our purposes because the boiling points of phosphorus trichloride and acrylyl chloride are within a degree of one another. We therefore adopted the method using benzoyl chloride for the preparation of aliphatic acid chlorides first reported by Brown.[5] This synthesis gave us good yields of a pure product.

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Experimental

A mixture of 216 g. (3 moles) of acrylic acid, 844 g. (6 moles) of benzoyl chloride, and 0.5 g. of hydroquinone was distilled at a fairly rapid rate through an efficient 25-cm. distilling column. The distillate was collected in a receiver containing half a gram of hydroquinone, immersed in ice. When the temperature at the top of the column, which remained between 60 and 70° for most of the distillation, had reached 85° the distillation was discontinued. The crude product, weighing between 215–225 g., was then redistilled through the same column and the fraction boiling at 72–74° at 740 mm. was collected. The weight of the final product was 185–195 g., or 68–72%.

(5) Brown, THIS JOURNAL, **60**, 1325 (1938).

DEPARTMENT OF CHEMISTRY
CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
PITTSBURGH 13, PENNSYLVANIA

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Preparation of 1-Phenyl-6-methylhendecane

BY WILLIAM E. TRUCE AND JOHN T. WISE

A pure sample of 1-phenyl-6-methylhendecane was desired for infrared and ultraviolet absorption studies. It was prepared by treating 1-phenyl-5-pentylmagnesium bromide with 2-heptanone, followed by dehydration and subsequent hydrogenation.

Experimental

1-Phenyl-5-pentanol[1] was prepared by treating 1-phenyl-3-propylmagnesium bromide with a two-fold excess[2] of ethylene oxide; yield 68%, b. p. 136° (5 mm.), $n^{20}D$ 1.5158.

1-Phenyl-5-bromopentane was prepared by treating the corresponding alcohol with anhydrous hydrogen bromide[3]; yield 80.3%, b. p. 144° (12 mm.), $n^{20}D$ 1.5332. *Anal.* Calcd. for $C_{11}H_{15}Br$: Br, 35.1. Found: Br, 35.1.

To the Grignard reagent prepared from 319.5 g. (1.40 m.) of 1-phenyl-5-bromopentane, 34.1 g. (1.40 m.) of magnesium and 600 ml. of ether, 159.6 g. (1.40 m.) of 2-heptanone was added over a period of five hours. After standing for thirty-six hours, the reaction mixture was hydrolyzed with cold, dilute hydrochloric acid. The alcohol was extracted with ether. After removing the ether, the crude product was refluxed for twenty hours with twice its volume of 90% formic acid.[4] The mixture was made alkaline with aqueous sodium hydroxide and the crude olefin(s) was extracted with ether. After removing the ether, the residue was distilled over sodium in an atmosphere of nitrogen; b. p. 158° (5 mm.), $n^{20}D$ 1.4979; 40.1% conversion based on 1-phenyl-5-bromopentane. The product gave positive tests for unsaturation with bromine and potassium permanganate. *Anal.* Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.9; H, 11.1.

A portion of the material (24.4 g.) was reduced practically quantitatively in the presence of Raney nickel catalyst in a Parr type hydrogenerator at 90–100° and 51 p. s. i. hydrogen pressure for four hours. The resulting hydrocarbon, 1-phenyl-6-methylhendecane, was filtered and distilled, b. p. 136–137° (1 mm.), $n^{20}D$ 1.4874. It gave negative tests for unsaturation with bromine and potassium permanganate. *Anal.* Calcd. for $C_{18}H_{30}$: C, 87.8; H, 12.2. Found: C, 88.0; H, 12.3.

Retention of the benzene ring was demonstrated by infrared analysis, and the ultraviolet absorption spectrum of the compound agreed well with that expected of a monoalkylbenzene.[5]

(1) v. Braun, *Ber.*, **44**, 2872 (1911).

(2) Huston and Langham, *J. Org. Chem.*, **12**, 90 (1947).

(3) v. Braun, Deutsch and Schmatloch, *Ber.*, **45**, 1258 (1912); "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 246.

(4) Soffer, Strauss, Trail and Sherk, THIS JOURNAL, **69**, 1684 (1947).

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(5) We are indebted to the Chemical Division of the Procter and Gamble Company for this information.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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Basic Ketals of Benzophenone

BY PRICE TRUITT AND W. D. COMPTON[1]

The recent success of Benadryl[2] as a potent histamine antagonist suggested the possibility that the structurally related diphenyl-di-(2-dialkylaminoethoxy)-methane might exhibit a similar potency.

