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THE SIMPLE HALOGEN DERIVATIVES OF FURAN

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Syntheses in the furan series are limited by the lack of direct methods for introducing organic radicals into the furan ring. For this reason the furan derivatives which have been most widely studied are largely those with substituent organic groups in the 2-position, for which furfural serves as a suitable starting material. A certain number of furan derivatives with organic substituents in the 2- and 5-positions are available from 5-methylfurfural and its derivatives,[1] and a few others may be obtained through various types of ring formation that lead to furan derivatives.[2]

3-Methylfuran[3] and 3-furoic acid[4] have been obtained from natural sources but the structure of these compounds has not been confirmed by synthesis. In fact, a review of the literature showed that no furan derivative with a single organic substituent in the 3-position has ever been synthesized. Although halogen, nitro and sulfonic acid groups may be introduced directly into the furan ring, the resulting compounds have not been studied further with the idea of introducing organic substituents by indirect methods. With the object of extending the methods of synthesis in the furan series through the use of these groups, a series of investigations was undertaken. The present paper deals with the preparation and properties of the simpler halogen derivatives of furan.

Although a number of halogenated furans containing two or more halogen atoms are known,[5] only one of the monohalogenated furans, 3-bromofuran,[6]

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[1] The synthesis of furan derivatives with a methyl group in the 5-position and substituent groups in the 2-position has been facilitated by the recent observation that certain replacement reactions of α-furfuryl chloride involve rearrangement of the α-furfuryl group into the 5-methyl-2-furyl group [Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930); Reichstein, *Ber.*, **63**, 749 (1930)].

[2] An excellent review of this subject is given by Marquis, *Ann. chim. phys.*, [8] **4**, 200–208 (1905); see also Benary, *Ber.*, **44**, 493 (1911).

[3] Asahina and Tanaka [*Acta Phytochim.*, **2**, 1 (1924); *C. A.*, **19**, 1139 (1925)] prepared 3-methylfuran by decarboxylation of 3-methyl-2-furoic acid, which had been obtained from the naturally occurring ketone, elscholtzione.

[4] Rogerson, *J. Chem. Soc.*, **101**, 1044 (1912); Power and Salway, *Pharm. J.*, **90**, 550 (1913); *C. A.*, **7**, 2659 (1913).

[5] These include 2,5- and 3,4-dibromofuran, 2,5-di-iodofuran, 2,3,4-tribromofuran, 2,3,4-tribromo-5-chlorofuran, tetrabromofuran and tetra-iodofuran.

[6] Canzoneri and Oliveri, *Gazz. chim. ital.*, **17**, 43 (1887). These authors obtained a small amount of 3-bromofuran in an attempt to prepare 3-hydroxyfuran or 3-hydroxyfuroic acid by heating 3-bromofuroic acid with excess calcium hydroxide. Although they stated an intention of preparing an hydroxyfuran from this compound and of preparing the isomeric 2-bromofuran, we were unable to find any further published results on this subject.

has been obtained in a state of purity. Several investigators have noted the formation of these compounds in small amounts but have not purified or characterized them.[7]

For the purpose of preparing the simple halogenated furans it appeared that the corresponding furoic acids would be the most satisfactory materials. Various chlorofuroic and bromofuroic acids have been prepared in a pure state by Hill and his collaborators,[8] and the positions of the halogens have been established with reasonable certainty. By decarboxylation of these acids, the corresponding halogenated furans of known constitution could be obtained. After a preliminary study it was found that this method was quite satisfactory and the chlorofurans and bromofurans could be obtained in excellent yields.

