It was not found possible to condense acetaldol with chloral to give a mixed paraldehyde.

Summary

1. Chloral either alone or, better, in the presence of a trace of hydrogen chloride, combines with acetaldehyde,[17] propionaldehyde, *iso*butyraldehyde and trimethylacetaldehyde to give paraldehydes corresponding to the general type ($2RCHO + CCl_3CHO$).

2. It apparently does not combine with acetaldol under similar conditions.

3. Attempts to prepare a mixed paraldehyde containing three different aldehydes were unsuccessful.

4. The possible rôle played by such derivatives in plant and animal life would seem to call for some consideration.

Montreal, Canada

[Contribution from the Chemical Laboratory of the Rice Institute]

ALPHA-FURFURYL CHLORIDE (FURYL-2-METHYL CHLORIDE) AND ITS DERIVATIVES.

I. THE PREPARATION AND PROPERTIES OF ALPHA-FURFURYL CHLORIDE AND A FEW ALPHA-FURFURYL ETHERS[1]

By W. R. Kirner

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The synthesis of many relatively simple derivatives of furan has hitherto been impossible or, at best, extremely difficult and complicated, due to the fact that reactive starting materials such as the ω-halogen derivatives of furan homologs have been practically unknown. A halogen in the side chain of a furan ring corresponds in reactivity to that possessed by a halogen in the side chain of a benzene ring.

Fenton and co-workers[1a] were the first to prepare a reactive halogen derivative of methylfuran when they succeeded in isolating 2-chloromethyl- and 2-bromomethyl-5-furfuraldehyde from a large variety of carbohydrates using a non-aqueous solvent (for example, ether, chloroform or carbon tetrachloride) saturated, respectively, with hydrogen chloride and hydrogen bromide. They pointed out the high order of reactivity of the halogen and prepared a number of derivatives in which the halogen was substituted by groups such as H, OH, $OCOCH_3$, $OCOC_6H_5$, C_6H_5 and $CH_2C_4H_2OCOH$, while subsequent workers[2] extended the list of sub-

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[1] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis meeting, April, 1928.

[1a] Fenton and Gostling, *J. Chem. Soc.*, **73**, 556 (1898); *ibid.*, **75**, 423 (1899); *ibid.*, **79**, 361, 807 (1901); Fenton and Robinson, *ibid.*, **95**, 1334 (1909).

[2] Erdmann, *Ber.*, **43**, 2392 (1910); Cooper and Nuttall, *J. Chem. Soc.*, **99**, 1197 (1911); E. Fischer and v. Neyman, *Ber.*, **47**, 974 (1914); see also Middendorp, *Rec. trav. chim.*, **38**, 23–38 (1919).

stitutions to include the OCH_3 and OC_2H_5 groups. Hill and Jennings[3] obtained the 2-bromomethylpyromucic acid by direct bromination under specific conditions and noted the easy hydrolysis to form the hydroxy compound.

Only recently has the preparation of the parent ω-halogen methylfuran been successful. Zanetti[4] has succeeded in preparing ethereal solutions of both the α-furfuryl bromide and iodide from α-furfuryl alcohol by simple procedures. In the case of the iodide at least 40% of the alcohol is transformed and 70% in case of the bromide. Using these reactive agents, Zanetti prepared five ethers which had previously been unknown. Zanetti did not isolate the bromide or iodide in a pure condition but merely obtained them in an ethereal solution. Von Braun and Köhler were the first to have prepared an ethereal solution of the bromide[5] by the treatment of α-furfurylethylmethylamine with cyanogen bromide, which resulted in an 80% conversion of the base (by weight) to the bromide. This method is not as convenient, however, as that of Zanetti. Von Braun and Köhler describe the properties of the ethereal solution, particularly its gradual decomposition on standing, and add that when an attempt was made to distil it, it completely decomposed. They consider it a surprisingly satisfactory result that α-furfuryl bromide is stable even for several hours. They also predicted that the same ease of decomposition would probably be found in the chloride.

