(III) with noval bromide (2-bromo-5-diethylaminopentane) according to the general procedure of Rohrman and Shonle,[3] compound (III) was converted to its *p*-toluenesulfonamido derivative (IV) which was alkylated successfully with 3-diethylaminopropyl chloride. However, hydrolysis of the alkylated product (V) gave material which could not be purified.

Barber and co-workers[2] similarly effected the propylation of compound (I) but the product (II) was then hydrolyzed and reduced. The resulting amine was reacted with 5-diethylamino-2,2-diethoxypentane followed by reduction to form their analog. The product was particularly susceptible to atmospheric oxidation and did not readily yield crystalline salts.[2]

Experimental[4]

3-Nitro-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (II).—A solution of 10 g. (0.032 mole) of 3-nitro-4-(*p*-toluenesulfonamido)-anisole[2] (I) and 4.6 g. (0.037 mole) of *n*-propyl bromide in 35 ml. of commercial absolute ethanol was refluxed with 4.5 g. (0.032 mole) of anhydrous potassium carbonate for seventeen hours.[5] The hot solution was filtered, the alcohol was evaporated and the deep red product was washed with a 10% sodium hydroxide solution and then with water. The yield of compound (II) as a tan-colored powder, melting at 105–106°, was 7.2 g. (64%). Two recrystallizations from ethanol–water gave white crystals melting at 107–108°; reported m. p. 108–109°.

Anal. Calcd. for $C_{17}H_{20}N_2O_5S$: C, 56.08; H, 5.54; N, 7.70; S, 8.81. Found: C, 56.25; H, 5.94; N, 7.85; S, 8.96.

3-Amino-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (III).—To a well stirred refluxing solution of 90 g. (0.247 mole) of 3-nitro-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (II) (m.p. 105–106°) in 1000 ml. of 85% ethanol (in a 2l. three-necked flask fitted with a reflux condenser and a mercury-sealed stirrer) was added 20 g. of ammonium chloride and, in small portions, 130 g. of zinc dust. After the reaction mixture had been stirred and refluxed for five hours, it was filtered and the insoluble material washed several times with small portions of hot 95% ethanol. To the combined ethanol solutions, 250 ml. of water was added and, after chilling, the precipitated white flocculent product was filtered and dried *in vacuo* to give 75 g. (91%) of amine (III) melting at 112°. Two recrystallizations did not raise the melting point.

Anal. Calcd. for $C_{17}H_{22}N_2O_3S$: C, 61.05; H, 6.63; N, 8.38; S, 9.59. Found: C, 61.08; H, 6.76; N, 8.41; S, 9.53.

3-(*p*-Toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (IV).—A solution of 60 g. (0.18 mole) of 3-amino-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (III) and 33.6 g. (0.18 mole) of *p*-toluenesulfonyl chloride in 120 ml. of pyridine was refluxed seven and one-half hours and allowed to stand overnight at room temperature. The addition of 120 ml. of 95% ethanol followed by the slow addition of 500 ml. of ice–water gave a heavy precipitate, which, after filtering, was washed with several portions of a 6 *N* hydrochloric acid until a sample of the washings, when made basic, was only slightly cloudy. After washing several times with water and drying in the oven at 70°, 78.5 g. (90%) of compound (IV) (m. p. 162–164°) was obtained. Several recrystallizations from ethanol–water gave white crystals melting at 167° cor.

Anal. Calcd. for $C_{24}H_{28}N_2O_5S_2$: C, 58.99; H, 5.78; N, 5.74; S, 13.12. Found: C, 59.21; H 6.01; N, 5.81; S, 13.05.

3-(N-γ-Diethylaminopropyl-*p*-toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (V).—A solution containing 78.5 g. (0.16 mole) of 3-(*p*-toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (IV) and 27.2 g. (0.184 mole) of 3-diethylaminopropyl chloride[6] in 215 ml. of dioxane was refluxed with 22.4 g. (0.16 mole) of anhydrous potassium carbonate for seventeen hours.[5] After the reaction mixture had been allowed to cool to room temperature, it was slowly poured with stirring into 600 ml. of ice–water. The resulting oil soon solidified. The solid was filtered, washed with water and dried in the oven at 80° to give 92.1 g. (96%) of product (V) melting at 152–154°. Rather surprisingly, several recrystallizations from dioxane–water gave white crystals melting at 130–133° which, however, analyzed for compound (V).

