[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

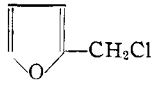
REARRANGEMENT OF THE ALPHA-FURFURYL GROUP. II. 5-METHYLFURFURYL CHLORIDE AND 5-METHYLFURYLACETIC ACID[1]

BY E. W. SCOTT AND JOHN R. JOHNSON

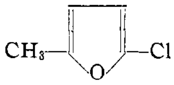
RECEIVED MARCH 23, 1932 PUBLISHED JUNE 6, 1932

It has been observed[2] recently that the nitrile obtained by the action of α-furfuryl chloride upon aqueous sodium cyanide produces 5-methylfuroic acid upon hydrolysis, but the experimental data are too meager to fix with certainty the exact stage at which the rearrangement occurs. The present study was undertaken with the object of establishing this point and of investigating the mechanism of the rearrangement.

The possibility of a rearrangement of α-furfuryl chloride (I) into the isomeric 5-methyl-2-chlorofuran (II), or a dynamic isomerism of these halides, was considered to be unlikely on theoretical grounds. The synthesis of 5-methyl-2-chlorofuran through the decarboxylation of 2-methyl-5-chloro-3-furoic acid[3] now excludes definitely this possibility, since the two halides are found to be entirely distinct individuals. The relationship between them is analogous to that of benzyl chloride and the chlorotoluenes; α-furfuryl chloride has the higher boiling point and the more labile halogen atom. Likewise, the possibility of a rearrangement during hydrolysis of the nitrile has now been excluded through the synthesis of authentic 5-methyl-2-furonitrile, by the dehydration of 5-methylfurfuraldoxime. A comparison of the physical properties of 5-methyl-2-furonitrile and of α-furfuryl cyanide with those of the nitrile obtained from α-furfuryl chloride and aqueous sodium cyanide, indicate that the latter is a mixture of approximately 85% 5-methyl-2-furonitrile and 15% α-furfuryl cyanide. This result demonstrates clearly that the rearrangement of the α-furfuryl group occurs in the production of the nitrile.



B. p. 49.6–50° at 27 mm.
I



B. p. 48–49° at 70 mm.
II

In dealing with the mechanism of rearrangement it seemed of interest to prepare a derivative of α-furfuryl chloride with a substituent in the 5-position and to observe its behavior toward aqueous sodium cyanide.

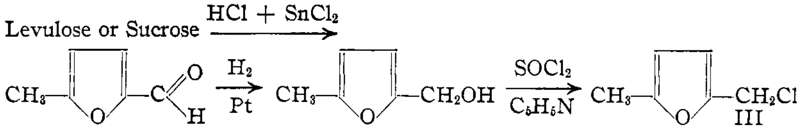
---

[1] This article is an abstract of a portion of a thesis submitted by E. W. Scott to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in July, 1931.

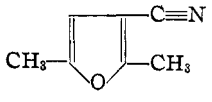
[2] (a) Reichstein, *Ber.*, **63**, 749 (1930); (b) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930).

[3] This synthesis was carried out by Mr. G. F. Rundel.

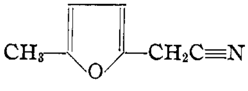
5-Methylfurfuryl chloride (III) was selected for this purpose and was synthesized through the reactions indicated below.



