three others are more or less completely in hand and will be offered for publication at an early date. The remaining member of this group, 3,4-dimethyl-1-pentene, is proving more difficult but may yet be obtained.

Space has not permitted an adequate discussion of the remarkable correlation between the physical properties and the structure of the above heptenes such as has been included in the earlier papers of this series. Such a discussion will form a part of a more general paper taking up this question as it relates to the olefins.

Summary

The bromo ether synthesis has been applied in a systematic survey of the heptenes. Eighteen of the twenty-seven heptenes are herein described, seventeen having been obtained by the above synthesis. Ten of these heptenes are new.

The seventeen corresponding bromoethoxyheptanes and eighteen dibromoheptanes, prepared incidentally to the synthesis and identification of the above heptenes, are also described. Sixteen of the ethoxy derivatives and fourteen of the dibromides are new.

COLUMBUS, OHIO

RECEIVED JANUARY 14, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Furan Mercurials

BY HENRY GILMAN AND GEORGE F. WRIGHT

Introduction

Apparently the only published study on pure furan mercurials is that by Ciusa and Grillo,[1] who prepared tetraacetoxy- and tetrachloromercurifurans, from which they obtained tetraiodofuran. They also reported the isolation of acetoxymercurifuran and chloromercurifuran by the action of mercuric salts on furoic acid, but they were unable to repeat the preparation of these mono-mercurials.

We find that a wide variety of furan mercurials can be conveniently prepared either by direct nuclear substitution or by replacement of a carboxyl group. The mercurials are reagents of choice for two purposes. First, they admirably bridge the gap between the unusually reactive and unusually inert substituted furans[2] and so render more accessible, by subsequent replacement reactions, important furan types. Second, they constitute at this time the best derivatives for the characterization of many furans, and for the stabilization of sensitive furans.

---

(1) Ciusa and Grillio, *Gazz. chim. ital.*, **57**, 323 (1927). See, also, Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930) for the preparation of a mixture of mercuration products from furoic acid; and the paper by Scheibler and co-workers, *J. prakt. chem.*, **136**, 232 (1933), which appeared just prior to receipt of proof, on the mercuration of furfural diacetate.

(2) Gilman and Young, *Rec. trav. chim.*, **51**, 761 (1932).

Preparation of Mercurials. (A) Direct Mercuration.—The ease of furan mercuration recalls the discovery by Volhard[3] that thiophene reacts at room temperatures with a buffered solution of mercuric chloride to give good yields of the α-thienylmercurial. The apparently more ready mercuration of furan types is part of the accumulating evidence which leads one of us to the opinion that furan has super-aromatic properties.[4] Furan itself mercurates normally to give a mixture of 2-chloromercurifuran and 2,5-dichloromercurifuran.[5] However, unlike the thiophene series where the formation of an intermediate does not appear except in β-mercuration, 2-methylfuran reacts with one equivalent of mercuric chloride and two of sodium acetate to give an intermediate which closely approximates that postulated by Steinkopf[6] for the complex from 2,5-dimethylthiophene. The furan intermediate addition compound, perhaps of a kind previously observed in halogenation,[7] is converted by boiling alcohol to 5-methyl-2-chloromercurifuran. If, however, four equivalents of sodium acetate are used, a 50% yield of the furan mercurial is obtained directly. Accordingly, experimental conditions can be varied to include or eliminate the intermediate addition compound.

The ability of substituted furans to form mercurials corresponds closely with that of the related thiophenes. Thus, neither 2,5-diiodofuran nor 2,5-diiodothiophene will react with mercuric chloride and sodium acetate; and 2-nitrofuran and 2-nitrothiophene are likewise resistant,[8] although 5-nitro-2-chloromercurifuran has been prepared from 5-nitro-2-furoic acid. Whereas an unusually wide variety of alkylfurans as well as compounds like 2-iodofuran, 4-iodo-2-methylfuran and difurylmethane react smoothly to give well defined mercurials, the compounds obtained from ethyl furoate, furfural, furfuryl alcohol and *sym*-2,2′-difurylethane have not as yet been identified as true mercurials.

(B) Replacement of Carboxyl by a Mercuri Group.—This procedure turns on the extraordinary ease of α-decarboxylation and is remindful of mercurial syntheses from aromatic acids of various types.[9]

$$2\text{-}C_4H_3OCO_2Na + HgCl_2 \longrightarrow 2\text{-}C_4H_3OHgCl + CO_2 + NaCl \qquad (1)$$

This reaction appears to be applicable with all α-furoic acids, but not with β-furoic acids. If the free acid and not the salt is used, the reaction becomes one of simple decarboxylation, undoubtedly as a consequence of scission effected by the hydrochloric acid.

---

(3) Volhard, *Ann.*, **267**, 172 (1892).

(4) Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

(5) An excess of mercurating agent promptly yields the tetra-mercurial.

(6) Steinkopf and Bauermeister, *Ann.*, **403**, 50 (1914).

(7) Gilman and Wright, THIS JOURNAL, **52**, 3349 (1930).

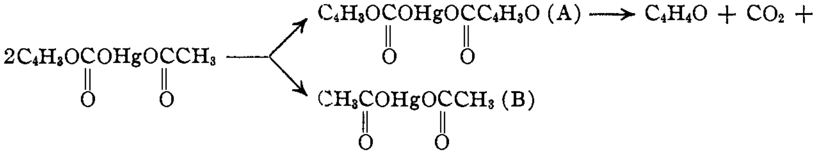
(8) It remains to be determined whether so-called forced conditions might not effect mercuration with those types resistant under moderate conditions.

(9) Peters, *Ber.*, **38**, 2567 (1905); Kharasch and Chalkley, THIS JOURNAL, **43**, 611 (1921); Michaelis and Becker, *Ber.*, **15**, 182 (1882); Whitmore and Fox, THIS JOURNAL, **51**, 3363 (1929); and Kerkhof, *Rec. trav. chim.*, **51**, 755 (1932). For an excellent, general account of mercuration, see Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921.

