2. The pure α-furfuryl iodide has not been isolated owing to its instability but it has been identified by using it in the synthesis of various α-furfuryl ethers.

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ALPHA FURFURYL ETHERS. I

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The α-furfuryl ethers have been but little investigated. Wissell and Tollens[1] prepared the methyl-, ethyl-, propyl- and *iso*-amyl-α-furfuryl ethers by acting on α-furfuryl alcohol with the corresponding iodides in the presence of potassium hydroxide solution. The writer has found that α-furfuryl bromide in ether solution, the preparation of which is described further, acts quite as well with alcohols with the formation of α-furfuryl ethers, according to the reaction $C_4H_3OCH_2Br + HOCH_2R \xrightarrow{KOH} C_4H_3OCH_2OR + HBr$.

This condensation has been studied with numerous alcohols, including α-furfuryl alcohol, with the result that the series of α-furfuryl ethers has now been considerably extended.

The reaction has been checked in several cases, as in that of the benzyl ether and of the butyl ethers by synthesizing these compounds with the alkyl and aryl bromides and α-furfuryl alcohol in the presence of potassium hydroxide, as well as with α-furfuryl bromide and the corresponding alcohols.

The ethers of this series are all colorless liquids with faint odors reminiscent of the alcohols, if these have characteristic odors, but as remarked before, in the case of esters of furoic acid[2] the α-furfuryl group has not so far shown any characteristic odor. The di-α-furfuryl ether, for example, is almost odorless, as was α-furfuryl furoate.

These ethers are extremely hygroscopic and when moist decompose rapidly. If kept sealed in glass containers under 2 mm. pressure they remain colorless for months but quickly turn dark if exposed to the air or even if, when sealed in a vacuum, sufficient time was not allowed to permit traces of moisture to boil from the liquids. The addition of traces of hydroquinone[3] stabilizes them even in the air; samples stabilized in this way have been kept in ordinary bottles side by side with non-stabilized

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[1] Wissell and Tollens, *Ann.*, **272**, 291 (1892).

[2] Zanetti and Beckmann, THIS JOURNAL, **48**, 1068 (1926).

[3] For a thorough presentation of this question of stabilization see Moureu and Dufraisse, *Chem. Rev.*, **3**, 113 (1926).

samples and have remained colorless after several weeks when the non-stabilized ones showed decomposition and darkening within 24 hours. The α-furfurylbenzyl ether is a notable exception, as it darkens in a few days even when traces of hydroquinone have been added.

Experimental Part

Preparation of α-Furfuryl Bromide Solution.—Twenty g. of freshly distilled α-furfuryl alcohol is dissolved in 200 g. of absolute ether and the solution treated with 20 g. of phosphorus tribromide dissolved in about 30 cc. of absolute ether. The α-furfuryl alcohol used must be freshly distilled or, at most, pale yellow in color; samples having a dark color are unsuitable and will yield mostly polymerization products. The phosphorus tribromide solution is added a few cc. at a time and the α-furfuryl alcohol solution kept cool during the whole addition by shaking it in a flask under a stream of running cold water. The addition of the tribromide should take about 20 minutes. If too rapid, the heat evolved will cause the solution to boil over. When about three-fourths of the tribromide has been added, a viscous substance begins to separate on the walls of the flask (phosphorous acid) and this separation continues for some time. If the ether has been thoroughly dried, the phosphorous acid settles on the walls of the flask as a white, waxy mass. If the ether was somewhat moist, it forms a dark, sirupy layer on the walls which gradually settles and, if ordinary ether is used, the mixture separates in two layers, the lower one containing the acid together with decomposition products from the α-furfuryl alcohol. In the last case mostly polymerization products are obtained. When the addition is complete, the mixture should be allowed to stand for half an hour at room temperature and then decanted into a clean flask. It is next treated cautiously, a little at a time, and with cooling, with about 50 cc. of 35–40% potassium or sodium hydroxide solution. The ether layer containing the α-furfuryl bromide is then slightly yellow. The ether layer is decanted off and treated with solid potassium or sodium hydroxide. This treatment removes most of the water and undecomposed α-furfuryl alcohol and the solution is then ready for use. It is fairly stable at room temperature and may be kept for several days undecomposed if tightly corked. The bromide has very decided lachrymatory properties as would be expected from its analogy in constitution to benzyl bromide.

