

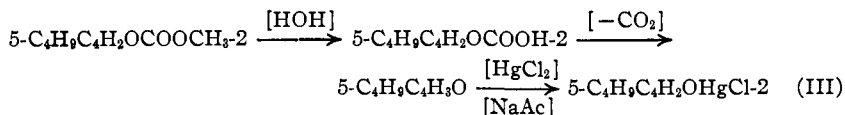
This preferential nuclear substitution, and the condensations with methyl furoate but not with methyl benzoate, together with the fact that benzene can be used as a medium for some Friedel-Crafts reactions of furan are advanced as supporting evidence for the concept that furan has super-aromatic properties.

As previously mentioned,¹ some benzenoid types are apparently more aromatic than others. This is especially true of benzene derivatives having amino and phenolic or substituted amino and substituted phenolic⁴ groups. In accordance with this general principle it has been found that methyl anisate (*p*-CH₃OC₆H₄COOCH₃), unlike methyl benzoate, undergoes the Friedel-Crafts reaction. Also, the correlation of the α -positions in naphthalene with the α -positions in furan⁵ finds support in the observation that the Friedel-Crafts reaction takes place with ethyl α -naphthoate.

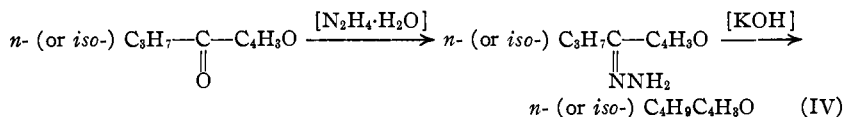
Constitution of Products.—The structure of 5-*tert*-butyl-2-furyl phenyl ketone was established by comparison with the product obtained by interaction of 5-*tert*-butyl-2-furoyl chloride with benzene and aluminum chloride.

The ketones obtained from furan and acid chlorides were identical with those prepared from 2-furylmercuric chloride and the acid halides, and from 2-furonitrile and the appropriate Grignard reagent.⁶

The alkylation products of methyl 2-furoate were somewhat unusual in the sense that the alkyl group appeared to undergo rearrangement so that, for example, each of the four butyl chlorides (as well as butylene) gave some of the same product: namely, methyl 5-*tert*-butyl-2-furoate. The structure of this compound was established by a process of exclusion. The *n*-butyl-, isobutyl-, and *sec*-butyl derivatives were synthesized and shown to be unlike the compound obtained by the Friedel-Crafts reaction which was characterized as follows



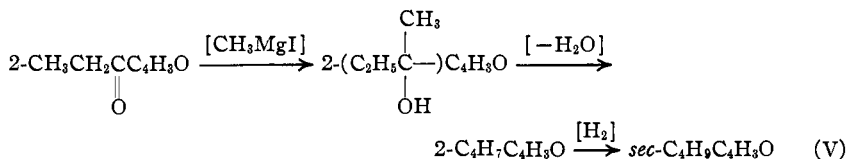
This mercurial as well as the butylfuran from which it was prepared were shown to be unlike the other three possible 5-butyl-2-furylmercuric chlorides and the corresponding 2-butylfurans. The *n*-butyl- and isobutylfurans were synthesized as follows



The following reactions illustrate the synthesis of *sec*-butylfuran

(5) Gilman and Wright, *Chem. Rev.*, **11**, 330 (1932).

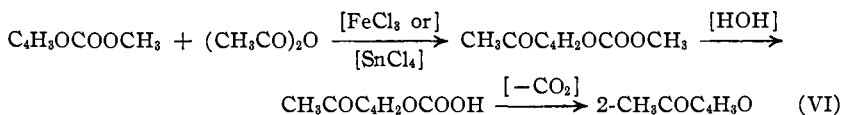
(6) Asahina and Murayama, *Arch. Pharm.*, **252**, 435 (1914).



This sequence of reactions is related to that used recently⁷ for the preparation of 2-isopropylfuran $\text{C}_4\text{H}_3\text{OCOOC}_2\text{H}_5 \xrightarrow{[\text{CH}_3\text{MgI}]} \text{C}_4\text{H}_3\text{OC}(\text{CH}_3)_2\text{OH} \xrightarrow{[-\text{H}_2\text{O}]} \text{C}_4\text{H}_3\text{OC}(\text{CH}_3)=\text{CH}_2 \xrightarrow{[\text{H}_2]} \text{C}_4\text{H}_3\text{OCH}(\text{CH}_3)_2$. Our isopropylfuran is identical with this compound, and thus gives added support to the generalization⁵ that nuclear substitution occurs in an α -position if one be available.

