

4,4'-diamidinostilbene, which is isolated in crystalline form as the dihydrochloride.

***p*-Iodobenzaldehyde.**—The following method<sup>4a</sup> is based on Williams' modification<sup>4b</sup> of the Stephen method.

Pure anhydrous *p*-iodobenzonitrile<sup>3</sup> (15.5 g.) was treated with 30 g. of stannous chloride in 200 cc. of absolute ether. After saturation with dry hydrogen chloride, the stannic chloride aldimine hydrochloride complex was collected and subjected to steam distillation. After repeated purification by steam distillation and recrystallization from dilute ethanol, a very pure product (ca. 10 g.) was obtained; white needles, m. p. 77–78°.

*Anal.* Calcd. for  $C_7H_5OI$ : I, 54.74. Found: I, 54.64. Semicarbazone, white needles from 50% ethanol, m. p. 225°; Willgerodt and Rieke<sup>5</sup> give 224.5°. Oxime, white needles from 50% ethanol, m. p. 111–112°; Patterson<sup>4a</sup> gives 111°. In the preparation of the azine, the use of hydrazine hydrate (40%) was preferable to hydrazine sulfate and alkali, as used by Willgerodt and Rieke<sup>5</sup>; yellow needles from 50% ethanol, m. p. 230–232° (dec.).

**4,4'-Diiodostilbene.**—(a) 4,4'-Diiodobenzaldazine (6 g.) was sublimed repeatedly until the melting point of the sublimate reached 258°. The sublimate was then crystallized from absolute ethanol-toluene, from which 2 g. of very pale yellow leaflets, m. p. 259–260°, separated. Meyer and Hofmann<sup>6</sup> give 257–259°.

(b) Twelve grams of pure 4,4'-diaminostilbene<sup>7</sup> was diazotized in dilute sulfuric acid solution, and the diazonium salt was decomposed with 20 g. of potassium iodide. The crude product (ca. 16 g.) was first sublimed and then recrystallized from ethanol-toluene. Pale yellow leaflets (ca. 10 g.), m. p. 258–260°, mixed with the product from (a), m. p. 258–260°.

*Anal.* Calcd. for  $C_{11}H_{10}I_2$ : I, 58.96. Found: I, 59.13.

**4,4'-Diamidinostilbene Dihydrochloride.**—To the Grignard reagent from 6 g. of 4,4'-diiodostilbene in absolute ether and 0.7 g. of pure magnesium, 15 cc. of ethyl ortho-carbonate was added, and the mixture was heated under reflux for two hours. After treatment with ice, extraction, drying, and removal of solvent, 2.5 g. of a sirupy oil was obtained. Analysis indicated that this oil was the impure bis-orthoester.

*Anal.* Calcd. for  $C_{28}H_{40}O_6$ : C, 76.32; H, 9.15. Found: C, 75.91; H, 8.70.

Since attempts to purify the ester resulted in decomposition, the crude material was treated directly with 100 cc. of absolute ethanol which had previously been saturated with dry ammonia. The mixture was heated at 30° for one week in a tightly stoppered thick-walled bottle. Removal of the solvent *in vacuo* on the water-bath left 1.2 g. of a brown micro-crystalline mass, of no sharp melting point or distinctive form.

(4a) Jackson and White, *Am. Chem. J.*, **3**, 32 (1881); Patterson, *J. Chem. Soc.*, **69**, 1005 (1896); Willgerodt and Bogel, *Ber.*, **38**, 3451 (1905); Willgerodt and Uckle, *J. prakt. Chem.*, [2] **86**, 276 (1912).

(4b) *THIS JOURNAL*, **61**, 2248 (1939).

(5) Willgerodt and Rieke, *Ber.*, **38**, 1479 (1905).

(6) Meyer and Hofmann, *Monatsh.*, **38**, 156 (1917).

(7) Elbs and Hoesmann, *J. prakt. Chem.*, [2] **39**, 502 (1889).

*Anal.* Calcd. for  $C_{16}H_{16}N_4$ : N, 21.20. Found: N, 20.98.

Attempts to purify a small sample of the crude amidine by sublimation resulted in decomposition, with the evolution of ammonia, and the sublimation of a small amount of 4,4'-dicyanostilbene, m. p. 276–278°, mixed with an authentic sample, no depression.

The remainder of the crude product was converted into the dihydrochloride by treatment with saturated ethanolic hydrogen chloride (100 cc.), boiling for one hour, decolorizing with charcoal, and concentrating *in vacuo*. The white micro-crystalline prisms thus obtained (800 mg.) did not melt below 300°.

