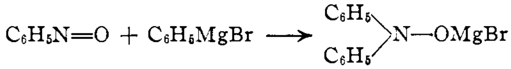
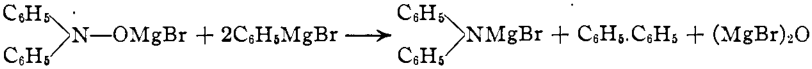
The procedures followed were those previously given in this paper. Again it was shown that about three equivalents of Grignard reagent are required. The quantity of phenol obtained is equal to that present in the original Grignard solution. Several runs were made under varying conditions of temperature. In one of the runs, at room temperature, there was obtained 24.7% of diphenyl and 26.4% of an oil that very probably consisted largely of *p*-dimethylaminodiphenylamine. In two other runs at higher temperatures the yield of diphenyl was 27.3 and 22.1%.

Summary

The following reactions are probably the chief ones that take place when phenylmagnesium bromide is added to nitrosobenzene.



$$C_6H_5N{=}O + C_6H_5MgBr \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!N{-}OMgBr \qquad (I)$$



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!N{-}OMgBr + 2C_6H_5MgBr \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!NMgBr + C_6H_5.C_6H_5 + (MgBr)_2O \qquad (II)$$

Reaction II corrects the mechanism reported previously by others.

AMES, IOWA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, COLUMBIA UNIVERSITY, No. 536]

ALPHA FURFURYL IODIDE (2-IODOMETHYL FURAN)

BY J. E. ZANETTI

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In this paper the name α-furfuryl chloride, bromide, etc., will be used to denote the 2-methyl furan derivatives. Two furfuryl derivatives, C_4H_3-OCH_2–, are possible, those where the CH_2 group occurs in the 2 and in the 3 position.

In order to avoid the much longer notation which would be necessary to describe these derivatives if the 2-methyl furan notation were used, it seems justifiable to employ the shorter one which has the further advantage of longer usage.

The α-furfuryl halides have been but little investigated owing to their instability. Von Braun and Köhler[1] obtained the bromo derivative by treating α-furfurylmethylamine with cyanogen bromide, and Gilman and Vernon[2] prepared a solution of the chloro derivative by acting on α-furfuryl alcohol with thionyl chloride and with hydrogen chloride in the presence of a drying agent. Von Braun and Köhler were not able to isolate the bromide in a pure state for as soon as the ether in which it had been prepared was evaporated, the residue turned black. Neither could Gilman and Vernon isolate the corresponding chloride which they identified

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

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

by synthesizing with it α-furfurylethyl ether previously made by Wissell and Tollens.[3] All attempts to isolate the pure compound resulted in its violent decomposition even at low temperature, as soon as the solvent in which it was prepared was evaporated. The yields were very small.

From the fact that the bromide did not decompose as violently as the chloride it was thought that possibly the stability of the iodide might be even greater. An experimental study of this question, while not successful in yielding a pure product, resulted in evolving a convenient method for preparing both the iodide and bromide in ether solutions with yields sufficient to make these compounds available for synthetic work, more specially for the study of the α-furfuryl ethers.

In preparing α-furfuryl iodide the essential reaction in the preparation of organic iodides, $PI_3 + 3ROH \longrightarrow 3RI + P(OH)_3$, was employed. The iodide, however, was not prepared *in situ* as in the case of the ordinary reaction, by acting on a mixture of red phosphorus and iodine with the alcohol, for fear of the possible formation of iodo addition products on the furan ring, but acting on α-furfuryl alcohol with phosphorus tri-iodide in anhydrous ether. The reaction is not, however, as simple as written above. Results so far obtained point to the formation of an oxy- or hydroxy-iodide of phosphorus, but as no such compounds are described in the literature and their isolation in a pure state from an organic reaction mixture presents difficulties, this matter has not yet been settled. When the α-furfuryl alcohol is added to the suspension of phosphorus iodide in ether, there is formed a crystalline orange or yellowish-brown precipitate while the supernatant solution which contains α-furfuryl iodide turns dark in color. If phosphorous acid were formed, as happens in the case of the action of phosphorus tribromide on α-furfuryl alcohol,[4] it would be colorless and not so decidedly crystalline as in the case of this compound. The yields of iodide are not as high as those of the bromide when one mole of α-furfuryl alcohol is allowed to react with three moles of phosphorus halide. As these yields, however, can be measured only in terms of the yields of di-α-furfuryl ether, and many side reactions doubtless interfere, the matter of the exact course of this reaction must be left in suspense until a more accurate method of measurement can be devised.

The ether solution of α-furfuryl iodide prepared by the above reaction and washed free of excess of phosphorus iodide by potassium hydroxide solution, as described in the experimental part, has a light yellow color and contains at least 40% of the α-furfuryl alcohol used transformed into α-furfuryl iodide.

The necessity of working in an anhydrous medium appears to be due not to any action of moisture on the iodide but to the well-known action of

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

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

aqueous mineral acids in polymerizing α-furfuryl alcohol. For this reason, when the excess of phosphorus iodide is destroyed by the use of potassium hydroxide solution, the potassium hydroxide must be concentrated in order to neutralize immediately any acid formed by the action of water.