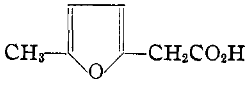
III



IV



V



VI

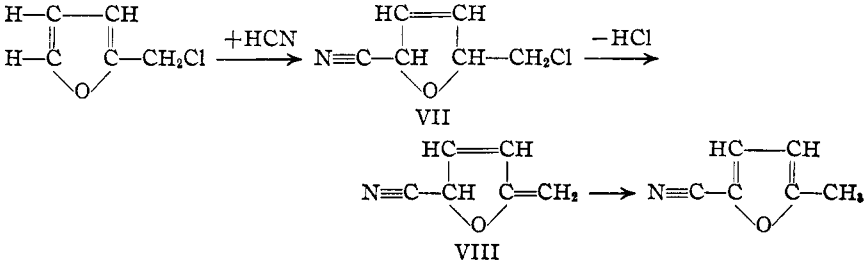
Since the 5-position in this halide is blocked, the reaction with sodium cyanide might give the normal product, 5-methylfuryl-2-acetonitrile (V), or a product of rearrangement, 2,5-dimethyl-3-furonitrile (IV), in which the cyano group entered the 3-position of the ring. Upon hydrolysis the latter would give rise to the known 2,5-dimethylfuroic acid (m. p. 134°), and the former would yield 5-methylfuryl-2-acetic acid. The nitrile actually obtained in this reaction, upon hydrolysis with aqueous potassium hydroxide and subsequent acidification, gave an acid melting at 57–58°, presumably 5-methylfuryl-2-acetic acid (VI). To establish the identity of this acid, an authentic specimen was synthesized from 5-methylfurfural, through the series of reactions which had been used to obtain 2-furylacetic acid from furfural.[2b,4] The authentic acid melted at 57–58° and showed no depression of the melting point when mixed with the acid obtained from 5-methylfurfuryl chloride.[5] This result indicates that the rearrangement requires the presence of a hydrogen in the 5-position, and that the 3- and 5-positions in the furan ring do not have the close relationship shown by the ortho and para positions in the benzene ring.

To account for the formation of 5-methylfuronitrile from α-furfuryl chloride, Reichstein[2a] has postulated an unstable intermediate compound (VIII) but has not proposed a mechanism to account for its production. The formation of this unstable structure (VIII) can be accounted for by rearrangement of the α-furfuryl group in the course of the reaction, but it seems more likely that the first step is a 1,4-addition of hydrogen cyanide

---

[4] In a private communication this result was reported to Dr. Reichstein, who informed us that he had carried out a similar investigation and had observed the same result. In a recent article Reichstein and Zschokke [*Helv. Chim. Acta,* **15**, 249 (1932)] have described a synthesis of 5-methylfuryl-2-acetic acid by an entirely independent method, from 5-methylfuroyl chloride. They reported that the synthetic acid melted at 61–62°, and was identical with the acid obtained from 5-methylfurfuryl chloride. This halide was prepared from 5-methylfurfuryl alcohol, obtained by reduction of 5-hydroxymethylfurfural.

[5] It is probable that none of the isomeric 2,5-dimethyl-3-furoic acid is produced from 5-methylfurfuryl chloride, since this acid is sparingly soluble in water and could be detected readily.



(VII). This addition would be followed by elimination of hydrogen chloride and rearrangement of the resulting 5-methylene-2,5-dihydro-2-furonitrile (VIII) into 5-methylfuronitrile.

The postulation of 1,4-addition to the furan ring finds support in the interpretation of the behavior of furan derivatives in halogenation, nitration and ring-opening reactions. 1,4-Addition of hydrogen cyanide to the furan ring may occur, likewise, in the synthesis of aldehydes[6] by the action of hydrogen cyanide on furan in the presence of hydrogen chloride. The observation that the aldehyde synthesis can be effected with furan derivatives containing one substituent in the 2- or 5-position, but is unsuccessful when substituents are present in both positions, can be explained satisfactorily by this hypothesis. An investigation of the addition of hydrogen cyanide to various types of furan derivatives and to conjugated aliphatic systems is now in progress.

In comparing the aromatic character of the benzene and furan rings it is of interest to note that the analogous benzene derivative, benzyl chloride, does not undergo rearrangement on treatment with sodium cyanide.[7] This difference can be interpreted as an indication of the ethylenic, or non-aromatic, character of the furan ring and places the simple furan derivatives in an intermediate position between the 1,3-butadienes and benzene. In the benzene series the aromatic[9] character of the ring is augmented by the presence of certain substituents (COOH, NO_2, SO_3H) and is decreased by the presence of others (OH, NH_2). In the furan series an analogous effect is observed: the presence of certain substituents (especially COOH) increases the aromatic character of the ring, and the pres-

[6] Reichstein, *Helv. Chim. Acta*, **13**, 345 (1930).

