droxide in diethylene glycol in a closed bottle at about 150–175°, followed by titrations of the excess alkali with standard acid. Series III formed gels when treated in this way. Titration of the excess alkali in the gel was difficult and led to variable results. Therefore, the molecular weights of the members of series III were determined ebulliometrically. The values given are those obtained by extrapolation to zero concentration.

The viscosities were obtained in a carefully calibrated Fenske pipet.

Summary

Three series of open chain chloromethylmethylpolysiloxanes were prepared and characterized. The boiling points, index of refraction, density, viscosity and freezing point of the polymers were determined.

RECEIVED AUGUST 9, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Some Aminodibenzothiophenes

BY HENRY GILMAN AND JOHN F. NOBIS

In connection with studies concerned with antimalarial and antituberculous compounds, some substituted dibenzothiophenes[1] were prepared.

2-Acetyldibenzothiophene[2] is an important starting material for the preparation of 2-amino- and 2-acetaminodibenzothiophenes. 2-Aminodibenzothiophene can be prepared in excellent yields by a Beckmann rearrangement of the oxime of 2-acetyldibenzothiophene followed by hydrolysis of the resulting acetamino compound. This amine can also be prepared by the nitration and reduction of the parent heterocycle, but the over-all yields are lower, although catalytic reduction of the 2-nitro compound gives high yields of the amine.

2,8-Diacetyldibenzothiophene[3] was prepared and was found to be a suitable intermediate in the preparation of 2,8-diaminodibenzothiophene. Formation of the dioxime of the diacetyl compound, treatment of the dioxime with phosphorus pentachloride, and hydrolysis of the resulting diacetamino compound (m. p. 304–305°) gave a good yield of the 2,8-diamino compound (m. p. 199.5–200°). These same melting points were recently reported.[4] The older literature reported the melting point of the diamino compound to be 178°[5] and 194°,[3] and the melting point of the diacetamino derivative as 237°[5] and 254°.[3]

In order to confirm the structure of the 2,8-diaminodibenzothiophene, an authentic specimen was prepared by nitration of 2-nitrodibenzothiophene followed by catalytic reduction of the resulting 2,8-dinitrodibenzothiophene. Acetylation of this diamino compound gave 2,8-diacetaminodibenzothiophene. The melting points of the latter two compounds were in agreement with the melting points of the compounds obtained from 2,8-diacetyldibenzothiophene, and mixed melting points were not depressed.

The oxidation of 2,8-diacetaminodibenzothiophene to the 5-dioxide was accomplished with either hydrogen peroxide or hypochlorous acid where it had been previously reported[4] that hydrogen peroxide oxidation was not possible.

The authors are grateful to Parke, Davis and Company for arranging for pharmacological tests, the results of which will be reported elsewhere.

Experimental

2-Nitrodibenzothiophene.—Since the previous directions[6] could not be duplicated to give the reported 40% yield, the following procedure was developed. To 10 g. (0.054 mole) of dibenzothiophene dissolved in 80 cc. of glacial acetic acid at 30° was added 10 cc. of fuming nitric acid (d., 1.51) over a period of thirty minutes. When the addition was complete the reaction mixture was stirred at room temperature for one hour and filtered. The yellow solid was refluxed for several hours with 100 cc. of 95% ethanol and the insoluble 2-nitrodibenzothiophene removed by filtration. The yield of product was 3.5 g. (28%) melting at 186–187°.

2,8-Dinitrodibenzothiophene.—The following procedure was worked out from the brief directions reported previously.[5] To 18 cc. of fuming nitric acid (d., 1.51) in 25 cc. of glacial acetic acid was added 7.2 g. (0.031 mole) of 2-nitrodibenzothiophene in small portions. When the addition was complete an additional 10 cc. of fuming nitric acid was added dropwise. The reaction mixture was stirred for one hour and poured into water; the resulting yellow product was recrystallized from glacial acetic acid to give 4 g. (47%) of product melting at 320–330°. Recrystallization from dioxane gave 3.2 g. (38%) of the dinitro compound melting at 339–340° (previously reported, 324–325°[5]).

One attempt to prepare this compound by direct nitration of dibenzothiophene gave only 12% of the 2-nitrodibenzothiophene.

2-Aminodibenzothiophene-5-dioxide.—2-Nitrodibenzothiophene-5-dioxide was prepared in 88% yield by refluxing the 2-nitro compound with an excess of hydrogen peroxide.[6] The crude product was recrystallized from dioxane and from acetone to give pure material melting at 255–256°. A mixture of 9 g. (0.034 mole) of this nitro compound, 23 g. of granular tin metal, 115 cc. of hydrochloric acid, and 100 cc. of ethanol was refluxed for one hour, cooled, and the amine hydrochloride removed by filtration. An 87% yield of the amine (m. p. 274–276°) was obtained by treatment of the salt with ammonium

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[1] Gilman and Avakian, THIS JOURNAL, 68, 1514 (1946); Gilman and Nobis, *ibid.*, 67, 1479 (1945).

