methyl-2-hydroxypropane dissolved in 60 cc. of chloroform was treated with 4.0 g. of thionyl chloride, and the solution was boiled under reflux for four hours. After distillation of the solvent, the residue was boiled with alcohol. A considerable quantity of insoluble substance, identified as bis-(2-nitro-4-chlorophenyl) disulfide, was removed by filtration. The concentrated filtrate was again freed of insoluble matter and left in the cold. It yielded crystals of m. p. 76–79° which, after two recrystallizations from ethanol, melted at 79–80°. The melting point of a mixture of this substance and the product from the addition of I to *i*-butylene (III) was undepressed.

Other Experiments

The following compounds could not be induced to react with either I or II: *trans*-dichloroethylene, phenanthrene, mesityl oxide, ethyl maleate, ethyl fumarate, benzalacetophenone, acrylonitrile, and cyclopropane. In several cases when I was employed, most of it was recovered.

1,1-Diphenyl-2-chloroethanol could not be prepared by the Grignard synthesis, reported by Klages and Kessler.[20]

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[20] Klages and Kessler, *Ber.*, **39**, 1754 (1906).

Summary

The addition of arylsulfenyl chlorides to olefins has been studied. The yields in favorable cases were nearly quantitative, but were greatly diminished or null in cases of olefins having electronegative substituents (such as phenyl or halogen) adjacent to the double bond. The arylsulfenyl chlorides did not add to double bonds conjugated with a carbonyl or nitrile group.

It was demonstrated that when arylsulfenyl chloride added to the double bond of isobutylene, the chlorine atom became linked to the less hydrogenated carbon atom while the sulfur atom became linked to the more hydrogenated carbon atom.

SUMMIT, NEW JERSEY
PHILADELPHIA, PENNSYLVANIA

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Acylation Studies in the Thiophene and Furan Series. II. Zinc Chloride Catalyst

BY HOWARD D. HARTOUGH AND ALVIN I. KOSAK[1]

The authors have previously reported that iodine and hydriodic acid catalyze the acylation of thiophene and furan with acid anhydrides and halides.[2]

Zinc chloride and zinc bromide have been found to be effective catalysts for the acylation of thiophene if employed in amounts ranging from 0.01 to 0.03 mole per mole of acylating agent. Yields as high as 87% of 2-acetylthiophene and 95% of 2-benzoylthiophene have been obtained from the respective acid anhydrides with an excess of thiophene using 0.03 mole of fused zinc chloride as catalyst. Higher concentration of catalyst caused decomposition of the 2-acetylthiophene. In two otherwise identical experiments yields of 11 and 78% of 2-acetylthiophene were obtained from reaction mixtures wherein 0.5 mole of zinc chloride was used and the reaction time varied from two hours to five minutes. Continued heating after the initial heat of reaction caused thiophene ring rupture with evolution of hydrogen sulfide and formation of unidentified tars. Zinc fluoride failed to catalyze this reaction. Aluminum chloride, ferric chloride, mercuric chloride and stannic chloride failed to promote acylation of thiophene with acetic anhydride when employed in amounts of 0.01 mole per mole of anhydride.

Furan also is acylated with acetic anhydride in a similar manner giving a 66% yield of 2-acetylfuran. The preferred reaction temperature is much lower, 0–20°, since two otherwise similar runs at 0–20° and 30–60° give yields of 66 and 40%, respectively, of 2-acetylfuran.

2-Acetylthiophene can be further acylated with acetic anhydride in the presence of zinc chloride to give about a 6% yield of 2,5-diacetylthiophene. Diacylation of the thiophene nucleus has previously been observed by v. Schweinitz[3] who reported that the acetylation of octylthiophene yielded some octyldiacetothienone. Attempts to improve the yield above 6% have not been successful.

The use of aliphatic and aromatic anhydrides is preferred to the corresponding acyl chlorides since higher yields are obtained with the anhydrides.

Attempts to acylate aromatic hydrocarbons under the conditions described herein have not been successful.

Zinc chloride is well known as a catalyst for the acylation of phenol and resorcinol,[4] but equimolar amounts of catalyst are required. The singular action of zinc chloride as a catalyst in this reaction indicates that it does not undergo complex formation with acyl halides and acid anhydrides in the same manner as aluminum chloride.[5]

Experimental

2-Acetylthiophene.—To 168 g. (2 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride was added 4.0 g. (0.03 mole) of fused zinc chloride, previously pow-

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[1] Present address: Department of Chemistry, Ohio State University, Columbus, Ohio.

[2] Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946).

[3] v. Schweinitz, *Ber.*, **19**, 646 (1886).

[4] Nencki, *et al.*, *J. prakt. Chem.*, [2] **23**, 147–546 (1881); Ward, *J. Chem. Soc.*, **119**, 852 (1921).