Anal. Calcd. for $C_{31}H_{41}N_3O_5S_2$: C, 61.87; H, 7.01; N, 6.98; S, 10.65. Found: C, 61.40; H, 7.28; N, 7.12; S, 10.88.

(3) Rohrman and Shonle, THIS JOURNAL, **66**, 1640 (1944).

(4) Microanalyses by Oakwold Laboratories, Alexandria, Virginia. Melting points are uncorrected.

(5) See Izmail'skii and Simonov, *J. Gen. Chem. (U.S.S.R.)*, **10**, 1580 (1940); *C. A.*, **35**, 2870 (1941).

(6) Breslow, Walker, Yost and Hauser, THIS JOURNAL, **67**, 1472 (1945).

DEPARTMENT OF CHEMISTRY
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The Catalytic Oxidation of Piperonyloin to Piperil

BY MARVIN WEISS AND MILDRED APPEL

In a previous article,[1] a statement was made that piperonyloin could not be oxidized to piperil by cupric acetate and ammonium nitrate in acetic acid, due to the formation of tars. This was similar to the observation of Perkin,[2] that when dilute nitric acid reacted with piperonyloin a large amount of oxalic acid was formed.

A study of the effects of increasing amounts of catalyst showed that a point could be reached where the reaction rate of cupric ion with a benzoin (reaction A) exceeded the reaction rate of ammonium nitrate with cuprous ion (reaction B). This manifested itself by the formation of a reddish-brown precipitate of copper oxide, which did not redissolve unless more ammonium nitrate was added.

(A) $RCH(OH)COR + 2Cu(OAc)_2 \longrightarrow RCOCOR + 2CuOAc + 2AcOH$

(B) $2CuOAc + NH_4NO_3 + 2AcOH \longrightarrow 2Cu(OAc)_2 + NH_4NO_2 + H_2O$

(C) $CH_2O_2C_6H_3CH(OH)COC_6H_3O_2CH_2 + NH_4NO_3 \longrightarrow (COOH)_2 +$ decomposition

This reversal of reaction rates led to the interesting speculation that, in the event the oxidation of piperonyloin was carried out under conditions just short of copper oxide formation, that is, where the reaction rate of A equalled B, one might expect that reaction C, being slower than a combination of A plus B, would be suppressed. That reaction C might be slower is suggested by the re-

(1) Weiss and Appel, THIS JOURNAL, **70**, 3666 (1948).

(2) Perkin, *J. Chem. Soc.*, **59**, 164 (1891).

action of benzoin with ammonium nitrate where only 40% was converted to benzil, while in the presence of cupric acetate a quantitative yield was obtained.[1] Experimentally, we have verified these ideas and have been able to prepare piperil in 89% yield.

Experimental

In a 250-cc. flask fitted with a reflux condenser are placed 4.5 g. of piperonyloin, 1.5 g. of cupric acetate, 1.5 g. of ammonium nitrate and 100 cc. of an 80% by volume acetic acid–water solution. The flask is heated gently, over an asbestos-covered wire gauze, agitating to prevent a local concentration of ammonium nitrate. Reflux gently for one hour. Toward the end of the reaction, a variable amount of cupric oxalate precipitates (*ca.* 20 mg.). The solution is filtered hot, with suction, before allowing the piperil to crystallize. When cool, 50 cc. of water is added to precipitate the remaining piperil. The piperil is collected on a Buechner funnel and washed well with water. The yield is 4.0 g. or 89%, m. p. 173–174° cor.; Fehling test negative.

The piperil was checked by cleaving it with sodium cyanide in aqueous alcohol. The piperonylic acid formed showed no melting point depression when mixed with piperonylic acid obtained by the oxidation of piperonal.

LABORATORY
AMERICAN PHARMACEUTICAL CO.
NEW YORK, N. Y. RECEIVED FEBRUARY 15, 1949

Mercaptans from Aldehydes

BY FRANK KIPNIS, ISIDORE LEVY AND JOHN ORNFELT

The method for the preparation of mercaptans by the interaction of aldehydes with hydrogen sulfide, followed by reduction of the disulfide, has been reported by several workers,[1,2] though details were not complete. During the present study, it was found possible to prepare previously unreported mercaptans by the above procedure, and indications are that the method is rather versatile for the preparation of difficulty available aromatic and heterocyclic mercaptans.

