ture 34.2 g. (0.262 mole) of furoyl chloride. Refluxing was maintained for four hours. The complex was decomposed with 60 ml. of sulfuric acid in ice, the organic layer separated and the aqueous extracted four times with 50-ml. portions of benzene. The organic layers were combined, washed thoroughly with 10% sodium carbonate solution and saturated sodium chloride solution, dried with calcium sulfate, filtered, and the solvent stripped, finally under reduced pressure. The residue was fractionated at 55–58° (3 mm.) to give 8 g. (27.7%) of 2-acetylfuran.

Furan-2-glyoxal. (a) From 2-Acetylfuran.—In a 1000-ml. 3-neck interjoint flask fitted with a sealed stirrer, reflux condenser and thermometer, was placed 39 g. (0.35 mole) of selenium dioxide, 220 ml. of dioxane and 7.5 ml. of water. The mixture was stirred at 50° until solution was complete. Thirty-eight grams (0.346 mole) of 2-acetylfuran was then added and the solution refluxed for four hours. The selenium was removed by filtration through a bed of Supercel and the solvent was removed from the filtrate by distillation through a short Vigreux column. Fractionation of the residue under a 30-cm. Vigreux column gave 20 g. (46.5%) of a yellow oil boiling at 65–66° (4 mm.).

b. From Furoyl Chloride.—2-Diazoacetylfuran and 2-chloroacetylfuran were prepared by the method of Burger.[2]

2-Furoylmethylpyridinium Chloride.—The chloroacetylfuran (9.4 g.) was mixed with 30 ml. of pyridine (dried over barium oxide), and warmed gently on the steam-bath. A vigorous reaction occurred, and a black tar was precipitated. Heating was maintained for one hour, at the end of which time the mixture was cooled and treated with anhydrous ether, leaving a gray powder which was recrystallized several times from *s*-butanol (Darco), giving 7.3 g. (50%) of white crystals melting at 178–179°.[13]

Anal.[14] Calcd. for $C_{11}H_{10}ClNO_2$: Cl, 15.85; N, 6.26. Found: Cl, 15.44; N, 6.31.

2-Furoyl-N-(4′-dimethylaminophenyl)-nitrone.—In a 500-ml. 3-neck flask fitted with a mechanical stirrer, thermometer, vent and dropping funnel was placed 7.3 g. (0.0326 mole) of the pyridinium chloride, 20 ml. of water and 5.35 g. (0.0356 mole) of *p*-nitrosodimethylaniline in 170 ml. of 95% ethanol. The solution was chilled to 0° and 36 ml. of 1 *N* sodium hydroxide was added during ten minutes, maintaining the temperature at 0 ± 3°. The mixture turned blood red in color and the odor of pyridine became apparent. Red crystals began to form within thirty minutes, and the crystallization was completed by the addition of cold water. The product was removed by filtration, washed thoroughly with water, air dried and recrystallized three times from a benzene–hexane mixture yielding 5.1 g. (61%) of deep red crystals melting at 123–125°.

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: N, 10.85. Found: N, 11.21.

Furan-2-glyoxal Hydrate.—One and eight-tenths grams (0.007 mole) of the nitrone was mixed in a small separatory funnel with 20 ml. of 5 *N* sulfuric acid and 5 ml. of water. The green solution was extracted six times with 30 ml. of ether. The solvent layer was washed with a little saturated sodium bicarbonate solution, dried with calcium sulfate and the volatiles removed by distillation, leaving a colorless crystalline mass which could be recrystallized from a small quantity of benzene to give 0.7 g. (71%) of furan-2-glyoxal hydrate melting at 68–69°.

A sample of the hydrate prepared by treatment of anhydrous furan-2-glyoxal with two moles of water melted at 69–70° and gave no depression in melting point when admixed with that produced from the nitrone. In addition, both products gave similar green-blue colorations upon solution in acetic anhydride and treatment with a drop of concentrated sulfuric acid.

Furan-2-glyoxal Mono-semicarbazone.—Furanglyoxal was heated with one molecular equivalent of semicarbazide hydrochloride according to the directions of Shriner and Fuson.[15] The derivative was recrystallized three times from 2-ethylbutanol to a constant melting point of 215° (dec.).

Anal. Calcd. for $C_7H_3N_3O_3$: C, 46.71; H, 3.89. Found: C, 46.11; H, 3.95.

---

[13] All melting points taken with a Fisher–Johns apparatus.

[14] Aanlyses by Oakwold Laboratories, Alexandria, Virginia.

