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, $n^{20}\text{D}$ 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.), $n^{20}\text{D}$ 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]

RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, N. J.
RECEIVED DECEMBER 29, 1949

---

[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.

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.

RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, N. J.
FRANK KIPNIS[4]
JOHN ORNFELT
RECEIVED DECEMBER 29, 1948

---

[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.

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] British Patent 588,377, May 21, 1947.

was refluxed and stirred for three hours. The solution was cooled and acidified to congo red with hydrochloric acid and then extracted five times with a total of 1 l. of ethyl ether. After drying over calcium sulfate, the solvent was removed by distillation from the steam-bath, and the residue was recrystallized several times from carbon tetrachloride giving 5 g. (61.5% yield) of product melting at 91–92°.

Anal.[2] Calcd. for $C_6H_6O_3S$: C, 45.56; H, 3.82. Found: C, 45.90; H, 3.77.

---

[2] Analyses by Oakwold Laboratories, Alexandria, Va.

RESEARCH LABORATORIES FRANK KIPNIS
AMERICAN HOME FOODS, INC. ISIDORE LEVY
MORRIS PLAINS, N. J. JOHN ORNFELT

RECEIVED DECEMBER 29, 1949

2-Acetylfuran Diethyl Mercaptol

In a cooled pressure bottle was placed 5.5 g. (0.05 mole) of 2-acetylfuran, 15 g. (0.234 mole) of ethyl mercaptan and 25 ml. of dry toluene containing 100 mg. of hydrogen chloride. The bottle was stoppered and shaken vigorously, a violet-colored water layer forming immediately. After refrigeration for three hours, the reaction mixture was extracted several times with a saturated solution of sodium bicarbonate, after which the organic layer was dried over potassium carbonate, filtered therefrom and then fractionated to give a yellowish oil boiling at 93–96° (2.5 mm.) in a yield of 4.2 g. (46.7%).

Anal.[1] Calcd. for $C_{10}H_{16}OS_2$: C, 55.51; H. 7.45; S, 29.64. Found: C, 56.11, H, 7.66; S, 29.73.

RESEARCH LABORATORIES FRANK KIPNIS[2]
AMERICAN HOME FOODS, INC. JOHN ORNFELT
MORRIS PLAINS, N. J.

RECEIVED DECEMBER 29, 1948

---

[1] Analyses by Oakwold Laboratories, Alexandria, Va.

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

Thiophene-2-methylisothiouronium Chloride and 2-(thiophene-2′-methylthio)-4-methyl-6-oxypyrimidine

Thiophene-2-methylisothiouronium Chloride.—In a 250-ml. three-neck flask fitted with a sealed stirrer and reflux condenser with drying tube, was placed 26.5 g. (0.2 mole) of thiophene-2-methyl chloride,[1] 15.2 g. (0.2 mole) of thiourea and 75 ml. of anhydrous ethanol. The solution was stirred and refluxed gently for five hours. At the end of that time, the volatiles were removed by distillation from the steam-bath under reduced pressure, and the residue washed thoroughly with anhydrous ether, giving 40.8 g. (98% yield) of a white crystalline product melting at 160–161°.[2] The material was of sufficient purity to be used in the subsequent reaction.

2-(Thiophene-2′-methylthio)-4-methyl-6-oxypyrimidine.—The procedure of Johnson and Bailey[3] for the synthesis of thiopyrimidines was used. In a 250-ml. three-neck flask fitted with a sealed stirrer, reflux condenser and drying tube, thermometer and dropping funnel was placed 16.7 g. (0.06 mole) of thiophene-2-methylisothiouronium chloride, 11 g. (0.085 mole) of freshly distilled ethyl acetoacetate and 60 ml. of anhydrous ethanol. The mixture was stirred and chilled to 0 ± 2°, and a solution of 3.7 g. (0.161 mole) of sodium in 100 ml. of anhydrous ethanol was added during one hour. The low temperature was maintained for an additional hour and the mixture was then allowed to stand overnight at room temperature. The solvent was removed by distillation at reduced pressure, the residue suspended in 50 ml. of water and acidified to litmus with glacial acetic acid, causing the formation of a precipitate. This was filtered by suction, washed with a little cold water and ether and recrystallized four times from ethanol to give 9.5 g. (50%) of a product melting at 161°.

