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.

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[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.

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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.

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[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.

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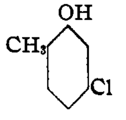
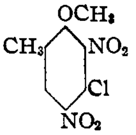
Some Derivatives of 1-Methyl-2-hydroxy-4-chlorobenzene

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



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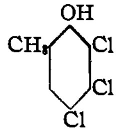
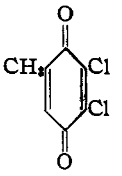
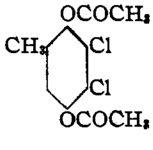


III



IV



V

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

By the oxidation of III 2-methyl-5,6-dichlorobenzoquinone-(1,4) (IV) resulted, which had been obtained by Angeletti and Oliveri[2] in another way. The reducing acetylation of IV gave the diacetate of 2,5-dioxy-3,4-dichlorotoluene (V).

Experimental

1-Methyl-2-hydroxy-4-chlorobenzene (I) and its Methyl Ether.—Ullmann and Panchaud[3] described the preparation of 1-methyl-2-hydroxy-3-chlorobenzene by diazotization of the corresponding amino compound. The diazotization of 1-methyl-2-amino-4-chlorobenzene can be carried out in the same way, giving a 60% yield of distilled 1-methyl-2-hydroxy-4-chlorobenzene, b. p. 225°.[4] The chlorophenol by reaction with sodium hydroxide and dimethyl sulfate in the usual way can be transformed into the methyl ether, b. p. 206–208° (yield 80%).

1-Methyl-2-methoxy-4-chloro-3,5-dinitrobenzene (II) (Chloro-dinitro-*o*-cresol Methyl Ether).—Four grams of 1-methyl-2-methoxy-4-chlorobenzene is introduced dropwise into 20 ml. of cooled, fuming nitric acid followed by 10 ml. of cooled sulfuric acid. After five minutes the mixture is poured onto ice and the nitro compound is filtered by suction. By crystallization from alcohol woolly needles, m. p. 70° (60%), are obtained.

Anal. Calcd. for $C_8H_7O_5N_2Cl$: C, 39.3; H, 2.84; N, 11.36. Found: C, 39.4; H, 2.94; N, 11.06.

1-Methyl-2-hydroxy-4-chloro-3,5,6-tribromobenzene.—I was brominated in the presence of iron as catalyst as described in previous papers.[5] The crude product was purified by crystallization from glacial acetic acid as prisms, m. p. 190° (yield 65%).

Anal. Calcd. for $C_7H_4OClBr_3$: C, 22.13; H, 1.05; halogen, 72.59. Found: C, 22.44; H, 1.04; halogen, 72.29.

1-Methyl-2-hydroxy-3,4,5-trichlorobenzene (III) and its Methyl Ether.—To a cool solution of one mole of I in ten times its weight of glacial acetic acid, two moles of chlorine are added. The mixture is diluted with water and the oily precipitate collected in ether. After the evaporation of the ether the residue distils from 261–265° (765 mm.); 90% yield. Recrystallization from petrol ether gives the trichloro product (III) m. p. 74° (Zincke[1] 77°). The methylation with dimethyl sulfate and sodium hydroxide gives a 90% yield of the methyl ether, b. p. 269–271° (752 mm.). The distillate is crystallized from alcohol in thin needles, m. p. 51.5°.

Anal. Calcd. for $C_8H_7OCl_3$: C, 42.75; H, 3.16; Cl, 47.22. Found: C, 42.40; H, 3.02; Cl, 47.40.