(15) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 142.

RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, NEW JERSEY
RECEIVED AUGUST 9, 1948

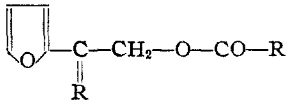
Acyloxyacetylfurans. II

BY HOWARD W. ALLCOCK,[1] FRANK KIPNIS,[1a] JOHN ORNFELT AND PAUL ALLEN, JR.

It has been reported by Kipnis and co-workers[2] that it is possible to prepare 2-acyloxyacetylfurans by the interaction of carboxylic acids with ω-diazoacetylfuran. The present work reports on the production of additional members of this series, synthesized by a variation of the original method. The diazoketone was transformed to 2-

TABLE I

ACYLOXYACETYLFURANS



R	R′	Yield, %	M. p.,[a] °C.	Empirical formula	Analyses,[b] % Calculated C	H	N	Found C	H	N
=O	$-CH_3$	59.5	31.5–32.5[c]	$C_8H_8O_4$	57.14	4.80		57.26	4.80	
=O	$-(CH_2)_2CH_3$	82.0	[d]	$C_{10}H_{12}O_4$	61.16	6.12		60.63	6.31	
=O	$-C_6H_5$	64.1	75.5–76	$C_{13}H_{10}O_4$	67.82	4.38		67.79	4.56	
$=NNHCONH_2$	$-CH_3$		95–95.5	$C_9H_{11}N_3O_4$			18.66			18.40
$=NNHCONH_2$	$-(CH_2)_2CH_3$		114–116	$C_{11}H_{15}N_3O_4$			16.59			16.46
$=NNHCONH_2$	$-C_6H_5$		180–182 dec.	$C_{14}H_{13}N_3O_4$			14.63			14.86
$=NNHCONH_2$	$-C_4H_3O$ (furan)		122–123 dec.	$C_{12}H_{11}N_3O_5$			15.16			14.90

[a] Melting points taken with Fisher–Johns apparatus. [b] Carbon and hydrogen analyses by The Microlab, Staten Island, N. Y.; Kjeldahl nitrogen analyses by H. W. A. [c] B. p. 70–75° (0.1 mm.). [d] B. p. 110–112° (0.03 mm.).

---

(1) Abstracted from a thesis submitted by H. W. A. to The Stevens Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

(1a) Present address: Oxford Products, Inc., Cleveland, Ohio.

(2) Kipnis, Soloway and Ornfelt, THIS JOURNAL, **70**, 142 (1948).

chloroacetylfuran following the procedure of Burger,[3] and this was then caused to react with the various carboxylic acids at a *p*H of about 6.5 in aqueous–ethanolic solution to give the products listed in Table I.

Experimental

In a 250-ml. 3-neck interjoint flask fitted with a sealed stirrer and reflux condenser was placed 0.12 mole of the carboxylic acid dissolved in a mixture of 40 ml. of water and 80 ml. of ethanol. The whole was adjusted to *p*H 6.5 ± 0.1 with 5% sodium hydroxide solution and 0.1 mole of chloroacetylfuran was added. After refluxing and stirring for eight hours the mixture was allowed to cool, poured into 800 ml. of ice-water and extracted three times with 200 ml. of ether. The organic layer was washed with sodium bicarbonate solution until basic, with water until neutral and then dried with calcium sulfate. After filtration from the desiccant, the volatiles were removed by distillation (finally under reduced pressure) and the residue was set aside until crystallization occurred. In the cases of the acetate and butyrate, fractionation under reduced pressure was required for purification. The solid esters were recrystallized from hexane for analytical samples.

The semicarbazones[4] were prepared in the usual manner and recrystallized from ethanol-water mixtures.

---

[3] Burger and Harnest, *ibid.*, **65**, 2382 (1943).

[4] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 142.

STEVENS INSTITUTE OF TECHNOLOGY
HOBOKEN, NEW JERSEY
RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, NEW JERSEY

RECEIVED AUGUST 9, 1948

α-Ketosulfides

BY FRANK KIPNIS[1] AND JOHN ORNFELT

During work on syntheses from 2-bromoacetylthiophene, it was found desirable to study its interaction with sodium mercaptides. The method of Newell and Calaway,[2] which had been used for the preparation of tolylmercaptopropanones from the various thiocresols with chloroacetone, was found to be adequate with suitable modifications, for the preparation of α-ketosulfides with a thiophene loading.