[2] (a) Gilman and Jacoby, *J. Org. Chem.*, 3, 108 (1938); (b) Burger and Bryant, *ibid.*, 4, 119 (1939).

[3] Burger, Wartman and Lutz, THIS JOURNAL, 60, 2628 (1938).

[4] Neumoyer and Amstutz, *ibid.*, 69, 1920 (1947).

[5] Courtot and Pomonis, *Compt. rend.*, 182, 893 (1926).

[6] Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1936).

hydroxide. Recrystallization from methanol gave 4.7 g. (59%) of product melting at 278–280°.

Anal. Calcd. for $C_{12}H_9O_2NS$: S, 13.84. Found: S, 13.50.

2-Acetyldibenzothiophene.—Conflicting reports[2] exist concerning the preparation and yield of this compound. The following procedure was developed.

One hundred and twenty grams (0.64 mole) of dibenzothiophene in 900 cc. of dry carbon disulfide was treated with 52 g. (0.64 mole) of acetyl chloride.[2a] The reaction product was distilled at reduced pressure (b. p. 183–185° (1 mm.)) to give 112.5 g. (78%) of crude compound. This material was refluxed for two hours with two successive 500-cc. portions of ether to give the desired 2-acetyldibenzothiophene melting at 109–110°. Recrystallization from methanol gave 60 g. (41%) of material melting at 111–111.5°.

2-Aminodibenzothiophene. A. From 2-Nitrodibenzothiophene.—A suspension of 13.5 g. (0.059 mole) of 2-nitrodibenzothiophene and one and one-half teaspoonfuls of Raney nickel catalyst in 150 cc. of absolute ethanol was hydrogenated at 50 p. s. i. The reaction was complete in eighteen hours; there was obtained 3.7 g. of amine melting at 133°. Dilution of the filtrate gave 7 g. of product melting at 129–131°, making a total yield of 91%. Reduction of the 2-nitro compound with tin and hydrochloric acid gave only a 66% yield of 2-aminodibenzothiophene melting at 125–126°.

B. From 2-Acetyldibenzothiophene.—Eighteen grams (0.075 mole) of the oxime of 2-acetyldibenzothiophene was treated with phosphorus pentachloride,[2a] yielding 2-acetaminodibenzothiophene quantitatively. This crude product was refluxed with 500 cc. of 1:1 hydrochloric acid for four hours and filtered hot. The residue was extracted with two liters of boiling water and the combined extracts were treated with ammonium hydroxide to give 10.7 g. (72%) of product melting at 129–131°.

2,8-Diacetyldibenzothiophene Dioxime.—2,8-Diacetyldibenzothiophene was prepared by an adaptation of the method of Burger, Wartman and Lutz.[3] To a mixture of 22.6 g. (0.1 mole) of 2-acetyldibenzothiophene and 53 g. (0.4 mole) of aluminum chloride in 500 cc. of dry carbon disulfide was added 7.8 g. (0.1 mole) of acetyl chloride over a period of ten minutes. The reaction mixture was refluxed for six hours, poured into an ice-hydrochloric acid mixture, and filtered; the crude yield was quantitative. The white solid was washed with 50 cc. of benzene and recrystallized from 95% ethanol to give 20.5 g. (76%) of pure product melting at 206–208°.

A mixture of 26.8 g. (0.1 mole) of 2,8-diacetyldibenzothiophene, 27.2 g. (0.4 mole) of hydroxylamine hydrochloride, 60 cc. of pyridine, and 250 cc. of absolute ethanol was refluxed for three hours. The solution was evaporated to one-half the volume and the remaining liquid poured into 1600 cc. of water. There was obtained, subsequent to filtration and washing with water, 28.5 g. (95%) of 2,8-diacetyldibenzothiophene dioxime melting at 266–267°.

2,8-Diacetaminodibenzothiophene. A. From 2,8-Diacetyldibenzothiophene Dioxime.—To 26.7 g. (0.09 mole) of the dioxime in 500 cc. of benzene was added 60 g. (0.287 mole) of phosphorus pentachloride at such a rate as to cause gentle refluxing. When the reaction had subsided, the mixture was poured onto ice and the suspension made alkaline with sodium carbonate. There was obtained 25 g. (93.5%) of crude diacetamino compound melting at 240–280°. (When this rearrangement was effected with hydrogen chloride[3] a 30% yield of crude product was obtained melting at 220–280°.) The crude diacetamino compound was hydrolyzed in the usual manner. The yield was 13.7 g. (76%) of 2,8-diaminodibenzothiophene melting at 197–198°. Two recrystallizations from 95% ethanol raised the melting point to 199.5–200°. A mixed melting point with 2,8-diaminodibenzothiophene obtained by reduction of 2,8-dinitrodibenzothiophene was not depressed.