Decarboxylation of 3-bromofuroic acid, 5-bromofuroic acid, 3,4-dichlorofuroic acid and 3,4,5-trichlorofuroic acid was effected simply by heating the substances at temperatures between 210 and 300°. 3-Chlorofuroic acid and 5-chlorofuroic acid proved to be more stable and could not be decarboxylated in this way. It was found that copper bronze or finely divided nickel, prepared by reducing the oxide at 300–400°, effectively catalyzed the decarboxylation[9] and in the presence of these catalysts 3-chlorofuroic acid and 5-chlorofuroic acid could be decarboxylated. The results of typical decarboxylation experiments are given in Table I.

It seemed likely that the pyrolysis of the halogenated furoic acids under the above conditions gave rise through secondary reactions to the formation of some free halogen acid, toward which the simpler furan derivatives are relatively sensitive. In order to avoid decomposition of the resulting halogenated furans, it appeared advisable to effect the decarboxylation in the presence of a base, which would combine with any free halogen acid formed during the pyrolysis. Quinoline was selected as a suitable base and proved to be quite satisfactory. The addition of quinoline made possible the isolation of 2-bromofuran, which we had not been able to accomplish in earlier experiments, and effected a marked improvement in the yields in other cases. The results of a series of semi-quantitative

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[7] (a) Henninger [*Ann. chim. phys.*, [6] **7,** 222 (1886)] states that the bromination of furan leads to a monobromofuran and a dibromofuran, but describes only the latter. (b) Hill and Jackson [*Proc. Am. Acad. Arts Sci.*, **24,** 320 (1888)] state that a small amount of a colorless liquid separated upon adding water to the first portions of the distillate obtained upon distilling the alcoholic alkali used in saponifying ethyl 5-chlorofuroate. This liquid, which they did not investigate further, may have been a monochlorofuran or a dichlorofuran.

[8] (a) Hill and Sanger, *ibid.*, **21,** 135 (1885); (b) Hill and Hartshorn, *Ber.*, **18,** 448 (1885); (c) Hill and Palmer, *Proc. Am. Acad. Arts Sci.*, **23,** 188 (1887); (d) Hill and Jackson, *ibid.*, **24,** 320 (1888); (e) Hill and Hendrixon, *ibid.*, **25,** 283 (1889); (f) Hill and Wheeler, *Am. Chem. J.*, **25,** 463 (1901).

[9] Sabatier, "Catalysis in Organic Chemistry," translated by E. Emmet Reid, D. Van Nostrand and Co., New York, **1922,** par. 831–839.

TABLE I

PYROLYSIS OF HALOGENATED FUROIC ACIDS

Substituted furoic acid	Decompn. temp. (approx.), °C.	Sample, g.	Substituted furan	Product, g.	Yield, %
3-Chloro-	260[a]	20	3-Chloro-	4.2	30
5-Chloro-	260[a]	20	2-Chloro-	6.7	47
3,4-Dichloro-	300	20	3,4-Dichloro-	9.6	63
3-Bromo-	260	20	3-Bromo-	7.4	48
5-Bromo-	210	20	2-Bromo-	0[b]	0

[a] One gram of copper bronze (Kahlbaum's "Naturkupfer C") was added in these experiments, since these acids did not decompose appreciably below 300° in the absence of catalysts.

[b] 5-Bromofuroic acid was readily decarboxylated but the resulting 2-bromofuran was converted into a black resin in the reaction tube. The resinification of the product was circumvented in later experiments (see Table II) and yields of 2-bromofuran as high as 90% of the theoretical were obtained.

experiments, in which the evolved carbon dioxide was measured, are shown in Table II.

TABLE II

PYROLYSIS OF HALOGENATED FUROIC ACIDS IN THE PRESENCE OF COPPER BRONZE AND QUINOLINE

Substituted furoic acid	Temp.,[a] °C.	Sample, g.	Carbon dioxide Found	Carbon dioxide Calcd.	Carbon dioxide Percentage of calcd.	Substituted furan	Percentage of theory[b]
3-Chloro-	250	5.00	1.45	1.50	96	3-Chloro-	79
5-Chloro-	240	10.00	3.19	3.01	106	2-Chloro-	91
3,4-Dichloro-	220	10.00	2.46	2.43	101	3,4-Dichloro-	97
5-Bromo-	220	15.00	3.38	3.45	98	2-Bromo-	75

[a] This column indicates the minimum temperature of the bath which was necessary to obtain vigorous decomposition. The acids decomposed slowly at somewhat lower temperatures.