Methyl chloride gave a dithio ester, as a consequence of interaction with the carbon disulfide;⁸ ethyl chloride and ethyl bromide apparently undergo a reaction like that observed with methyl chloride; both *n*-propyl and isopropyl chloride gave the same isopropyl derivative [methyl 5-isopropyl-2-furoate], so that smooth alkylation of methyl furoate really starts with the propyl halides; and the amyl and hexyl derivatives, prepared from *n*-amyl chloride and *n*-hexyl bromide, probably are branched chain types by analogy with the formation of *tert*-butylfuran from each of the four isomeric butyl halides.

The structures of the acylation products of methyl furoate were established as follows, using acetic anhydride as a type



The chief problem in determining the constitution of a monoacylated nuclear substituted product of a di- α -substituted furan having like substituents concerns the integrity of the furan nucleus. The nucleus is not cleaved significantly in a Friedel-Crafts reaction. This was established in the case of the acetylated 2,5-dimethylfuran by preparing the same compound from 2,5-dimethylfurylmercuric chloride and acetyl chloride. The resulting 2,5-dimethyl-3-furyl methyl ketone was prepared earlier by the condensation of succinic acid and acetic anhydride with zinc chloride.⁹

An anomalous reaction takes place between 2-furfural and isopropyl chloride. The product is not 5-isopropyl-2-furfural, but appears to be a related dihydrofuran or possibly a compound formed by nuclear cleavage.

Experimental Part

2-Furyl Phenyl Ketone and *tert*-Butyl Chloride.—Eight grams (0.05 mole) of 2-furyl

(7) Reichstein, Zschokke, Gehring and Rona, *Helv. Chim. Acta*, **15**, 1118 (1932).

(8) Jorg, *Ber.*, **60**, 1466 (1927).

(9) Magnanini and Bentivoglio, *Gazz. chim. ital.*, **24**, I, 435 (1894).

phenyl ketone in carbon disulfide were brought into reaction with *tert*-butyl chloride and aluminum chloride under the conditions described later [see "Alkylation of Methyl 2-Furoate"], with the exception that no ice-bath was used. The resulting 5-*tert*-butyl-2-furyl phenyl ketone (30% yield) is unusually stable; b. p. 180–182° (20 mm.) and 187–189° (22 mm.); d_{25}^{25} 1.065; n_D^{25} 1.5665.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.06. Found: C, 79.06; H, 7.54.

The same compound was obtained in a 70% yield by condensing 5-*tert*-butyl-2-furoyl chloride (0.1 mole), aluminum chloride (0.1 mole) and 100 cc. of benzene.

The 5-*tert*-butyl-2-furoyl chloride was obtained (51% yield) by refluxing 5-*tert*-butyl-2-furoic acid with thionyl chloride; b. p. 220°; d_{25}^{25} 1.108; n_D^{25} 1.5091.

Anal. Calcd. for $C_9H_{11}O_2Cl$: Cl, 19.03. Found: Cl, 19.37.

2-Furfural and Isopropyl Chloride.—In an experiment with 0.5 mole of furfural, 0.5 mole of isopropyl chloride, and 0.6 mole of aluminum chloride in carbon disulfide no external cooling was applied. There was a marked evolution of hydrogen chloride, and but very little charring was noted. Subsequent to hydrolysis of the reaction mixture, the carbon disulfide layer was washed first with water and then with sodium acetate. Then 200 cc. of a saturated solution of sodium acetate was added, and the resulting aldehyde steam distilled. This aqueous distillate was extracted with the carbon disulfide which first distilled over, washed with sodium bicarbonate, dried over sodium sulfate, and the aldehyde, after removing carbon disulfide, was distilled under reduced pressure.

The yield was 8 g. of aldehyde distilling at 101–103° (21 mm.); d_{25}^{25} 1.023; n_D^{25} 1.5041. The constitution of this aldehyde has not yet been established, but it appears to be a dihydrofuran derivative.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.52; H, 8.64. Found: C, 69.49; H, 8.38.