Aluminum amalgam seems to be the reducing agent of choice, though zinc in acetic acid has been used in the reduction of the disulfide[2] from piperonal.

Experimental

5-Methylfurfurylmercaptan.—In a 1000-ml. three-neck flask fitted with a sealed stirrer, reflux condenser and drying tube, was placed 24 g. (0.22 mole) of 5-methylfurfural[3] and 500 ml. of an ethanolic solution of ammonium hydrogen sulfide.[4] The mixture was stirred at room temperature for five hours, heated on a water-bath for one hour and allowed to stand overnight. The volatiles were removed by distillation from the steam-bath at reduced pressure, leaving a brown residue.

Without further purification, the presumed disulfide was transferred to a 1000-ml. three-neck flask containing a sealed stirrer, reflux condenser and dropping funnel. Five hundred milliliters of solvent ether was added, together with aluminum amalgam[5] prepared from 30 g. of aluminum turnings. The stirrer was started and 30 ml. of water was added to the suspension during ten minutes. The reduction commenced almost immediately and continued steadily, the mixture being heated from time to time with a warm water-bath when the reaction showed signs of slackening. After standing overnight, the aluminum sludge was separated by filtration, washed with 100 ml. of ether, the filtrate and washings combined, dried with calcium sulfate, filtered and the solvent stripped, finally under reduced pressure. The residue was fractionated at 70° (3 mm.) to give 8 g. (28.4% yield) of a colorless liquid, $n^{20}D$ 1.5258.

Anal.[6] Calcd. for C_6H_8OS: C, 56.22; H, 6.28. Found: C, 56.71; H, 6.43.

3-Methoxy-5-hydroxybenzyl Mercaptan.—bis-(3-Methoxy-4-hydroxybenzyl) disulfide, m. p. 129–130°, was prepared from vanillin according to the method of Manchot,[2] and reduced with aluminum amalgam as above to give a 59% yield of a colorless oil distilling at 75–80° (0.03 mm.), $n^{20}D$ 1.5940.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.44; H, 5.92; S, 18.84. Found: C, 56.57; H, 6.21; S, 18.95.

It was reported that the disulfide was not reduced with zinc and acetic acid.[2]

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NEW COMPOUNDS

D-Glucose-thiophene-2′-methyl Mercaptal

The procedure used was based on the methods devised by Levene[1] and Wolfrom.[2] In a 300-ml. pressure bottle, 18 g. (0.1 mole) of D-glucose was dissolved in 27 ml. of concentrated hydrochloric acid. To this was added 27 g. (0.207 mole) of thiophene-2-methyl mercaptan. The bottle was stoppered and shaken at 35° for thirty minutes, after which time the contents were poured into 500 ml. of ice-water, causing the precipitation of a semicrystalline product. The precipitate was removed by filtration, washed with much cold water and then recrystallized successively from hot water, aqueous methanol and much isopropyl ether to give 20 g. (47.4% yield) of a product melting at 130–131°.

Anal.[3] Calcd. for $C_{16}H_{22}O_5S_4$: C, 45.47; H, 5.25; S, 30.35. Found: C, 45.66; H, 5.50; S, 30.38.

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5-Mercaptomethylfuroic Acid

A solution of 12.6 g. (0.05 mole) of 2-carbomethoxyfuran-5-methylisothiouronium chloride,[1] 5 g. (0.125 mole) of sodium hydroxide, 50 ml. of ethanol and 20 ml. of water

(1) Staudinger and Reichstein, U. S. Patent 1,715,795 (1929); 1,748,527 (1930).

(2) Manchot and Zahn, *Ann.*, **345**, 315 (1906).

(3) Rinkes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 393.

(4) Prepared as follows: 500 ml. of absolute ethanol was saturated with anhydrous ammonia at 15°. The solution was divided into two equal portions and dry hydrogen sulfide was passed into one portion until crystallization began, after which the two solutions were mixed and used immediately.

(5) Hartman and Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 233.

(6) Analyses by Oakwold Laboratories, Alexandria, Va.

(1) Levene and Meyers, *J. Biol. Chem.*, **74**, 695 (1927).

(2) Wolfrom, THIS JOURNAL, **52**, 2466 (1930).

(3) Analyses by Oakwold Laboratories, Alexandria, Va.

(4) Present address: Oxford Products, Inc., Cleveland 3, Ohio.

(1) British Patent 588,377, May 21, 1947.