[b] The yields given here are based upon the weights of the products after purification by two steam distillations.

The monohalogen derivatives of furan are colorless liquids with a pleasant sweet odor closely resembling that of chloroform and bromoform. With strong aqueous hydrochloric acid they produce at first a green coloration, and on longer standing change to resins. 3,4-Dichlorofuran does not give this coloration with hydrochloric acid, but forms a resin on standing in contact with this reagent. The halogen atoms in these compounds are surprisingly unreactive; all attempts to carry out metathetical reactions were entirely unsuccessful.. Such reagents as aqueous sodium hydroxide and sodium cyanide solutions, metallic sodium, mercury dimethyl and zinc dimethyl were without action.[10] In one case, however, it was possible to obtain a Grignard reagent. 2-Bromofuran in ethereal solu-

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[10] Several of the experiments mentioned here were carried out by Mr. E. B. Reinbold, who also found that the bromine atom of ethyl 5-bromofuroate was extremely unreactive.

tion, on treatment with a highly activated magnesium–copper alloy,[11] gave 2-furylmagnesium bromide. The latter was characterized by the formation of 2-furoic acid by the action of carbon dioxide, and of 2-furoic anilide by the action of phenyl isocyanate. The use of this Grignard reagent in synthesis should render available a number of furan derivatives that cannot be prepared by the usual methods, such as difurylcarbinol, trifurylcarbinol, and others.

Experimental Part

Preparation of Halogenated Furoic Acids.—The methods used for the preparation of the various halogenated acids were essentially those of Hill and his collaborators,[8] with slight modifications in a few details. The acids used in this work were free from isomeric acids according to the criteria of Hill, and their purity was checked by halogen determinations.

Substituted furoic acid	M. p., °C. (corr.)	Percentage of halogen[a]		
		Calcd.	Found	
3-Chloro-	148.5–149.5	Cl, 24.20	24.04	23.99
5-Chloro-	179–180	Cl, 24.20	24.29	23.90
3,4-Dichloro-	169.5–170.5	Cl, 39.19	39.00	38.33
3,4,5-Trichloro-	174.5–175.5	Cl, 49.39	48.97	48.73
3-Bromo-[c]	127–129	Br, 41.85	......[c]	
5-Bromo-	184–186	Br, 41.85	40.87[b]	

[a] Halogen determinations by the Parr peroxide bomb method.

[b] 5-Bromofuroic acid was purified conveniently as the ethyl ester, which was readily prepared through the acid chloride. The latter method was more satisfactory than direct esterification with ethyl alcohol and sulfuric acid. Forty-eight grams (0.25 mole) of 5-bromofuroic acid was heated for one and one-half hours with 57 g. (0.275 mole) of phosphorus pentachloride, and part of the resulting oxychloride was removed by distillation from an oil-bath at 125–130°. The residue was treated cautiously with 100 cc. of absolute alcohol and warmed for three or four hours. The crude ester was washed with a large volume of water, then sodium bicarbonate solution, dried and distilled. There was obtained 48 g. (87% yield) of ethyl 5-bromofuroate, b. p. 134–136° at 34 mm. (Br analysis, calcd., Br, 36.51. Found: Br, 36.62, 36.85). Similarly, 3,4-dichlorofuroic acid gave ethyl 3,4-dichlorofuroate in 90% yield.

