SOME REACTIONS OF 5-CHLOROMERCURI-2-FURFURYL ALCOHOL¹

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The simple furans, especially those with saturated substituent groups, are so sensitive towards acidic reagents employed in nuclear substitution that such reactions usually lead either to low yields or complete decomposition. This difficulty can often be circumvented by indirect substitution involving an intermediate mercuration step (1). The present work is an extension of this method to the sensitive compound 2-furfuryl alcohol, from which only one substitution-product, 5-nitrofurfuryl alcohol, has been reported (2). The successful preparation of mercurated furfuryl alcohol as outlined in this paper thus provides a means of obtaining such compounds as 5-bromo- and 5-aceto-furfuryl alcohol, which cannot yet be obtained by bromination or by the Friedel and Crafts reaction. The oxidation of mercurated furfuryl alcohol likewise leads through mercurated furfural to products obtainable by replacement of the halomercuri group.

When furfuryl alcohol, I, was mercurated by the prescribed procedure (1) the product was chiefly an infusible non-crystallizable precipitate. If, however, a threefold excess of the alcohol was employed, a 50% yield of 5-chloromercurifurfuryl alcohol, II, was obtained and the production of infusible material was minimized. The object in using this excess of alcohol was, of course, to reduce poly- in favor of mono-substitution, but the infusible material evidently contains more than simple substitutionproducts. Evidence for this lies in the observation that it is partially soluble in dilute alkali; the solution when carefully acidified with hydrochloric acid yields 5-chloromercurifurfuryl alcohol. A part of the infusible precipitate must therefore be an intermediate of type III, by analogy with similar intermediates which have been isolated (1, 3) in both the furan and thiophene series.

The foregoing description concerning preparation of 5-chloromercurifurfuryl alcohol indicates its characteristic property of solubility in alkali. When it was treated with one equivalent of 5% sodium hydroxide it dissolved at once, but a compound, presumably the hydroxymercuri deriva-

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tive, IV, precipitated immediately. This compound could not be purified satisfactorily for analysis, owing to its tendency to retain the elements of potassium or sodium chloride and to decompose with formation of mercurous salt. It was somewhat soluble in water and very soluble in excess alkali, from which solution the chloromercuri derivative could be regenerated by cautious addition of hydrochloric acid. Since the odor of furfuryl alcohol during such treatment attested the extreme lability of the C—Hg linkage in this compound, a better regeneration of the chloromercuri derivative, II, was effected with carbon dioxide in a solution saturated with sodium chloride.

This solubility of chloromercurifurfuryl alcohol was at first somewhat surprising to us. We have since found that this is an extreme instance of a general though little-known property of hydroxymercurials. Thus phenylmercuric chloride dissolves with some difficulty by heating in 10%alkali and, if the solution be diluted sufficiently, the hydroxymercuri derivative does not precipitate. The solubility of RHgOH types depends, however, upon the presence of coordinating groups. This is especially noticeable in the case of α -methoxymercurials, many of which are so easily dissolved in sodium hydroxide that a neutralization equivalent can be carried out with a compound such as 1-chloromercuri-2-methoxycyclohexane (4). The furyl nucleus must also have this property, since furylmercuric chloride (1) is very soluble in 5% aqueous sodium hydroxide, from which it can be recovered unchanged by careful acidification with hydrochloric acid. In this connection, we see no reason to assume with Reissert (5) that the ready solubility of o-nitrobenzylmercuric chloride results from formation of an acinitro salt, since this characteristic solubility



could be explained equally satisfactorily as due to the effect of the coordinating nitro group on the hydroxymercuri linkage. It must be admitted, however, that such an unelaborated concept does not explain the report that *o*-nitrophenylmercuric chloride $(6)^2$ as well as some α -methoxymercurials are not soluble in alkali, nor that an excess of alkali is required to retain 5-hydroxymercurifurfuryl alcohol in solution.

² More recent work in this laboratory indicates that o-nitrophenylmercuric chloride can be dissolved in warm alkali and reprecipitated from this solution with hydrochloric acid.



