Experimental[3]

2-Benzenesulfonylaminodibenzothiophene.—To an ice-cold solution of 4 g. (0.02 mole) of 2-aminodibenzothiophene,[4] m.p. 132–133°, in 20 ml. of pyridine was added dropwise 3.0 ml. (0.024 mole) of benzenesulfonyl chloride. The violet solution was refluxed for one hour. The mixture was cooled and then poured into 200 ml. of dilute hydrochloric acid. A brown oil precipitated. Within two hours the oil solidified. Two crystallizations from acetic acid gave 5.1 g. (76%) of lustrous white crystals, m.p. 171–172°. The compound was soluble in alcohol, acetone, benzene, pyridine and acetonitrile. It was moderately soluble in chloroform and very slightly soluble in heptane.

Anal. Calcd. for $C_{18}H_{13}NO_2S_2$: N, 4.13; S, 18.9. Found: N, 4.03; S, 18.9.

3-Benzenesulfonylaminodibenzothiophene.—This compound was prepared from 3-aminodibenzothiophene,[5] m.p. 124–125°, by the procedure used for the 2-isomer. Crystallization from chlorobenzene and then alcohol gave 71% colorless needles, m.p. 198–199°.

Anal. Calcd. for $C_{16}H_{13}NO_2S_2$: N, 4.13; S, 18.9. Found: N, 4.06; S, 18.8.

3-(N^4-Acetylsulfanilamido)-dibenzothiophene.—The same procedure was followed as for the other sulfonamines. Slightly more than a molar equivalent of pure *p*-acetylaminobenzenesulfonyl chloride[6] was used. Crystallization from aqueous acetic acid gave a 78% yield of colorless crystals, m.p. 269–270°.

Anal. Calcd. for $C_{20}H_{16}N_2O_3S_2$: N, 7.07. Found: N, 6.94.

2-(N^4-Acetylsulfanilamido)-dibenzothiophene.—Crystallization from acetic acid gave a 58% yield of colorless crystals, m.p. 215–216°.

Anal. Calcd. for $C_{20}H_{16}N_2O_3S_2$: N, 7.07. Found: N, 6.93.

2-Sulfanilamidodibenzothiophene.—To 1.5 g. (0.0038 mole) of 2-(N^4-acetylsulfanilamido)-dibenzothiophene suspended in 40 ml. of boiling alcohol was added slowly 15 ml. of concentrated hydrochloric acid. The clear solution was refluxed for one hour. Colorless needles precipitated. An almost quantitative yield of the hydrochloride was obtained, m.p. 252 dec. To the hydrochloride suspended in water an excess amount of dilute ammonium hydroxide was added. The gummy precipitate was crystallized out of methanol. Colorless crystals (1.2 g., 90%) were obtained, m.p. 175–176°.

Anal. Calcd. for $C_{18}H_{14}N_2O_2S_2$: N, 7.91. Found: N, 7.87.

3-Sulfanilamidodibenzothiophene.—To a suspension of 1.0 g. (0.0025 mole) of 3-(N^4-acetylsulfanilamido)-dibenzothiophene in 40 ml. of boiling alcohol was added 15 ml. of concentrated hydrochloric acid. The mixture was refluxed an hour. Charcoal was added to the clear solution. The mixture was refluxed an additional half-hour and filtered hot. Dilute ammonium hydroxide was added to the clear hot solution until a definite turbidity was formed. The solution was allowed to cool. The crystals were collected on a buchner funnel and washed with water. Colorless microcrystals (0.80 g., 90%) were obtained, m.p. 254–255° dec.

Anal. Calcd. for $C_{18}H_{14}N_2O_2S_2$: N, 7.91. Found: N, 7.97.

***n*-Propyl N-2-Dibenzothienylcarbamate.**—To an ice-cold solution of 1.00 g. (0.005 mole) of 2-aminodibenzothiophene in 10 ml. of pyridine was added dropwise 1.85 g. (0.015 mole) of *n*-propyl chlorocarbonate. The mixture was allowed to stand at ice-water temperature for 30 minutes and was then poured into cold dilute hydrochloric acid. Crystallization from heptane gave 0.72 g. (51%) of colorless glistening needles, m.p. 117.5–119°.

Anal. Calcd. for $C_{16}H_{15}NO_2S$: S, 11.23. Found: S, 11.10.

***n*-Propyl N-3-Dibenzothienylcarbamate.**—This compound was prepared from 3-aminodibenzothiophene by the procedure used for the 2-isomer. Crystallization from heptane gave an 84% yield of colorless crystals, m.p. 103–104°.

Anal. Calcd. for $C_{16}H_{15}NO_2S$: S, 11.23. Found: S, 11.48.