Von Braun and Köhler attempted to make α-furfuryl chloride by the well known Von Braun reaction which, in this case, consisted in the treatment of the benzoyl derivative of α-furfurylmethylamine with phosphorus pentachloride. The reaction resulted only in the complete resinification of the substances present, the same result being obtained with phosphorus pentabromide. Gilman and Vernon[6] also attempted to prepare the chloride by treatment of an ethereal solution of α-furfuryl alcohol with thionyl chloride at low temperature and by passing dry hydrogen chloride into an ethereal solution of the alcohol in the presence of a dehydrating agent (calcium carbide). The yield in the first case was 10% (based on the amount of α-furfuryl ethyl ether obtained) and 5% in the second case. Both of these methods are therefore decidedly unsatisfactory and impractical. Gilman and Vernon state that "all efforts to distil the chloride were futile. After some 80–90% of the ether had been distilled at reduced pressure, the contents of the flask suddenly and violently decomposed into a hard, intractable tar. The temperature of the water-bath in which the flask was immersed did not exceed 30°."

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[3] Hill and Jennings, *Am. Chem. J.*, **15**, 180 (1893).

[4] Zanetti, THIS JOURNAL, **49**, 1061, 1065 (1927).

[5] Von Braun and Köhler, *Ber.*, **51**, 87 (1918).

[6] Gilman and Vernon, THIS JOURNAL, **46**, 2576 (1924).

It is the purpose of this paper to demonstrate that *under certain conditions it is possible to prepare the chloride and isolate it in a pure state by vacuum distillation, to obtain a satisfactory analysis, determine its physical properties and prepare derivatives of it.* Zanetti has shown that the bromide is more stable than the iodide toward potassium hydroxide[7] and in this work it is proved that the chloride is more stable toward potassium hydroxide than the bromide The relative stabilities of these furfuryl halides thus coincide with the order usually given for organic halides, namely, chloride > bromide > iodide. Although the chloride is a relatively unstable substance it is of a much higher order of stability than the statements of previous investigators would lead one to believe.

Since the furan nucleus is sensitive to halogen acids, it is imperative in the successful preparation of the furfuryl halides to avoid so far as possible the presence of halogen acids in an uncombined state. The Darzens method for the preparation of chlorides from alcohols,[8] which consists in the treatment of the alcohol in a solution of a tertiary amine (pyridine was used in this work) with thionyl chloride, is ideal in this case since the hydrogen chloride which is liberated from the alcohol and thionyl chloride is immediately taken up by the base and therefore causes no decomposition of the sensitive alcohol. By this method *α-furfuryl alcohol has been converted into α-furfuryl chloride with a 63% yield of distilled material.* The boiling point observed was 49.6–50° at 27 mm. The substance distils as a water-white liquid which is sufficiently stable, in the absence of moisture, to permit its analysis and the determination of its density and refractive index. It is insoluble in water but soluble in the common organic solvents. It possesses a characteristic odor and is a weak lachrymator. On standing it gradually turns yellow, then green and finally black and deposits a black, resinous precipitate. An ethereal solution remains nearly colorless for several days at room temperature and gradually turns yellow with the formation of a black, gummy precipitate. There is no difficulty whatsoever in preparing and keeping the substance long enough for use in any reaction.

From the pure chloride a number of ethers were prepared using the procedure given by Zanetti.[4] The ethers were chosen as the first derivatives to be prepared since Zanetti has recently prepared a considerable number of them by a convenient procedure and in good yield. They are listed below together with their boiling point, density, yield, refractive index and calculated and observed molecular refraction. It is interesting to note that Zanetti was unable to prepare the allyl ether by treatment of the α-furfuryl bromide with allyl alcohol; he states "the heat of formation was so great as to decompose the α-furfuryl bromide, giving only resinous

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[7] Ref. 4, p. 1067.

[8] Darzens, *Compt. rend.*, **152,** 1314 (1911).

products." Using the chloride no difficulty whatsoever was experienced; in fact, the highest yield of the eight ethers prepared was obtained in this case.