The ether solution of the iodide can be kept for days without change in a tightly stoppered bottle, but it gradually decomposes, liberating iodine and separating a black corrugated film which adheres tightly to the sides of the flask. The formation of these black films, as well as their possible nature, is interesting and appears to be characteristic. If about 5 cc. of the solution is allowed to evaporate in the air in a small glass evaporating dish, there is left behind a thick, yellow oil with a pungent odor and sharp lachrymatory properties. In a few moments several dark spots appear in the oil and suddenly the whole mass decomposes with a puff, giving off a dense violet smoke. There is left behind a thin, black, shiny film which, if carefully separated from the dish, will preserve its exact form. The film if held in a Bunsen flame will crinkle somewhat, giving off a little smoke, but there remains a shiny graphitic carbon film which will not burn if heated to redness in the oxidizing zone of the flame.

The α-furfuryl iodide in its ether solution is very reactive and will form α-furfuryl ethers if treated with an alcohol and solid potassium hydroxide with the separation of potassium iodide and evolution of heat, the ether boiling briskly as soon as the alcohol and potassium hydroxide are added. The yields are not high, and there is always a considerable amount of di-α-furfuryl ether formed. This may come from the excess of α-furfuryl alcohol which was not acted upon by the phosphorus iodide, some of which is left in the ether solution even after the washing with concd. potassium hydroxide solution, and also from the formation of α-furfuryl alcohol by the action of potassium hydroxide on the α-furfuryl iodide.

In spite of these side reactions the yields obtained are much higher than those of Gilman and Vernon when working with the α-furfuryl chloride solution. These authors obtained yields of α-furfuryl ethyl ether when working with α-furfuryl chloride solution of 10% of the α-furfuryl alcohol, whereas with the α-furfuryl iodide yields of 30% of methyl-α-furfuryl ether, 33% of the ethyl ether, figured on the same basis, were obtained.

By synthesizing with α-furfuryl iodide in its ether solution a series of α-furfuryl ethers and the analogy of its behavior with other known α-furfuryl halogen derivatives, the fact is established that this compound has now been obtained in its ether solution.

Experimental Part

Preparation of α-Furfuryl Iodide Solution.—To 45 g. (0.12 mole) of phosphorus tri-iodide in suspension in 200 cc. of anhydrous ether, 30 g. (0.3 mole) of colorless, freshly distilled α-furfuryl alcohol is added, a few cc. at a time and with constant cooling and shaking. The phosphorus iodide should be in the form of powder. In a dry atmosphere the iodide may be quickly ground in a mortar and the powder immediately dropped in the anhydrous ether without any serious loss due to absorption of moisture, but on a moist day this can be accomplished only by gradually breaking the lumps under the ether with a glass rod. If large lumps are used, the yields will be low owing to the fact that these become quickly covered with a powdery yellowish-brown or orange precipitate which prevents their complete reaction with the α-furfuryl alcohol. After the alcohol has been added, the mixture is allowed to stand for half an hour with occasional shaking and cooling. The ether solution is then decanted into a clean flask. Owing to the violence with which the α-furfuryl iodide decomposes when the ether has been evaporated, care should be taken in decanting the solution to avoid wetting the mouth of the flask into which the solution is being decanted or letting any of the ether solution spill on the outside of the flask. The ether solution, which has a dark brown color, is then treated carefully with about 50 cc. of 30–40% potassium hydroxide solution, with cooling and shaking. The solution becomes a light yellow and contains about 40–45% of the α-furfuryl alcohol transformed into the iodide. Because of the ease of decomposition of the iodide mentioned above, it is best not to separate the ether layer from the potassium hydroxide layer by a separatory funnel but to decant it off into another flask. This ether solution can then be used directly for the syntheses of ethers as described below.

Preparation of α-Furfuryl Ethers, Using α-Furfuryl Iodide.—The solution of α-furfuryl iodide in ether prepared as above is treated with 25–30 g. of solid potassium hydroxide broken into small pieces and the alcohol, whose ether is desired, added gradually in excess and with constant shaking. The reaction starts almost immediately the solution begins to boil and cooling must be resorted to in cases to prevent boiling over. Voluminous precipitation of potassium iodide takes place. The end of the reaction can be determined by allowing a drop of the mixture to evaporate either on a watch glass or a glass rod. As long as any α-furfuryl iodide is left, marked darkening will take place. When the iodide has been used up, the ether is distilled off on the water-bath and the residue treated with 300 cc. of water. The α-furfuryl ether separates in a layer and can be separated with a separatory funnel. It is then dried with calcium chloride and fractionated. The yields are poor.

On fractionation, a little of the alcohol used distils first. The thermometer then rises rapidly to the boiling point of the α-furfuryl ether prepared, which distils within a narrow range. The residue which amounts to about 30% of the mixture consists of di-α-furfuryl ether. Small amounts of α-furfuryl alcohol (less than 5%) are always present.

If the boiling point of the ether synthesized is near the boiling point of α-furfuryl alcohol, the ether fraction must be shaken several times with three or four times its volume of diluted potassium hydroxide solution to remove the alcohol before being redistilled.

The following α-furfuryl ethers were synthesized with α-furfuryl iodide (the yields are figured on the basis of the amount of furfuryl alcohol used in the preparation of the iodide): methyl,[3] b. p. 131–133° (760 mm.), yield 27%; ethyl,[3] b. p. 149–151° (765 mm.), yield 23%; *n*-propyl,[3] b. p. 164–169° (760 mm.), yield 28%; α-furfuryl,[4] b. p. 99–102° (2 mm.), yield 42%.

Summary

1. A method of preparing α-furfuryl iodide in ether solution is described.

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).