2-(*o*-Carboxybenzoylamino)-dibenzothiophene.—To a suspension of 9.4 g. (0.064 mole) of phthalic anhydride in 80 ml. of warm xylene, a solution of 12 g. (0.06 mole) of 2-aminodibenzothiophene in 80 ml. of warm xylene was added. The mixture was warmed for half an hour and then allowed to stand at room temperature for half an hour. The pasty precipitate was collected on a buchner funnel and dissolved in 10% sodium hydroxide solution. The filtered solution was acidified with dilute hydrochloric acid. Crystallization of the precipitate from methanol gave 10 g. (48%) of colorless microcrystals, m.p. 208–210° dec.

Anal. Calcd. for $C_{20}H_{13}NO_3S$: S, 9.22. Found: S, 9.39.

3-(*o*-Carboxybenzoylamino)-dibenzothiophene.—This compound was prepared from 3.0 g. of 3-aminodibenzothiophene by the procedure used for the 2-isomer. Crystallization from methanol gave 2.9 g. (57%) of colorless microcrystals, m.p. 286–289° dec.

Anal. Calcd. for $C_{20}H_{13}NO_3S$: S, 9.22. Found: S, 9.42.

2-Benzalaminodibenzothiophene.—A solution of 0.20 g. (0.001 mole) of 2-aminodibenzothiophene in 3 ml. of alcohol was refluxed for 15 minutes with 0.10 ml. (0.001 mole) of benzaldehyde. Solidification took place when the cooled supersaturated solution was scratched or seeded. Crystallization from aqueous methanol gave 0.23 g. (80%) of colorless plates, m.p. 121–122°.

Anal. Calcd. for $C_{19}H_{13}NS$: S, 11.2. Found: S, 11.0.

3-Benzalaminodibenzothiophene.—This compound was prepared from 3-aminodibenzothiophene by the procedure used for the 2-isomer. Crystallization from hexane gave a 90% yield of yellow needles, m.p. 160°.

Anal. Calcd. for $C_{19}H_{13}NS$: S, 11.2. Found: S, 11.1.

3-(4′-Dimethylaminobenzalamino)-dibenzothiophene.—A solution of 0.40 g. (0.002 mole) of 3-aminodibenzothiophene in 8 ml. of alcohol was refluxed for one hour with 0.30 g. (0.002 mole) of *p*-dimethylaminobenzaldehyde. The Schiff base was precipitated by adding the cooled mixture to excess water. Two crystallizations from methyl cellosolve gave 0.53 g. (80%) of yellow crystals, m.p. 195–196°.

Anal. Calcd. for $C_{21}H_{18}N_2S$: S, 9.70. Found: S, 9.51.

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(3) All melting points are uncorrected.

(4) H. Gilman and J. F. Nobis, THIS JOURNAL, **71**, 274 (1949).

(5) R. K. Brown, R. G. Christiansen and R. B. Sandin, *ibid.*, **70**, 1748 (1948).

(6) S. Smiles and J. Stewart, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 8.

Preparation of Lithium Fluoborate

BY I. SHAPIRO[1] AND H. G. WEISS[1]

RECEIVED MARCH 13, 1952

In the course of studying the reaction of lithium aluminum hydride with boron trifluoride etherate[2] it became necessary to prepare a quantity of pure lithium fluoborate. In addition to the well-known methods of preparing lithium fluoborate from aqueous solutions,[3] Baumgarten and Bruns[4] prepared lithium fluoborate in milligram quantity by the reaction of gaseous boron trifluoride with lithium carbonate heated at 300°.

$$3Li_2CO_3 + 9BF_3 \xrightarrow{300°} 6LiBF_4 + 3CO_2\uparrow + (BOF)_3\uparrow \quad (1)$$

The product was found to contain about 4% lithium fluoride. This impurity can be attributed to

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(2) I. Shapiro, H. G. Weiss, M. Schmich, Sol Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(3) Since fluoborate ion is known to hydrolyze, the lithium fluoborate that can be obtained from an aqueous solution is of questionable purity.

(4) P. Baumgarten and W. Bruns, *Ber.*, **72B**, 1753 (1939).

the dissociation of lithium fluoborate since at 300° the calculated dissociation pressure is *ca.* 675 mm.[5]

We have found it possible to prepare pure lithium fluoborate by using the same reactants given in eq. 1 but by carrying out the reaction in an ethereal solution at 35°. From measurements of the volume of gas evolved after each addition of small portions of boron trifluoride etherate to a slurry of lithium carbonate in anhydrous ethyl ether (Fig. 1), the stoichiometry of the reaction was ascertained to be

$$3Li_2CO_3 + 8BF_3 \xrightarrow{\text{ether}} 6LiBF_4 + 3CO_2\uparrow + B_2O_3 \quad (2)$$

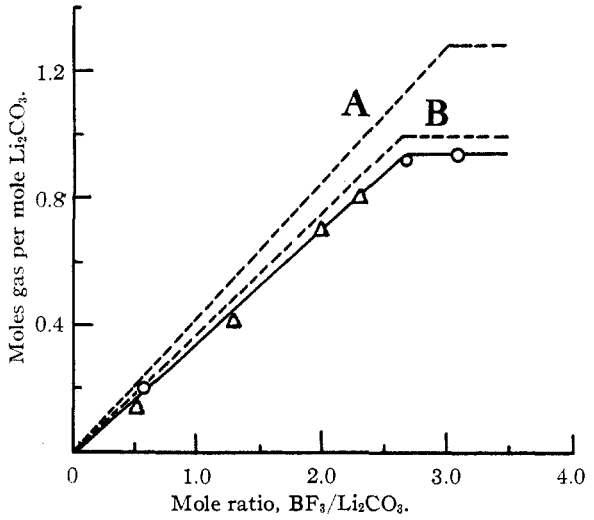

Fig. 1.—Gas evolution as a function of mole ratio of reactants: A, eq. (1); B, eq. (2).