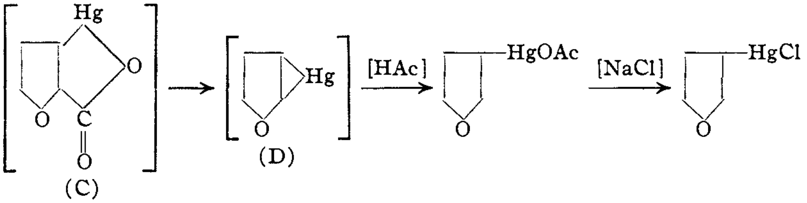
$$2\text{-}C_4H_3OCOOH + HgCl_2 \longrightarrow (2\text{-}C_4H_3OHgCl + HCl + CO_2) \longrightarrow C_4H_4O + HgCl_2 \quad (2)$$

This is an improved procedure for decarboxylation and is recommended for those types which are pyrolyzed with difficulty or in poor yields because of secondary transformations. In some cases, as with 5-nitro-2-furoic acid, where scission of the mercurial is relatively difficult, the reaction is carried out stepwise. It is surprising that none of the furoic acids seems to form insoluble mercuric salts. The methylfuroic acids show a slight tendency to salt formation, but in no case have we been able to isolate mercuric furoate or a nuclear substituted mercuric furoate. The success of the reaction is undoubtedly dependent on this fact. Conversely, the ready formation of a mixed mercuric salt affords a satisfactory method of β-mercuration.

When a solution of furoic acid is treated with aqueous mercuric acetate, the mixed salt (acetoxymercury furoate) is formed. This was identified by analysis and by the regeneration on treatment with alkali of the requisite amount of furoic acid. Although this salt decomposes in boiling water with formation of furan and the precursor of the β-mercurial, we have elected to employ dry pyrolysis. If the salt is heated to 135°, the ortho rearrangement characteristic of aromatic mercury salts occurs, although the reaction in this case is more complex. The yield of furan (the expected product since the temperature of pyrolysis of furoic acid is exceeded) and the volume of carbon dioxide evolved indicate that the reactions proceed as follows:



$$2C_4H_3O\underset{\overset{\|}{O}}{C}OHgO\underset{\overset{\|}{O}}{C}CH_3 \longrightarrow \begin{cases} C_4H_3O\underset{\overset{\|}{O}}{C}OHgO\underset{\overset{\|}{O}}{C}C_4H_3O\ (A) \longrightarrow C_4H_4O + CO_2 + \\ CH_3\underset{\overset{\|}{O}}{C}OHgO\underset{\overset{\|}{O}}{C}CH_3\ (B) \end{cases}$$



(3)

Acetoxymercury furoate acts here as if it were a mixture of the two symmetrical salts (A) and (B). The ready decarboxylation of the hypothetical anhydro-3-hydroxymercuri-2-furoic acid (C), which cannot be prevented by stopping the pyrolysis after one equivalent of carbon dioxide is evolved, recalls the formation of organomercury compounds from salts of easily decarboxylated acids.[10] The absence of acetic acid evolution or of any gaseous product other than furan and carbon dioxide opposes a mechanism which involves directly the mixed salt. The acetic acid α-cleavage of

---

(10) Kharasch, THIS JOURNAL, **43**, 2238 (1921).

(D) appears reasonable in view of the more ready scission by hydrochloric acid of an α-carbon–mercury linkage when compared with β-furan mercurials.

Reactions of Mercurials.—In the furan and thiophene series, unlike the benzene series, RHgX compounds are more accessible than R_2Hg compounds. Consequently the reactions studied by us were largely confined to chloromercuri compounds. In general, the reactions with organic and inorganic acid halides do not proceed so smoothly as with the related thienylmercurials. Acetyl chloride and other aliphatic acid chlorides with 2-chloromercurifuran give the corresponding ketones, but the mercurial is recovered unchanged after treatment with furoyl chloride. Furfuryl chloride, in agreement with its highly reactive halogen,[11] gives difurylmethane, whereas the related benzyl chloride underwent no reaction under corresponding conditions. Incidental to confirming the identity of the difurylmethane, we found, contrary to other observations,[12] that the Wolff–Kischner reduction of difuryl ketone gave an excellent yield of the methane. The greater stability of our methane over that obtained otherwise[12] may be due to the fact that our synthesis does not involve contamination with di-2-furylcarbinol, which compound we prepared from furfural and 2-furylmagnesium iodide and found to be extremely unstable.

Chloromercurifuran and its congeners react smoothly with bromine (in non-aqueous solution) and iodine. The reaction with iodine provides an improved source of 2-iodofuran,[13] and is far superior to our former method for the preparation of 3-iodofuran which involves the stripping of three atoms of iodine from tetraiodofuran. The lesser activity of β-furan mercurials is obvious in the fact that 3-chloromercurifuran absorbs iodine about one-fifth as rapidly as 2-chloromercurifuran. The same ratio in reactivity was observed in the dilute hydrochloric acid scission of the two mercurials, the α-isomer hydrolyzing more rapidly. The corresponding isomeric iodofurans exhibit a similar difference in reactivity: the 3-iodofuran is much more stable than 2-iodofuran, and is apparently inert toward magnesium and sodium, but it does react slowly with sodium–potassium alloy to give an organo-alkali compound which when carbonated yields traces of 3-furoic acid. The dichloromercurifurans investigated are infusible, insoluble compounds. Their reaction with iodine is not only a convenient way of identifying them, but also a good source of di-iodofurans.

The action of dimethyl sulfate on 2-chloromercurifuran and 5-iodo-2-furylmagnesium iodide is one which is not quite clear.[14] It indicates that the furan nucleus decomposes in apparently anhydrous media to give

---

(11) Gilman and Wright, THIS JOURNAL, **54**, 4108 (1932).