When the alkaline solution of chloromercurifurfuryl alcohol was treated with hydrobromic acid the product contained both bromine and chlorine. A better method of preparing bromomercurifurfuryl alcohol, (V), involved repeated treatment of chloromercurifurfuryl alcohol, (II), with sodium bromide in ethanol. Both II and V were smoothly acetylated with acetic anhydride in pyridine to yield 5-bromomercurifurfuryl acetate, (VI), and 5-chloromercurifurfuryl acetate, (VII).

This compound VII was desired in order that it might be treated with ketene to produce 5-acetofurfuryl acetate, (VIII), from which the corresponding alcohol, (IX), could be prepared. This step seemed necessary because no product could be obtained by reaction of II with ketene in acetone except for a small amount of VII. When the acetate, (VII), was

TABLE I	
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Preparation of 2-Furyl Methyl Ketone in Various Solvents by the Action of Ketene upon 2-Chloromercurifuran

RUN	BOLVENT	MOLES KETENE	% YIELD 2-FURYL METHYL KETONE	M.P. 2,4- DINITBOPHEN- YLHYDRAZONE, °C.	YIELD KETENE POLYMER, GRAMS
1	Acetone	0.536	34.5 27.0	165–174 212–214ª	0.64
2	Diethyl sulphide	0.57	20.9	190-194	0.39
3	Glycol dimethyl ether	0.346	13.8	189-192	0.23
4	Pyridine	0.36	None		21.5
5	Acetone + hydroquinone	0.56	34.5	164 - 168	0.59
6	Carbon tetrachloride	0.528	11.8	200 - 215	None
7	Chloroform	0.624	31.7	199-203	None

^a Purified crude dinitrophenylhydrazone from Expt. 1 by crystallization.

likewise treated with ketene in acetone none of the product VIII could be isolated.

The method (7) was, however, known to be erratic and seemed to warrant further investigation. The work of Rice and Greenberg (8) suggested that solvents other than acetone might reduce the tendency towards ketene polymerization. Table I shows, by comparison of apparent furyl methyl ketone 2,4-dinitrophenylhydrazone yields with the crude melting points, that solvents such as carbon tetrachloride and chloroform are most satisfactory for this reaction of organomercurials with ketene. The latter solvent is to be preferred because it dissolves organomercurials with greater ease than does carbon tetrachloride.

When chloroform was used as solvent in the reaction between chloromercurifurfuryl acetate, (VII), and ketene, a 14% yield of 5-acetofurfuryl acetate, (VIII), was obtained. In addition to VIII considerable furfuryl acetate was obtained, which was not unexpected owing to the lability of the C—Hg linkage in these mercurials. Compound VIII was identified by saponification to acetofurfuryl alcohol (IX), by preparation of its oxime, and oxidation to dehydromucic acid, (X).

The bromination of 5-chloromercurifurfuryl acetate, (VII), produced an oil containing both chlorine and bromine. It was better, therefore, to use 5-bromomercurifurfuryl acetate, (VI), in order to obtain a fair yield of pure 5-bromofurfuryl acetate, (XI). This ester had a pleasant fruity odor. It was slowly saponified at room temperature to give the odorless, low-melting solid 5-bromofurfuryl alcohol, (XII). This compound was extremely unstable and difficult to purify. After futile attempts to stabilize XII with urea or with hydroquinone, it was found that conversion to the bromomagnesium alkoxide by means of the Grignard reagent, followed by regeneration of the alcohol with dilute acetic acid, rendered XII much more amenable to purification techniques. Nevertheless, the isolated compound was exceedingly unstable. It decomposed slowly at room temperature, and immediately at 65°, to form a greenish-black tar. \mathbf{It} was more stable in solution; indeed, it survived a five-hour reflux period in benzene containing suspended sodium acetate. It seems, however, to be a property of halofurans that decomposition is autocatalytic. Hence the presence of sodium acetate, which effectively removes traces of halogen acid, might be expected to retard decomposition.