Preparation of α-Furfuryl Ethers, Using α-Furfuryl Bromide.—When prepared as above, the α-furfuryl bromide solution may be estimated to contain 70% of the original α-furfuryl alcohol as bromide. The solution is evaporated to about one-third of its volume (or two-thirds of the ether distilled) together with an excess of solid potassium or sodium hydroxide in small pieces, and an excess of the alcohol whose ether is desired then added to it. The evaporation is continued, the solution becoming deep orange and when the ether is finally all boiled off, the α-furfuryl ether formation takes place rather suddenly with evolution of heat and voluminous separation of potassium or sodium bromide. Some decomposition takes place and the reaction mixture is either dark brown or black but the yields are good, being usually 80%, calculated on the basis of a 70% yield of the bromide. Water is then added to wash out the excess of alkali, and the ether layer separated. If the density of the ether is near that of the solution, salting out or, better, extraction with ordinary ether must be resorted to.

If the alcohol used is very volatile as, for example, methyl alcohol, the heat evolved when the ether is formed will cause boiling over, and in such cases the alcohol should be added in small portions and a large excess used. In some cases, notably in the formation of α-furfuryl-allyl ether, and others which are not described in the present paper, the heat of formation is so great that the α-furfuryl bromide is entirely decomposed. In such cases this method is not suitable.

The dark layer consists essentially of the excess of alcohol used and the ether prepared. As it is possible to treat the α-furfuryl bromide solution with solid potassium hydroxide without any appreciable decomposition, any excess of α-furfuryl alcohol left after the action of phosphorus tribromide is removed before the solution is used so that no appreciable amounts remain to interfere with the fractionation. The small residue which remains after the ether has been distilled off (less than 5%) may contain di-α-furfuryl ether but its presence has not been established. This is in striking contrast to the syntheses of ethers with α-furfuryl iodide where about 30% of the ether mixture consisted of di-α-furfuryl ether and shows definitely the much greater stability of the α-furfuryl bromide towards potassium hydroxide.

Five new α-furfuryl ethers were synthesized by the above method and their properties and analyses are shown in Table I. The allyl ether could not be prepared by that method as the heat of formation was so great as to decompose the α-furfuryl bromide, giving only resinous products, but it was readily obtained by treating allyl bromide with α-furfuryl alcohol in the presence of potassium hydroxide. The heptyl ether was similarly prepared and the butyl and benzyl ethers were prepared by both methods.

The boiling points at ordinary pressures are given only in the case of the more volatile ethers. The others showed much decomposition when heated above 200° and no definite boiling points could be obtained at atmospheric pressure.

TABLE I

α-FURFURYL ETHERS

Name	Formula	B. p., °C.	Press., mm.	D^{20}_{0}	H, % Calcd.	H, % Found	C, % Calcd.	C, % Found
n-Butyl-	$C_9H_{14}O_2$	189–190	765	0.955	9.09	9.28	70.13	69.77
						9.41		69.96
*iso*Butyl-	$C_9H_{14}O_2$	179–180	755	.946	9.09	9.16	70.13	69.90
						9.38		70.20
n-Heptyl-	$C_{12}H_{20}O_2$	99–101	2	.925	10.20	10.47	73.47	73.48
						10.07		73.25
Allyl-	$C_8H_{10}O_2$	172–173	757	1.005	7.24	7.82	69.56	69.71
						7.45		69.45
Benzyl-	$C_{12}H_{12}O_2$	118–120	2	1.092	6.38	6.60	76.60	76.09
						6.68		76.60
Cinnamyl-	$C_{14}H_{14}O_2$	138–140	2	1.075	6.54	6.70	78.50	77.85
						6.77		78.44
α-Furfuryl-	$C_{10}H_{10}O_3$	101–102	2	1.137	5.62	5.73	67.41	67.27
						5.91		67.33

Work on the α-furfuryl ethers is being continued in this Laboratory.

Summary

1. A new method is described for the preparation of α-furfuryl bromide in its ether solution and the subsequent preparation of α-furfuryl ethers.
2. The *n*-butyl-, *iso*butyl-, heptyl-, allyl-, benzyl- and cinnamyl-α-furfuryl ethers and the di-α-furfuryl ether have been prepared and their properties reported.

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