(12) Reichstein, Grüssner and Zschokke, *Helv. Chim. Acta*, **15**, 1066 (1932).

(13) Gilman, Mallory and Wright, THIS JOURNAL, **54**, 733 (1932).

(14) Mention should be made of the fact that 5-methyl-2-furylmagnesium iodide does react with dimethyl sulfate to give 2,5-dimethylfuran.

water or other active hydrogen compounds. Such instability is most pronounced with 2,5-disubstituted furans, and is one of the reasons underlying the use, wherever possible, of dehydrating solvents like acetic anhydride in nuclear substitution reactions.

As might have been predicted,[4] β-difurylmercury is more stable than the α-isomer.

Incidentally, it is interesting to note that hydrazine hydrate effects a quantitative conversion of 2-chloromercurifuran and phenylmercuric chloride to the corresponding R_2Hg compounds.

Experimental Part

I. Directly Mercurated Furans and their Chemical Behavior

2-Chloromercurifuran, 2-C_4H_3OHgCl.—A solution of 540 g. (2 moles) of mercuric chloride in 8 liters of water was added to 1088 g. (8 moles) of sodium acetate trihydrate in 4 liters of water; the resulting solution was thoroughly chilled, and to it was added quickly 136 g. (2 moles) of furan in 850 cc. of alcohol. The tightly stoppered bottle was allowed to stand, precipitation commencing in three to four minutes and completing itself in two days, after which the mixture of mercurials was filtered[15] by suction and extracted with 4 liters of boiling ethanol. Hot filtration by suction left chiefly 2,5-dichloromercurifuran (164 g.). The cooled alcoholic filtrate yielded 202 g. or 33.5% of 2-chloromercurifuran melting at 148°. This was sufficiently pure for most operations, and crystallization from hot ethanol raised the m. p. to 151°.

Anal. Calcd. for C_4H_3OHgCl: Hg, 66.01. Found: Hg, 65.83.

The 2,5-dichloromercurifuran is almost insoluble in organic solvents and purification was effected by eight hours of extraction with acetone.

Anal. Calcd. for $C_4H_2O(HgCl)_2$: Hg, 74.71. Found: Hg, 74.65.

When 53.6 g. of the residues from the crystallization of the crude mercuration product was treated with an iodine–potassium iodide solution (0.2 mole), there was obtained 1.32 g. of tetraiodofuran (m. p. 158°) and 12 g. of 2,5-diiodofuran (b. p. 115–116° (12 mm.), m. p. 47°); the latter was isolated by steam distillation of the reaction mixture and the former by alcoholic extraction of the residues from steam distillation, and no triiodofuran was isolated. An ether suspension of 2,5-dichloromercurifuran was treated for two days with benzoyl chloride to yield a trace of 2,5-dibenzoylfuran (m. p. 107–108°).

The relative amounts in grams of mono- (M) and poly-mercurated (P) furans from 2 moles of furan were as follows: with 2 moles of mercurating solution and two days, 202 (M) and 164 (P); in one day, 144 (M) and 124 (P); and with 4 moles of mercurating solution and two days, 106 (M) and 495 (P).

In each of the following reactions of 2-chloromercurifuran, 31.3 g. (0.1 mole) was used unless otherwise stated.

(1) **Acetyl Chloride.**—The dropwise addition of 0.1 mole of acetyl chloride to a suspension of the mercurial in 50 cc. of acetone evolved heat, and dissolved the mercurial with considerable darkening; after refluxing half an hour, the cooled solution was poured into ice, made alkaline with sodium carbonate solution, filtered by suction, the precipitate washed thoroughly with ether, the filtrate extracted twice with 50-cc. portions of ether to yield on distillation 21% of furyl methyl ketone melting at 32° and boil-

---

[15] Some furan can be recovered by siphoning off the supernatant liquid and distilling it with steam.

ing at 80° (30 mm.). The yield with ether as the solvent was 10.5%, and reaction without solvent resulted in complete decomposition.

(2) **Furfuryl Chloride.**—From 0.4 mole of the mercurial, 0.4 mole of furfuryl chloride[16] and 750 cc. of ether, stirred for twenty-four hours, was obtained 5.7. g. or 9.5% of difurylmethane: b. p. 94° (22.5 mm.); d_4^{20} 1.102; n_D^{20} 1.5049; n_D^{25} 1.5026.

Anal. Calcd. for $C_9H_8O_2$: C, 72.97; H, 5.4. Found: C, 72.58; H, 5.66.

No furan or 2-methylfuran was isolated in this experiment, and it is noteworthy that no difurylethane was found, inasmuch as furfuryl chloride with methylmagnesium iodide gave a 50% yield of *sym*-difurylethane. The difurylmethane resisted alkaline permanganate oxidation, and did not react with ethyl nitrite and sodium ethylate to yield difuryl ketoxime. The furyl 5-chloromercurifurylmethane (probably mixed with a complex of the type reported with 2-methylfuran) was obtained in 80% yield from 0.01 mole of difurylmethane, and melted at 149.5° when crystallized twice from an alcohol–water–acetone mixture and finally from benzene.

Anal. Calcd. for $C_9H_7O_2HgCl$: Hg, 52.37. Found: Hg, 53.32.

When this mercurial was cleaved with boiling dilute acid only difurylmethane distilled. When iodinated in aqueous solution a 70% yield of 5-iodo-2,2′-difurylmethane was isolated; b. p. 123° (9 mm.); n_D^{20} 1.5843.

Anal. Calcd. for $C_9H_7O_2I$: I, 46.35. Found: I, 46.42.