A deliberate attempt to decompose bromofurfuryl alcohol, (XII), either spontaneously or with sulfuric acid, to produce acetylacrylic acid has thus far not been successful. This would be the expected product in view of the formation of benzalcrotonolactone, (XVIII), from the ether of chlorofuryl phenyl carbinol (9), (XVII). The fact that XVIII will not add hydrogen halide whereas acetylacrylic acid undergoes this addition may contribute to the failure to isolate the latter compound from 5-bromofurfuryl alcohol, (XII). It was observed that the decomposition of XII in sulfuric acid did not produce the hydrogen halide observed in the comparable reaction with XVII.



Oxidation of bromofurfuryl alcohol failed to yield a characterizing derivative, but the structure of this compound was proved by synthesis via the Cannizzaro method from 5-bromofurfural, (XIX). This reaction did not succeed using an equivalent quantity of 30% sodium hydroxide, but was effected when a large excess of this alkali and a trace of hydrogen peroxide was employed. The demonstrated catalytic effect of peroxide on the Cannizzaro reaction (10) is significant here because furfurals, unlike benzaldehydes, do not form peroxides in the air. Thus, furfurals do not autooxidize to furoic acids as benzoic acids are formed from benzaldehydes.

No chloromercurifuroic acid could be isolated when 5-chloromercurifurfuryl alcohol was oxidized with permanganate, although a 1-2% yield of 5-chloromercurifurfural was obtained. This aldehyde, (XV), was more conveniently obtained by the following series of reactions. Chloromercurifurfuryl alcohol, (II), with sodium thiosulfate gave a good yield of *bis*-5-hydroxymethyl-2-furylmercury, (XIII). The structure of this compound was demonstrated by conversion with mercuric bromide to bromomercurifurfuryl alcohol, (V), in a state of purity which demonstrated that passage from one halomercuri derivative to another is best effected in this series through the R_2Hg intermediate. When *bis*-5-hydroxymethyl-2-furylmercury was oxidized with permanganate, a 22% yield of *bis*-5-formyl-2-furylmercury was obtained, which could be converted quantitatively with mercuric chloride to 5-chloromercurifurfural, (XV).

This compound, XV, was identified by bromination to 5-bromofurfural (11), (XIX), and was further characterized by iodination to 5-iodofurfural, (XVI). The latter substance melted 18° higher than the compound to which Scheibler and co-workers (12) assigned this structure. Since their compound was prepared from a substance which they describe as triacetoxyfurfural (although the analysis is none too satisfactory for this designation) it is possible that their compound is either a β -substituted furfural or an impure sample of the iodofurfural which we have prepared. Our compound has been converted to 5-iodofuroic acid by a Cannizzaro reaction, in which the fraction containing the iodofurfuryl alcohol was discarded because of the evident extreme instability of this compound.

EXPERIMENTAL

5-Chloromercuri-2-furfuryl alcohol. To a solution of 815 g. (3 moles) of mercuric chloride, and 1632 g. (12 moles) of sodium acetate trihydrate in 15 liters of water was added 882 g. (9 moles) of freshly distilled, water-soluble furfuryl alcohol. After stirring for thirty-five hours, the crude product, 789 g., m.p. 144°, was filtered off. Extraction with boiling alcohol and subsequent recrystallization from the same solvent yielded 490 g., m.p. 144.5-145.5°. This 49% yield of pure product may be augmented both by evaporation of the crystallizing liquors, and by solution of the ethanol-insoluble residue, remaining after ethanol extraction of the crude product, in 4% sodium hydroxide (150 cc. per 20 g.). After filtering and chilling this alkaline solution it was stirred while exactly one equivalent of 4% hydrochloric acid was added dropwise. These additional yields, m.p. 137-138°, were difficult to purify, but were suitable for the preparation of the R₂Hg compounds.

Anal. Calc'd for C₅H₅ClHgO₂: C, 18.0; H, 1.51.

Found: C, 17.8; H, 1.54.