The aldehyde is relatively unstable and darkens on atmospheric exposure. When oxidized by alkaline silver oxide it gives a carboxylic acid which is unlike 5-isopropyl-2-furoic acid.⁷ This new acid, which may be a dihydro-isopropylfuroic acid or a ring scission product, melts at 76–77° when crystallized from 40% ethyl alcohol. In an orienting experiment the supposed dihydroisopropylfuroic acid was heated with phosphorus pentachloride to remove two hydrogens and give the known 5-isopropyl-2-furoic acid; however, the original acid was recovered after alkaline hydrolysis. *Neutralization equivalent.* Calcd., 156; found, 155.

Anal. Calcd. for $C_8H_{12}O_2$: C, 61.49; H, 7.75. Found: C, 61.71; H, 7.45.

The semicarbazone of the aldehyde melts at 174–176° when crystallized from 30% alcohol, and its analysis agrees for a dihydro derivative.

Anal. Calcd. for $C_8H_{15}O_2N_3$: C, 54.79; H, 7.66. Found: C, 54.65; H, 7.42.

The unknown aldehyde was condensed with sodium acetate and acetic anhydride to give a 40% yield of an acid which analyzes for a dihydroisopropylfurylacrylic acid. This acid melts at 102–103° when crystallized from water and alcohol. *Neutralization equivalent.* Calcd., 182.1; found, 180.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.89; H, 7.74. Found: C, 65.93 and 65.93; H, 7.75 and 7.66.

Furan and Acid Chlorides.—To 26.6 g. (0.2 mole) of aluminum chloride in 250 cc. of carbon disulfide contained in a three-necked flask provided with a mechanical stirrer was added 0.2 mole of the acid chloride. The flask and contents were then chilled with an ice-bath. Furan (0.2 mole), prepared in accordance with recent directions,¹⁰ contained in 50 cc. of carbon disulfide was added dropwise over a twenty-five minute period;

(10) Gilman and Lousinian, *Rec. trav. chim.*, **52**, 156 (1933).

the mixture turned dark brown, and after about one-third of the furan had been added copious quantities of hydrogen chloride were evolved. Stirring was continued for fifteen minutes in the ice-bath, and then for ten minutes at room temp., after which the mixture was poured upon 300 g. of cracked ice, and steam distilled; the distillate was made alkaline with potassium hydroxide, extracted with ether, dried over sodium sulfate, and the alkyl 2-furyl ketone distilled under reduced pressure. The data are given in Table I.

TABLE I
ALKYL 2-FURYL KETONES FROM FURAN AND ACID CHLORIDES

Alkyl 2-furyl ketone	RCOCl used	Yield, %	B. p. (mm.), °C.	d_{25}^{25}	n_D^{25}
1 Ethyl	<i>n</i> -Propionyl	36.3	78-80 (17) m. 27-28°
2 <i>n</i> -Propyl	<i>n</i> -Butyryl	51.8	95-97 (19)	1.041	1.4922
3 Isopropyl	Isobutyryl	45.3	86-87 (18)	1.032	1.4888
4 <i>n</i> -Butyl	<i>n</i> -Valeryl	23	108-109 (18)	1.012	1.4900
5 <i>n</i> -Amyl	<i>n</i> -Caproyl	39	116-119 (16)	0.9954	1.4864

	Analyses, %				M. p., °C.	Semicarbazone and analyses			
	Calcd.		Found			Carbon		Hydrogen	
	C	H	C	H		Calcd.	Found	Calcd.	Found
1	67.71	6.50	67.65	6.66	188-190	(a)		(a)	
2	69.52	7.30	70.02	7.40	190	(a)		(a)	
3	69.52	7.30	69.45	7.63	
4	71.01	7.96	71.32	8.15	158-159	57.22	57.22	7.22	6.73
5	72.24	8.49	71.77	8.76	110-112	54.68	54.97	7.66	7.41

TABLE II
ALKYLATION OF METHYL 2-FUROATE

Methyl 5-alkyl 2-furoate	Alkyl halide used	Yield, %	B. p. (mm.), °C.	d_{25}^{25}	n_D^{25}
1 5-Isopropyl-	<i>n</i> -Propyl chloride ^b	48	110-112 (20)	1.076	1.4851
2 5- <i>tert</i> -Butyl-	<i>n</i> -Butyl chloride ^c	45	110-114 (15)	1.037	1.4792
3 5-Amyl-	<i>n</i> -Amyl chloride	31	112-116 (13)	1.032	1.4804
4 5-Hexyl-	<i>n</i> -Hexyl bromide	57.1	132-136 (19)	1.016	1.4814