This iodo compound did not react with magnesium nor with silver nitrate. The position of the iodine (and of the chloromercuri group) is assumed to be that designated on the basis of the stability of the iodo compound which is intermediate to that expected for lateral and β-nuclear substituted furans. Incidental to this study it was found that the addition of precipitated calcium carbonate in the reaction mixture markedly increased the yield of iodo compound. It is a curious coincidence that the HCN-HCl reaction for inserting aldehydic groups introduces a different number of substituents than does mercuration or nitration with 2,2′-difuryl and 2,2′-difurylmethane: one aldehydic or two nitro groups being introduced into difuryl, and one mercuri group or two aldehydic groups into difurylmethane.

Difurylmethane was also prepared by reduction of di-2-furyl ketone which was synthesized as follows: 0.097 mole of 2-furonitrile in 25 cc. of ether was added to 0.097 mole (by acid titration) of 2-furylmagnesium iodide,[13] the solution refluxed for one hour, chilled with an ice–water bath, and hydrolyzed by 0.1 mole of sulfuric acid in 100 cc. of water to yield 73.3% of ketone distilling at 113° (6 mm.) and melting at 33°. To 0.1 mole of the ketone in 50 cc. of methyl alcohol was added 0.2 mole of hydrazine hydrate. No hydrazone precipitated, even on chilling; and after one hour 0.2 mole of coarsely ground potassium hydroxide was added, the flask heated on a water-bath to promote nitrogen evolution, and the temperature raised gradually so that at the end of a four-hour period the water-bath was boiling. The methyl alcoholic distillate was poured into saturated calcium chloride and the solution extracted with ether and from this by customary procedures was isolated a 92% yield of difurylmethane (b. p. 80.5° (19.5 mm.)), the mercurial of which showed no depression in a mixed m. p. determination with that described above.

(3) **Iodine.**—For the preparation of 2-iodofuran[13,17] it is preferable to use the mixture of mercurials obtained in the mercuration of furan rather than the pure com-

---

(16) Kirner, THIS JOURNAL, **50**, 1955 (1928). It is suggested that in a 2 mole preparation of furfuryl chloride by this procedure, the ether solution be evaporated under reduced pressure and the residue strongly chilled to remove a solid prior to distillation. The solid is as yet unidentified, but at least a part of it contains nitrogen and may be a pyridinium salt.

(17) Gilman and Franz, *Rec. trav. chim.*, **51**, 991 (1932). Subsequent experience indicates that the iodide should be distilled under diminished pressure rather than merely dried over barium oxide.

pounds in order to obtain the optimum yield. This mixture, as filtered from the 2-mole run previously described, is suspended in 4 liters of water and stirred vigorously during the slow addition of a solution of 358.4 g. (1.4 moles) of iodine and 465 g. (2.8 moles) of potassium iodide in 2 liters of water. A slight excess of iodine at the end of the reaction was reduced with sodium thiosulfate. The mixture was steam distilled from a 12-liter balloon flask, and the iodofurans in the distillate were separated, poured into a 250-cc. distilling flask containing 45 g. of anhydrous calcium chloride and distilled in an atmosphere of dry nitrogen. The iodofuran fraction distilling between 39–50° (14 mm.) weighed 118.6 g. and represents 32% of the furan initially used. The residue in the distillation flask was quickly covered with water, sodium thiosulfate added, and the mixture steam distilled to yield impure diiodofuran which when crystallized from a hot water–alcohol solution weighed 43.5 g. We were unable to prepare a satisfactory mercurial from 2,5-diiodofuran, but mercuration of 2-iodofuran proceeded smoothly. The 5-iodo-2-chloromercurifuran was prepared in 50% yield by shaking for four days a solution of 0.162 mole of 2-iodofuran with 810 cc. of the stock mercurating solution,[18] filtering by suction and crystallizing from a water–alcohol solution and then successively from alcohol and benzene to give a compound melting at 173°.

Anal. Calcd. for $C_4H_2OClIHg$: Hg, 46.76. Found: Hg, 47.19.

When this iodo-mercurial was heated with copper powder above its melting point and under nitrogen, total decomposition occurred instead of coupling. An attempted reduction with an excess of aluminum amalgam in ether-methyl alcohol solution did not yield 2-chloromercurifuran; the chloromercuri group was evidently removed since there was no mercurial remaining at the end of the reaction.

(4) **Dimethyl Sulfate.**—No reaction occurred when 0.1 mole of 2-chloromercurifuran was suspended in 0.1 mole of recently purified dimethyl sulfate. The temperature was gradually raised and at 160° a reaction set in which was complete at 170°. The condensate was 2.72 g. of furan, identified by conversion to 2-chloromercurifuran, and no trace of 5-methyl-2-chloromercurifuran was detected in the preparation of the derivative. The unexpected course of this reaction makes it advisable to report a similar anomalous formation of 2-iodofuran from 5-iodofuryl-2-magnesium iodide. An ether solution of this Grignard reagent,[19] which consistently gives a 29% yield of RMgI as determined by acid titration, was treated with an excess of freshly distilled dimethyl sulfate. Subsequent to hydrolysis with 10% ammonium chloride solution it gave a 72% yield of 2-iodofuran which was identified by conversion to 2-furoylanilide by way of 2-furylmagnesium iodide and phenyl isocyanate.

(5) **Coupling to 2,2′-Difurylmercury.**—To a solution of 50 g. of sodium thiosulfate in 200 cc. of water was added at once 0.1 mole of the mercurial; the mixture was shaken vigorously for a few minutes, and after eight hours the precipitate was filtered to give a 95% yield of crude difurylmercury which may be purified by crystallization from a hot acetone–water solution or by a careful distillation under diminished pressure, the material sometimes decomposing violently. The compound distils at 156° (7 mm.) and melts at 114°.

Anal. Calcd. for $C_8H_6O_2Hg$: C, 28.69; Hg, 59.95. Found: C, 28.23; Hg, 60.34.