When the alcohol was dissolved in 1 equivalent of 5% sodium hydroxide an immediate precipitate appeared. This precipitate, m.p. 155–157°, was soluble in an excess of alkali. Although it was undoubtedly the hydroxymercuri compound, it contained small amounts of sodium and halogen and has not yet been satisfactorily purified for analysis. When its water solution was saturated with sodium chloride and treated with carbon dioxide, pure 5-chloromercurifurfuryl alcohol was precipitated. The alcohol could likewise be obtained by acidifying the alkaline solution with hydrochloric acid, although the odor of furfuryl alcohol was always apparent. The lability of this C—Hg linkage was likewise demonstrated by treating a pyridine solution of the alcohol II with an equivalent of trityl chloride. The product, trityl furfuryl ether, m.p. 138–140° was identified by mixed melting point (13).

5-Chloromercurifurfuryl acetate. An unsatisfactory yield of this compound can be obtained by treating an acetone solution of the alcohol with gaseous ketene. It is more conveniently prepared by treating 33.3 g. (0.1 mole) of chloromercurifurfuryl alcohol in 47 g. (0.6 mole) of pyridine (dried over barium oxide) with 41 g. (0.4 mole) of acetic anhydride at 0° for four days. Subsequent addition of 1% hydrochloric acid until the pyridine was neutralized produced a precipitate weighing 36.5 g. (97% yield) melting at 126-127°. This yielded 29 g. m.p. 131-131.5°, after crystallization from 7:1 benzene-petroleum ether (b.p. 60-70°). Subsequent crystallization did not raise the melting point.

Anal. Calc'd for C₇H₇ClHgO₈: C, 22.4; H, 1.87; Hg, 53.5; Cl, 9.5.

Found: C, 22.3; H, 1.86; Hg, 53.6; Cl, 9.1.

bis-5-Hydroxymethyl-2-furylmercury. To a solution of 337 g. (1.34 mole) of sodium thiosulfate pentahydrate in 900 cc. of water was added 150 g. (0.453 mole) of 5-chloromercuri-2-furfuryl alcohol at once with vigorous agitation. After standing for twenty-two hours the precipitate was filtered off and re-treated with the same quantity of fresh thiosulfate solution. The resulting mixture was filtered after twelve hours. A weight of 106 g. (theoretical, 88.6 g.) and melting point of 130-135° indicated an incomplete reaction. Crystallization from 2:1 methanol-ethyl acetate yielded 55 g., m.p. 147.5-148.5° (yield, 62%) which was sufficiently pure for most purposes. Repeated crystallization from this solvent, and from benzene raised the melting point to 153-154°.

Anal. Calc'd for C10H10HgO4: C, 30.4; H, 2.56.

Found: C, 30.4; H, 2.65.

The compound was also obtained in 61% yield when 5-chloromercurifurfuryl alcohol in methanol was treated with an excess of diazomethane (14).

5-Bromomercuri-2-furfuryl alcohol. a. From bis-5-hydroxymethyl-2-furylmercury. A solution of 0.39 g. (0.001 mole) of the R_2Hg compound with 0.36 g. (0.001 mole) of mercuric bromide in 8 cc. of ethanol was refluxed for ninety minutes. Vacuum evaporation of the solvent left 0.74., m.gp. 124-130°. Crystallization from 1:1 chloroform-ethanol yielded 0.63 g., m.p. 139-140°. Yield of this pure material was therefore 84%.

Anal. Calc'd for C₅H₅BrHgO₂: C, 15.9; H, 1.33. Found: C, 15.8; H, 1.43.

b. From 5-chloromercuri-2-furfuryl alcohol. A solution of 33.3 g. (0.1 mole) of the alcohol in 450 cc. of 95% ethanol was treated with 20.6 g. (0.2 mole) of sodium bromide in 25 cc. of water. Vacuum evaporation of the solvent, followed by thorough washing of the residue with water yielded a solid, m.p. 137-138° which still contained chlorine. Repetition of the entire process yielded a crude product, m.p. 138°, in 70.8% yield.

5-Bromomercuri-2-furfuryl acetate. This preparation, identical with that outlined for the chloro compound except that hydrobromic acid was used to neutralize the pyridine, yielded a crude product melting at 90-95° which was crystallized from 1:7 benzene-petroleum ether (b.p. 60-70°) to the constant melting point 108-109°. Yield of the purified product was 88%.

Anal. Calc'd for C7H7BrHgO3: C, 20.0; H, 1.67.

Found: C, 20.4; H, 1.81.

