added dropwise over a period of 3 hr., since the heat of reaction is high and the temperature range must be kept at −3 to −10°. Then an additional reaction time of 1 hr. was allowed, after which air was blown through the solution to remove bromine and oxides of nitrogen.

The solution was made strongly alkaline with cold 40% sodium hydroxide, filtered with suction and the filtrate and residue each extracted with four 100-ml. portions of carbon tetrachloride. The extracts were combined and allowed to evaporate dry at room temperature. The yield of crude 2-bromopyrimidine was 9.1 g. (0.057 mole, 26.6%). A double crystallization from purified petroleum ether (b.p. 60–70°) yielded 7.2 g. of white crystals, m.p. 55.50–57.0°.

Anal. Calcd. for $C_4H_3BrN_2$: C, 30.2; H, 1.9; Br, 50.4; N, 17.6. Found: C, 30.14; H, 2.11; Br, 50.68; N, 17.45.

II. Use of Phosphorus Oxybromide.[13]—A 6.0-g. portion (0.06 mole) of 2-pyrimidinol was brought to boil with 140 ml. of toluene, and 10 ml. was distilled to remove any moisture present. Then 40 g. (0.14 mole) of purified liquid phosphorus oxybromide at 80° was introduced. After heating the mixture at reflux for 1.75 hr., it was placed in an ice bath, cooled to 40°, and 50 ml. of ice water was added over a period of 10 min. with shaking. The aqueous layer was separated, the toluene extracted with 20 ml. of dilute hydrobromic acid and the aqueous layers combined.

The solution was made strongly alkaline with 40% sodium hydroxide at a temperature below 50°. This solution was then extracted with four 50-ml. portions of carbon tetrachloride, which were combined and allowed to evaporate to dryness at room temperature. The yield of crude 2-bromopyrimidine, 0.7 g., was taken up in 150 ml. of boiling petroleum ether (b.p. 60–70°). This was cooled to 0°, filtered to remove phosphorus-containing impurities, evaporated to 30 ml., cooled again to 0°, and filtered to yield 0.5 g. (5%) of white crystalline 2-bromopyrimidine, m.p. 56-57.5°.

Anal. Calcd. for $C_4H_3BrN_2$: C, 30.2; H, 1.9; Br, 50.4; N, 17.6. Found: C, 30.6; H, 2.1; Br, 49.5; N, 17.2.

Synthesis of 2,2′-Bipyrimidine.—All glassware was oven-dried at 140°. Into a 300-ml. flask, fitted with a stirrer, reflux condenser (protected with a calcium chloride tube), and nitrogen inlet were added 30 g. of activated Natural Copper Fine 44-F, 20 g. (0.126 mole) of 2-bromopyrimidine, and 100 ml. of dimethylformamide (distilled from calcium hydride). The mixture was purged with nitrogen for 10 min. with stirring, the nitrogen inlet was then replaced with a thermometer, and the solution brought rapidly to reflux by a mantel. After 3.5 hr., 5 g. of activated copper was added to the gently refluxing solution. Stirring was maintained at all times. At the end of 8 hr., the mixture was cooled to 10° and filtered through coarse paper with suction.[14] The copper residue was placed in a large beaker and extracted for 2 min. by stirring in a 200-ml. solution of concentrated ammonium hydroxide to which had been added 40 g. of potassium cyanide. The mixture was separated by suction filtration, and the extraction then repeated on the residue with a fresh ammonical potassium cyanide solution. To the combined filtrates was added 2 g. of potassium cyanide. This solution was then extracted with four 200-ml. portions of chloroform. The chloroform was placed in an evaporating dish and evaporated in a high velocity hood.[15]

Enough ethyl acetate was added to the tarry, semicrystalline residue to dissolve it, then a few milliliters excess. A small amount of carbon black (Darco) was added and the mixture was held at reflux for 15 min. The hot mixture was filtered. Then enough hot petroleum ether (b.p. 90–100°) was added to the ethyl acetate solution until a slight permanent cloudiness occurred at 80°. This mixture was slowly cooled to 0° with stirring, and filtered again to yield 5.1 g. of tan crystalline solid. The purification steps were repeated to give 3.5 g. (0.022 mole), 35% theory, of white crystalline 2,2′-bipyrimidine, m.p. 113.0–115.0° after vacuum drying. (In other runs, the yield varied from 10 to 50%.)

Anal. Calcd. for $C_8H_6N_4$: C, 60.7; H, 3.82; N, 35.5. Found: C, 60.40; H, 3.53; N, 35.41.

Molecular weight, determined in distilled water by a Mechrolab osmometer, Model 301A, was 306, indicating a dimer; in benzene it was 160, indicating the monomer.