The yield by reaction of 2-chloromercurifuran with sodium iodide in acetone solution is 70%. It is interesting to observe that excess hydrazine hydrate converts 2-chloromercurifuran to difurylmercury. This new reaction which is equally effective

---

(18) The mercurating solution was prepared by adding a solution of 272 g. (2 moles) of sodium acetate trihydrate in 400 cc. of water to 135 g. (0.5 mole) of mercuric chloride dissolved in 1.5 liters of water, filtering, if necessary, and then diluted to a volume of 2500 cc. to give a solution 0.2 molar in mercuric chloride equivalent.

(19) Gilman and Wright, *Iowa State College J. of Sci.*, **5**, 85 (1931). One equivalent of aluminum amalgam also reduces diiodofuran preferentially to give a 60% yield of 2-iodofuran and no furan.

with phenylmercuric chloride gives an almost quantitative yield of exceptionally pure product, together with precipitation of one-half of the mercury as the metal.

The difurylmercury was also prepared by adding to 0.04 mole of filtered 2-furylmagnesium iodide in 150 cc. of ether, 0.02 mole of mercuric chloride by the method of extraction from a Soxhlet.[20] This operation was complete in ten hours, after which the mixture was hydrolyzed by 10% ammonium chloride solution to give a 24% yield of difurylmercury.

When difurylmercury mixed with copper powder was heated to 270°, at which point the mercurial started to distil, mercury droplets were noted, but no di-2-furyl distilled and one-half of the difurylmercury was recovered. Also, when difurylmercury was heated to 200° in pyridine solution only a trace of mercury was precipitated; steam distillation gave no product, and no mercurial could be recovered from the residues.

(6) **Miscellaneous Experiments with 2-Chloromercurifuran.**—Furan was obtained in an 82% yield by heating at 100° with 4% hydrochloric acid in an alcohol–water medium.

Sulfuryl chloride at 20° in ether gave a very small quantity of 2-chlorofuran.

Bromine at 10° in an ether–ligroin mixture gave 14.5% of 2-bromofuran and a trace of 2-chlorofuran.

No product was isolated in reactions with furoyl chloride or benzoyl chloride in acetone at 56° and in benzene at 80°, but the recovery of 2-chloromercurifuran was 20 g. and 30 g., respectively. No product was isolated with benzyl chloride in acetone at 56° and in ether at 20°, other than 26 g. of the mercurial. With benzenediazonium chloride at 15° in water 15 g. was recovered, and with pyridine alone at 116°, 30 g. was recovered. There was no recovery of mercurial and no isolation of reaction product in the following experiments: nitrosyl chloride at −30° in chloroform; ethyl bromoacetate alone at 140°; ethyl chloroacetate at 116° in pyridine; phosgene at 20° in acetone; nitric acid at −10° in acetic anhydride; sulfuric acid alone at 10°; and nitrous anhydride at −20° in chloroform.

5-Methyl-2-chloromercurifuran, 5-$CH_3C_4H_2OHgCl$.—A solution of 164 g. (2 moles) of 2-methylfuran in 800 cc. of alcohol was added to the mercuric chloride–sodium acetate solution identical with that used with furan. A turbidity appeared in about one minute and after two days the precipitate was filtered and crystallized from 3.5 liters of boiling alcohol to yield 154 g. of residue and 254 g. (from the alcoholic filtrate) of crystalline 5-methyl-2-chloromercurifuran melting at 131°. The mother liquors when diluted with water yielded an additional 60 g. (m. p. 127°) making a total yield of 50%. When purified by crystallization from alcohol or an acetone–water mixture it melted at 134°.

Anal. Calcd. for C_5H_5OHgCl: Hg, 63.28. Found: Hg, 63.40.

Inasmuch as no method could be found for purifying the infusible, alcohol insoluble residue it was not analyzed, but from the iodination reaction described later it was shown to be a mixture of 5-methyl-β,2-dichloromercurifuran and an intermediate addition compound or complex of a mono-mercurated 2-methylfuran. This addition compound could be obtained as the principal product of mercuration if 2 instead of 4 moles of sodium acetate were used for each mole of 2-methylfuran. It decomposed during fusion at 164°, and gave a yellow precipitate of mercuric oxide with alkali. When boiled with alcohol for several hours, the filtered extract when diluted with water yielded 5-methyl-2-chloromercurifuran melting at 131°. The intermediate is soluble in ether, and from this solution, which was evaporated under diminished pressure, was isolated the pure compound, the analysis of which approximates that required for a complex of 2-methylfuran, basic mercuric chloride and mercuric chloride.[6]

---

[20] Gilman and Brown, THIS JOURNAL, **52**, 3314 (1930).

Anal. Calcd. for $C_5H_6OHg(OH)Cl \cdot HgCl_2$: Hg, 66.20. Found: Hg, 66.78.

The fact that 2-methylfuran, but not 2-methylthiophene, readily forms this stable intermediate supports a generalization which can be deduced from other reactions in the two series: namely, that addition compounds are more readily formed with furans than with thiophenes.

An investigation is being made of the possibility that this intermediate may be related to the isomeric sylvans reported recently by Kischner.[21]

The 154 g. of alcohol insoluble compound was treated with an iodine–potassium iodide solution to yield a mixture of iodofurans which when distilled under diminished pressure gave 9.4 g. of 5-iodo-2-methylfuran and a highly unstable residue which must have been a diiodo-2-methylfuran, for when an ether–methanol solution was reduced with aluminum amalgam it gave a 55% yield of β-iodo-2-methylfuran. We believe this compound to be 3-iodo-2-methylfuran. This iodo compound was quite stable: b. p. 57° (28 mm.); n^{20}_{D} 1.5489, n^{25}_{D} 1.5456; d^{20}_{4} 1.860. The aluminum amalgam reduction is generally useful for the preferential removal of α-iodine. The bromine in 5-bromo-2-furfural is untouched by this reagent.

Anal. Calcd. for C_5H_5OI: I, 61.02. Found: I, 61.28.