[c] For our first experiments on the preparation of 3-bromofuran we used pure 3-bromofuroic acid, m. p. 127–129°, which was obtained according to Hill's procedure by the reduction of 3,5-dibromofuroic acid, prepared by the bromination of furoic acid. In later experiments in an attempt to improve the preparation of 3,5-dibromofuroic acid, we brominated furoyl chloride and obtained a dibromofuroic acid which was apparently not pure 3,5-dibromofuroic acid. The dibromofuroic acid from furoyl chloride gave on reduction a monobromofuroic acid or a mixture of monobromofuroic acids which melted indefinitely at 110–118° instead of 128–129°. Bromine determinations and neutralization values showed that the material in hand corresponded to a monobromofuroic acid or a mixture of monobromofuroic acids (Br: calcd., 41.25; found, 41.60; neutralization value: calcd., 190.9; found, 191.3, 192.9), and decarboxylation gave 3-bromofuran. It appears that bromination of furoyl chloride gives rise to a mixture of 3,5-dibromofuroic acid and 4,5-dibromofuroic acid. Reduction of

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[11] Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

these would produce 3-bromofuroic acid and 4-bromofuroic acid, both of which would yield 3-bromofuran on decarboxylation. Since Hill and his collaborators have not described 4-bromofuroic acid or 4,5-dibromofuroic acid, further work is being done to determine the nature of the products of bromination of furoyl chloride and of the monobromofuroic acid obtained therefrom.

Preparation of Halogenated Furans. General Procedure.—Decarboxylation of the halogenated furoic acids was carried out by heating the acids in a large pyrex tube, 25 × 200 mm., bearing a side tube which was provided with a small condenser and a receiver for the liquid distillate. The decomposition tube was closed with a cork holding a glass tube drawn out to a narrow tip reaching to within 60–80 mm. of the bottom of the tube. Dry nitrogen was passed through the small tube to provide an inert atmosphere and to remove the volatile products as rapidly as possible from the zone of high temperature. The decomposition tube was heated in a bath of Wood's metal at temperatures varying from 210–300° (see Tables I and II). It was found that better yields were obtained by decomposing the acids in small portions of about 5 g. each.

Five grams of the halogenated furoic acid, 10 g. of quinoline and 1 g. of copper bronze (Kahlbaum's "Naturkupfer C") were placed in the reaction tube, which was lowered into a previously heated bath of Wood's metal. The bath was maintained at such a temperature that a vigorous evolution of carbon dioxide took place. The decarboxylation proceeded smoothly and the halogenated furan distilled into the receiving flask. When the acid was completely decarboxylated, as shown by cessation of gas evolution, the tube was raised from the bath and allowed to cool. A second portion of 5 g. of the halogenated acid was added and the above process repeated. In this way 20–30 g. of the acid could be decarboxylated before dismantling the apparatus. In cases where the decomposition temperature of the halogenated furoic acid was relatively high, it proved advantageous to use a base of higher boiling point than quinoline (b. p. 238°) in order to avoid distilling traces of the base into the receiving flask. For this purpose a high-boiling fraction of crude coal tar bases, b. p. 285–310°, proved entirely satisfactory.[12] The halogenated furans were purified by two steam distillations and were dried over fresh calcium oxide. After trial experiments had shown that these substances did not react with metallic sodium, certain of them were dried by means of this metal, *e. g.*, 3-chlorofuran and 2-bromofuran. The yields of the halogenated furans varied from 75–95% of the calculated amounts

The halogenated furans are slightly soluble in water and soluble in organic solvents such as alcohol, ether and benzene; they have an odor very similar to that of chloroform or bromoform. The purified products were colorless liquids when freshly distilled but darkened on standing and eventually changed completely to insoluble resins.[13]

It was found that the products could be kept for months without appreciable decomposition by covering them with an alkaline solution of hydroquinone and storing in corked bottles. Determinations of physical constants were made on freshly distilled specimens of the pure liquids boiling over less than 0.5° temperature range, and samples for analysis were sealed in small bulbs within thirty minutes of the time of distillation. Halogen determinations were made by the Parr bomb method on samples sealed in thin-walled glass bulbs.[14] The physical constants and analyses of the halogenated furans are shown in Tables III and IV.