	Analyses, %				M. p., °C.	5-Alkyl-2-furoic acid and analyses			
	Calcd.		Found			Calcd.		Found	
	C	H	C	H		C	H	C	H
1	64.24	7.20	63.87	7.36	65-66	62.29	6.54	62.45	6.44
2	65.90	7.74	66.20	7.91	104-105	64.24	7.20	64.51	7.40
3	67.34	8.16	67.10	8.21	69.70	65.90	7.44	66.3	7.95
4	68.34	8.63	68.45	8.51	36-37	67.34	8.16	67.1	7.99

^a These semicarbazones were prepared and analyzed by Asahina and Murayama.⁸
^b The yield of methyl 5-isopropyl-2-furoate from isopropyl chloride was 42%. ^c From 12.6 g. (0.1 mole) of methyl furoate, 0.1 mole of *tert*-butyl chloride, 0.12 mole of ferric chloride in place of aluminum chloride and 100 cc. of carbon disulfide there was isolated but two fractions: one of these (8 g.) was recovered methyl furoate and the other a 41.3% yield of methyl 5-*tert*-butyl-2-furoate. The yield of methyl 5-*tert*-butyl-2-furoate from isobutyl bromide was 66%; from *sec*-butyl bromide, 1.6%; and from *tert*-butyl bromide, 46%.

The several ketones were also prepared by interaction of 2-furyl-mercuric chloride and the appropriate acid chloride, in accordance with recent directions.¹¹ The ketones

(11) Gilman and Wright, THIS JOURNAL, 55, 3302 (1933).

prepared by these two methods were identical, as established by mixed melting point determinations of the semicarbazones. The yields of alkyl 2-furyl ketones prepared from 2-furylmercuric chloride were as follows: ethyl, 24.2%; *n*-propyl, 18.1%; isopropyl, 14.5%; and *n*-amyl, 18%.

In accordance with Steinkopf's¹² directions for the preparation of 5-ethyl-2-thienyl ethyl ketone from ethylthiophene, propionyl chloride and phosphorus pentoxide, a reaction was attempted between furan, ethyl chlorocarbonate and phosphorus pentoxide. The furan was recovered practically quantitatively.

The difficulty in *alkylating* furan with *n*-butyl chloride, aluminum chloride and carbon disulfide or furan itself as a medium may be due in part to a coating which formed on the aluminum chloride.

Alkylation of Methyl 2-Furoate.—In these experiments 0.1 mole of methyl furoate and 0.1 mole of alkyl halide was added dropwise over a twenty-five minute period to 0.1–0.2 mole of aluminum chloride and 200 cc. of carbon disulfide contained in a three-necked flask provided with a mechanical stirrer and cooled by an ice-bath. A dark, viscous oil separated in each case leaving a clear supernatant liquid, and hydrogen chloride was evolved promptly with the lower halides but more slowly with the higher ones. When addition was complete, the ice-bath was removed and the mixture allowed to stand for twenty-four hours. Because the evolution of hydrogen halide is very slow with *n*-hexyl bromide, the ice-bath was removed directly after admixing the reactants. The reaction product was poured upon 500 g. of cracked ice with *vigorous* stirring to prevent extreme local heating, the solvent separated, and the aqueous layer extracted three times with 200-cc. portions of ether. The ether and carbon disulfide solutions were combined, washed with 200 cc. of water and then with 200 cc. of a saturated sodium bicarbonate solution, dried over sodium sulfate, and the heavy residual liquid (after removing the solvents) was fractionated in a Claisen flask with indentations. It was found desirable to fractionate at least three times in order to obtain a product which on hydrolysis would yield a solid acid; otherwise, oily acids are obtained which are very difficult to crystallize. In view of the difficulty of fractionation it appears altogether reasonable to conclude that isomeric 2-butyl esters were formed.