Preparation of 2-Chloropyrimidine by Reverse Addition Diazotization.—This procedure was the same as for 2-bromopyrimidine except that sodium chloride and hydrochloric acid were substituted for sodium bromide and hydrobromic acid, respectively. It is important not to let the temperature get and stay below −10°, as an efficient salt–ice bath might tend to do in this case.

Preparation of 2-Pyrimidinol.—A 30-g. portion of 2-aminopyrimidine was refluxed for 16 hr. in 200 ml. of 10 *M* sodium hydroxide with two clay plate chips keeping the phases mixed. The mixture was cooled to 0°, whipped to a "cream," and filtered on paper with suction. The solid sodium oxypyrimidine was scraped into a large beaker, placed in an ice bath on a magnetic stirrer, and slowly acidified to pH 3.7 by stirring in dilute ice-cold sulfuric acid. Removal of the solvent was begun immediately at room temperature by slowly reducing the pressure to 5 mm. All attempts to remove the water by evaporation on a steam plate, as proposed by Brown, led to decomposition and loss of product. When the solids appeared rather dry from the outside, they were removed, crushed, and further dried at 0.5 mm. and 50° until the hydrates began to release their water and spatter around in the flask. After crushing the solids again, an additional 0.5 hr. of drying was required to remove all of the water of hydration. This was necessary to prevent decomposition during the extraction step.

The dry solid was then refluxed for 30 min. each with three 2-l. increments of dry ethyl acetate. Each increment was decanted through paper, cooled to 0°, and filtered again to obtain the white crystals. The filtrate was saved for future use as it still contained 0.5 g. of 2-pyrimidinol per liter.

The 2-pyrimidinol obtained by several repetitions of the above procedure was consistently pure, m.p. 178–179° (lit., 178–179°[11]) with yields of 21–27 g., 65–90%. Ultraviolet spectra agreed with those of Brown.[11]

(13) The phosphorus oxybromide was supplied with the compliments of the Great Lakes Chemical Corporation. It was purified by distillation, b.p. 60–65°/5–7 mm., and by crystallization, m.p. 56–60°, from 60–70° petroleum ether.

(14) This filtration is slow, but it is necessary to wait until all of the dimethylformamide is removed from the copper bipyrimidine complex; otherwise it interferes in subsequent steps. This solvent is used for the reaction because of its solvent power and because its boiling point lies below the decomposition temperature of 2-bromopyrimidine, but above that necessary to initiate the reaction.

(15) The chloroform forms a stable complex with the 2,2′-bipyrimidine. Evaporation of the last 50 ml. or so is very slow. Azeotropic distillation with portions of carbon tetrachloride may also be used. In both cases some 2,2′-bipyrimidine is lost with the solvent in evaporation.

The Preparation of Furan-2,5-dicarboxylic Acid[1]

GEORGE GONIS AND E. D. AMSTUTZ

Wm. H. Chandler Laboratory of Chemistry, Lehigh University, Bethlehem, Pennsylvania

Received January 22, 1962

Although dehydromucic acid (furan-2,5-dicarboxylic acid) has been known since before 1900,

there has never appeared in the literature any simple, clear cut, synthetic procedure for it. Since this compound was needed for further work, it was desirable to find a convenient method of preparation that would afford the compound in reasonable yield and high purity.

Among the earliest preparations of this compound is that involving the reaction of mucic or saccharic acids (or their salts) with concentrated hydrobromic acid solution. This reaction does not give the desired product in good yield (20–30%) and furthermore, involves a tedious work-up to afford pure material. Many papers appear in the literature[2] which describe the preparation of dehydromucic acid by oxidation of compounds such as aldehydopyromucic acid, 5-acetoxymethylfurfural, 5-chloromethylfurfural, 5-formyloxymethylfuroic acid, and 5-methoxymethylfurfural. In each case the authors either do not report any yield or fail to identify properly their product. Often, the starting materials are not easily obtainable.

A study of the action of nitric acid on derivatives of 5-hydroxymethyl-2-furoic acid was carried out with the hope that oxidation of one of these substances would lead to the desired dicarboxylic acid in good yield. Moldenhauer, *et al.*,[3] reported that oxidation of methyl 5-formyloxymethyl-2-furoate with 65% nitric acid gave a 74% yield of the diacid. The compound was identified merely by its failure to melt up to 220°.

No analysis or neutralization equivalent was reported, and in many attempts to prepare the diacid by this method, we consistently obtained grossly impure product (neutralization equivalent 105–115).