5-Bromofurfuryl acetate. A solution of 7.18 g. (0.017 mole) of 5-bromomercuri-2furfuryl acetate in 150 cc. of chloroform stirred at 0° was treated dropwise but rapidly with 2.75 g. (0.017 mole) of bromine in 30 cc. of chloroform. After the addition, the precipitated mercuric bromide was filtered off and the filtrate washed successively with 50 cc. of saturated sodium sulfite, 50 cc. of 10% sodium carbonate, and twice with water. Distillation of the solution dried with magnesium sulfate, finally at 110-112° (17-18 mm.) gave 2.39 g. which was redistilled at 106-107° (13 mm.) to yield (58% of theoretical) a colorless oil having a pleasant fruity odor, d_{25}^{25} , 1.51; n_{p}^{25} , 1.4991; M_p Calc'd 42.69, Found 42.57.

Anal. Calc'd for C₇H₇BrO₈: Br, 36.5. Found: Br, 36.7.

5-Bromofurfuryl alcohol. a. From bromofurfuryl acetate. A solution of 2.54 g. (0.01 mole) of the acetate and 2.6 g. (0.05 mole) of potassium hydroxide in 11 cc. of methanol and 14 cc. of water was let stand for four days until the odor of the acetate was very slight. The methanol was removed at 10 mm., and the aqueous residue extracted with ether. The ether solution, dried with magnesium sulfate, was evaporated to leave 1.78 g. of orange-colored oil. This was crystallized under nitrogen repeatedly from 1:8 ether-petroleum ether (b.p. $40-60^{\circ}$) from $+20^{\circ}$ to -80° . After eight crystallizations and final evacuation at 0° to remove solvent the compound weighed 0.54 g. and melted at 43-44°. This wasteful process was improved as described below. The resulting compound was extremely unstable; it became slightly green after a short time and then rapidly decomposed to a green tar. The green, slightly decomposed samples gave a red solution when dissolved in alcohol. Addition of 1% of hydroquinone or urea lowered the melting point without stabilizing the compound. Boiling with excess sodium acetate in benzene for five hours did not decompose the substance, which was recovered unchanged. Decomposition over a one day period in either concentrated sulfuric acid or 85% phosphoric acid did not yield a recognizable product. When an ether solution of the alcohol was refluxed overnight with acetyl chloride, a good yield of bromofurfuryl acetate was obtained by steam distillation. The alcohol could be dissolved in water at 60° but would not crystallize on cooling although it could be recovered by ether extraction. Such a homogeneous water solution could be refluxed for some hours without destruction of the substance. However when more than would dissolve in the water was heated to 65° under water the undissolved portion decomposed instantly with formation of a green tar; the aqueous solution gave a dinitrophenylhydrazone test and iodoform test (comparable tests with furfuryl alcohol were negative) but no product could be isolated. When the alcohol was refluxed in ethanol solution for two days and the solvent subsequently removed at 12 mm., the residue distilled at 91-94°, 12 mm. This compound is being investigated; it seems not to contain a carbonyl group and is not soluble in water or in saturated sodium bicarbonate solution. Because of difficulty in freeing bromofurfuryl alcohol from solvent without decomposing it, the analyses were not good.

Anal. Calc'd for C₅H₅BrO₂: Br, 45.2. Found: Br, 44.2.

b. From 5-bromofurfural. The disappearance of bromofurfural in this Cannizzaro reaction was followed by testing the supernatant ether solution for the characteristic yellow color with aniline acetate. A suspension of 17.5 g. (0.1 mole) of bromofurfural in 100 cc. of ether was stirred with 400 cc. of 30% sodium hydroxide. The time of reaction varied from one to four days, but the reaction could be brought quickly to completion by addition of a drop of 30% hydrogen peroxide. When the test for bromofurfural was negative, water was added to dissolve the sodium bromofuroate, and the alkaline solution extracted five times with ether, after which it was acidified, yielding 76% of the possible amount of 5-bromofuroic acid. The ether extract, washed with ferrous ammonium sulfate solution, sodium bisulfite, and water, was dried with magnesium sulfate to which was added a little charcoal. The ether solution was then treated with 0.1 mole of filtered ethylmagnesium bromide in ether. Treatment with phenylmagnesium bromide for two days gave the same results. After two hours this was poured into iced dilute acetic acid. The ether solution obtained by five-fold extraction of this hydrolysate was washed with 2% alkali, dried with magnesium sulfate to which charcoal was added, and evaporated at 10 mm. to yield 7.12 g. (80%) of bromofurfuryl alcohol melting at 35°. This was purified by solution in 10 cc. of benzene and seeding of the solution rendered turbid by addition of 60 cc. of petroleum ether (b.p. 26-30°) to yield 5.25 g., m.p. 43-44°. A mixed melting point with the compound obtained from the mercurial was not lowered.

