2-(4-Nitrophenyl)-3-(2-phenethyl)-4-thiazolidine-1-dioxide.—Ten grams of 2-(4-nitrophenyl)-3-(2-phenethyl)-4-thiazolidone was dissolved in hot acetic acid (200 ml.) and cooled. The solution was treated with potassium permanganate as described for the 3-isopropyl compound above. The crude product (10 g.) was recrystallized from isopropyl alcohol, (7 g., 64%), m. p. 147–148° cor.

Anal. Calcd. for $C_{17}H_{16}N_2O_5S$: S, 8.89; N, 7.77. Found: S, 8.98; N, 7.89.

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RECEIVED JUNE 22, 1948

The Preparation of Methyl *p*-Benzyloxyphenyl Acetate

BY PHILIP WEISS[1]

During the course of an investigation on aryl oxyphenylacetic acids, it was necessary to synthesize methyl *p*-benzyloxyphenyl acetate. The preparation of this compound was effected in the following manner.

***p*-Benzyloxyacetophenone** was prepared according to the method of Priestley and Moness[2] by refluxing *p*-hydroxyacetophenone[3] with benzyl chloride in the presence of sodium ethoxide. This same product was obtained, in lower yields, by effecting the condensation in aqueous alkali. By means of a modified Willgerodt reaction[4,5] using morpholine and sulfur, *p*-benzyloxyacetophenone was converted to *p*-benzyloxyphenylthioacetmorpholide. Hydrolysis with aqueous potassium hydroxide yielded *p*-benzyloxyphenylacetic acid. In this conversion to the acid there was no advantage gained in purifying the crude thioacetmorpholide. Esterification was effected by refluxing *p*-benzyloxyphenylacetic acid in a methanol–chloroform solution using *p*-toluenesulfonic acid as a catalyst. A soxhlet apparatus was used to remove water that was produced in the reaction, thus increasing the yield by shifting the equilibrium to the right.

Experimental[6]

***p*-Benzyloxyphenylthioacetmorpholide.**[4,5]—Twenty-four and nine-tenths grams (0.11 mole) of *p*-benzyloxyacetophenone reacted with 13.9 g. (0.16 mole) of morpholine and 5.1 g. (0.16 mole) of sulfur to yield 27.8 g. of the desired thioacetmorpholide. This was recrystallized from dilute methanol, m. p. 118–119°.

Anal. Calcd. for $C_{19}H_{21}NO_2S$: C, 69.72; H, 6.42; N, 4.28; S, 9.78. Found: C, 69.99; H, 6.65; N, 4.31; S, 9.71.

***p*-Benzyloxyphenylacetic Acid.**[4]—To 250 ml. of 10% potassium hydroxide solution was added 22.5 g. (0.07 mole) of *p*-benzyloxyphenylthioacetmorpholide and the mixture was refluxed for fourteen hours. The product was isolated as described by Schwenk and Bloch[4] for the *o*-isomer. Recrystallization of the crude product from benzene–petroleum ether (30–60°) yielded 6.5 g. of *p*-benzyloxyphenylacetic acid, m. p. 114°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found: C, 74.18; H, 6.03.

Methyl *p*-Benzyloxyphenyl Acetate.—Five grams (0.02 mole) of *p*-benzyloxyphenylacetic acid, 0.2 g. of *p*-toluenesulfonic acid, 25 ml. of methanol, and 25 ml. of chloroform were refluxed in a soxhlet apparatus for six hours. Anhydrous magnesium sulfate was placed in the thimble of the soxhlet apparatus in order to remove the water from the reaction mixture as it was being produced by the reaction. Water was added to the mixture until two distinct layers were formed. The chloroform layer was washed with water, and then extracted twice with a saturated sodium bicarbonate solution to remove any unreacted *p*-benzyloxyphenylacetic acid. The chloroform extract was again washed with water until neutral, and then dried over anhydrous sodium sulfate. After filtering the solution, the chloroform was removed by distillation under diminished pressure. The colorless oily residue solidified on cooling in an ice-bath, and was recrystallized from dilute methanol: m. p. 58.5–59°; yield 4.5 g.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.25. Found: C, 75.28; H, 6.54.

Saponification of methyl *p*-benzyloxyphenyl acetate by means of alcoholic potassium hydroxide yielded *p*-benzyloxyphenylacetic acid, m. p., 113.5–114°; mixed melting point of this acid with a sample of *p*-benzyloxyphenylacetic acid gave no depression.

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RECEIVED JULY 17, 1948

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[1] Present address: Wallace and Tiernan Products, Inc., Belleville 9, New Jersey.