In general, it was found that the sodium salts of thiophenols and aralkyl mercaptans gave higher yields of product with 2-bromoacetylthiophene than did the alkyl compounds. In this respect, it may be noted that while sodium aryloxides interact with phenacyl halides to yield ω-aryloxyacetophenones,[3] sodium alkoxides give "halo-diphenacyls."[4] It is not improbable that the same distinction applies in the mercaptide series, but no attempt was made to isolate any product other than the ketone sulfides.

Experimental

2-(2′-Benzylthio)-acetylthiophene.—To a 500-ml. 3-neck interjoint flask fitted with a sealed Hershberg stirrer, thermometer, dropping funnel and reflux condenser with drying tube, was added 2.3 g. (0.1 gram atom) of sodium and 200 ml. of anhydrous toluene. The mixture was heated to reflux and the sodium was powdered by stirring. The mixture was cooled to 10° and a solution of 12.4 g. (0.1 mole) of benzyl mercaptan in 50 ml. of toluene was added with stirring during one-half hour, maintaining the temperature at 15–20°. After the addition was completed, refluxing and stirring were continued for an additional two hours until the reaction was complete. To the suspension of sodium benzyl mercaptide cooled to 10° was added during ten minutes a solution of 20.5 g. (0.1 mole) of 2-bromoacetylthiophene in 50 ml. of toluene. The mixture turned yellow and warmed. After stirring for one hour at room temperature, the suspension was refluxed for four hours and filtered hot. The residue of sodium bromide was washed with toluene, the filtrate and washings combined, washed with 50 ml. of saturated sodium chloride solution, dried with sodium sulfate, filtered, and the toluene removed by distillation under reduced pressure. The residue was caused to crystallize by scratching, and it was recrystallized twice from hexane and once from carbon tetrachloride–hexane to give 76% of a product melting at 78–79°.[5]

Anal. Calcd. for $C_{13}H_{12}OS_2$: C, 62.87; H, 4.87. Found: C, 62.20; H, 4.90.

2-(2′-Phenylthio)-acetylthiophene.—Light yellow oil; b. p. 165–70° (3 mm.); 38% yield. *Anal.* Calcd. for $C_{12}H_{10}OS_2$: C, 61.50; H, 4.30; S, 27.37. Found: C, 61.90; H, 4.62; S, 27.89.

2-(2′-Butylthio)-acetylthiophene.—Light yellow oil (tends to darken); b. p. 122–126° (3 mm.); 43% yield. *Anal.* Calcd. for $C_{10}H_{14}OS_2$: C, 56.05; H, 6.58; S, 29.90. Found: C, 55.90; H, 6.48; S, 29.51.

---

[1] Present address: Oxford Products, Inc., Cleveland, Ohio.

[2] Newell and Calaway, THIS JOURNAL, **69**, 116 (1947).

[3] Vandervelde, *Bull. acad. roy. Belg.*, 205 (1899); Mohlau, *Ber.*, **15**, 2498 (1882).

[4] Widman, *Ber.*, **42**, 3266 (1909); Fritz, *ibid.*, **28**, 3032 (1895); Paul and Stern, *ibid.*, **32**, 531 (1899).

[5] All melting points were taken with a Fisher–Johns apparatus.

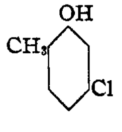
RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, NEW JERSEY

RECEIVED AUGUST 9, 1948

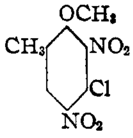
Some Derivatives of 1-Methyl-2-hydroxy-4-chlorobenzene

BY MORITZ KOHN AND EMIN SYREIA

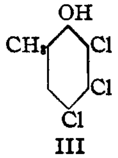
In connection with other work on halogenated phenols the preparation of some new derivatives of 1-methyl-2-hydroxy-4-chlorobenzene (I) was necessary. Diazotization of 1-methyl-2-amino-4-chlorobenzene gave I. The nitration of the methyl ether of I yielded 1-methyl-2-methoxy-4-chloro-3,5-dinitrobenzene (II); the bromination of I the 1-methyl-2-hydroxy-4-chloro-3,5,6-tribromobenzene. By chlorination of I 1-methyl-2-hydroxy-3,4,5-trichlorobenzene[1] (III) was prepared.



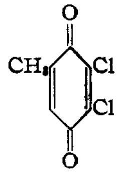
I



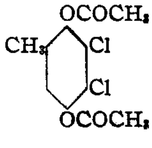
II



III



IV



V

---

[1] Th. Zincke, *Ann.*, **417**, 205 (1918).