The best results that could be obtained involved the use of 60% nitric acid and a reaction time of two days. The product obtained from these reactions had a neutralization equivalent of 82–84 and even this material could not be purified, without great loss, through simple recrystallization. It was found convenient to esterify this crude material, distil, and then saponify the dimethyl ester obtained. On several occasions we were able to isolate 5-hydroxymethyl-2-furoic acid (m.p. 168–169°, neut. equiv. 142.6, reported[4] m.p. 166–167°, neut. equiv. 142) at this point which indicates the contaminant present in the dibasic acid obtained by Moldenhauer's procedure.

Experimental

Methyl 5-Acetoxymethyl-2-furoate.—Methyl 5-chloromethyl-2-furoate was prepared essentially according to the method of Moldenhauer.[3] Yields of product boiling at 117–124° at 7 mm. varied between 80 and 87%.

One hundred grams (0.57 mole) of the chloromethyl compound and 70 g. (0.86 mole) of anhydrous sodium acetate were refluxed in 143 ml. of glacial acetic acid for 2 hr. in a 500-ml. flask fitted with reflux condenser and stirrer. After this time, the flask was set for distillation and about 100–125 ml. of acetic acid was distilled under diminished pressure. The solution was kept stirred during this distillation in order to prevent bumping. The remaining solution was cooled and poured into 200 ml. of ice-cold water. A solid mass formed within the flask and was taken up into 150 ml. of ether by stirring and warming the solution. The ether layer was then removed, and the aqueous layer was extracted four times with 50-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and then distilled to remove the solvent. The residue was distilled at reduced pressure and the product collected at 135–137°/5 mm., m.p. 142–143°. The yields in this reaction were 80–90% based on the chloromethyl compound used (in six runs).

Anal. Calcd. for $C_9H_{10}O_5$: C, 54.5; H, 5.05. Found: C, 54.6; H, 5.15.

Furan-2,5-dicarboxylic Acid.—One hundred grams of methyl 5-acetoxymethyl-2-furoate was heated with a solution of 100 ml. of water and 450 ml. of concentrated nitric acid (70%) in a 2-l. one-neck flask fitted with a reflux condenser. The reflux condenser was connected to a trap containing 10% sodium hydroxide solution. Heating was continued until the exothermic reaction began, and then the flask was cooled in an ice water bath to control the vigorous oxidation. When the reaction subsided, heat was again applied and the solution was refluxed for 48 hr. After the first few hours of refluxing, a white solid began to separate. At the end of the reflux time the reaction mixture was cooled in an ice bath and then filtered. The product collected was washed well with water and then dried in an oven at 110°. The yield was 55.0 g. of material having a neutralization equivalent of 82 (calcd. neut. equiv. 78). Purification of this material by recrystallization from water or acetic acid could not be effected without seriously affecting the yield.

The crude diacid was next esterified by refluxing with 400 ml. of absolute methanol containing 10 ml. of concentrated sulfuric acid for a total of 5 hr.

After this time about 300–325 ml. of alcohol was distilled and the remaining solution was poured into 500 ml. of cold water. The solid which separated was filtered off and washed by slurrying with 10% sodium bicarbonate solution and then with water. This product amounted to 60.0 g. after drying overnight in a desiccator over sodium hydroxide. Distillation of this solid gave 41.5 g. of product, b.p. 140–145°/10 mm. A residue of 12 g. of the monomethyl ester was recovered, re-esterified, and combined with the distilled portion. Saponification with 10% sodium hydroxide gave 35 g. (45%) of the desired product having neut. equiv. 78.7–79.0 after being crystallized once from water.

(1) The authors gratefully acknowledge the interest of Mr. Andrew P. Dunlop and the financial assistance of The Quaker Oats Co. in support of this and other work.

(2) Dunlop and Peters, "The Furans," A.C.S. Monograph series No. 119, Reinhold Publishing Corp., New York, N. Y., 1953, pp. 572–573.

(3) O. Moldenhauer, G. Trautmann, R. Pfluger, and H. Doser, *Ann.*, **580**, 179 (1953).

(4) T. Reichstein, *Helv. Chim. Acta*, **9**, 1066 (1926).

Investigation of a Reported Synthesis of 1,3-Diphenylcyclobutadiene

SUBRAMANIA RANGANATHAN AND HAROLD SHECHTER

Department of Chemistry,
The Ohio State University, Columbus, Ohio

Received March 21, 1962

It has been recently reported[1] that 1,3-diphenylcyclobutadiene[2] is obtained in good yield by

(1) A. Chatterjee, S. K. Srimany, and (Miss) B. Chaudhury, *J. Chem. Soc.*, 4576 (1961).