5,6-Dichloro-2-methylbenzoquinone-(1,4) (IV) and Diacetate of 2,5-Dioxy-3,4-dichlorotoluene (V).—To a solution of 15 g. trichloro-*o*-cresol in 150 ml. glacial acetic acid and 45 ml. water 11 g. chromic anhydride is added. The mixture is stirred and slowly heated until a sample poured into water gives a pure green color. The solution is then diluted with water whereby a reddish, at first oily, substance is precipitated which later changes to a resinous cake. The mixture is kept in the refrigerator overnight and filtered by suction. By steam distillation of the crude product an orange oil is obtained which very soon solidifies and which on crystallization from alcohol gives sulfur yellow, thin, prismatic needles, m. p. 80°, undoubtedly identical with the quinone (m. p. 83°) prepared by Angeletti and Oliveri.[2]

Anal. Calcd. for $C_7H_4O_2Cl_2$: Cl, 37.17. Found: Cl, 36.98, 37.52.

The yield is poor because of the resinous by-products of the reaction which form the residue of the steam distillation. But the corresponding hydroquinone diacetate can be prepared in very good yield from the quinone by boiling the quinone with zinc dust, acetic anhydride and glacial acetic acid under reflux (goggles). In order to decolorize it completely, fresh zinc dust and acid mixture are added. The residual zinc dust is removed by filtration and the filtrate precipitated by adding water and stirring until the excess of acetic anhydride is decomposed. The crude product is filtered by suction, dried in vacuum and crystallized from alcohol; prisms, m. p. 118°.

Anal. Calcd. for $C_{11}H_{10}O_4Cl_2$: C, 47.65; H, 3.61; Cl, 25.63. Found: C, 47.69; H, 3.6; Cl, 25.55.

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[2] Angeletti and Oliveri, *Gazz. chim. ital.*, **70**, 789–795 (1940).

[3] Ullmann and Panchaud, *Ann.*, **350**, 112 (1906).

[4] All boiling points are uncorrected.

[5] M. Kohn and G. Dömötör, *Monatsh.*, **47**, 212 (1926).

The Rate of Esterification of Primary Alcohols by Dibasic Acid Anhydrides

BY THEODORE F. LAVINE AND CARLOTA HERKNESS

Siegel and Moran[1] recently claimed that dibasic acid anhydrides react instantaneously with primary alcohols at room temperature to form acid esters, *i. e.*

$$R'(CO)_2O + ROH \longrightarrow R'(COOR)COOH \qquad (A)$$

This conclusion could not be confirmed in this Laboratory and appears to have been the result of misinterpretation of the experimental data. The latter were obtained by titration of the reaction mixtures with alcoholic potassium hydroxide which was tacitly assumed to be a neutralization of the acid ester. The equally rapid reaction of alcoholates with anhydrides, however, was not considered, *i. e.*

$$R'(CO)_2O + OR^- \longrightarrow R'(COOR)COO^- \qquad (B)$$

although it has been utilized repeatedly for the titrimetric estimation of anhydrides[2–6] and for preparative purposes.[7,8] Since both the acid ester and the anhydride react with one equivalent of alcoholate, it is evident that this reagent can yield no information concerning the rate or extent of Reaction (A) (*i. e.*, the titration value remains constant). On the other hand, two equivalents of aqueous alkali are necessary for the neutralization of an anhydride

$$R'(CO)_2O + 2OH^- \longrightarrow R'(COO^-)_2 + H_2O \qquad (C)$$

and during the course of Reaction (A) the titer of the solution in terms of aqueous alkali will continue to decrease until a limiting value equivalent

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[1] Siegel and Moran, THIS JOURNAL, **69**, 1457 (1947).

[2] Caudri, *Rec. trav. chim.*, **48**, 778 (1929).

[3] Lavine and Toennies, *J. Biol. Chem.*, **101**, 727 (1933).

[4] Toennies and Elliot, THIS JOURNAL, **57**, 2136 (1935); **59**, 902 (1937).

[5] Bryant and Smith, *ibid.*, **58**, 2452 (1936).

[6] Kolthoff and Stenger, "Volumetric Analysis. II," Interscience Publishers, New York, N. Y., 1947, pp. 212, 228.

[7] Heitman, THIS JOURNAL, **34**, 1591 (1912).

[8] Chattaway, *J. Chem. Soc.*, **2495** (1931).