Anal.[4] Calcd. for $C_{10}H_{10}N_2OS_2$: C, 50.40; H, 4.23. Found: C, 49.68; H, 4.09.

The technical assistance of Mr. Herbert Landesman is gratefully acknowledged.

RESEARCH LABORATORIES FRANK KIPNIS[5]
AMERICAN HOME FOODS, INC. JOHN ORNFELT
MORRIS PLAINS, N. J.

RECEIVED DECEMBER 29, 1948

---

[1] Blicke and Leonard, THIS JOURNAL, 68, 1934 (1946).

[2] All melting points were taken with a Fisher-Johns apparatus.

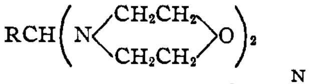
[3] Johnson and Bailey, THIS JOURNAL, 35, 1007 (1913).

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

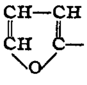
[5] Present address: Oxford Products, Inc., Cleveland 3, Ohio.

Some Derivatives of Morpholine

The compounds listed in the table were prepared by heating for five minutes on a steam-bath 0.02 mole of the appropriate aldehyde, dissolved in 5 ml. of 95% ethyl alcohol, with 3.5 g. of morpholine. The solution was then cooled in an ice-bath and seeded or scratched to induce crystallization; the crude product was removed by filtration and recrystallized from a small volume of ethyl alcohol, acetone or diethyl ether. The yields were essentially quantitative if additional crops were recovered by evaporating the mother liquors. These compounds are soluble in all the common organic solvents; they are readily hydrolyzed.



$$RCH\left(N\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}O\right)_2$$

R	Formula	M. p., °C. (cor.)	N Analyses, %[a] Calcd.	Found
2-$NO_2C_6H_4$–	$C_{15}H_{21}O_4N_3$	130.5–131.5	13.68	13.48
3-$NO_2C_6H_4$–	$C_{15}H_{21}O_4N_3$	132–133	13.68	13.46
2-ClC_6H_4–	$C_{15}H_{21}O_2N_2Cl$	98–99	9.44	9.43
4-ClC_6H_4–	$C_{15}H_{21}O_2N_2Cl$	135–136	9.44	9.25
2-HOC_6H_4–	$C_{15}H_{22}O_3N_2$	123–124	10.07	10.09
4-$CH_3OC_6H_4$–	$C_{16}H_{24}O_3N_2$	114.5–115.5	9.58	9.58
4-$(CH_3)_2NC_6H_4$–	$C_{17}H_{27}O_2N_3$	130.5	13.76	13.68
3,4-$CH_2O_2C_6H_3$–	$C_{16}H_{22}O_4N_2$	109–110	9.15	9.14
	$C_{13}H_{20}O_3N_2$	120–120.5	11.10	11.17

[a] Micro-Dumas method.

Non-crystallizable sirups were formed under these conditions with 3- and 4-methylbenzaldehyde, 3-hydroxybenzaldehyde and 2-methoxybenzaldehyde.

A 1:1-addition product was isolated when 0.04 mole of morpholine was added slowly with agitation to 0.04 mole of furfural at 0°. The solid product, after extraction with small quantities of cold absolute diethyl ether, melted at 49–50° with decomposition.

Anal. Calcd. for $C_9H_{13}O_3N$: N, 7.64. Found: N, 7.92.

On standing, this addition product decomposed to furfural and 4,4′-furfurylidenedimorpholine, m. p. 120–120.5°. 2-Chlorobenzaldehyde and salicylaldehyde also yielded very unstable 1:1-addition products with morpholine.

4,4′-Benzylidenedimorpholine–Sulfur Dioxide Addition Product.—A solution of 5 g. of benzylidenedimorpholine[1] in 60 ml. of diethyl ether was cooled in a salt-ice mixture and saturated with dry sulfur dioxide. A white solid precipitated almost immediately; it was recovered by filtration and washed with three 10-ml. portions of ether; m. p. 131–133°. This material was water soluble

---

[1] Zief and Mason, *J. Org. Chem.*, 8, 5 (1943); Herlocker, Kleinholz and Watkins (to Sinclair Refining Co.), U. S. Patent 2,388,058 (1945).