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[12] The authors wish to express their thanks to Mr. W. R. Gerges of the Chemical Department of the Barrett Company, Philadelphia, for supplying a generous sample of this material.

[13] Compare Moureu, Dufraisse and Johnson, *Ann. chim.*, [10] **7**, 28 (footnote) (1927).

[14] Lemp and Broderson, THIS JOURNAL, **39**, 2069 (1917).

TABLE III

PHYSICAL CONSTANTS OF HALOGENATED FURANS

Halogenated furan	Boiling point, °C. Temp. (corr.)	Press. mm.	d_4^{20}	n_D^{20}	Molecular refraction[a] Obs.	Calcd.	MR$_D$ (obs.) − MR$_D$ (calcd.)
2-Chloro-	77.2–77.5	744	1.1923	1.45687	23.40	24.05	−0.65
3-Chloro-	79.0–79.4	742	1.2094	1.46005	23.21	24.05	−0.84
3,4-Dichloro-[b]	122.8–123.1	744	1.4136	1.48612	27.82	28.92	−1.10
2,3,4-Trichloro-	151.7–152.7	734	1.5471	1.5057	32.90	33.78	−0.88
2-Bromo-	101.9–102.2	744	1.6500	1.49805	26.11	26.95	−0.84
3-Bromo-[c]	102.5–102.6	745	1.6606	1.49575	25.84	26.95	−1.11

[a] The molecular refractions of these compounds were calculated from the revised values of Eisenlohr for the atomic refractions [Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th ed., Vol. II, **1923**, p. 985]. The observed molecular refractions were calculated by the Lorentz–Lorenz formula.

[b] 3,4-Dichlorofuran solidified when cooled in an ice-bath, and the m. p. was found to be 3.8–4.0° (corr.) with the thermometer immersed in the liquid.

[c] Other physical constants of 3-bromofuran are: b. p. 50° at 110 mm., 38.5° at 40 mm.; d_0^0 1.6957; n_C^{20} 1.49185.

TABLE IV

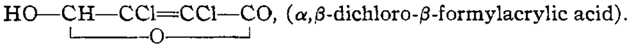
ANALYSIS OF HALOGENATED FURANS

Halogenated furan	Carbon, % Calcd.	Found		Hydrogen, % Calcd.	Found		Halogen, %	Calcd.	Found	
2-Chloro-	46.84	46.95	46.70	2.95	3.00	2.90	Cl	34.60	34.48	34.41
3-Chloro-	46.84	47.17	47.01	2.95	2.95	2.97	Cl	34.60	34.54	34.52
3,4-Dichloro-	35.05	34.86	34.84	1.47	1.52	1.46	Cl	51.79	51.51	51.68
2,3,4-Trichloro-	...	...	...	..	..	..	Cl	62.08	61.60[a]	61.56
2-Bromo-	32.67	32.62	32.76	2.06	2.06	2.10	Br	54.39	54.41	54.48
3-Bromo-	...	...	...	..	..	..	Br	54.39	53.15[b]	53.48

[a] The combustion analyses of this compound were unsatisfactory, probably on account of the difficulty of achieving complete combustion and complete retention of the halogen.

[b] Analysis for bromine in this particular compound was effected by the method of Stepanow [*Ber.*, **39**, 4056 (1906)] and the low results are probably due to loss of bromofuran by volatilization. The Stepanow method for halogen determinations was replaced by the Parr bomb method for all other compounds, but the analyses of 3-bromofuran were not repeated since this compound had previously been described and analyzed.