Table I

α-Furfuryl Ethers

Name	B. p., °C.	Press., mm.	Density, 20°/4°	Yield, %	Refractive index, $N_D^{20°}$ (Abbé)	Molecular refraction Obs.	Calcd.
Methyl	134–135	762	1.0163	66[a]	1.4570	30.031	30.060
Ethyl	149.5–150.5	770	0.9844	81	1.4523	34.573	34.678
n-Propyl	168–170	767	0.9656	79	1.4523	39.164	39.296
n-Butyl	189–191	777	0.9516	78	1.4522	43.707	43.914
Allyl	173.5–174.5	772	1.0025	88	1.4718	38.554	38.829
Benzyl	108–109	1	1.0865	83	1.5372	54.082	54.167
α-Furfuryl	88–89	1	1.1405	84	1.5088	46.604	47.041
Cinnamyl	141–142	1	1.0802	85	1.5661	64.670	62.936

[a] Some material was lost accidentally.

Experiments are already under way in this Laboratory using the chloride for the preparation of a large number of other furan derivatives such as the amines, acetoacetic and malonic ester derivatives, those obtained from the Grignard reagent, etc.

I wish to thank my friend, Dr. John R. Johnson of Cornell University, for the first generous sample of furfuryl alcohol used in this work.

Experimental

A. Preparation of α-Furfuryl Chloride

The α-furfuryl alcohol was always freshly distilled just before using; it boiled at 84.5–85.0° at 26 mm. The pyridine was obtained from the Eastman Kodak Company, and was thoroughly dried over solid potassium hydroxide and distilled. The thionyl chloride was distilled from cotton seed oil through a Glinsky column and then re-distilled; it was practically water white.

The following procedure is typical of a number of experiments which were made: 46.2 g. (0.47 mole) of freshly distilled furfuryl alcohol was placed in a 500cc. three-necked Pyrex round-bottomed flask, the center neck being fitted with a stirrer, one side neck with a 50cc. dropping funnel and the other with a loosely stoppered thermometer: 44.7 g. (0.565 mole, 20% excess) of pyridine was added, which caused a slight evolution of heat, and then 50 cc. of dry ether (prepared in the same way as one prepares Grignard ether). The flask was immersed in an ice-bath and the stirrer started. When the temperature fell to about 2–3°, 61.7 g. (0.52 mole, 10% excess) of thionyl chloride dissolved in 50 cc. of dry ether was added from the dropping funnel, dropwise, in 10cc. portions, to the mixture in the flask, each 10cc. portion being added over a period of about twenty minutes. In this way the temperature of the reaction mixture remained at 7–9° during practically the entire reaction. The reaction was very vigorous, each drop of thionyl chloride producing a hissing noise and a spattering of the liquid.

During the addition of the second 10cc. portion, each drop of thionyl chloride produced a local turbidity and after about half of this portion had been added a heavy, oily layer started to separate. During the addition of the seventh portion the lower layer crystallized and the temperature rose rapidly to about 15° and then gradually fell again. After this portion was all added the thermometer was temporarily removed while a bent glass rod was inserted to break up the crystalline lumps as much as possible. The last portions of the thionyl chloride caused the crystalline material, which was originally a light brown color, to turn greenish-black. After all of the thionyl chloride had been added the mixture was stirred for an additional twenty-five minutes.