Although Fourneau and Chantalou[3] have reported certain similar cyclic acetals, namely, 2-phenyl-4-dialkylaminomethyldioxalane-1,3, their method of synthesis was unsuccessful when applied to preparation of the compounds reported in this paper.

Even though other procedures gave some of the desired ketals, the preferred method of synthesis was by the addition of anhydrous potassium carbonate to a refluxing solution of diphenyldichloromethane and the appropriate 2-dialkylaminoethanol. The diphenyl-di-(2-dialkylaminoethoxy)-methanes prepared in this manner were very viscous liquids which hydrolyzed rapidly when in contact with diluted hydrochloric acid. Benzophenone was obtained from this hydrolysis. It was necessary to prepare the disuccinates or dimethiodides of these basic ketals in order to obtain pure crystalline products.

Neither of the disuccinate salts prepared in this work showed appreciable antihistamine activity.

Experimental[4]

The 2-dimethylaminoethanol, 2-diethylaminoethanol and 2-piperidinoethanol were obtained from Eastman Kodak Company and distilled before use.

(1) Present address: Department of Chemistry, Arlington State College, Arlington, Texas.

(2)(a) Parke, Davis & Co. Trade Mark. (b) Rieveschl and Huber, Paper 41, Division of Medicinal Chemistry, American Chemical Society Meeting, Atlantic City, 1946.

(3) Fourneau and Chantalou, *Bull. soc. chim.*, **12**, 845 (1945).

(4) Melting points were taken with a Fisher-Johns melting point apparatus.

Diphenyl-di-(2-dimethylaminoethoxy)-methane.—A solution of 18 g. (0.2 mole) of 2-dimethylaminoethanol, 27 g. (0.1 mole) of diphenyldichloromethane[5] in 100 ml. of xylene was refluxed for one hour then 18 g. of powdered anhydrous potassium carbonate added. This mixture was refluxed with vigorous stirring for five days. Potassium carbonate was added at twenty-four hour intervals until a total of 72 g. of carbonate had been introduced. The product was separated by distillation *in vacuo*. Redistillation gave 15 g. (44%) of the desired ketal, b. p. 190–195° (5 mm.)

Anal. Calcd. for $C_{21}H_{30}O_2N_2$: N, 8.19. Found: N, 7.87.

Diphenyl-di-(2-dimethylaminoethoxy)-methane Disuccinate.—A solution of 3.42 g. (0.01 mole) of the preceding ketal in 20 ml. of acetone and 2.36 g. (0.02 mole) of succinic acid in 50 ml. of absolute ethanol gave a crystalline product. Two recrystallizations of this product from acetone yielded 3.9 g. (68%) of very hygroscopic crystals, m. p. 97–100°.

Anal. Calcd. for $C_{29}H_{42}O_{10}N_2$: N, 4.85. Found: N, 4.85.

Diphenyl-di-(2-diethylaminoethoxy)-methane.—This compound was prepared in 51% yield from 2-diethylaminoethanol and diphenyldichloromethane in the manner previously described, b. p. 217–223° (5 mm.).

Anal. Calcd. for $C_{25}H_{38}O_2N_2$: N, 7.03. Found: N, 6.75.

Diphenyl-di-(2-dimethylaminoethoxy)-methane Dimethiodide.—A solution of diphenyl-di-(2-dimethylaminoethoxy)-methane in benzene was added to an excess of methyl iodide. The white precipitate was filtered to give 88% of the dimethiodide, m. p. 232–233° (dec.).

Anal. Calcd. for $C_{23}H_{36}O_2N_2I_2$: N, 4.47. Found: N, 4.31.

Diphenyl-di-(2-piperidinoethoxy)-methane.—This substance was prepared by the above method. The yield was 23% of the theoretical, b. p. 215–230° (1 mm.).

Anal. Calcd. for $C_{27}H_{38}O_2N_2$: N, 6.64. Found: N, 5.96.

Diphenyl-di-(2-piperidinoethoxy)-methane Disuccinate.—This salt was prepared from the above ketal as in the previous experiments, m. p. 76–78°.

Anal. Calcd. for $C_{35}H_{50}O_{10}N_2$: N, 4.25. Found: N, 4.36.

(5) Gattermann and Schultze, *Ber.*, **29** 2944 (1896).

DENTON, TEXAS RECEIVED NOVEMBER 25, 1949

Preparation of Gentisic Acid

BY FRANK J. VILLANI AND JOSEPH LANG[1]

The recent publication of Morris[2] on the synthesis of 2,5-dihydroxybenzoic acid, gentisic acid, (I) prompted us to report some of the work carried out in our laboratory on the synthesis of this compound. Two methods were studied for the preparation of this compound. Hydroquinone monomethyl ether on treatment with carbon tetrachloride and concentrated sodium hydroxide in the presence of catalytic quantities of copper powder under the conditions of the Reimer–Tiemann reaction gave 70–75% of 2-hydroxy-5-methoxybenzoic acid (II), Method A.[3] The demethylation of II with hydrobromic acid yielded gentisic acid in yields of 60–65%.