Oxidation of 3,4-Dichlorofuran.—(a) Ten grams of pure 3,4-dichlorofuran was added slowly to 28 g. of nitric acid (sp. gr. 1.42) at room temperature. The oxidation proceeded slowly at first and then became extremely vigorous. On standing the solution deposited crystals, which were filtered and crystallized from hot water. After drying in a vacuum desiccator the product weighed 3 g.; m. p. 124–125° (corr.). The melting point and chlorine analysis indicate that this compound is mucochloric acid,



$HO{-}\underbrace{CH{-}CCl{=}CCl{-}CO}_{O}$, ($\alpha,\beta$-dichloro-$\beta$-formylacrylic acid).

Anal. Subs., 0.1792, 0.2966: 20.60, 34.20 cc. of 0.1018 *N* $AgNO_3$. Calcd. for $C_4H_2O_3Cl_2$: Cl, 41.98. Found: Cl, 41.50, 41.62.

(b) Seven grams of pure 3,4-dichlorofuran was added slowly to 21 g. of fuming nitric acid (sp. gr. 1.49) at room temperature. A transient green coloration was developed and oxides of nitrogen were evolved in large quantity. After standing for two days the crystals that had separated were filtered, pressed on a porous plate and dried in a vacuum desiccator. The crude dichloromaleic anhydride weighed 5 g. and melted at 110–115°; it was identified by the procedure of Salmony and Simonis,[15] by heating with aniline. The resulting anil of anilidochloromaleic anhydride, after crystallization from alcohol, formed greenish-yellow crystals, which discolored on heating and melted to a brown liquid at 188.7–190.2° (corr.). Salmony and Simonis reported that the anil of anilidochloromaleic anhydride began to turn brown at 175° and melted to a brown liquid at 188°.

Attempt to Prepare 2-Iodofuran.—A number of experiments were made in an effort to prepare a mono-mercurated furan, from which an iodofuran might be obtained by treatment with iodine in aqueous potassium iodide. Ciusa and Grillo[16] succeeded in obtaining tetrachloromercuri-furan and in converting it to tetra-iodofuran by this method. In one experiment they obtained a mono-mercurated furan but were unable to repeat this preparation, and were consequently unable to obtain a mono-iodofuran. In our experiments we used a mixture of mercuration products and attempted to separate the mixture of iodo derivatives obtained therefrom. The following experiment illustrates the methods used.

A solution of 318 g. of mercuric acetate in 1300 cc. of water was added slowly, while stirring vigorously, to a solution of 150 g. of furoic acid in 2 liters of water at 80°. Bubbles of carbon dioxide were evolved and a heavy precipitate was formed. After standing for twelve to twenty-four hours to complete the reaction, the precipitate was filtered with suction and washed thoroughly with water. To convert the mercuri-acetate to the corresponding mercuri-chloride, the moist precipitate was stirred with a solution of 75 g. of sodium chloride in 1 liter of water, and allowed to stand for thirty minutes. The resulting precipitate was filtered with suction, suspended in 4–5 liters of water, and treated dropwise with a solution of iodine in aqueous potassium iodide, until a faint color indicated the presence of an excess of iodine. The amount of iodine added corresponded to 0.80–0.85 mole for each mole of furoic acid used. The resulting suspension was extracted several times with ether and, after drying and distilling off the solvent, a semi-solid residue remained. In a preliminary experiment, when this material was distilled through a fractionating column, a small amount of liquid distilled at 120–125°; the temperature then rose sharply and the residue decomposed rapidly with the evolution of violet vapors. For this reason, in subsequent experiments the residual mixture of iodofurans was subjected to three or four steam distillations in order to effect a partial separation of the liquid products from the solids. In this way there was obtained 3 g. of a liquid fraction (sp. gr. > 1) which was dried over anhydrous sodium sulfate and distilled at atmospheric pressure. About 2 g. of an almost colorless liquid, with an odor resembling that of iodoform, distilled at 120–140°. Since the liquid acquired a green color very rapidly, samples were sealed at once for analysis. Within thirty minutes of the time of distillation both the sealed samples and the material that had been allowed to stand in the air had completely resinified. For this reason the halogen determinations were not satisfactory.