Darzens recommends that, after the addition of the thionyl chloride to the alcohol-pyridine mixture, the mixture be heated until evolution of sulfur dioxide ceases. In this case such a procedure was not possible for it was found that the heating resulted in nothing but a black tar; presumably the furan ring was destroyed or else polymerization occurred. Since heating was not required in this case to give a fair yield it may not be necessary in other cases in which, following Darzens, heating is usually carried out. The removal of the ethereal solution from the flask fortunately was extremely easy since the brownish lumps were rather large and pasty. The thermometer was removed and in its place a glass siphon tube was tightly stoppered, the short end of which reached to the very bottom of the flask. By having an electric light bulb behind the flask so as to be able to see through the ethereal solution the siphon tube could be placed in a space cleared up by the stirrer. Slight air pressure was then applied through the dropping funnel and the ethereal solution completely siphoned off into an Erlenmeyer flask. The ethereal solution was light yellow in color and transparent. The siphon tube was removed, 50 cc. of dry ether added to the reaction flask and the mixture stirred for five minutes after again breaking up the lumps with a bent glass rod. Then the ethereal solution was again siphoned off. This extraction was repeated three times, the last time the flask being removed from the ice-bath to permit it to warm up slightly. The total ethereal solution, which reacted acid to litmus paper, was thoroughly extracted with 50 cc. of 50% potassium hydroxide solution, everything being kept very cold and the potassium hydroxide solution being added in small portions in order not to cause undue heating. The ethereal solution was then removed and dried over anhydrous sodium carbonate.

In the distillation of the furfuryl chloride 75cc. portions of the ethereal solution were used and the distilled product was converted into the various ethers described later. The ether solution was added in portions to a 25cc. Claissen fractionating flask the side arm of which was fitted with a short water condenser, a 50cc. distilling flask being used as the receiver. The air entering the flask during the distillation was dried with a soda lime tube and a similar large soda lime tube was placed between the receiver and manometer; a water pump furnished the suction. It is the custom in this Laboratory to clean glass apparatus by immersion in a bath of very hot sulfuric acid. It was found that unless certain precautions were taken some of the acid remained adsorbed on the walls of the apparatus and that when the furfuryl chloride was distilled decomposition occurred in the side arm and receiver. This difficulty was overcome by carefully washing all apparatus a large number of times in tap water followed by washing with distilled water, then allowing the apparatus to soak in a large bath of distilled water overnight and subsequently re-washing with distilled water. The distilling flask was also steamed to remove completely any acid from the side arm and indentations of the fractionating column. The apparatus was then dried in an oven at 130°.

After removal of the ether in vacuum in the apparatus described above, a yellowish-brown, oily residue remained. On distilling this from a water-bath the liquid distilled very readily and yielded a water-white distillate. Various boiling points observed were: 49.1–49.4° (26 mm.); 49.6–50.0° (27 mm.); 54.0–54.4° (33 mm.), $d_{20}^{20} = 1.1804$; $d_{4}^{20} = 1.1783$; $N_{D}^{20} = 1.4941$ (Abbé). M_D, calcd. = 28.666; M_D, obs., = 28.788.

Anal. Subs., 0.2072, 0.2253; AgCl, 0.2538, 0.2747. Calcd. for C_5H_5OCl: Cl, 30.436. Found: 30.299, 30.16.

The analyses are slightly low due to the fact that during the time necessarily required to weigh out the sample and introduce it into the Carius tube some decomposition was taking place. This was evident from the fact that the sample gradually turned yellow.

B. Preparation of α-Furfuryl Ethers

The ethers were prepared by treating a given weight of the distilled chloride in 75 cc. of dry ether with 100% excess of dry, pulverized potassium hydroxide and with 200% excess of the desired alcohol, the alcohol being added in portions. In the case of methyl and α-furfuryl alcohol the reactions were vigorous enough to cause the ether to boil, so that cooling was necessary; large amounts of a flocculent precipitate of potassium chloride formed. In the case of the other alcohols the reaction proceeded more slowly and only small quantities of heat were evolved and small amounts of potassium chloride deposited. The reaction mixtures were allowed to stand overnight. Then the ether was evaporated on a hot-plate until the temperature of the flask contents reached 75°. The flask was then heated in a water-bath at 75–80° for a half hour, cooled, 100 cc. of distilled water added and the oily layer which separated removed with a separatory funnel. The aqueous layer was extracted four times with 25cc. portions of ether and the total oily layer–ether extract was dried over anhydrous sodium carbonate.

