

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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RECEIVED APRIL 17, 1942

#### *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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RECEIVED MARCH 30, 1942

#### 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

(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).

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).

with ether and the oil left after removing the ether was distilled under reduced pressure. There was obtained a 45.7% yield (based on the diazonium fluorosulfonate) of nearly colorless oil, distilling at 135–137° (5 mm.);  $d_{25}^{25}$  1.2905;  $n_D^{25}$  1.5508. When cooled to  $-78^\circ$  the oil crystallized, m. p. 33–34.5° (uncor.). The compound had a slightly aromatic odor and was soluble in acetone, methanol, chloroform, benzene and hexane; it was insoluble in

water and ethylene glycol.

*Anal.* Calcd. for  $C_{12}H_9SO_3F$ : F, 7.53; hydrolysis value, 7.59 ml. of 0.5221 *N* NaOH. Found: F, 7.40; hydrolysis value, 7.27 ml. of 0.5221 *N* NaOH.<sup>3</sup>

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RECEIVED MARCH 2, 1942

## COMMUNICATIONS TO THE EDITOR

### THE SYNTHESIS OF LACTOSE AND ITS EPIMER

*Sir:*

Referring to our articles which describe the syntheses of epi-cellobiose and cellobiose [THIS JOURNAL, **63**, 1724 (1941); **64**, 1289 (1942)], we now report that the combination of acetone-D-mannosan with acetobromo-D-galactose has been accomplished, and that by reactions which are entirely like those used in the indicated syntheses, we have produced, first, the epimer of lactose and, second, lactose itself. The yield of synthetic crystalline  $\alpha$ -epi-lactose octaacetate by the indicated combination was 30% and the deacetylation of the octaacetate generated synthetic epi-lactose which is identical with that produced from lactose. Synthetic epi-lactose octaacetate was converted to acetobromo-epi-lactose, which was in turn reduced to the known lactal hexaacetate, from which  $\beta$ -lactose octaacetate was obtained in good yield by oxidation with perbenzoic acid, followed by acetylation. Deacetylation of this octaacetate generated lactose. Publication of the full details will follow. The syntheses of epi-lactose and lactose were announced at the Memphis meeting of the Society in the Division of Organic Chemistry, April 21, 1942.

DIVISION OF CHEMISTRY  
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RECEIVED MAY 14, 1942

### POLAROGRAPHIC DETERMINATION OF CITRININ

*Sir:*

In view of the growing interest in anti-bacterial substances obtained from molds,<sup>2</sup> it seems desir-

(1) Taken from the thesis of H. W. Hirschy, submitted in partial fulfillment for a Master's Degree in Chemistry, June, 1941.

(2) (a) Abraham, Baker, Chaiu, Florey, Holiday and Robinsou. *Nature*, **149**, 356 (1942); (b) Dawson, Hobby, Meyer and Chaffee. *Jour. Clin. Invest.*, **20**, 433 (1941); (c) Oxford, Raistrick and Smith, *Chem. and Ind.*, **61**, 22 (1942); (d) Raistrick and Smith, *ibid.*, **60**, 828 (1941); (e) Waksman, *Bact. Rev.*, **5**, 253 (1941); (f) Wiesner, *Nature*, **149**, 356 (1942)

able to publish at this time the results of some preliminary physico-chemical studies on the metabolic product of *Penicillium citrinum*: namely, citrinin, which recently has been shown to inhibit the growth of *Staphylococcus aureus*.<sup>2d</sup>

Citrinin,  $C_{13}H_{14}O_6$ , a yellow crystalline solid, m. p. 170–171° (with decomposition), was isolated and purified by the method of Hethering and Raistrick.<sup>3</sup> It was obtained from the culture, *P. citrinum* #136-5730.6.<sup>4</sup> The characteristic properties of our product were in good agreement with those reported previously.<sup>3</sup>

We have found that citrinin in concentrations of 0.001–0.003 *M* gives well-defined current-voltage curves at the dropping mercury cathode in acid, 75% ethanol solutions, buffered and unbuffered. The limiting current was found to be proportional to the concentration of citrinin. The half-wave potential in the buffered alcoholic solution (*pH* 2.05) is in the range of  $-0.80$  to  $-0.82$  volt applied *versus* the saturated calomel reference electrode. Citrinin is also reduced in 0.1 *N* KCl-75% ethanol solution. It is not reduced in acetate alcoholic buffer (*pH* 6.0) nor in phosphate alcoholic buffer (*pH* 7.4). The manual apparatus used in these studies was similar to that described previously.<sup>5</sup> Attempts to use standard potentiometric procedures with  $TiCl_3$ <sup>6</sup> as a reducing agent proved unsuccessful since stable potentials were never reached within a reasonable and workable length of time.

(3) Hethering and Raistrick, *Roy. Soc. Phil. Trans.*, **B220**, 269 (1931).

(4) Furnished through the courtesy of Dr. K. B. Raper, U. S. Department of Agriculture. The A. T. C. collection #6202 failed to give little more than traces of citrinin.

(5) Smith, Kolthoff, Wawzonek and Ruoff, THIS JOURNAL, **63**, 1018 (1941).

(6) (a) Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 355; (b) Knecht and Hibbert, "Volumetric Analysis," Longmans, Green and Co. London, 1925, p. 53.