From molecular weight determinations and vapor tension measurements (28 mm. at −111.8°) the gas was identified as (pure) carbon dioxide. The amount of boric oxide present as an end-product of the reaction was shown by titration to be in good agreement with that expected from eq. 2. Before dissolving the boric oxide all boron present as the fluoride complex was removed by ignition. The ignited solids were dissolved in water, the *p*H of the solution was adjusted to the phenolphthalein endpoint and the boric oxide was titrated with standard hydroxide after the addition of mannitol. Chemical analysis of the solid obtained by evaporation of the filtered ethereal solution indicated lithium fluoborate of 99.5% purity. The analysis consisted of measuring the loss in weight (boron trifluoride evolved) upon heating the solid, and then converting the resulting lithium fluoride to lithium sulfate.

The apparatus and techniques employed in this study have been described previously.[2] A typical experiment for preparing lithium fluoborate was as follows: To a slurry of 8.15 g. (0.110 mole) of lithium carbonate[6] in 400 ml. of dry ether was added dropwise 25 ml. (0.198 mole) of boron trifluoride etherate. The mixture was stirred vigorously and the ether refluxed during the addition of the boron trifluoride (0.5 hour) and for a period of three hours following the addition. After 20 minutes standing to permit settling of the solids, the supernatant liquid was transferred to a flask where the ether was evaporated under vacuum at room temperature. The lithium fluoborate was washed with a small quantity of ether and then dried, first, by passing dry nitrogen gas over the solid and, finally, by heating overnight in an oven at 80–90°. A further recovery of the lithium fluoborate remaining in the original solid was made by an extraction with ether. Six and one-half grams of lithium fluoborate was obtained from the original filtrate and one extraction. This quantity was only slightly less than that expected from the solubility of lithium fluoborate which was found by precipitation as nitron fluoborate[7] to be 1.3 g./100 ml. of ether at 25°.

The spacings and intensity of lines for powder diffraction data on lithium fluoborate are included here since these data apparently have not been published previously. The X-ray diffraction data were obtained with a cylindrical camera of 5.73 cm. radius using CuK_α radiation filtered through nickel foil. Line intensities were estimated visually as follows: 4.76 ms, 3.33 s, 3.19 s, 2.57 f, 2.39 s, 2.37 f, 2.27 f, 2.03 s, 1.89 vvf, 1.81 f, 1.73 f, 1.68 f, 1.59 f, 1.46 vvf, 1.43 vf, 1.36 vvf, 1.31 vvf, 1.28 vf, 1.22 vf, 1.18 vvf, 1.13 vvf, 1.06 vvf, 1.02 vvf, 0.994 vvf, 0.942 vvf, 0.931 vvf, 0.906 vvf, 0.849 vvf, 0.828 vvf.

Acknowledgment.—The authors are grateful to Dr. L. A. Burkardt for preparing and measuring the X-ray photographs.

(5) Calculated from the data of Klinkenberg as reported by H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 98.

(6) The purification of all reagents has been described in detail in ref. 2.

(7) W. Lange, *Ber.*, **59**, 2107 (1926).

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Preparation of Isoasparagine by the Phthaloyl Method

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RECEIVED SEPTEMBER 26, 1952

Recent methods developed for the syntheses of phthaloylglutamine[2] and of glutamine itself[3] based upon the γ-directive influence of the N-phthaloyl group coupled to the smooth procedures[4,5] for its removal, led us to attempt a similar approach for the aspartic acid homolog. This mode of asparagine formation has already been described in detail by King and Kidd.[6] Corollary to these experiments we had noted that the intermediary compound N-phthaloylaspartic anhydride (I), yields upon reaction with ammonia followed by dephthaloylation, asparagine (II), isoasparagine (III) or a mixture of the two; the direction of ring opening being dependent upon the nature of the solvent used during ammonolysis. It may be of some theoretical and practical interest to record conditions under which the different isomers are formed and to delineate the preparation and identification of isoasparagine.

The selective ring opening of phthaloylaspartic anhydride with ammonia in aqueous alcohol to give predominantly N-phthaloylisoasparagine is in contradistinction to what takes place with phthaloylglutamic anhydride under the same conditions.[2] Furthermore, ammonolysis in aqueous ether yields a mixture of N-phthaloylasparagine and N-phthal-

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