulfonamide	113.5	57	$C_4H_4ClNO_2S_2$	7.09	7.08
Sodium N-chloro-5-chloro-2-thiophenesulfonamide	124.5 dec.	71	$C_4H_2Cl_2NNaO_2S_2\cdot 3H_2O$	4.53	4.53
N-Methyl-5-chloro-2-thiophenesulfonamide	44	33[c]	$C_5H_6ClNO_2S_2$	6.64	6.40
N-Ethyl-5-chloro-2-thiophenesulfonamide	52[d]	33[e]	$C_6H_8ClNO_2S_2$	6.22	6.20
N-Propyl-5-chloro-2-thiophenesulfonamide	14[f]	9	$C_7H_{10}ClNO_2S_2$	5.82	5.57
N-(1-Methylethyl)-5-chloro-2-thiophenesulfonamide	41	18	$C_7H_{10}ClNO_2S_2$	5.82	5.83
N-Butyl-5-chloro-2-thiophenesulfonamide	19[f]	22	$C_8H_{12}ClNO_2S_2$	5.59	5.36
N-Amyl-5-chloro-2-thiophenesulfonamide	32	31	$C_9H_{14}ClNO_2S_2$	5.25	5.05
N-Hexyl-5-chloro-2-thiophenesulfonamide	47	42[e]	$C_{10}H_{16}ClNO_2S_2$	4.98	4.96
N-Heptyl-5-chloro-2-thiophenesulfonamide	46	46	$C_{11}H_{18}ClNO_2S_2$	4.75	4.72
N-Phenyl-5-chloro-2-thiophenesulfonamide	83[g]	28	$C_{10}H_8ClNO_2S_2$	5.12	5.09

[a] All melting points are corrected. [b] Analyses by semi-micro Kjeldahl method. [c] Recrystallized from methanol–water. [d] Benzene used instead of ether as solvent. [e] Recrystallized from ethanol–water. [f] Liquid at room temperature; decomposed slowly on standing. [g] Recrystallized from 50% ethanol.

5-Chloro-2-thiophenesulfonamide was prepared by heating for fifteen minutes on a steam-bath a stirred mixture of 8.5 g. (0.039 mole) of 5-chloro-2-thiophenesulfonyl chloride and excess dry ammonium carbonate. After addition of a small amount of ice-water the mixture was extracted with ether. The residue after evaporation of the ether was dissolved in hot water, treated with Norit A, filtered and cooled, yielding the sulfonamide.

Sodium N-chloro-5-chloro-2-thiophenesulfonamide was prepared by adding to 1 g. (0.00506 mole) of 5-chloro-2-thiophenesulfonamide 9 g. (0.00607 mole) of 5.25% sodium hypochlorite solution and 15 ml. of saturated sodium chloride solution. The precipitate was filtered, washed with saturated salt solution, and extracted with absolute ethanol. The ethanol solution was filtered and allowed to evaporate, yielding sodium N-chloro-5-chloro-2-thiophenesulfonamide trihydrate.

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COMMUNICATIONS TO THE EDITOR

A NEW VALENCE STATE OF AMERICIUM, AM(VI)[1]

Sir:

Evidence has been obtained for the existence of americium in the formal valence of plus six:

1. Americium(III) is completely oxidized by ammonium peroxydisulfate in 0.2 *M* nitric or chloric acids to a non fluoride-precipitable state. At a concentration of 200 μg of element per 100 microliters (2 g./l.), the characteristic pink of Am(III) changes to a strong yellow color.

2. The absorption spectrum of such an oxidized solution was measured with a Beckman model DU spectrophotometer using quartz micro cells and 0.1 sensitivity scale. The solution shows no Am(III) absorption at 504 and 811 mμ, or Am(V) absorption at 514 and 714 mμ. There is a narrow and prominent peak at 991–992 mμ, and strong ultraviolet absorption. The decrease with time of these new absorption peaks is attended by a growth of Am(V) absorption but no increase in the Am(III) absorption. The rate of decrease of the 991 peak is much greater in the absence of sulfate, and the ultraviolet absorption is altered.

3. By the addition of sodium acetate, a yellow compound of tetrahedral structure was obtained which was isomorphous with the analogous $NaMO_2Ac_3$ compounds (M is U or Pu). The refractive index of sodium americyl acetate has the expected value of 1.528 (compared with 1.501 and 1.518 for the uranium and plutonium compounds, respectively). There were no Am(III) or Am(V) absorption lines in this compound. The compound was dried with acetone, treated with excess ferrous ammonium sulfate and back-titrated with ceric sulfate. The amount of americium was determined by radio-assay. A value of 2.9 was obtained for the number of equivalents on reducing Am(VI) to Am(III).

4. X-Ray analysis showed a cubic structure with an a_0 of 10.6 which is the same as that of the uranium and plutonium analogs.

5. Ether extraction after removal of sulfate with barium and salting with ammonium nitrate and nitric acid gave essentially complete extraction.

6. Hexone (methyl isobutyl ketone) extraction was also successful, but less complete, apparently due to reduction by the solvent.

7. Addition of sulfuric acid (sufficient to make 4 *M* sulfuric acid) to a solution of Am(V) in 0.3 *M* perchloric acid caused rapid disappearance of

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(1) This document is based on work performed at the Los Alamos Scientific Laboratory of the University of California under AEC contract W-7405-eng-36.