The ether was removed in vacuum and the residue subjected to fractional distillation, either at atmospheric pressure or in vacuum, depending on the boiling point of the furfuryl ether. The boiling points and densities, in general, agree quite well with those given by Zanetti except in the case of the α-furfuryl and benzyl ethers. In these cases the boilng points observed were about 10° lower than reported by Zanetti; his distillations were made at 2 mm., while in this work the pressure was 1 mm. The fact that the boiling points of the cinnamyl ethers agree even though distilled at two slightly different pressures makes it probable that the 10° difference in the boiling points in these two instances does not correspond to the decrease occasioned by a 1mm. change in pressure. Both of these ethers were systematically fractionated twice and they boiled very uniformly over the small range of temperature indicated. The close agreement between the calculated and observed molecular refractions indicates that the substances were pure. The value obtained for the refractive index of the ethyl ether does not agree with the value ($N^{20} = 1.4316$) given by Gilman and Vernon. They do not state their light source, but assuming that they used the D line their observed molecular refraction is 33.046, which is quite far from the calculated value of 34.678. It thus appears that their value for the refractive index is incorrect or their substance was impure. The agreement between the observed and calculated values for the molecular refraction of the substances listed is good in all cases except the cinnamyl ether. In this case there is the usual exaltation due to the conjugated system present in the cinnamyl group. It is also interesting that the refractive indices of the ethyl, *n*-propyl and *n*-butyl ethers are almost identical.

Using the iodide for the preparation of ethers Zanetti obtained a mixture of ethers which contained as much as 30% of the di-α,α′-furfuryl ether formed by the reaction of the iodide with furfuryl alcohol. The latter was present, either because it was not reacted upon during the preparation of the iodide, or was formed by the hydrolysis of the iodide. Using the bromide practically no di-α,α′-furfuryl ether appeared to be formed. This is also true in the case of the synthesis using the choride. The crude ethers are nearly pure and leave practically no residue when distilled.

The remarks of Zanetti concerning the instability of the furfuryl ethers have been confirmed. When placed in tubes at atmospheric pressure they gradually darken, but if sealed off in tubes at about 1 mm. pressure with a trace of hydroquinone, they remain nearly colorless for a considerable length of time.

Summary

1. α-Furfuryl chloride has been isolated in a pure state, analyzed and its physical properties have been determined. It is a relatively unstable substance but of sufficient stability to be distilled in a vacuum and used in a variety of reactions. It seems obviously more stable than the corresponding bromide and iodide. This is the first time the parent ω-halogen methyl furan has been obtained in a pure, free condition, having previously been known only in solution.

2. The chlorine atom possesses a high order of reactivity, comparable to that of the chlorine in benzyl chloride. Eight ethers have been prepared from the α-furfuryl chloride and their physical properties determined. The allyl-α-furfuryl ether has been prepared by the direct reaction between the chloride and allyl alcohol.

3. The synthesis of this reactive chloride has opened up new possibilities in the furan series and investigations of other reactions using α-furfuryl chloride are being continued.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

A METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION OF LIQUID–LIQUID SYSTEMS[1]

BY F. E. BARTELL[2] AND F. L. MILLER[3]

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Recently the authors were confronted with the problem of measuring the interfacial tension between water and a series of crude petroleum oils. Some of these oils were very dark, practically black; consequently, the methods most generally used for interfacial tension measurements were not satisfactory. With the more transparent oils the Reynolds capillary tube method[4] was used, but with the darker oils the liquid interface within the capillary could not be seen. After considerable experimentation a method was developed by means of which it was possible to determine the interfacial tension between the dark oils and water and subsequently it was found that this method gave results which checked well with what

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[1] This paper contains preliminary results obtained in an investigation on the "Displacement of Petroleum Oils from Oil Bearing Sands by Means of Selected Aqueous Solutions," listed as Project No. 27 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Reynolds, *Trans. Chem. Soc.*, **119**, 460–466 (1921).