Hydrolysis was effected by heating 10 g. of the ester at 80° with a 20% solution of alcoholic potassium hydroxide for ten minutes. The mixture was then poured into 100 g. of cracked ice in 200 cc. of water, and acidified slowly by the addition, with stirring, of 50% iced sulfuric acid. Solution in cold dilute potassium hydroxide and reprecipitation with cold sulfuric acid is sometimes desirable. Crystallization is effected from an alcohol–water mixture. The yields on hydrolysis are in excess of 75%. Unnecessary heating should be avoided to prevent the precipitation of the acids as oils. The data are given in Table II.

The best method for the preparation of 5-*tert*-butyl-2-furoic acid is probably that one involving the use of isobutyl bromide. The actual reaction is completed in three hours (and the entire preparation in five hours); but one fraction is obtained and this distils at 110–116° (20 mm.) to give a 77% yield. Redistillation gives a 66% yield of ester distilling at 112–114° (20 mm.).

In the reaction with methyl chloride, the gas was bubbled into a mixture obtained by adding 63 g. or 0.5 mole of methyl furoate to 1 mole of aluminum chloride in 300 cc. of carbon disulfide. The reaction product yielded 35 g. of the original methyl furoate and 25 g. of a red viscous oil which when finally crystallized from an alcohol–water mixture melted at 102–103°. This experiment was checked. However, when petroleum ether (b. p. 30–60°) was used as a medium in place of carbon disulfide, only methyl furoate was isolated (65% recovery). The deep red compound is uncommonly stable under ordinary conditions, and the color was not discharged by heating for one

(12) Steinkopf, *Ann.*, **430**, 105 (1923).

hour with 30% hydrogen peroxide. The compound may be 5-carbomethoxy-2-carbo-dithiomethoxyfuran (5-CH₃CO₂C₄H₂OCS₂CH₃).

Anal. Calcd. for C₈H₈O₃S₂: S, 29.63. Found: S, 28.71 (by Carius), and 29.10 (by Parr bomb).

In an attempted alkylation of diethyl 2,5-furandicarboxylate with *n*-butyl chloride and aluminum chloride, the dibasic ester was recovered.

Sec-Butyl-2-furan from Ethyl 2-Furyl Ketone.—The ethyl furyl ketone (0.42 mole) was added slowly to methylmagnesium iodide and hydrolysis was effected by iced dilute acetic acid to give a 66.3% yield of methylethyl-2-furylcarbinol (Reaction (V)); b. p. 77–78° (19 mm.); d_{25}^{25} 1.023; n_D^{25} 1.4729.

Anal. Calcd. for C₈H₁₂O₂: C, 68.52; H, 8.64. Found: C, 68.90; H, 9.02.

The tertiary alcohol (0.34 mole) was dehydrated by refluxing with acetic anhydride (0.5 mole) for twenty minutes. The oil obtained subsequent to hydrolysis by iced potassium hydroxide, ether extraction and drying was fractionated. That part distilling at 145–150° was probably a mixture of the two possible furylbutylenes, and because of its relative instability was reduced at once by Adams' method to give the 2-*sec*-butylfuran distilling at 132–135°. This compound and its mercurial were analyzed (see Table III).

Alkylation of 2-Furoic Acid.—In an orienting experiment, 0.5 mole of furoic acid, 1 mole of aluminum chloride and 0.5 mole of *n*-butyl chloride were allowed to react in carbon disulfide. The oily product yielded 6% of 5-*tert*-butyl-2-furoic acid. This yield can be improved considerably, but the reaction with the ester is preferred because of the apparent greater ease of purifying the liquid ester mixture rather than the mixture of solid acids.

Alkyl-2-furans.—Decarboxylation of 10 g. quantities of the alkyl-2-furoic acids was effected by Johnson's procedure, using quinoline and copper bronze, the distillate being collected in iced 5% sulfuric acid. The alkylfurans were then recovered by the customary procedures.