[5] Groggins, Nagel and Stirton, *Ind. Eng. Chem.*, **26**, 1317 (1934).

dered in a mortar under thiophene. The reaction mixture was maintained at a reflux temperature of 94–103° over a period of four hours, cooled to 50° and 200 ml. of water added. The material was thoroughly washed with water and finally neutralized with sodium carbonate solution. Water and unreacted thiophene were removed by distillation from a Vigreux-modified Claisen flask. The 2-acetylthiophene was rectified under vacuum, b. p. 77–78° at 4 mm.,[6] to give 109 g. (87% yield) of product.

2-Benzoylthiophene.—A mixture of 1.5 moles of thiophene, one mole of benzoyl chloride and 0.02 mole of fused zinc chloride powdered as described above was heated together at 110–115° for four hours. The reaction mixture was processed as described above under 2-acetylthiophene with the exception that the product was washed with 10% sodium hydroxide solution and distilled in an apparatus suitable for distillation of crystalline compounds. The 2-benzoylthiophene, 136 g. (73% yield),[7] b. p. 143–144° at 4 mm., was recrystallized once from 50% alcohol, m. p. 56.5–57°.[8]

2,5-Diacetylthiophene.—To 63 g. (0.5 mole) of 2-acetylthiophene was added 107 g. (1 mole) of 95% acetic anhydride and 2.0 g. (0.015 mole) of zinc chloride. The mixture was heated at 100–105° for two hours. The product was worked up by procedures listed under 2-acetylthiophene, thiophene being added to reduce loss. Forty-one grams of 2-acetylthiophene was recovered and 5 g. of 2,5-diacetylthiophene was collected as a solid product in the condenser boiling from 138–145° (5 mm.). The product was purified by dissolving in ethyl acetate, treating with decolorizing charcoal and recrystallizing by the addition of petroleum ether. Pure white plate-like crystals melting at 172–173° were obtained.

Anal. Calcd. for $C_8H_8O_2S$: S, 19.05. Found: S, 19.17.

5-Acetyl-2-thiophenecarboxylic acid was prepared by oxidation of 2,5-diacetylthiophene with sodium hypochlorite,[9] after recrystallization from water the pure white crystals melted at 142–143°.

Anal. Calcd. for $C_7H_6O_3S$: neut. equiv., 170. Found: neut. equiv., 174.

2,5-Thiophenedicarboxylic acid was prepared from the 2,5-diacetylthiophene by a modification of the above method[9] which consisted of heating 1.25 g. of product with a five-fold excess of sodium hypochlorite at 80–85° for one hour. The product was recrystallized from water. Since no melting point was listed in the literature due to sublimation, a melting point was run in a sealed tube on a melting point block, m. p. 358.5–359.5°. A mixed melting point with an authentic sample (prepared by oxidation of 5-methyl-2-thiophenecarboxylic acid with alkaline permanganate) showed no depression.

The deep red di-(2,4-dinitrophenylhydrazone) of 2,5-diacetylthiophene, prepared according to a standard procedure, melted at 311–312° after recrystallization from alcohol.

Anal. Calcd. for $C_{20}H_{16}N_8O_8S$: N, 21.21; S, 6.1. Found: C, 21.16; S, 6.2.

2-Acetylfuran.—One mole of acetic anhydride and 0.5 mole of furan were cooled to 0° in an ice-bath. Zinc chloride (2 g., 0.015 mole) was added and the temperature maintained at 0–5° for one hour, and then at 15–20° for three hours. The product, 36 g. (66%), was obtained by the method listed under 2-acetylthiophene; b. p. 45–48° (5 mm.), m. p. 30–32°. A mixture melting point with a sample prepared by an authentic method[10] showed no lowering.

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Summary

Catalytic quantities of zinc chloride have been shown to promote the acylation of furan and thiophene.

2-Acetylthiophene and 2-benzoylthiophene were obtained in high yields by interaction of thiophene with acetic and benzoic anhydride, respectively, in the presence of catalytic amounts of zinc chloride.

2-Acetylfuran has been prepared from furan and acetic anhydride in 66% yields.

2,5-Diacetylthiophene has been prepared in low yields from the action of 0.015 mole of zinc chloride on 0.5 mole of 2-acetylthiophene and one mole of acetic anhydride.

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(6) Steinikopf and Bauermeister, *Ann.*, **403**, 69 (1914), lists b. p. of 91–92° at 13 mm.

(7) The use of benzoic anhydride gave a 95% yield of 2-benzoylthiophene.

(8) Steinkopf and Schubert, *Ann.*, **424**, 19 (1920), lists m. p. of 56–57°.

(9) "Organic Synthesis," Coll. Vol. II, 428 (1943).

(10) Gol'farb and Smorgonskii, *J. Gen. Chem.* (*U.S.S.R*), **8**, 1523 (1938); *C. A.*, **33**, 4593 (1939).