The mercurial prepared from 0.01 mole of the β-iodo-2-methylfuran, namely, 5-methyl-β-iodo-2-chloromercurifuran, weighed 2.56 g. and melted at 193.5° when crystallized from hot alcohol.

Anal. Calcd. for $C_5H_4OClIHg$: Hg, 45.28. Found: Hg, 45.50.

The 5-methyl-2-chloromercurifuran (0.1 mole) with an iodine-potassium iodide solution gave a 48% yield of 5-methyl-2-iodofuran; b. p. 59° (18 mm.); n^{20}_{D} 1.5571; d^{20}_{4} 1.861. In distilling the 5-methyl-2-iodofuran the same precautions should be observed as with 2-iodofuran.

Anal. Calcd. for C_5H_5OI: I, 61.06. Found: I, 61.36.

The iodide was used in the preparation of the corresponding Grignard reagent in 90% yield, slow addition of the RI compound being necessary. The chilled solution of 5-methyl-2-furylmagnesium iodide was carbonated to give a 33% yield of 5-methyl-2-furoic acid (mixed m. p.). The same Grignard reagent with α-naphthyl isocyanate gave 5-methyl-2-furoyl naphthalide melting at 149.5° and identical by mixed m. p. with the compound prepared from 5-methyl-2-furoyl chloride (which distilled with difficulty, because of excessive foaming, at 93° (20 mm.)) and α-naphthylamine.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.49; H, 5.15. Found: C, 76.64; H, 5.62.

II. Preparation and Chemical Behavior of Mercurials from Furoic Acids

General Procedure.—A solution of one mole of the sodium 5-substituted-2-furoate (prepared by dissolving the acid in exactly one equivalent of sodium hydroxide) in 0.5 to 5.0 liters of water was added to a solution of 270 g. (1 mole) of mercuric chloride in 5 liters of water at room temperature. After one hour the mixture was filtered and then boiled until the evolution of carbon dioxide was complete. On cooling, the mercurial was filtered and crystallized from alcohol. In Table I equivalent molecular proportions of furoic acid and mercuric chloride were used.

Reactions of 5-Bromo-2-chloromercurifuran.—The mercurial with acetyl chloride gave, in acetone or in ether, a very low yield of 5-bromo-2-furyl methyl ketone, 5-BrC_4H_3-$OCOCH_3$. Reaction without solvent results in complete decomposition.

When a suspension of 5-bromo-2-chloromercurifuran in boiling water is treated dropwise with 1:1 hydrochloric acid, 2-bromofuran distils in almost quantitative yields.

Decarboxylation of 5-Bromo-2-furoic Acid.—A suspension of 19.1 g. (0.1 mole)

---

(21) Kischner, *J. Gen. Chem.* (U. S. S. R.), **1**, 1212 (1931); *Chem. Abstracts*, **26**, 5299 (1932).

TABLE I

MERCURIALS BY REPLACING —COONa BY —HgCl

Acid	Moles	% Yield of mercurial	M. p. °C. Crude	M. p. °C. Pure	By-product
5-Bromo-2-furoic[a]	0.2	76	175–176	177	None
5-Methyl-2-furoic[b]	.01	58	127	134	Unidentified
5-Iodo-2-furoic[c]	.0025	71	160	169.5	Unidentified
2-Furoic[c,d]	.1	30	140	151	2,5-Dichloromercurifuran

[a] The yield of 5-bromo-2-chloromercurifuran was increased 5% by the use of 2 equivalents of mercuric chloride. *Anal.* Calcd. for $C_4H_2OClBrHg$: Hg, 52.51. Found: Hg, 52.67.

[b] 5-Methyl-2-furoic and 2-methyl-3-furoic acids gave a precipitate, presumably the mercuric salt, on addition of the sodium salt to mercuric chloride solution. Neither of these supposed salts yielded an anhydro-hydroxymercurifuroic acid on heating.

[c] Mixed m. p. determinations with the mercurials prepared from the corresponding furans showed no depression.

[d] This yield, which was higher when smaller quantities were employed, was so decreased when molar proportions were used that the method is considered suitable only for the identification of furoic acid.

of 5-bromo-2-furoic acid in a solution of 27 g. (0.1 mole) of mercuric chloride in 200 cc. of water was boiled in a distilling flask provided with a condenser, and the oil which steam distilled over was separated, dried and distilled to give a 65.5% yield of 2-bromofuran. Similar results were obtained with furoic acid.[22] However, the reaction failed with 5-nitro-2-furoic acid, even on heating to 160–180°.

5-Nitro-2-chloromercurifuran.—An aqueous solution of sodium 5-nitro-2-furoate (0.4 mole), prepared from sodium bicarbonate, was heated to 50° and then to it was added 0.8 mole of mercuric chloride. The stirred solution was heated to boiling, but no precipitate appeared. Consequently the solution was then heated at 150–160° (70–80 pounds steam pressure) in an autoclave for one hour, the hot solution filtered immediately and the precipitate dried and extracted with 150 cc. of boiling alcohol for several hours. The hot alcoholic extract was filtered to remove an as yet unidentified insoluble material, and evaporated to yield 5.2 g. of mercurial melting at 208°. The aqueous filtrate from the reaction mixture was chilled and filtered to yield 30.3 g. melting at 195°, and the 5-nitro-2-chloromercurifuran was purified by solution in acetone and evaporation of part of the solvent. The total yield was 35 g. or 25% of mercurial melting at 208°. From the aqueous filtrate there was recovered 50% of the original 5-nitro-2-furoic acid.

Anal. Calcd. for $C_4H_2O_3NClHg$: Hg, 57.64. Found: Hg, 57.59.

A suspension of 5-nitro-2-chloromercurifuran when boiled with 1:1 hydrochloric acid gave a quantitative yield of 2-nitrofuran.