Some alkyl-2-furans were prepared by the Wolff-Kischner procedure from the alkyl 2-furyl ketones by first heating the ketone and hydrazine hydrate in dry methyl alcohol, and then adding potassium hydroxide pellets and heating again until gas evolution ceased. The alkylfurans were characterized as their mercurials, *n*-propylfuran, for

TABLE III
2-ALKYLFURANS AND 5-ALKYL-2-FURYL MERCURIC CHLORIDES

2-Alkylfurans	Method of preparation		Yield, %	B. p., °C.	d_{25}^{25}	n_D^{25}
	Calcd.	Found				
1 2- <i>n</i> -Propyl-	Reduction of ketone		36	114–116	0.882	1.4410
2 2-Isopropyl-	Decarboxylation		55	106–109	.8771	1.4466
3 2- <i>n</i> -Butyl-	Reduction of ketone		53.8	137–138	.8983	1.4460
4 2-Isobutyl-	Reduction of ketone		32	123–127	.886	1.4425
5 2- <i>sec</i> -Butyl-	Reduction of 2-butenylfuran			132–135
6 2- <i>tert</i> -Butyl-	Decarboxylation		60	119–120	.8708	1.4380

	Analyses, %				M. p., °C.	5-Alkyl-2-furyl-mercuric chloride Hg analyses, %	
	Calcd.	H	Found	H		Calcd.	Found
1	76.29	9.09	75.81	9.36	99	58.11	58.01
2	76.29	9.09	75.95	9.57	117–118	58.11	58.22
3	77.36	9.83	77.28	9.64	79–80	55.84	55.35
4	77.36	9.83	77.45	9.71	95–96	55.84	55.41
5	77.36	9.83	77.50	10.20	88	55.84	56.0
6	77.36	9.83	77.01	10.10	136–137	55.84	55.52

example, giving 5-*n*-propyl-2-furylmercuric chloride. The yields of mercurials prepared by the general method described recently¹¹ were about 35%. Data on the alkylfurans and their mercurials are contained in Table III.

Acylation of Furoic Esters.—In sharp contrast with the alkylation of methyl furoate, aluminum chloride appeared to be ineffective in a Friedel-Crafts reaction of the ester with acetic anhydride or acetyl chloride. It is possible that the quality of aluminum chloride has a marked effect in such condensations if one may judge by pronounced variations in yield in the reaction between furoic acid, benzene and aluminum chloride.¹³ However, both ferric chloride and stannic chloride worked satisfactorily with acid anhydrides to introduce an acyl group in the α -position.

Ethyl 5-acetyl-2-furoate was prepared in 30% yield from 0.4 mole of ethyl furoate, 0.4 mole of acetic anhydride, 0.8 mole of stannic chloride and 250 cc. of dry thiophene-free benzene. The fraction distilling between 125–170° (20 mm.) was crystallized from 80% alcohol to give the keto ester, which melted at 85–86°.

Anal. Calcd. for C₉H₁₀O₄: C, 59.31; H, 5.55. Found: C, 59.68; H, 5.97.

The corresponding keto acid, obtained by alkali hydrolysis of the ester, did not melt up to 230°, but decomposed gradually with blackening. *Neutralization equivalent.* for 5-acetyl-2-furoic acid: calcd., 154; found, 153.5. Decarboxylation of the keto acid by heating in the presence of copper bronze gave methyl 2-furyl ketone. This ketone was characterized by its semicarbazone (mixed m. p.).

Methyl 5-*n*-butyryl-2-furoate was prepared from methyl furoate, *n*-butyric anhydride and stannic chloride in benzene. The fraction distilling between 145–160° (20 mm.) when recrystallized from alcohol and water gave a 25% yield of keto ester melting at 67–68°.

Anal. Calcd. for C₁₀H₁₂O₄: C, 61.19; H, 6.17. Found: C, 61.31; H, 6.20.

Hydrolysis of the ester gave 5-*n*-butyryl-2-furoic acid; m. p. 172°. *Neutralization equivalent.* Calcd., 182; found, 181.4. Decarboxylation of the keto acid gave *n*-propyl 2-furyl ketone which was characterized by its semicarbazone (mixed m. p.).

2,5-Dimethylfuran with Acetic Anhydride, Benzoyl Chloride and Benzoic Anhydride.¹⁴—The yield of 2,5-dimethyl-3-furyl methyl ketone from 2,5-dimethylfuran (0.14 mole), ferric chloride and acetic anhydride was 42%. The same compound (b. p. 94–96° (18 mm.); m. p. and mixed m. p. of oximes, 78°) was obtained in a 22% yield from 2,5-dimethyl-3-furylmercuric chloride¹⁵ (0.05 mole) and acetyl chloride.