[7] No *o*- or *p*-tolunitrile could be detected in the nitrile produced by the reaction of benzyl chloride or benzyl iodide with sodium cyanide. On the other hand, benzylmagnesium chloride undergoes abnormal reaction with certain substances and gives rise to *o*-tolyl derivatives.[8]

[8] Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); Austin and Johnson, *ibid.*, **54**, 647 (1932).

[9] It is difficult to formulate a concise definition of the term aromatic. It is used here to mean a closely integrated, cyclic, conjugated system (containing two or more double bonds) characterized by a marked tendency to resist alteration of the conjugated system and rupture of the ring (especially through oxidation).

ence of others (OH, NH_2) causes a marked decrease of stability and a closer approach to the unsaturated aliphatic type. Since the thiophene ring is generally considered to be one of the most highly aromatic heterocycles, it would be of interest to investigate the behavior of the thiophene analog of α-furfuryl chloride, 2-chloromethylthiophene, toward aqueous sodium cyanide. A study of this reaction is in progress.

Experimental

5-Chloro-2-methyl-3-furoic Acid.—Ethyl 2-methyl-3-furoate was obtained by Benary's[10] modification of the Feist synthesis, from 1,2-dichloroethyl ether and acetoacetic ester. It was found advantageous to use aqueous pyridine[11] in effecting this reaction instead of ammonia, since the production of a pyrrole derivative is thereby obviated and the yield of the furan derivative is increased to 50–60% of the theoretical.

The chlorination of ethyl 2-methyl-3-furoate was carried out in the manner described by Hill and Jackson[12] for the chlorination of ethyl furoate. The ester was heated in a distilling flask in an oil-bath at 145°, and a stream of dry chlorine was introduced beneath the surface of the liquid. When the gain in weight attained 80–90% of the amount calculated for the introduction of one chlorine atom, the chlorination was stopped. The reaction mixture was saponified by heating with an excess of alcoholic sodium hydroxide solution, and after adding water the alcohol was distilled off. After pouring into dilute hydrochloric acid, the crude acid was filtered with suction and washed with a small quantity of water. After recrystallization from hot water, 5-chloro-2-methyl-3-furoic acid separated in glittering plates, m. p. 122–123° (uncorr.). The yield was 35–50% of the theoretical.

Anal. Calcd. for $C_6H_5O_3Cl$: Cl, 22.1. Found: Cl (Parr bomb), 21.85, 22.00. Neutralization equivalent: calcd., 160.5; found, 161.3.

In this product the chlorine is shown to be attached in the ring and not in the side chain since it is not removed by heating with alcoholic sodium hydroxide solution. It is inferred with reasonable certainty that the halogen entered the 5-position in preference to the 4-position, since the introduction of halogens always occurs by preference in an α-position of the furan ring. Experiments are in progress with a view to establishing the position of the halogen by means of a direct proof of structure.

5-Methyl-2-chlorofuran.—5-Chloro-2-methyl-3-furoic acid was decarboxylated in 5-g. portions by heating in the presence of high-boiling coal tar bases (b. p. 150–200° at 16 mm.) and copper bronze.[13] The decomposition began at 250–260°, and was quite rapid at 260–270°. From 33 g. of the acid there was obtained 12 g. of 5-methyl-2-chlorofuran (50% yield). The purified product was a colorless liquid with an odor resembling that of chloroform; b. p. 108–110° at 740 mm., 48–49° at 70–75 mm., n^{20}_{C} 1.4579, n^{20}_{D} 1.4611, n^{20}_{F} 1.4714, n^{20}_{G} 1.4781, d^{20}_{20} 1.1204, d^{20}_{4} 1.1184; MR_D (calcd.) 28.67, (obs.) 28.56.

Anal. Calcd. for C_5H_5OCl: Cl, 30.44. Found: Cl (Parr bomb), 29.90, 30.55.

This halide is distinctly different from α-furfuryl chloride, for which Kirner[14] re-

---

[10] Benary, *Ber.*, **44**, 493 (1911).

[11] This modification was developed by Mr. M. O. Baker. Details of the method will be published elsewhere.

[12] Hill and Jackson, *Proc. Am. Acad. Arts Sci.*, **24**, 320 (1888).

[13] Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930).