With acetone or ether as a solvent for acetyl chloride, the mercurial was recovered unchanged. With acetic anhydride as solvent or with acetyl chloride alone, an infusible compound was obtained and this has not been identified.

The nitro-mercurial (0.01 mole) with 0.01 mole iodine and 0.02 mole sodium iodide in 20 cc. of water was allowed to stand eighteen hours, and then was steam distilled after removing the excess iodine by thiosulfate to yield 17% of 5-nitro-2-iodofuran melting at 76°.

Anal. Calcd. for $C_4H_2O_3NI$: I, 53.14. Found: I, 53.20.

---

(22) Subsequent studies by others in this Laboratory have shown that the reaction is of general utility for halogen and alkyl-substituted 2-furoic acids.

The nitro-iodofuran is a strong lachrymator, sternutator and vesicant. It was also prepared as follows by the nitration of 2,5-diiodofuran. A solution of 16 g. (0.05 mole) of diiodofuran in 51 g. of acetic anhydride was slowly added to a solution of 17.5 g. (0.25 mole) of fuming nitric acid (sp. gr. 1.52) in 25 cc. of acetic anhydride, the temperature being held between −5 and −10°. When reaction was complete the solution was poured into ice and water and then filtered to yield 87% of the total quantity of iodine (pure) in the initial diiodofuran. The filtrate was extracted with ether and the extract washed with sodium thiosulfate and sodium bicarbonate, dried and evaporated under reduced pressure to give 0.5 g. of the 5-nitro-2-iodofuran (mixed m. p.). No attempt was made to isolate any other reaction products, but in a similar nitration of 2,5-dibromofuran, a quantitative yield of fumaric acid was obtained.

3-Chloromercurifuran.—Acetoxymercury furoate, $C_4H_3OCOHgOCOCH_3$, or its equivalent, was prepared by adding a solution of 336 g. (3 mole) of furoic acid in 3 liters of water to a stirred solution of 477 g. (1.5 moles) of mercuric acetate in 7.5 liters of water. The precipitate was filtered by suction[23] and dried by a strong air draft. It weighed 490 g., an 88.3% yield, and was analyzed without further purification.

Anal. Calcd. for $C_7H_6O_5Hg$: Hg, 54.05. Found: Hg, 53.58.

Seven hundred and forty grams (2 moles) of the mercuric acetofuroate was stirred in a 5-liter three-necked flask equipped with a mercury-sealed stirrer, thermometer and outlet tube leading to a flask containing 30% sodium hydroxide solution. This flask was connected to a condenser and chilled receiver wherein the furan was collected. The reaction flask was heated by an oil-bath which was gradually raised to 210° over a ten-hour period. The internal temperature remained at 110° until near the end of the reaction when it reached 135°. After ten hours no more gas evolution was observed. It is imperative that the temperatures be held closely between the specified limits, otherwise a sudden decomposition may take place. The yield of furan was 95% of the expected quantity (see Reactions (III)), and 1.6 equivalents of carbon dioxide was evolved, but there was no trace of methane or other gas. The weight of the residue was 547 g.[24] The analysis did not conform with any plausible structure, and the compound or compounds were not of constant composition. It was insoluble in organic solvents, except acetic acid, and did not dissolve even after long heating in aqueous potassium hydroxide.

The residue (547 g.) was suspended in 900 cc. of 95% acetic acid, and after twenty-four hours it dissolved with slight heat evolution. This solution was poured into 8 liters of water, filtered by suction, and the filtrate treated with sodium chloride until no further precipitate formed. The precipitate was filtered, washed with water, and dried over a steam plate to yield about 270 g. of solid which was extracted with ether in a Soxhlet for eight to ten hours. The ether was evaporated leaving 94.5 g. of 3-chloromercurifuran melting at 168°, and on crystallization from 1500 cc. of hot alcohol it melted at 184.5°. A small quantity was recovered by adding water to the crystallizing liquor. The weight of purified 3-chloromercurifuran was 87.5 g. or 12% as based on the mercuric acetate originally used in the series of reactions.

Anal. Calcd. for C_4H_3OHgCl: Hg, 66.01. Found: Hg, 66.25.

---

(23) Throughout this series of reactions, the dense, fine nature of the precipitates made filtration difficult and the device recommended by Gortner]THIS JOURNAL, **36**, 1967 (1914)] was used to effect more rapid drying of these precipitates.

(24) If large quantities of the compound are required and time is not an important factor the preparation can be simplified by spreading the acetoxymercury furoate in a thin layer over the bottom of a suitable container which is placed on a steam plate (140°) for two days. The same yield is secured. The furan may be collected by using a closed container which is connected to two wash bottles, the first holding sodium hydroxide and the second mercuric acetate solution. The furan may be regenerated from the chlormercurifurans so formed by boiling with dilute hydrochloric acid.

The following reactions were carried out with the 3-chloromercurifuran. A suspension of 6.04 g. (0.02 mole) in 2 cc. of concd. hydrochloric acid, 18 cc. of water and 2 cc. of alcohol was placed in a distilling flask attached to a condenser and receiver cooled by ice and salt. The mixture was boiled for one hour to yield 63% of furan which was subsequently identified as 2-chloromercurifuran.

Unsuccessful acetylations were attempted with acetyl chloride in acetone, ether and no solvent.

3,3′-Difurylmercury was prepared by adding 30.3 g. (0.1 mole) of the 3-chloromercurifuran to 50 g. of sodium thiosulfate in 200 cc. of water contained in a separatory funnel. The mixture was shaken vigorously for ten minutes, and then after standing for twelve hours the suspension was extracted with two 100-cc. portions and one 50-cc. portion of ether. The ether solution was dried, the ether removed by evaporation, and the residue distilled to give 12.1 g. or a 72% yield of the difurylmercury distilling at 152–153° (8.5 mm.) and melting at 72°. Crystallization from water–alcohol raised the melting point to 73°.