Anal. Calcd. for $C_{12}H_{10}N_2S$: S, 14.95. Found: S, 14.90.

One-tenth gram (0.0004 mole) of 2,8-diaminodibenzothiophene in 25 cc. of benzene was refluxed for one hour with a few drops of acetic anhydride. There was obtained 0.11 g. (92%) of the diacetamino compound melting at 299–301°. Recrystallization from dilute ethanol gave a melting point of 303°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2S$: N, 9.39. Found: N, 9.44.

B. From 2,8-Diaminodibenzothiophene.—2,8-Diaminodibenzothiophene (m. p. 194–196°) was prepared in 46% yield by catalytic reduction of 2,8-dinitrodibenzothiophene in the manner previously described for the preparation of 2-aminodibenzothiophene. (Reduction of the 2,8-dinitro compound with tin and hydrochloric acid gave a 35% yield of impure material.) A mixed melting point with the material obtained from the Beckmann rearrangement was not depressed.

One-tenth gram (0.0004 mole) of this diamine was treated with acetic anhydride to give 0.1 g. of 2,8-diacetaminodibenzothiophene (m. p., 301–302°) after recrystallization from dilute methanol. A mixed melting point with the material prepared from 2,8-diacetyldibenzothiophene dioxime was not depressed.

2,8-Diacetaminodibenzothiophene-5-dioxide.—One gram (0.003 mole) of 2,8-diacetaminodibenzothiophene was dissolved in 20 cc. of glacial acetic acid by warming to 70°. To this solution was added 2 cc. of 30% hydrogen peroxide; the temperature was slowly raised to 93°. At the end of three hours, during which time an additional 2 cc. of hydrogen peroxide was added, the reaction mixture was poured onto ice. There was obtained 1 g. (95%) of dioxide melting at 330–331°. This material was refluxed first with 75 cc. of 95% ethanol and then with 100 cc. of dioxane to give a melting point of 356–357°. This oxidation method had been previously reported[4] to give no isolable product.

Anal. Calcd. for $C_{16}H_{14}O_4N_2S$: S, 9.70. Found: S, 9.65.

2,8-Diaminodibenzothiophene-5-dioxide.—A mixture of 0.8 g. (0.002 mole) of 2,8-diacetaminodibenzothiophene-5-dioxide and 100 cc. of 18% hydrochloric acid was refluxed for thirty minutes. The clear solution was diluted with an equal volume of water and filtered hot. Treatment of the filtrate with ammonium hydroxide gave 0.6 g. of material melting at 306–308°. Recrystallization from 95% ethanol gave 0.3 g. (51%) of the 2,8-diamino compound melting at 327–328°.

In another preparation, 10 g. (0.034 mole) of crude 2,8-diacetaminodibenzothiophene was suspended in 300 cc. of glacial acetic acid at 80° and 100 cc. of freshly prepared sodium hypochlorite solution[7] was added over a period of fifteen minutes. The reaction mixture was poured into one liter of water and a quantitative yield of crude dioxide was obtained by filtration. This crude product was refluxed for two hours with 300 cc. of 18% hydrochloric acid and allowed to stand overnight. The insoluble material was extracted with two one-liter portions of water and the combined extracts were treated with decolorizing carbon. Neutralization of the filtrate with ammonium hydroxide precipitated 4 g. (48% based on the 2,8-diacetaminodibenzothiophene) of 2,8-diaminodibenzothiophene-5-dioxide melting at 325–326°.

Anal. Calcd. for $C_{12}H_{10}O_2N_2S$: S, 13.0. Found: S, 13.4.

4-Methoxydibenzothiophene-5-dioxide.—An 85% yield of this dioxide was obtained by refluxing 4-methoxydibenzothiophene[2a] with an excess of hydrogen peroxide. After recrystallization from 95% ethanol the melting point was 191–192°.

Anal. Calcd. for $C_{13}H_{10}O_3S$: S, 13.00. Found: S, 13.33.

Reaction of Dibenzothiophene with Aluminum Halides.—In attempts to obtain a dibenzothiophenecarboxylic acid, dibenzothiophene was heated with various aluminum halides in sealed tubes under a variety of conditions. No

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(7) Weijlard, This Journal, 67, 1031 (1945).

acid was obtained by carbonation of the reaction mixtures, although 2-dibenzofurancarboxylic acid was isolated in similar reactions with dibenzofuran.[8]

Summary

New procedures are given for the preparation of some aminodibenzothiophenes and aminodibenzothiophene-5-dioxides. Additional proof is presented for the structure of 2,8-diacetyldibenzothiophene.

Ames, Iowa Received July 26, 1948

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(8) Gilman and Haubein, *ibid.*, **67**, 1033 (1945).

