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.

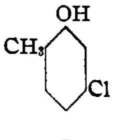
RESEARCH LABORATORIES
AMERICAN HOME FOODS, INC.
MORRIS PLAINS, NEW JERSEY

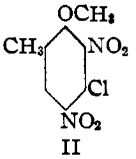
RECEIVED AUGUST 9, 1948

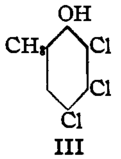
Some Derivatives of 1-Methyl-2-hydroxy-4-chlorobenzene

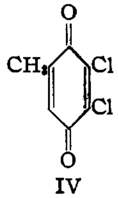
BY MORITZ KOHN AND EMIN SYREIA

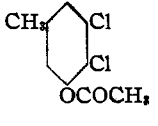
In connection with other work on halogenated phenols the preparation of some new derivatives of 1-methyl-2-hydroxy-4-chlorobenzene (I) was necessary. Diazotization of 1-methyl-2-amino-4-chlorobenzene gave I. The nitration of the methyl ether of I yielded 1-methyl-2-methoxy-4-chloro-3,5-dinitrobenzene (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).