Anal. Calcd. for $C_8H_6O_2Hg$: Hg, 59.95. Found: Hg, 60.42.

3-Iodofuran was prepared by the slow addition of a solution of 25.6 g. (0.1 mole) of iodine and 33.2 g. (0.2 mole) of potassium iodide in 400 cc. of water to a stirred suspension of 30.3 g. (0.1 mole) of 3-chloromercurifuran in 400 cc. of water. The reaction proceeded much slower than with 2-chloromercurifuran. The excess of iodine was removed with thiosulfate, the mixture steam distilled, and the oil in the distillate dried with calcium chloride and distilled under reduced pressure from the drying agent. The yield was 12.23 g. or 62% distilling at 37–38° (22 mm.). It was redistilled at 132.2° (732 mm.).

Anal. Calcd. for C_4H_3OI: I, 65.46. Found: I, 65.57.

3-Iodofuran was also prepared by partially dissolving 160 g. (0.28 mole) of tetraiodofuran in a solution of 750 cc. of ether and 100 cc. of methyl alcohol, and then adding 22.95 g. (0.85 mole) of aluminum amalgam, slight cooling being necessary at first. After three days the precipitate was recovered by suction filtration and thoroughly washed with ether. After evaporation of the ether, the residue was steam distilled, dried and fractionally distilled, collecting the fraction up to 43° (14 mm.). The residue, boiling at 112–114° (20 mm.), was re-worked with aluminum amalgam. The total yield was 46% of the same boiling point as that prepared by the above method. Other constants are: n_D^{20} 1.5610: n_D^{25} 1.5592; d_4^{20} 2.045; MR_D calcd. 55.7, found, 53.2. This is to be compared with MR_D of 2-iodofuran: found, 54.2. The difference in exaltation corresponds with the values previously reported for α- and β-isomeric furans.[25]

3-Iodofuran did not react with either ordinary or re-activated magnesium or with lithium in ether. When heated with magnesium in a sealed tube for sixteen hours at 150°, all of the 3-iodofuran was recovered unchanged. Under corresponding conditions chlorobenzene reacts with magnesium to give a good yield of phenylmagnesium chloride.[26]

Acknowledgments.—The authors are grateful to the Research Council of Iowa State College for assistance from the Rockefeller Fluid Research Fund and one of us (G. F. W.) for a Research Fellowship.

They are also indebted to E. A. Zoellner and W. M. Selby for assistance in the preparation of the Grignard reagents.

Summary

α- and β-furan mercurials, prepared by direct mercuration and by decarboxylation, have been used for the characterization and stabilization

---

(25) Hughes and Johnson, THIS JOURNAL, **53**, 737 (1931).

(26) Gilman and Brown, *ibid.*, **52**, 3330 (1930).

of furans and for the preparation of new and hitherto inaccessible types, particularly iodofurans. Attention is directed to essential differences in reactivities between α- and β-substituted furans.

AMES, IOWA
RECEIVED FEBRUARY 13, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

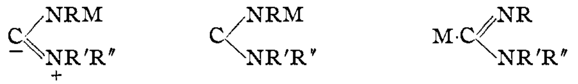
Attempts to Prepare Some Nitrogenous Derivatives of Divalent Carbon[1]

BY DENNISTOUN WOOD, JR., AND F. W. BERGSTROM

Introduction

The Nef formula for hydrocyanic acid, HN=C, represents, according to Franklin,[2] an ammono (meta) carbonous acid, and it was indeed found that many of its chemical properties are in harmony with this view.[3] Granting the existence of an ammonometacarbonous acid—at least in the form of its esters, the isocyanides—it appears not unreasonable to anticipate the existence of derivatives of ammonoorthocarbonous acid, $C(NH_2)_2$, in which at least three of the hydrogen atoms are replaced by alkyl or aryl groups.

In casting about for a method of synthesizing this class of compounds, we were interested by Scheibler's announcement[4] of the preparation of carbon monoxide diethylacetal, $C(OC_2H_5)_2$, (a diethyl aquocarbonite) which may be made from ethyl formate as a starting material. On the basis of analogy, it would logically follow that the esters of ammono orthocarbonous acid might similarly be prepared from substituted formamidines, $H{\cdot}C(=NR)NR'R''$, that is, from esters of an ammonoformic acid, $H{\cdot}C(=NH)NH_2$. To this end it was first desired to prepare metallic salts of a number of substances of this type, which would correspond to one or more of the structures[5]



(M is a monovalent metal)

---

(1) Abstracted from the doctoral dissertation of Dennistoun Wood, Jr., Stanford University, 1930.

(2) Franklin, *J. Phys. Chem.*, **27**, 167–186 (1923).

(3) It is of course recognized at the present time that this tautomer represents only a very minor proportion of ordinary hydrocyanic acid.

(4) Scheibler, *Ber.*, **59**, 1022–1032 (1926); **60**, 554–557 (1927); *Z. angew. Chem.*, **40**, 1072–1081 (1927).

(5) Within the past few years an increasing tendency has been noted to discard the older ideas of divalent carbon and ascribe to substances of this class formulas in which the carbon and nitrogen are united by three conventional non-polar single bonds and by one electrovalency, as in $^{-}C\equiv O^{+}$. (a) Langmuir, THIS JOURNAL, **41**, 903 (1919); (b) Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 127; (c) Sugden, "The Parachor and Valency," Routledge and Sons, 1930, p. 171; (d) Hammick, New, Sidgwick and Sutton, *J. Chem. Soc.*, 1876–1887 (1930); (e) Lindemann and Wiegrebe, *Ber.*, **63**, 1650 (1930). Pauling [*Proc. Natl. Acad. Sci.*, **18**, 294 (1932); THIS JOURNAL, **54**, 1000–1001 (1932)] regards carbon monoxide as a resonance mixture of the two forms, $^{-}C\equiv O^{+}$ and $C=O$, of which the first is the more important.