[Contribution from the Department of Chemistry, State University of Iowa]

The Alcoholysis of Sugar Derivatives

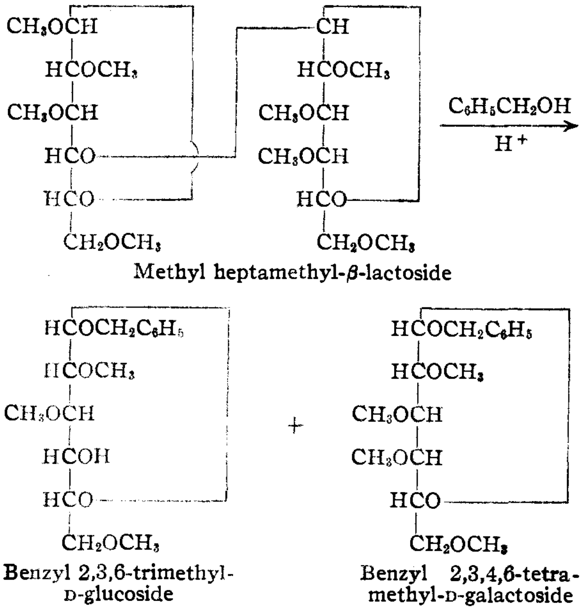
By Elmer E. Combs,[1] Chester M. McCloskey, Robert L. Sundberg and George H. Coleman[2]

The study of the alcoholysis reaction was undertaken in this Laboratory with the object of developing a method for the preparation of 2,3,6-trimethylglucose. The method was found to be satisfactory enough to warrant investigation of a larger field than originally planned with the object of obtaining a practical method of separation of the alcoholysis products of methylated disaccharides.

Berner[3] investigated the methyl alcoholysis of sucrose and other carbohydrates. From sucrose he obtained glucose and methyl fructofuranoside. Voss and Wachs[4] investigated the reaction rates of alcoholysis, acetolysis and hydrolysis of phenyl glucosides and found that the length of time required for completion of the reaction increased in the order mentioned with the reaction constant for methyl alcoholysis being over one-hundred times as great as that for hydrolysis. Methyl alcohol was used by the above workers and by others[5]; however, the use of methyl alcohol had the disadvantage that the hydrolysis rate of the methyl glycoside approximated that of the original compound. Considerable decomposition of the free sugars sometimes resulted during hydrolysis making it difficult to obtain crystalline compounds.

Richtmyer[6] studied the conditions under which benzyl glycosides are cleaved by catalytic hydrogenation. He found that palladium catalysts in glacial acetic acid, at room temperature and atmospheric pressure were capable of cleaving benzyl glycosides giving a quantitative yield of the free sugar. Methylated benzyl glycosides have been shown to be capable of distillation under high vacuum.[7,8] Studies of the benzyl alcoholysis of methyl α-fructofuranoside and of fructose have been described.[9] In view of these findings benzyl alcohol was selected for use in this investigation of the alcoholysis reaction.

The general procedure of benzyl alcoholysis is illustrated using methyl heptamethyl-β-lactoside.



Methyl heptamethyl-β-lactoside

Benzyl 2,3,6-trimethyl-D-glucoside

Benzyl 2,3,4,6-tetramethyl-D-galactoside

The benzyl glycosides obtained were distilled under vacuum and the separate fractions redistilled. In eleven runs the yield of the benzyl tetramethylglycoside averaged 87.7% and the yield of the benzyl trimethylglycoside averaged 46.1%. The lower yield of the trimethyl fraction was probably due to its higher boiling point and to the fact that it was subjected to high temperatures of distillation for a longer period of time. For this reason smaller runs generally gave better percentage yields than did larger runs. After separation the benzyl glycosides were catalytically reduced to the free sugar using palladium-charcoal catalyst in glacial acetic acid. In every case a nearly quantitative yield of the free sugar was obtained.

The methylated disaccharides used in this in-

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(1) Abstract of a portion of the dissertation submitted to the Graduate College of the State University of Iowa by Elmer E. Combs in partial fulfillment of the requirement for the degree of Doctor of Philosophy. Deceased Nov. 13, 1948.

(2) Present address, Institute of Textile Technology, Charlottesville, Virginia.

(3) Berner, *Ber.*, **66B**, 1076 (1933).

(4) Voss and Wachs, *Ann.*, **522**, 240 (1936).

(5) Coleman, Rees, Sundberg and McCloskey, This Journal, **67**, 381 (1945).

(6) Richtmyer, *ibid.*, **56**, 1633 (1934).

(7) Hess and Hwang, *Ber.*, **72B**, 1906 (1939).

(8) Hess and Gramberg, *ibid.*, **72B**, 1898 (1939).

(9) Purves and Hudson, This Journal, **59**, 49–56, 1170–1174 (1937).