2-Furyl methyl ketone 2,4-dinitrophenylhydrazone. This preparation was used to check the effect of solvents on the reaction of mercurials with ketene. Into a solution of 2-chloromercurifuran in the selected dry solvent maintained at 64° was passed ketene from an Ott lamp at the rate of 0.06-0.08 mole per hour for eight hours. The solvent was then removed under reduced pressure and the residue steam distilled until the distilling liquid no longer gave a dinitrophenylhydrazone test. The distillate was extracted with ether which, after drying, was evporated to leave a residue of ketone. This was weighed and then converted to the 2,4-dinitrophenylhydrazone by the method of Iddles and Jackson (15). A sample of pure furyl methyl ketone treated by this procedure gave a crude melting point of 210-212° and a high melting point of 223° after repeated crystallization from 3:1 ethyl acetate-ethanol. The results shown in Table I indicate that carbon tetrachloride or chloroform are the best solvents for the reaction. It may be noted that addition of hydroquinone to the solvent acetone did not increase the yield of ketone nor decrease the yield of polymer.

Anal. Calc'd for C12H10N4O5: C, 49.6; H, 3.47.

Found: C, 49.0; H, 3.70.

5-Acetofurfuryl acetate. A solution of 11.2 g. (0.03 mole) of 5-chloromercuri-2furfuryl acetate in 165 cc. of chloroform dried with calcium chloride was treated with ketene (0.6 moles) at 64° for twelve and one-half hours. The chloroform solution was then filtered and the solvent removed under reduced pressure. The residue was steam distilled until the distillate gave a negative dinitrophenylhydrazone test. The ether extract of the distillate was dried and evaporated to yield 3.23 g. of oil, which was fractionated at 11-12 mm. to give 1.47 g., b.p. 73-74° and 1.13 g., b.p. 100-140°. The latter fraction was purified by crystallization from 1:1 methanol-petroleum ether (b.p. 40-60°) and melted at 44-46°, 0.87 g. or 14% of theoretical. Three further crystallizations from a methanol-petroleum ether-ethyl ether mixture raised this melting point to 46.5-47°.

Anal. Calc'd for C₂H₁₀O₄: C, 59.3; H, 5.53.

Found: C, 59.2; H, 5.84.

Oxidation with alkaline permanganate gave a 2% yield of dehydromucic acid, identified by its yellow ferric chloride test and by conversion with diazomethane to its dimethyl ester, m.p. 107-108° after crystallization from water.

5-Acetoxymethyl-2-furyl methyl ketone semicarbazone. When the ester was treated with an excess of semicarbazide at pH 8, the precipitated semicarbazone melted at 169-170°. Two crystallizations from 4:1 benzene-ethanol raised this to 173-174°.

Anal. Calc'd for C10H14N3O4: C, 50.0; H, 5.82.

Found: C, 50.3; H, 5.79.

5-Acetofurfuryl alcohol. A 62% yield was obtained by saponifying the acetate with one equivalent of potassium hydroxide in 1:1 methanol-water for two days. Removal of the methanol *in vacuo* and extraction with ether gave 0.05 g. of solid, m.p. 42°, after this dried solution was evaporated. This compound was crystallized from 1:3 methanol-petroleum ether (b.p. 40-60°) and melted at 43-44°. A mixed melting point with the original acetate was lowered 20°.

Anal. Calc'd for C7H8O8: C, 60.0; H, 5.75.