*Anal.* Calcd. for  $C_{16}H_{18}N_4Cl_2$ : N, 16.62. Found: N 16.56.

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## NEW COMPOUNDS

### N,N'-Di-acetylsulfanilyl- and N,N'-Di-sulfanilyl-*l*-cystine

**N,N'-Di-acetylsulfanilyl-*l*-cystine.**—This compound was prepared from *l*-cystine by the method described by Kies, *et al.*,<sup>1</sup> for the preparation of di-*p*-toluenesulfonyl-cystine. The quantities of material used were: 14.4 g. of *l*-cystine dissolved in 125 cc. of *N* NaOH; 35 g. of *p*-acetylaminobenzenesulfonyl chloride; 100 cc. of ether, and an additional 125 cc. of 2 *N* NaOH. The reaction was completed in three hours. The acetylsulfanilyl cystine came out in a gummy mass which solidified around the stirring rod upon cooling. The moist gummy solid was dissolved in 100 cc. of boiling 95% alcohol and decolorized with Merck activated charcoal. Upon evaporation of the alcohol under reduced pressure white crystals separated; yield, 21–25 g. (56–66% of theoretical, based on cystine). The material was purified by solution in ammonia and precipitation with hydrogen chloride. The gummy mass which separated was dissolved in a minimum quantity of boiling 95% alcohol and decolorized with charcoal. On addition of ether the compound was precipitated in white crystals and dried in a vacuum desiccator over sulfuric acid. The acetylsulfanilylcystine gave a negative Sullivan test for cystine and a positive nitroprusside reaction after reduction with sodium cyanide. It gave a negative reaction with 1,2-naphthoquinone-4-sodium sulfonate.<sup>2</sup> The substance dried in an oven at 120° melted at 204–206° (uncor.) with foaming and decomposition. The desiccator dried sample was used for the analysis.

*Anal.* Calcd. for  $C_{22}H_{26}O_{10}S_4N_4$ : S, 20.20; N, 8.83. Found: S, 20.27; N, 8.93.

**N,N'-Di-sulfanilyl-*l*-cystine.**—3.6 g. of the acetylsulfanilyl-*l*-cystine was refluxed with 25 cc. of 10% hydro-

(1) Kies, Dyer, Wood and Du Vigneaud, *J. Biol. Chem.*, **128**, 207 (1939).

(2) Schmidt, *ibid.*, **122**, 757 (1937–38).

chloric acid for twenty minutes, transferred to an evaporating dish, and heated for an additional fifteen minutes on the water-bath. It was decolorized with charcoal and neutralized with 5 *N* NaOH to pH 3.5. After cooling in ice, the sulfanilylcystine, colorless needles, was filtered off, washed with ice cold water, 95% alcohol, and ether; yield, 2.1 g. (68%). Dried in a vacuum desiccator over sulfuric acid, it melted at 165–166° (uncor.) with foaming and decomposition. The loss in weight of the desiccator dried material upon further drying in a pistol at the boiling point of toluene indicated a mole of water of hydration, and the melting point became 193–194° (uncor.) with foaming and decomposition. The sulfanilyl-*L*-cystine is negative to the Sullivan reaction for cystine and positive to the nitroprusside test after reduction with sodium cyanide. It gave a positive reaction with 1,2-naphthoquinone-4-sodium sulfonate.<sup>2</sup> The desiccator dried sample was used for the analysis.

*Anal.* Calcd. for  $C_{18}H_{22}O_8S_4N_4$ : S, 23.27; N, 10.18. Found: S, 23.12; N, 10.11.

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#### *p*-Cyclohexylphenyl-phenylsulfone

Ten grams of phenylcyclohexane and 11.6 g. of benzene-sulfonyl chloride were placed together with 50 ml. of carbon disulfide in a small flask. Ten grams of aluminum chloride was added gradually in small amounts. No immediate reaction occurred, but after a short time the mixture turned dark red and a vigorous reaction ensued with copious evolution of hydrogen chloride. The mixture was allowed to stand overnight, whereupon the product was poured onto crushed ice. The organic layer was washed with water and the solvent allowed to evaporate. The sulfone was recrystallized four times from 95% ethanol and twice from high boiling ligroin. Glistening white leaflets were formed which melted at 108–109.5°; yield, 50%.

*Anal.* Calcd. for  $C_{18}H_{20}O_2S$ : S, 10.67. Found: S, 10.82.

The position of the cyclohexyl group was determined by oxidation with chromic acid.<sup>1</sup> The resulting carboxylic acid was obtained in almost quantitative yield. It melted at 273–274° and had properties similar to the *p*-phenylsulfonylbenzoic acid of Newell.