2,5-Dimethyl-3-furyl phenyl ketone was prepared in 7% yield from 2,5-dimethylfuran, benzoyl chloride, aluminum chloride, and carbon disulfide; in like yield from 2,5-dimethylfuran, benzoic anhydride, and ferric chloride and carbon disulfide; and in 29% yield when benzoic anhydride and stannic chloride were used in benzene; b. p. 140° (15 mm.), 152° (17 mm.); d_4^{20} 1.152; n_D^{25} 1.5602.

Anal. Calcd. for C₁₃H₁₂O₂: C, 77.96; H, 6.05. Found: C, 77.56 and 77.52; H, 6.30 and 6.32.

General Observations on the Stability of the Products.—The alkyl 2-furoates are relatively stable, but they often darken on standing. However, the α -alkylated alkyl furoates are quite stable and retain their water clear transparency or darken only to a golden-yellow upon standing for two years in the presence of air, which generally has a deleterious effect on many furan compounds. The opposite effect is observed with 2-alkylfurans which polymerize to a resinous yellow-brown solid on standing for a long period in an ice box, under conditions where furan itself is stable. These observations indicate that the stability is greatest when the two α -positions are occupied by certain

(13) King, *THIS JOURNAL*, 49, 565 (1927), and private communication from Dr. E. J. King.

(14) These experiments were carried out by Nelson E. Sanborn.

(15) Kindly provided by Robert R. Burtner.

groups, and this finds support with some other di- α -substituted furans. The alkenyl furan polymerized overnight.

The 2-furyl ketones were of moderate stability, and gradually darkened. It is interesting to note that as they assumed a darkened color they developed a very pleasant odor. The agreeableness of this bouquet appears to increase with the lengthening of the alkyl group, and this applies both to the freshly prepared ketones as well as to those which had aged for several months.

The alkylated 2-furylmercuric chlorides were less stable than one might have expected. After three months they underwent significant decomposition to insoluble compounds containing a high percentage of mercury.

Methyl Anisate and Isopropyl Chloride.—From 0.075 mole of methyl anisate, 0.075 mole of isopropyl chloride, 0.15 mole of aluminum chloride and 225 cc. of carbon disulfide there was obtained a 33.6% yield of methyl 3-isopropyl-4-methoxybenzoate (assuming normal orientation); b. p. 162–165° (25 mm.); d_{25}^{25} 1.074; n_D^{25} 1.5236.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 69.15; H, 7.74. Found: C, 69.31; H, 8.19.

Hydrolysis by alcoholic potassium hydroxide gave an acid which when crystallized from alcohol and water melted at 162–163° with softening at 158°. *Neutralization equivalent.* Calcd., 194.1; found, 195, 195. *Methoxyl.* Calcd., 17.17; found, 16.74.

Ethyl α -Naphthoate with Isopropyl and *n*-Butyl Chlorides.—From 0.05 mole of ethyl α -naphthoate, 0.05 mole of isopropyl chloride, 0.1 mole of aluminum chloride and 215 cc. carbon disulfide there was obtained a 33% yield of ethyl isopropyl- α -naphthoate; b. p. 198–203° (20 mm.); d_{26}^{25} 1.077; n_D^{25} 1.5760.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 79.27; H, 7.51. Found: C, 79.15; H, 7.32.

Hydrolysis by alcoholic potassium hydroxide gave a mixture of acids which when crystallized from water and alcohol melted between 68–72°. The calcd. neutralization equivalent for $C_{14}H_{14}O_2$ is 214; found, 213.4. In a corresponding preparation using *n*-butyl chloride, an ethyl butyl- α -naphthoate was obtained; b. p. 230–235° (18 mm.); d_{25}^{25} 1.0131; n_D^{25} 1.5552.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.62; H, 7.88. Found: C, 79.91; H, 7.75.

Summary

1. The Friedel-Crafts reaction, involving the nuclear introduction of alkyl and acyl groups, has been effected with a miscellany of furan compounds.

2. The same reaction has been shown to take place with some negatively substituted benzenoid types having pronounced aromatic characteristics.

3. The preferential and exclusive substitution in the furan nucleus of a symmetrical ketone like 2-furyl phenyl ketone, and the alkylation and acylation of ethyl furoate but not of ethyl benzoate, together with the fact that benzene can be used as a medium for some Friedel-Crafts reactions of furan are advanced as additional supporting evidence for the concept that furan has super-aromatic properties.