[14] Kirner, THIS JOURNAL, **50**, 1959 (1928).

ported the following constants: b. p. 49.6–50° at 27 mm., d_{20}^{20} 1.1804, d_4^{20} 1.1783, n_D^{20} 1.4941; MR_D (obs.) 28.788. 5-Methyl-2-chlorofuran is considerably more stable than α-furfuryl chloride toward metathetical reagents, has no lachrymatory action and does not undergo rapid spontaneous decomposition on standing. Samples of this halide have been kept for more than six months (under alkaline hydroquinone) without appreciable resinification.

5-Methylfurfural.—After preliminary experiments had been made, in which 5-chloromethylfurfural was isolated and reduced with stannous chloride, it was found that the desired aldehyde could be obtained directly by heating levulose, inulin or sucrose with dilute mineral acid in the presence of stannous chloride. Although the yield is low, this modification decreases the time required and is far less tedious than other methods.

In a 12-liter round-bottomed flask fitted with a separatory funnel and a short fractionating column, 500 g. of technical stannous chloride crystals, 2 kg. of sodium chloride and 4 liters of 12% sulfuric acid were mixed thoroughly and heated to boiling over a large gas-plate. When vigorous ebullition began, a solution of 800 g. of sucrose in 1 liter of hot water was added slowly through the separatory funnel over a period of thirty to forty-five minutes. The aldehyde distils out rapidly as it is formed, and an efficient condenser is necessary to avoid loss. The distillation was continued after all the sucrose had been added, until the distillate came over colorless. The entire distillate was carefully neutralized with sodium carbonate, saturated with sodium chloride and distilled. From the second distillate, which had separated into two layers, the methylfurfural was removed by several extractions with benzene. After distilling off practically all of the benzene, the residue was distilled under reduced pressure; b. p. 94–95° at 52 mm., 106–107° at 60 mm. The freshly distilled methylfurfural is an almost water-white liquid, but it darkens quickly on standing; it distils under atmospheric pressure at 179–184°, with slight decomposition. The yields in the above preparation varied from 8–14% of the theoretical (on the basis of the levulose residue only); usually 27–35 g. (10–13% yield) of 5-methylfurfural was obtained in a single preparation.

The 5-methylfurfural was identified by several reactions. On treatment with aqueous ammonia it gave methylhydrofuramide, m. p. 84–85° (reported 86–87°); with hydroxylamine it gave an oxime (described below). This aldehyde underwent the Cannizzaro reaction with the production of 5-methylfuroic acid, m. p. 107–108°, and 5-methylfurfuryl alcohol; in the Perkin reaction with acetic anhydride and sodium acetate it gave 5-methylfurylacrylic acid, m. p. 153–154°.

5-Methylfuronitrile from 5-Methylfurfural.—In order to obtain a pure specimen of 5-methylfuronitrile for comparison with the nitrile obtained from furfuryl chloride this substance was prepared by the dehydration of 5-methylfurfuraldoxime.

Twenty-two grams (0.2 mole) of freshly distilled 5-methylfurfural was mixed with a solution of 25 g. of hydroxylamine sulfate and 35 g. of sodium acetate crystals in 250 cc. of water, and the mixture was allowed to stand at 20°. After the first hour a heavy semi-solid mass had separated but after twenty-four hours the reaction mixture contained a mass of long pale yellow needles. These were filtered with suction and found to melt at 110–112°, corresponding to the form described by Fromherz and Meigen[15] as the *syn*-form of the oxime (m. p. 112°). Ether extraction of the aqueous filtrate gave an additional quantity of crystals which melted at 104–108°. The two fractions, amounting to 25 g., were combined for the next preparation.