The second procedure, Method B, involves the sodium hypochlorite oxidation of 2,5-dimethoxyacetophenone (III) to 2,5-dimethoxybenzoic acid (IV) and subsequent demethylation of IV to gentisic acid. The over-all yield in this method was 65–70%. Compound III was obtained by the Friedel–Crafts acylation of hydroquinone dimethyl ether.[4]

The melting point of gentisic acid has been reported by several authors[5] to be between 196–200°. Our preparation of gentisic acid, which was purified by sublimation under reduced pressure and final recrystallization from an ether–petroleum ether mixture, melted at 204.5–205°. This melting point is in agreement with that reported by Morris.[2]

Experimental

Method A. 2-Hydroxy-5-methoxybenzoic Acid.—A mixture of 62 g. (0.5 mole) of hydroquinone monomethyl ether, 100 g. of carbon tetrachloride, 300 cc. of 50% aqueous sodium hydroxide and 2 g. of copper powder was heated with stirring under reflux for eight hours. The mixture was cooled, poured into water, acidified with concentrated hydrochloric acid and filtered. The precipitate was dissolved in dilute sodium bicarbonate, treated with charcoal, filtered and the filtrate acidified with hydrochloric acid. The product was filtered and recrystallized from water, yield 66 g. (74%), m. p. 142–144°, m. p. lit.[6] 143.5°.

Gentisic Acid.—Twenty-five grams of 2-hydroxy-5-methoxybenzoic acid was heated under reflux for four hours with a mixture of 30 cc. of 48% hydrobromic acid and 30 cc. of glacial acetic acid. The glacial acetic acid was removed by vacuum concentration and the residue was extracted with ether until the aqueous solution produced no coloration with a ferric chloride solution. After removing the ether, the residue was triturated with petroleum ether and filtered. The yellowish-white crystalline product was dissolved in the minimum quantity of ethyl acetate, treated with charcoal and precipitated with petroleum ether; yield 14 g. (65%), m. p. 189–191°, m. p. lit.[5] 196–200°.

Method B. 2,5-Dimethoxyacetophenone.—This procedure is a modification of that reported in ref. 4a by which the yield of the product has been increased from 46 to 71%.

To a well-stirred ice-cold solution of 27.6 g. (0.2 mole) of hydroquinone dimethyl ether, 18.7 g. of acetyl chloride and 50 cc. of carbon disulfide, 60 g. (0.45 mole) of anhydrous aluminum chloride was added portionwise under anhydrous conditions. After all the aluminum chloride had been added (three-quarters to one hour), the flask was removed from the ice-bath, and allowed to warm to room temperature and finally heated on the steam-bath for three hours. The thick, viscous mixture was poured onto ice and the carbon disulfide removed by warming on the steam-bath. After cooling, the residue was extracted with ether, the ether extracts dried and distilled. There was obtained 25.5 g. (71%) of a yellow oil boiling at 156–160° (15 mm.), b. p. lit.[4] 155–158° (14 mm.).

2,5-Dimethoxybenzoic Acid.—Chlorine gas was bubbled into a solution of 60 g. (1.5 moles) of sodium hydroxide in 85 cc. of water and 350 g. of ice until 44.7 g. (1.26 atoms) was absorbed. This mixture was warmed to 50° and 25 g. (0.14 mole) of 2,5-dimethoxyacetophenone was added

(1) Present address: Florida State University, Tallahassee, Florida.

(2) Morris, THIS JOURNAL, **71**, 2056 (1949).

(3) The carboxylation of hydroquinone to gentisic acid is described in German Patent 258,887 (1912). We were unable to duplicate this procedure employing hydroquinone, but excellent results were obtained with hydroquinone monomethyl ether.

(4) (a) Klages, *Ber.*, **37**, 3996 (1904); (b) Kauffmann and Beisswenger, *ibid.*, **38**, 789 (1905).

(5) Senhofer and Sarlay, *Monatsh.*, **2**, 448 (1881); Miller, *Ann.*, **220**, 113 (1883); Tiemann and Müller, *Ber.*, **14**, 1988 (1881); Raistrick and Simonart, *Biochem. J.*, **27**, 628 (1933); Mauthner, *J. prakt. Chem.*, **156**, 150 (1940).

(6) Graebe and Martz, *Ann.*, **340**, 215 (1905).