

$d_4^{20}$  1.0718,  $d_4^{23}$  1.0537,  $d_4^{23}$  1.0490,  $n_D^{20}$  1.46535,  $n_D^{20}$  1.46897,  $n_F^{20}$  1.47812,  $n_G^{20}$  1.48607;  $MR_D$  (calcd.) 43.93, (obs.) 44.43. This ester has previously been described by Brühl,<sup>22</sup> who reported:  $n_D^{23}$  1.46862,  $d_4^{23}$  1.0478.

Two grams of the ester was hydrolyzed by refluxing for several hours with 2 g. of potassium hydroxide dissolved in 50% alcohol. After distilling off the alcohol, the cooled alkaline solution was poured into ice-cold 5% hydrochloric acid. The precipitated 2,5-dimethylfuroic acid was filtered with suction and dried; without further purification the acid melted at 132.5–133.5 (corr.). After crystallization from petroleum benzene (b. p. 100–110°), the acid formed white needles, m. p. 134°. This acid has previously been obtained by several methods; the melting points reported by various investigators lie in the range 133–135°.<sup>23</sup>

### Summary

It has been shown that rearrangement of the  $\alpha$ -furfuryl group into the 5-methylfuryl group occurs in the reaction of  $\alpha$ -furfuryl chloride with aqueous sodium cyanide. The resulting nitrile contains approximately 85% of 5-methyl-2-furonitrile and 15% of  $\alpha$ -furfuryl cyanide.

5-Methylfurfuryl chloride was synthesized and was found to react normally with aqueous sodium cyanide to give 5-methylfuryl-2-acetonitrile. The latter upon hydrolysis gave 5-methylfuryl-2-acetic acid. This acid was also synthesized by an independent method from 5-methylfurfural.

It is suggested that the mechanism of the rearrangement reaction involves 1,4-addition of hydrogen cyanide to the furan ring.

<sup>22</sup> Brühl, *J. prakt. Chem.*, [2] 50, 143 (1894).

<sup>23</sup> Wislicenus and Stadnicky, *Ann.*, 146, 306 (1868); Böttinger, *ibid.*, 172, 241 (1874); Harrow, *ibid.*, 201, 145 (1880); Fittig and v. Eynern, *ibid.*, 250, 190 (1889); Fittig and Parker, *ibid.*, 267, 212 (1892).

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### NOTES

#### The Preparation of Tetrathioptone

By STEPHEN A. KARASIEWICZ

In the course of attempts to iodize oleic acid by means of hydrogen sulfide and iodine, employing acetone as solvent, it was observed that white crystals of tetrathioptone,  $C_{15}H_{28}S_4$ , were formed as a by-product of the reaction. This substance was first described by Fromm and Baumann.<sup>1</sup>

The course of the reaction between iodine, hydrogen sulfide and acetone is probably analogous to the method of Fromm and Baumann, who used concentrated hydrochloric acid, hydrogen sulfide and acetone, since there is

<sup>1</sup> Fromm and Baumann, *Ber.*, 22, 1044 (1889).

conversion of iodine into hydriodic acid during the reaction. A larger yield is obtained from the new method, as 20 g. of tetrathio-pentone is obtained from 60 cc. as compared to 16 g. from 100 cc. of acetone. In repeating the Fromm and Baumann method only 3 g. of tetrathio-pentone was obtained. The method of preparation and purification used for tetrathio-pentone during this study also appeared easier. The substance crystallizes readily from the acetone and when filtered and washed with fresh acetone is pure.

When tetrathio-pentone was reduced in liquid ammonia with sodium, isopropyl mercaptan was isolated and identified as the 3,5-dinitrobenzoyl derivative.<sup>2</sup>

**Experimental.**—Twenty grams of pulverized iodine is dissolved in 60 cc. of acetone and a stream of hydrogen sulfide is passed through this solution for seven hours. Fresh acetone should be added to replace that evaporated by the heat evolved at the beginning of the reaction. The completion of the reaction is marked by a reddish-brown discoloration of the solution and by the appearance of white crystals, which increase in number upon standing in the refrigerator. The crystals are filtered and carefully washed with acetone, in which they are sparingly soluble. When 30 cc. of oleic acid is added to the above solution and hydrogen sulfide used as previously, there appear at the interface between the two non-miscible layers very pure crystals of tetrathio-pentone.