(1) Newell, *Am. Chem. J.*, **20**, 304 (1898).

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#### Fluorine Derivatives of Biphenyl

Two sulfonyl fluorides of biphenyl<sup>1</sup> were prepared by the method of Steinkopf<sup>2</sup> for sulfonyl fluorides of the benzene and naphthalene series.

**4-Biphenylsulfonyl Fluoride.**—This sulfonyl fluoride was prepared from biphenyl and fluorosulfonic acid by the

procedure used for  $\alpha$ -naphthalenesulfonyl fluoride.<sup>3</sup> It was recrystallized several times from hexane to give a 3.1% yield of tiny colorless plates, m. p. 76–78°, uncor.

*Anal.* Calcd. for  $C_{12}H_9SO_2F$ : F, 8.04; hydrolysis value, 8.11 ml. of 0.5221 *N* NaOH. Found: F, 8.17; hydrolysis value, 8.18 ml. of 0.5221 *N* NaOH (method of Davies and Dick<sup>3</sup>).

The structure was established by conversion with aluminum chloride<sup>2</sup> to 4-biphenylsulfonyl chloride; m. p. 113–115°, uncor. (Gabriel and Deutsch<sup>4</sup> give 115°). This compound was identical with a sample of the sulfonyl chloride prepared from potassium 4-biphenylsulfonate, m. p. and mixed m. p. 113–115°.

**4,4'-Biphenyldisulfonyl Fluoride.**—To 777 g. (7.8 moles) of colorless, freshly distilled fluorosulfonic acid in a Pyrex flask was added 195 g. (1.26 moles) of biphenyl, with stirring. The addition at 70° required about four hours and heating was continued for three hours longer. After standing for fourteen hours at room temperature, the reaction mixture was poured into ice water and the disulfonyl fluoride extracted by shaking the whole with methylene chloride. The solvent was removed from the methylene chloride layer by distillation and the residue dissolved in a methylene chloride-hexane mixture (equal volumes of each). After decolorizing with carbon the product was crystallized by cooling in a salt-ice mixture. A yield of 264.5 g. (66%) of the crude disulfonyl fluoride, m. p. 185–200°, was obtained. After two additional crystallizations from methylene chloride-hexane the 4,4'-biphenyldisulfonyl fluoride melted at 197–200°, uncor. Under the microscope the fine white powder appears as colorless prisms. The compound is soluble in methylene chloride, ethanol, acetone, benzene and nitrobenzene, slightly soluble in carbon bisulfide and carbon tetrachloride, and insoluble in hexane and in water. It is stable when boiled with water and with 0.5 *N* sulfuric acid. When heated on a copper bar it is entirely stable at 260°; very slight browning is evident at 285°.

*Anal.* Calcd. for  $C_{12}H_8F_2S_2O_4$ : F, 11.94; hydrolysis value, 12.04 ml. of 0.5221 *N* NaOH. Found: F, 12.00; hydrolysis value, 12.13 ml. of 0.5221 *N* NaOH.<sup>3</sup>

The structure was established by conversion with aluminum chloride<sup>2</sup> to 4,4'-biphenyldisulfonyl chloride, m. p. 202–204°, uncor. (Gabriel and Deutsch<sup>4</sup> give 203°).

**2-Biphenyl Fluorosulfonate.**—This compound was prepared by the method of Lange<sup>5</sup> for aryl fluorosulfonates. To a well-stirred solution of the diazonium chloride prepared from 169 g. of 2-aminobiphenyl, 200 cc. of concentrated hydrochloric acid, 76 g. of sodium nitrite and 300 cc. of water, was added 117 g. of solid ammonium fluorosulfonate<sup>6</sup> at 0°. The precipitated diazonium fluorosulfonate was filtered, washed with water, alcohol and ether and dried *in vacuo*: yield 207 g. (73.9%); decomposition point 83–84°. The diazonium fluorosulfonate (0.4 to 0.6 mole) was decomposed in small portions at 95°, and the residue was steam-distilled. The distillate was extracted

(3) Davies and Dick, *J. Chem. Soc.*, 2104 (1931).

(4) Gabriel and Deutsch, *Ber.*, **13**, 386 (1880).

(5) Lange, *ibid.*, **60**, 962 (1927); Lange and Müller, *ibid.*, **63**, 2653 (1930).

(6) Prepared according to the procedure of Traube, Hoerenz and Wunderlich, *ibid.*, **52**, 1272 (1919).

(1) The reaction of fluorosulfonic acid with biphenyl was investigated at the suggestion of Mr. Gaston DuBois.

(2) Steinkopf, *et al.*, *J. prakt. Chem.*, **117**, 1 (1927).