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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[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.

Acknowledgment.—The authors are indebted to Drs. R. T. Major and Max Tishler for their kind encouragement and advice.

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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).

RESEARCH LABORATORIES
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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.

A red coloration was developed with aqueous and alcoholic ferric chloride solution.

5-Hydroxy-4-pyrone-2-methylisothiouronium Chloride.—To a solution of 9.6 g. (0.06 mole) of chlorokojic acid in 100 ml. of absolute ethanol was added 4.6 g. (0.06 mole) of thiourea, and the mixture was refluxed with stirring for one and one-half hours, a crystalline precipitate forming after approximately fifteen minutes. The mixture was cooled to 15°, filtered, washed with anhydrous ether and recrystallized twice from ethanol to give 6 g. (49.3% yield) of a product melting at 155°.

Anal. Calcd. for $C_7H_9ClN_2O_3S$: N, 11.84. Found: N, 11.52.

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[3] Present address, Oxford Products, Inc., Cleveland, Ohio.

Syntheses from Acetoheterocycles

During a preliminary study on syntheses from 2-acetofuran, 2-acetothiophene and 2-acetopyridine, it was found desirable to prepare the pyruvic esters and glycidic esters derived therefrom. A search of the literature has revealed that only thenoylpyruvic ester[1] had been synthesized and investigated. It has been found possible to prepare the desired glycidates by the interaction of the appropriate ketone with ethyl bromoacetate in the presence of sodium ethoxide,[2] and the acyl pyruvates were made from the ketone and diethyl oxalate using the same condensing agent.

Experimental

Ethyl Furoylpyruvate.—The method of Darzens[2] was followed, with modifications as indicated below.

Anhydrous sodium ethoxide under toluene was prepared in the usual manner in a 500-ml. three-neck flask fitted with a sealed Hershberg stirrer, dropping funnel, thermometer and reflux condenser with drying tube, from 3.6 g. (0.16 mole) of sodium, 7.5 g. (0.16 mole) of anhydrous ethanol and 100 ml. of anhydrous toluene. The alkoxide suspension was chilled to 0° and a solution of 16.5 g. (0.15 mole) of 2-acetylfuran and 23.4 g. (0.16 mole) of diethyl oxalate in 50 ml. of anhydrous toluene was added at that temperature with vigorous stirring during thirty minutes. The heavy suspension was stirred at 0 + 5° for an additional hour and at room temperature for two hours. After filtration by suction, the precipitate was washed thoroughly with anhydrous ether, dissolved in cold water and acidified with glacial acetic acid. Extraction with ether, drying and removal of the solvent by distillation left a solid which, on several crystallizations from hexane, gave 10 g. (31.7% yield) of yellow crystals melting at 70°.[3]

Anal.[4] Calcd. for $C_{10}H_{10}O_5$: C, 57.15; H, 4.80. Found: C, 56.69; H, 4.54.

Ethyl Nicotinoylpyruvate.—From 3-acetopyridine and diethyl oxalate as above, except that the aqueous solution, after acidification with glacial acetic acid, was brought to *p*H 7.1 with sodium carbonate solution before extraction with ether; m. p. 66°; 51% yield (recrystallized from hexane).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.08. Found: C, 59.81; H, 4.53.

Both new compounds gave red colorations with aqueous and alcoholic ferric chloride solutions.

Ethyl β-Methyl-β-(2′-thienyl)-glycidate.—Alcohol-free sodium ethoxide was prepared in the usual manner from 0.75 mole of sodium and 0.75 mole of anhydrous ethanol in 250 ml. of dry toluene.

To a 1000-ml. interjoint flask containing a sealed Hershberg stirrer, dropping funnel (drying tube) and reflux condenser (drying tube), was added 63 g. (0.5 mole) of 2-acetothiophene, 83.5 g. (0.53 mole) of ethyl bromoacetate and 250 ml. of anhydrous toluene. Stirring was initiated and the mixture was chilled to 0–5°. The sodium ethoxide suspended in toluene was added during five hours at that temperature and, after addition was complete, that temperature was maintained for an additional two hours. After standing overnight at room temperature, the mixture was poured into 500 ml. of ice and water with stirring, cautiously acidified with glacial acetic acid and separated. The aqueous layer was extracted with 100 ml. of toluene, which was then added to the initial toluene fraction. The combined organic layer was washed with dilute sodium bicarbonate solution, dried over sodium sulfate and fractionated to give 54 g. (51% yield) of a product boiling at 122–125° (2 mm.). A considerable amount of 2-acetothiophene was recovered in the forecut.

Anal. Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.75. Found: C, 56.30; H, 5.56.

Ethyl β-Methyl-β-(3′-pyridyl)-glycidate.—From 3-acetopyridine and ethyl bromoacetate as above. The acidified reaction mixture was brought to *p*H 7.1 with 10% sodium carbonate solution. The remainder of the procedure followed the directions above; yield, 30%; b. p. 110–112° (2 mm.).

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32. Found: C, 64.03; H, 6.02.

Ethyl β-Methyl-β-(2′-furyl)-glycidate.—From 2-acetofuran and ethyl bromoacetate; yield, 42.1%; b. p. 122–9° (2 mm.).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16. Found: C, 60.90; H, 6.21.

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[1] Angeli, *Gazz. chim. ital.*, **21**, 444 (1891).

[2] Darzens, *Compt. rend.*, **139**, 1215 (1904).

[3] Melting points were taken on a Fisher–Johns apparatus.

[4] Analyses by Oakwold Laboratories, Alexandria, Virginia.

[5] Present address, Oxford Products, Inc., Cleveland, Ohio.

6-Chloro-2-naphthylmethylcarbinol, 6-Chloro-2-vinylnaphthalene and Related Compounds

6-Chloro-2-naphthylmethylcarbinol.—6-Chloro-2-acetonaphthone (4.6 g., m. p. 81–82°[1]) and 8 g. of aluminum isopropylate were boiled in 50 ml. of acetone for one and one-half hours. After hydrolysis, the product was taken up in ether, washed, dried and the solvent evaporated to leave 3.8 g. (82.5%) of white solid carbinol, m. p. 99–100.5°. Recrystallization from Skellysolve "F" raised the melting point to 101.8–102.2°.

Anal. Calcd. for $C_{12}H_{11}ClO$: C, 69.75; H, 5.35; Cl, 17.16. Found: C, 69.78; H, 5.31; Cl, 17.30.

The same product, obtained in 75–80% yield by reduction with lithium aluminum hydride, was purified by distillation, b. p. 135° (0.3 mm.).

The β-naphthylurethan, prepared in benzene solution, melted at 153–154°.

Anal. Calcd. for $C_{23}H_{17}ClNO_2$: C, 73.69; H, 4.57; N, 3.74; Cl, 9.46. Found: C, 73.66; H, 4.72; N, 3.86; Cl, 9.45.

6-Chloro-2-naphthylmethylcarbinyl Chloride.—The carbinol (20 g.), dissolved in 200 ml. of ether, was treated with 250 ml. of concentrated hydrochloric acid. A precipitate formed immediately, which was collected and recrystallized from Skellysolve "F" to give crops of crystals, totalling 22.7 g. (84%), melting from 79–81°. Two recrystallizations from the same solvent raised the melting point to 80.5–81.5°.

Anal. Calcd. for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.48. Found: C, 64.15; H, 4.44.

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[1] Jacobs, Winstein, Ralls and Robson, *J. Org. Chem.*, **11**, 30 (1946).