

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,²² who reported: $n_D^{23.1}$ 1.46862, $d_4^{23.1}$ 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°.²³

Summary

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

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

²³ 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 Tetrathiopentone

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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 tetrathiopentone, $C_{15}H_{28}S_4$, were formed as a by-product of the reaction. This substance was first described by Fromm and Baumann.¹

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

¹ 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.²

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).³ 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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² Wertheim, THIS JOURNAL, 51, 3662 (1929).

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