Anal. Subs., 0.2978, 0.2054: 15.70, 9.10 cc. of 0.1018 N $AgNO_3$. Calcd. for C_4H_3OI: I, 65.5. Found: I, 68.11, 57.37.

2-Furylmagnesium Bromide.—Preliminary experiments indicated that 2-bromofuran in ethereal solution did not react with ordinary magnesium nor with magnesium activated by heating with iodine. It was found, however, that 2-bromofuran would react with a magnesium–copper alloy[11] that had been activated by heating with half

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[15] Salmony and Simonis, *Ber.*, **38**, 2588 (1905).

[16] Ciusa and Grillo, *Gazz. chim. ital.*, **57**, 323 (1927).

its weight of iodine. In solution in di-*n*-butyl ether[17] no reaction occurred with the activated magnesium-copper alloy, even on heating to 100°.

A solution of 8 g. of 2-bromofuran in 20 cc. of anhydrous ether was treated in small portions with 3 g. of magnesium-copper alloy that had been heated gently with 1.5 g. of iodine. The addition of each portion of the alloy was accompanied by a vigorous reaction but a considerable excess of magnesium remained undissolved when the reaction subsided. The ethereal solution of 2-furylmagnesium bromide which resulted was red-brown in color and gave a strong color test for R-MgX with Michler's ketone, by the procedure of Gilman and Schulze.[18]

2-Furoic Anilide.—The solution obtained above was decanted from the residual magnesium-copper alloy and an ethereal solution of 1.2 g. of phenyl isocyanate was added dropwise, with constant stirring. A vigorous reaction occurred and after thorough shaking the solution still gave a strong test for R-MgX. It is advisable to avoid an excess of phenyl isocyanate, since the diphenylurea formed upon subsequent hydrolysis is difficultly separated from the anilide. The reaction product was hydrolyzed in the usual way, and the crude 2-furoic anilide was crystallized twice from alcohol, with the addition of decolorizing charcoal, and finally from water; m. p. 121-122° (corr.). For comparison, a sample of 2-furoic anilide was prepared from furoyl chloride and aniline; m. p. 121-122° (corr.). A mixture of the two specimens melted at the same temperature, 121-122° (corr.). The melting point of this compound is reported by previous investigators as 123.5°.[19]

2-Furoic Acid.—A solution of 2-furylmagnesium bromide prepared as above from 5 g. of 2-bromofuran gave a curdy precipitate when treated with carbon dioxide. The reaction mixture was decomposed with dilute sulfuric acid and the ether layer extracted with sodium hydroxide solution. The alkaline extract was acidified and extracted repeatedly with ether. The ether extracts on evaporation left a residue of crystals mixed with a tarry impurity. Sublimation gave crystals of 2-furoic acid, which was identified by comparison with furoic acid obtained from furfural.

Summary

A satisfactory method has been devised for the preparation of the simple halogenated furans from the corresponding halogenated furoic acids. 2-Chloro-, 3-chloro-, 3,4-dichloro-, 2,3,4-trichloro- 2-bromo- and 3-bromofuran have been prepared in a state of purity and their properties described.

The halogen atoms in these compounds were found to be extremely unreactive. No metathetical reactions could be effected with a number of reagents either in aqueous or anhydrous media.

A Grignard reagent, 2-furylmagnesium bromide, was prepared from 2-bromofuran in ethereal solution. This substance reacts normally with carbon dioxide and with phenyl isocyanate to produce 2-furoic acid and 2-furoic anilide.

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[17] Marvel, Blomquist and Vaughn, THIS JOURNAL, **50**, 2810 (1928).

[18] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[19] Schiff, *Ann.*, **239**, 367 (1887); Leimbach, *J. prakt. Chem.*, [2] **65**, 35 (1902); Baum, *Ber.*, **37**, 2954 (1904).