Twenty-five grams of crude 5-methylfurfuraldoxime was dissolved in 42 g. of acetic anhydride and the solution was boiled gently for three minutes. After cooling

---

[15] Fromherz and Meigen, *Ber.*, **40**, 403 (1907).

the solution was poured carefully into a slight excess of sodium carbonate solution and was subjected to steam distillation. The 5-methylfuronitrile was extracted from the distillate with ether, and after drying over anhydrous magnesium sulfate was distilled under reduced pressure; b. p. 65–67° at 15 mm. The yield was 13 g. (67% yield, based upon 5-methylfurfural). 5-Methylfuronitrile is a colorless liquid with an agreeable aromatic odor; it is appreciably soluble in water and is miscible with the usual organic solvents. For analysis and determination of physical constants, the material was carefully refractionated under diminished pressure: b. p. 74–75° at 27 mm., n^{20}_{D} 1.4848, d^{20}_{4} 1.0399, d^{25}_{4} 1.0348; MR_D (calcd.) 28.24, MR_D (obs.) 29.49. A Kjeldahl analysis gave 12.77% N; calcd. for C_6H_5ON, N, 13.08.

For comparison, the physical properties of the nitrile obtained from α-furfuryl chloride (A), pure 5-methyl-2-furonitrile (B) and α-furfuryl cyanide (C) are given.

(A) Nitrile from $C_4H_3O\text{-}CH_2Cl$:[16] b. p. 74–75° (26 mm.); d^{20}_{4} 1.0463; n^{20}_{D} 1.4833; MR_D (obs.) 29.24

(B) 5-Methyl-2-furonitrile: b. p. 74–75° (27 mm.); d^{20}_{4} 1.0399; n^{20}_{D} 1.4848; MR_D (obs.) 29.49

(C) α-Furfuryl cyanide: b. p. 78–80° (20 mm.); d^{25}_{4} 1.0854; n^{25}_{D} 1.4715; MR_D (obs.) 27.60

A rough calculation from these data indicates that the nitrile from α-furfuryl chloride described by Kirner and Richter[16] contained approximately 85% of 5-methylfuronitrile and 15% of α-furfuryl cyanide.

5-Methylfurfuryl Alcohol.—5-Methylfurfural was converted into the corresponding alcohol by catalytic hydrogenation, following the method of Adams and Kaufmann[17] for the preparation of furfuryl alcohol from furfural. After careful fractionation, the alcohol distilled at 70–73° (6 mm.), or 97–99° (36 mm.). The yields were 65–70% of the theoretical. The preparation of this alcohol has been described previously by Blanksma,[18] who obtained it by treating 5-methylfurfural with strong potassium hydroxide solution. He reported a boiling-point of 100° at 11 mm., which is widely different from that observed in the present work, but gave no other physical constants.

5-Methylfurfuryl alcohol is a colorless liquid of pleasant odor; it is quite soluble in water and is miscible with alcohol and ether. Under atmospheric pressure (744 mm.) it boils with slight decomposition at 194–196°. A sample freshly distilled under reduced pressure had the following constants: d^{20}_{4} 1.0769, n^{20}_{D} 1.4853; MR_D (calcd.) 29.94, (obs.), 29.83. The diphenylurethan was prepared by heating for thirty minutes 1 g. of the alcohol and 1 g. of diphenylcarbamyl chloride in 5 cc. of pyridine. After two crystallizations from petroleum benzine (b. p. 60–70°), the diphenylurethan was obtained as a white crystalline solid, m. p. 52–53°.

5-Methylfurfuryl Chloride.—5-Methylfurfuryl alcohol was converted into the chloride by the method that Kirner used for the preparation of furfuryl chloride from furfuryl alcohol.[14] Since this chloride appeared to be even more unstable than furfuryl chloride, the product was not isolated but was prepared in ethereal solution and used directly for the next step.

5-Methylfurfuryl Cyanide (5-Methylfuryl-2-acetonitrile) and 5-Methylfuryl-2-acetic Acid.—An ethereal solution of 5-methylfurfuryl chloride, prepared from 18 g. (0.15 mole) of 5-methylfurfuryl alcohol, was treated with aqueous sodium cyanide according to the procedure of Kirner and Richter.[16] Steam distillation of the reaction

---

[16] Kirner and Richter, This Journal, **51**, 3131 (1929).

[17] Adams and Kaufmann, *ibid.*, **45**, 3029 (1923).

[18] Blanksma, *Chem. Weekblad*, **9**, 186 (1912).

mixture gave 2.0 g. (11% yield) of 5-methylfurfuryl cyanide, which separated as a pale straw colored liquid sparingly soluble in water.