[2] Priestley and Moness, *J. Org. Chem.*, **5**, 357 (1940).

[3] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928).

[4] Schwenk and Bloch, THIS JOURNAL, **64**, 3052 (1942).

[5] Newman, *J. Org. Chem.*, **9**, 521 (1944).

[6] All melting points given are uncorrected.

Preparation of 1,1,1-Trichloro-2,2-bis-(4'-aminophenyl)-ethane

BY MOSHE WEIZMANN, SHALOM ISRAELASHVILI AND RAPHAEL PAPO

Kirkwood and Phillips[1] report the synthesis of 1,1,1-trichloro-2,2-bis-(4'-aminophenyl)-ethane (I) by catalytic reduction of 1,1,1-trichloro-2,2-bis-(4'-nitrophenyl)-ethane (II). Conditions have now been found permitting preparation of (I) by reduction of (II) with stannous chloride and hydrochloric acid (yield 71%). The 4,4'-diamino compound (I) responds to the characteristic reactions of aromatic amines, *i. e.*, diazotization and coupling. The structure of (I) is further proved by its conversion to the known compound 1,1,1-trichloro-2,2-bis-(4'-hydroxyphenyl)-ethane of m. p. 202°,[2] and acetylation to the 1,1,1-trichloro-2,2-di-(4'-acetaminophenyl)-ethane, m. p. 268°.[1]

Experimental

1,1,1-Trichloro-2,2-bis-(4'-aminophenyl)-ethane (I).—Twenty-five grams of (II) was added with stirring over a period of two hours at 0° to a solution of 200 g. of anhydrous stannous chloride in 500 g. of glacial acetic acid saturated with gaseous hydrogen chloride. The resulting precipitate was filtered, washed first with concentrated and then with dilute hydrochloric acid. A dilute solution of sodium hydroxide was added to the suspension of the precipitate in water until *p*H 8 was obtained. The precipitate was washed with water, immediately extracted with acetone and dried over anhydrous sodium sulfate. The diamino compound residue (15 g.), after removal of the solvent, recrystallized from ethanol–water as colorless needles, m.p. 150° (dec.).

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[1] Kirkwood and Phillips, THIS JOURNAL, **69**, 934 (1947).

[2] ter Meer, *Ber.*, **7**, 1201 (1874); Elbs, *J. prakt. Chem.*, **47**, 60 (1874); Stephenson and Waters, *J. Chem. Soc.*, 399 (1946).

Anal. Calcd. for $C_{14}H_{13}Cl_3N_2$: C, 53.5; H, 4.1; N, 8.9. Found: C, 54.0; H, 4.3; N, 9.1.

The diamine is very soluble in acetone and warm ethanol; soluble in benzene, ether and chloroform; slightly soluble in petrol-ether (80°), very slightly soluble in water; soluble in dilute hydrochloric and sulfuric acids. It darkens on exposure to air or when its solutions are heated.

1,1,1-Trichloro-2,2-bis-(4′-acetaminophenyl)-ethane.—When a benzene solution of the diamine (I) was added to acetic anhydride at room temperature a colorless precipitate of the diacetyl derivative was immediately formed in quantitative yield, m.p. 268°.

Anal. Calcd. for $C_{18}H_{17}O_2N_2Cl_3$: C, 54.1; H, 4.3. Found: C, 54.6; H, 4.4.

Diazotization of (I).[3]—A solution of 0.47 g. sodium nitrite in 1 cc. of water was added dropwise with shaking to a solution of 1.052 g. (0.003 mole) of (I) in 6 cc. of water and 1 cc. of hydrochloric acid (25%) at 0–5°. After the diazonium solution had been carefully neutralized with sodium bicarbonate, a solution of α-naphthol was added, and a dark cherry-red precipitate was obtained.

When a diazonium solution of (I), prepared in a similar way, was warmed on a water-bath during two hours, the known bis-phenol precipitated. Recrystallization from benzene–ethanol gave a product of m.p. 202° (dec.).[2]

The nitrilation of the diazonium solution, prepared as above, gave a coke-like brown mass, from which we were unable to isolate a pure product either by crystallization or sublimation in high vacuum.

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RECEIVED[4] DECEMBER 16, 1947

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(3) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 514.