These crystals, recrystallized from acetone or alcohol, melted sharply at 170–171°. The mixture melting point of equal amounts of tetrathio-pentone made by both methods was 170–171°.

*Mol. wt.* (Camphor method).<sup>3</sup> Calcd. for  $C_{15}H_{28}S_4$ : 336. Found: 333.4, 337.0.  
*Anal.* Calcd. for  $C_{15}H_{28}S_4$ : S, 38.09. Found: S, 37.92, 38.13.

To 150 cc. of dry liquid ammonia in a Dewar flask is added 1 g. of powdered tetrathio-pentone, which is treated with 0.3 g. of metallic sodium. After disappearance of the blue color ether is added and the ammonia allowed to evaporate. The remaining white precipitate is quickly filtered and covered with fresh ether. The suspension obtained is cooled in a salt-ice freezing mixture, while hydrogen chloride gas is passed through. When the ether solution was neutralized and the ether distilled, isopropyl mercaptan was isolated according to Wertheim's procedure. The lead salt of isopropyl mercaptan was also prepared.

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<sup>2</sup> Wertheim, *THIS JOURNAL*, **51**, 3662 (1929).

<sup>3</sup> Rast in Houben's "Die Methoden der organischen Chemie," Leipzig, 1925, Vol. I, p. 933.

### Furan Reactions. III. Absorption of Furan Vapors

BY CHARLES D. HURD AND A. R. GOLDSBY

Mixtures of furan and air were made by introducing furan from a pipet into a 2-liter flask. Using a stopcock attachment, this gas was readily transferred into the buret of a modified Orsat type apparatus.<sup>1</sup> Fuming sulfuric acid (8% SO<sub>3</sub>) was found to absorb the furan quickly and quantitatively, hence it was used to determine the percentage by volume of furan in the gas. The mixtures which were studied below contained about 10% of furan. The fuming acid is immediately darkened in color as the furan reaches it.

Using 40% potassium hydroxide solution in an absorption pipet, only one-third of the furan content of the gas was removed after thirty passes in and out of the reagent. With alkaline potassium iodomercurate (the reagent for acetylene) or 52% sulfuric acid solution, about 35 to 40% of the furan was removed by seven two-minute passes. With 62.5, 67.5 and 72.5% sulfuric acid, the percentage of furan removed after seven passes, respectively, was 57, 90 and 95. Using 82.5% sulfuric acid, the furan was absorbed completely in three passes. The 82.5% acid is the reagent which is used for the absorption of propylene,  $\alpha$ - and  $\beta$ -butylenes, butadiene, etc. Furan was also removed quantitatively with mercuric acetate solution (50 g. in 225 cc. of water) thereby forming<sup>2</sup> tetraacetoxymercurifuran, C<sub>4</sub>O(HgOAc)<sub>4</sub>. Unfortunately for its use in separating furan from other gases, this reagent also removes carbon dioxide and unsaturated hydrocarbons.

**Conclusions.**—Furan (gas) may be absorbed quantitatively by 82.5% sulfuric acid. A mixture of furan and ethylene could be analyzed in this manner since ethylene is not absorbed unless fuming sulfuric acid is used. The absorption method is not applicable for the quantitative analysis of furan when it is admixed with other unsaturated hydrocarbon gases. With such mixtures, liquefaction and distillation (by precise methods of fractionation) would be necessary for exact analysis.

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<sup>1</sup> Hurd and Spence, *THIS JOURNAL*, **51**, 3357 (1929).

<sup>2</sup> Ciusa and Grilla, *Gazz. chim. ital.*, **57**, 323 (1927).