The nitrile was hydrolyzed by boiling with 20% potassium hydroxide solution, and after acidification the acid was removed by ether extraction. After two recrystallizations from petroleum benzine, there was obtained 0.5 g. (25% yield) of colorless crystals of 5-methylfuryl-2-acetic acid, m. p. 57–58°. This acid showed no depression of the melting point when mixed with an equal quantity of authentic 5-methylfuryl-2-acetic acid synthesized from 5-methylfurfural. None of the isomeric 2,5-dimethylfuroic acid (m. p. 134°) was detected in the reaction products.

5-Methylfuryl-2-acetic Acid from 5-Methylfurfural.—This synthesis was effected through the series of reactions used previously for the preparation of 2-furylacetic acid from furfural.[2b] Fifty-five grams (0.5 mole) of 5-methylfurfural was condensed with 30.5 g. of nitromethane (0.5 mole) in the presence of aqueous potassium hydroxide, according to the procedure of Thiele and Landers.[19] After one crystallization from benzene, the 5-methylfurylnitroethylene was obtained in yellow crystals, m. p. 75–76°. An ethereal solution of this substance was reduced with zinc and acetic acid to 5-methylfuryl-2-acetaldoxime. The crude oxime was boiled for three minutes with an excess of acetic anhydride and the resulting solution was poured into an excess of sodium carbonate solution. Steam distillation of the alkaline solution gave 3 g. of 5-methylfurfuryl cyanide, which was hydrolyzed by boiling for one hour with an excess of 30% aqueous potassium hydroxide. Upon acidification there was obtained 1.5 g. of 5-methylfuryl-2-acetic acid, which after two crystallizations from petroleum benzine (b. p. 60–70°) formed colorless needles, m. p. 57–58°. This acid is moderately soluble in cold water, and is very soluble in alcohol, acetone and ether. The observed neutralization equivalent was 142.0 (calcd. 140).

2,5-Dimethylfuroic Acid.—For purposes of comparison, this isomer of 5-methylfuryl-2-acetic acid was prepared from the monoethyl ester of methronic acid (5-methyl-4-carboxyfuryl-2-acetic acid), which was obtained by warming ethyl acetoacetate with sodium succinate and acetic anhydride.[20] Since it is not known definitely whether the esterified carboxyl group in this ester is the one attached in the ring or that in the side chain, the reactions were carried out in such a way that the position of the esterified carboxyl group could be determined. This was accomplished by subjecting the monoethyl ester to decarboxylation, hydrolyzing the resulting ester and identifying the corresponding acid. Since the latter proved to be 2,5-dimethylfuroic acid, the esterified carboxyl in monoethyl methronate is shown definitely to be the one attached in the ring. If the side chain carboxyl had been esterified, 5-methylfuryl-2-acetic acid would have been the final product.

The decarboxylation of monoethyl methronate was followed in an approximately quantitative manner, as described previously for the decarboxylation of 2-furylacetic acid.[2b] A sample of 5.222 g. (0.026 mole) of monoethyl methronate (m. p. 73–74.5°) on heating for thirty minutes in an oil-bath at 290–300° gave 0.860 g. (0.020 mole) of carbon dioxide and 3.462 g. (0.021 mole) of ethyl 2,5-dimethylfuroate. These quantities correspond, respectively, to 77 and 80% of the theoretical. The liquid distillates from several decarboxylations were united, washed with dilute alkali to remove undecomposed acid, dried and distilled under diminished pressure. Upon redistillation ethyl 2,5-dimethylfuroate (ethyl pyrotritarate)[21] was obtained as a colorless liquid with a very characteristic aromatic odor: b. p. 83–85° at 6 mm., 99–101° at 14 mm.,

---

[19] Thiele and Landers, *Ann.*, **369**, 303 (1909).

[20] Fittig and v. Eynern, *ibid.*, **250**, 178 (1889).

[21] We are indebted to Dr. R. C. Tallman for the determinations of several of the physical constants here reported.

d_4^0 1.0718, d_4^{20} 1.0537, d_4^{23} 1.0490, n_C^{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 benzine (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).

ITHACA, NEW YORK

NOTES

The Preparation of Tetrathiopentone

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 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).