

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.*<sup>2</sup> Calcd. for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>S: C, 45.56; H, 3.82. Found: C, 45.90; H, 3.77.

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

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### 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.*<sup>1</sup> Calcd. for C<sub>10</sub>H<sub>16</sub>OS<sub>2</sub>: C, 55.51; H, 7.45; S, 29.64. Found: C, 56.11, H, 7.66; S, 29.73.

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

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

### Thiophene-2-methylisothiuronium Chloride and 2-(thiophene-2'-methylthio)-4-methyl-6-oxypyrimidine

**Thiophene-2-methylisothiuronium 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,<sup>1</sup> 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°.<sup>2</sup> 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<sup>3</sup> 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-methylisothiuronium chloride, 11 g. (0.085 mole) of freshly distilled ethyl acetate 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.*<sup>4</sup> Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>OS<sub>2</sub>: C, 50.40; H, 4.23. Found: C, 49.68; H, 4.09.

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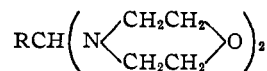
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
(4) Analyses by Oakwold Laboratories, Alexandria, Va.

(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.



R	Formula	M. p., °C. (cor.)	N Analyses, % <sup>a</sup>	
			Calcd.	Found
2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sub>3</sub>	130.5–131.5	13.68	13.48
3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sub>3</sub>	132–133	13.68	13.46
2-ClC <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> Cl	98–99	9.44	9.43
4-ClC <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> Cl	135–136	9.44	9.25
2-HOC <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N <sub>2</sub>	123–124	10.07	10.09
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N <sub>2</sub>	114.5–115.5	9.58	9.58
4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> -	C <sub>17</sub> H <sub>17</sub> O <sub>2</sub> N <sub>2</sub>	130.5	13.76	13.68
3,4-CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub>	109–110	9.15	9.14
	C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> N <sub>2</sub>	120–120.5	11.10	11.17

<sup>a</sup> 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<sub>9</sub>H<sub>13</sub>O<sub>3</sub>N: 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<sup>1</sup> 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) 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).

(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).