Found: C, 59.6; H, 5.82.

Oxidation of this compound with iodine in alkaline solution at 25° gave iodoform. bis-5-Formyl-2-furylmercury (XIV). Finely powdered potassium permanganate (40.6 g., 0.257 mole) was gradually added over a three-hour period to a stirred solution of 50.7 g. (0.128 mole) of bis-5-hydroxymethyl-2-furylmercury in 1900 cc. of permanganate-purified acetone. When no unchanged permanganate remained after thirty-six hours, the mixture was filtered and the filtrate evaporated at 10 mm., leaving a residue, m.p. 128-133°. This residue was extracted twice with 475 cc. of saturated sodium sulfite made slightly acidic with acetic acid.

The bisulfite extracts were treated with sodium carbonate, giving 17.4 g. of the dialdehyde, m.p. 238-240° (22.5% of theoretical). Repeated crystallization from dioxane raised the melting point to 262-263°. After boiling with hydrochloric acid, the aniline acetate test, characteristic of furfural, was obtained.

Anal. Calc'd for C10H6HgO4: C, 30.8; H, 1.55.

Found: C, 30.8; H, 1.63.

The compound slowly dissolved in a methanol solution of hydroxylamine. Vacuum evaporation of the solution left a solid, which was dissolved in 1% aqueous alkali and reprecipitated with carbon dioxide, giving 52% yield of a compound which was presumably the oxime, m.p. 114-116°, although we were unsuccessful in attempts to purify this compound for analysis.

5-Chloromercurifurfural. A 5% yield of the aldehyde m.p. $211-212^{\circ}$ was obtained by oxidizing an alkaline solution of the alcohol with one equivalent of permanganate. A better method of preparation involved refluxing equivalent quantities of bis-5formyl-2-furylmercury and mercuric chloride in ethanol for five hours. A 96% yield of crude product m.p. 200° was decreased to 66% after crystallization from 1:1 ethanol-chloroform m.p. 218-219°. Anal. Calc'd for C₅H₃ClHgO₂: C, 18.1; H, 0.91. Found: C, 18.5; H, 1.50.

5-Bromofurfural was obtained from this compound by treating a chilled chloroform suspension with one equivalent of bromine. After vacuum evaporation of the chloroform and steam distillation of the residue, the ether extract of the distillate gave on evaporation a 62% yield, m.p. 82°. A mixed melting point with the bromofurfural prepared from furfural was not lowered.

5-Iodofurfural. To a suspension of 1 g. (0.003 mole) of 5-chloromercurifurfural in 15 cc. of dioxane (distilled from sodium benzophenone) was added 0.76 g. (0.003 mole) of iodine in 24 cc. of dioxane. After ninety-six hours the dioxane was removed at 10 mm. and the residue steam distilled, yielding 0.46 g. m.p. 98-102°. This was washed with 5% potassium iodide solution and crystallized from acetone-water and dioxane-water, m.p. 127.5°, weight 0.31 g. or 46%.

Anal. Calc'd for C₅H₂IO₂: C, 27.0; H, 1.36; I, 57.2.

Found: C, 27.0; H, 1.43; I, 57.2.

A mixture of 0.16 g. (0.0008 mole) of this compound with 4 cc. of 30% sodium hydroxide solution containing a trace of peroxide yielded, after four days, 0.03 g. (32%) of 5-iodofuroic acid, m.p. 197°, which was crystallized from 1:1 benzenepetroleum ether (b.p. 60-70°), m.p. 197-198°. A mixed melting point carried out by Dr. Henry Gilman with the compound prepared from 2,5-diiodofuran (16) was not depressed. It was found in this connection that these samples must be introduced about 5° below the melting point in order to avoid decomposition. This accounts for the melting point 192° previously reported for this compound.

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SUMMARY

1. Monomercurated furfuryl alcohol and furfural have been prepared and characterized.

2. 5-Acetofurfuryl alcohol and 5-bromofurfuryl alcohol have been prepared from these mercurials. The latter compound has also been synthesized from 5-bromofurfural.

3. 5-Iodofurfural has been prepared from 5-chloromercurifurfural.

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