(4) An earlier version of this manuscript was received on February 27, 1947.—*The Editor.*

2-Chloro-4-aminoquinazoline

BY F. J. WOLF, R. H. BEUTEL AND J. R. STEVENS[1]

In the course of an investigation of quinazoline derivatives, 2-chloro-4-methoxyquinazoline was treated with ammonia in an effort to prepare 2-amino-4-methoxyquinazoline. However, none of the desired product was isolated from the reaction mixture. Instead, 2-chloro-4-aminoquinazoline was obtained in good yield. The ester-like properties of alkoxy groups in the 4-position of 2,4-disubstituted quinazolines has been noted,[2,3] although treatment of 2-chloro-4-methoxyquinazoline with aniline at moderate temperature yields the expected 2-anilino-4-methoxyquinazoline.[3]

2-Chloro-4-aminoquinazoline.—A solution of 2.5 g. of 2-chloro-4-methoxyquinazoline[4] in 50 ml. of methanol saturated with anhydrous ammonia at 5° was heated at 100° for eighteen hours. The mixture was concentrated to dryness *in vacuo* and the residue dissolved in hot 2.5 *N* hydrochloric acid. The product, 1.7 g. (74% yield), was obtained by neutralization with dilute ammonium hydroxide. The product melted at 239° and was analytically pure.

Anal.[5] Calcd. for $C_8H_6N_3Cl$: C, 53.50; H, 3.36; N, 23.4. Found: C, 53.76; N, 3.20; N, 23.7.

The compound was more readily obtained by treating 2,4-dichloroquinazoline[6] with aqueous ammonia.

A mixture of 300 ml. of 28% ammonium hydroxide and 30 g. of 2,4-dichloroquinazoline was allowed to stand three hours at room temperature and then heated on a steam-bath for one hour. After cooling, the precipitate was filtered and dissolved in 500 ml. of boiling 0.5 *N* hydrochloric acid. The crude product, m. p. 234–235°, obtained on neutralization of the solution, was recrystallized from 350 ml. of 95% ethanol, yielding light yellow product, m. p. 237°, 13 g. (48% yield). When mixed with the product from 2-chloro-4-methoxyquinazoline, no depression in the melting point was observed.

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(1) Present address: J. T. Baker Co., Phillipsburg, New Jersey.

(2) Lange and Sheibley, THIS JOURNAL, **54**, 4305 (1932); **55**, 1188 (1933).

(3) Lange and Sheibley, *ibid.*, **54**, 1994 (1932).

(4) Lange, Roush and Asbeck, *ibid.*, **52**, 3699 (1930).

(5) Microanalyses were kindly carried out by R. N. Boos and W. K. Humphrey.

(6) Gabriel and Colman, *Ber.*, **38**, 3561 (1905); Bogert and Scatchard, THIS JOURNAL, **41**, 2061 (1919).

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RECEIVED MAY 28, 1948

NEW COMPOUNDS

Kojic Acid Derivatives

2-(s-Butylthiomethyl)-5-hydroxy-4-pyrone.—Two and eight-tenths grams (0.12 mole) of sodium in 100 ml. of anhydrous toluene was powdered in the usual manner in a 250-ml. interjoint flask fitted with a sealed Hershberg stirrer, reflux condenser (soda lime tube), dropping funnel and thermometer. After cooling to about 70°, a solution of 10.8 g. (0.12 mole) of *s*-butyl mercaptan in 50 ml. of toluene was added during fifteen minutes with vigorous stirring. The mixture was stirred and refluxed for two hours, at the end of which time it was cooled to 10°, 18.5 g. (0.115 mole) of chlorokojic acid[1] was added and after remaining at that temperature for one hour, refluxing was initiated and maintained for three hours. After cooling, the mixture was transferred to a separatory funnel, cautiously diluted with 100 ml. of ice-water, shaken thoroughly and separated. The toluene layer was dried with sodium sulfate, filtered, and the solvent removed by distillation at reduced pressure, leaving a crystalline solid (12.1 g., 49% yield). This was recrystallized three times from hexane, giving a product melting at 93°.

Anal.[2] Calcd. for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.58. Found: C, 56.32; H, 6.52.

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(1) Chlorokojic acid (m. p. 166°) has been prepared by Yobuta, *J. Chem. Soc.*, **125**, 575 (1924), from kojic acid and thionyl chloride in the absence of a solvent. It has been found more convenient to prepare this compound by the interaction of one mole of kojic acid (supplied by the Northern Regional Research Laboratory, Peoria, Illinois) with two moles of purified thionyl chloride in anhydrous chloroform under gentle reflux, followed by cooling, filtration and recrystallization of the compound from water. The yield of product melting at 166° was 78%.

(2) Analyses by Oakwold Laboratories, Alexandria, Virginia.