chloride melted at 186–187° after recrystallization from acetone; the mixed m. p. with material prepared from 2-(3-thianaphthenylmethylamino)-pyridine[4] was 186–187°.

Anal. Calcd. for $C_{18}H_{22}ClN_3S$: Cl, 10.19; N, 12.08. Found: Cl, 10.42; N, 12.12.

Summary

Among the derivatives of thianaphthene described in this paper are 2-hydroxymethyl-, 2-chloromethyl- and 2-cyanomethylthianaphthene and thianaphthene-2-acetic acid. In addition, 3-hydroxymethylthianaphthene, 3-thianaphthenyloxyacetic acid, 3-(β-diethylaminoethoxy)-thianaphthene and 3-(β-dimethylaminopropionyl)-thianaphthene were obtained.

Procedures for the preparation of N,N-dimethyl-N'-phenyl-N'-(2-thianaphthenylmethyl)-ethylenediamine, N,N-dimethyl-N'-(2-pyridyl)-N'-(2-thianaphthenylmethyl)-ethylenediamine and the corresponding 3-thianapththenylmethyl derivatives have been reported.

ANN ARBOR, MICHIGAN RECEIVED MARCH 9, 1949

[CONTRIBUTION FROM THE KNIGHT CHEMICAL LABORATORY, UNIVERSITY OF AKRON]

The Reaction of 2-Thienylmagnesium Bromide with Chloral and Butyl Chloral

BY VAUGHN W. FLOUTZ

Several publications[1,2,3] have appeared recently which deal with the condensation of thiophene and a number of its derivatives with chloral. These investigations have been directed largely to the preparation of thienyl analogs of DDT in the course of studies of the insecticidal values of such compounds.

It seems timely, therefore, to report the preparation of two secondary alcohols from the reaction of the Grignard reagent, 2-thienylmagnesium bromide, with chloral and butyl chloral. The preparation of the acetates and benzoates derived from these carbinols is also reported in this paper. To the best of the author's knowledge all of these are new compounds.

Several investigations[4,5,6] have pointed out that chloral and butyl chloral react abnormally with a number of Grignard reagents to give a primary alcohol by reduction of the aldehyde and an oxidation product from the Grignard reagent. The Grignard reactions in this investigation were found to proceed normally with the formation of the expected secondary alcohols. No other reaction products were detected. This bears out the conclusion of Gilman and Abbott,[7] namely, that the reduction of chloral to trichloroethanol predominates in the case of Grignard reagents which can be oxidized with the loss of two hydrogen atoms and the formation of a carbon-to-carbon double bond. In other cases, where such an oxidation is not possible, the reaction predominating is that of normal addition.

Experimental

Chloral and 2-Thienylmagnesium Bromide.—The Grignard reagent was prepared in the usual manner by the addition of 0.25 mole of 2-bromothiophene, dissolved in a like volume of dry ether, to 0.25 gram-atom of magnesium turnings in 250 ml. of dry ether. During reactions an atmosphere of nitrogen was maintained. A 0.25-mole portion of chloral, dissolved in a like volume of anhydrous ether, was then added to the Grignard reagent. Hydrolysis was accomplished by pouring the reaction mixture into ice and water, and then adding sufficient 5% aqueous acetic acid to clear the mixture. The ether layer was removed, and washed and dried in the usual way.

After removal of the ether by distillation the residual oil was distilled under diminished pressure in an atmosphere of nitrogen. In this way there was obtained 36 g. (62%) of an oily, viscous liquid, b. p. 140–142° at 10 mm. This compound, trichloromethyl-2-thienylcarbinol, distilled as a colorless oil, but after standing it developed a green color.

Anal.[8] Calcd. for $C_6H_5OSCl_3$: C, 31.12; H, 2.18; S, 13.85; Cl, 45.94. Found: C, 31.09; H, 2.20; S, 13.97; Cl, 45.80.

Butyl Chloral (α,α,β-Trichlorobutyraldehyde) and 2-Thienylmagnesium Bromide.—The procedure followed was identical with that described for chloral and 2-thienyl magnesium bromide. Reactants were used in 0.25-mole portions. Distillation under reduced pressure in nitrogen atmosphere yielded 48 g. (74%) of a viscous liquid distilling at 152–155° at 4 mm. This product, 2,2,3-trichloro-1-(2-thienyl)-1-butanol, distilled as a colorless oil, but turned yellow after standing.

Anal. Calcd. for $C_8H_9OSCl_3$: C, 37.01; H, 3.49; S, 12.35; Cl, 40.98. Found: C, 36.72; H, 3.52; S, 12.47; Cl, 40.95.

Preparation of the Acetates and Benzoates.—The acetate of trichloromethyl-2-thienylcarbinol was prepared by refluxing a solution of 10 g. of the carbinol in 10 ml. of acetyl chloride for five hours. The excess of acetyl chloride was then removed and the residual oil was poured into water. After neutralization with sodium bicarbonate the product was extracted with ether, and the ether solution dried. After removal of the ether distillation of the residue under reduced pressure gave the ester, b. p. 138° at 8 mm. Upon standing the distillate solidified to give 10.3 g. (87%) of crystalline product. Two crystallizations from ethanol yielded a product melting at 63.5°.

Anal. Calcd. for $C_8H_7O_2SCl_3$: Cl, 38.88. Found: Cl, 38.71.

The acetate of 2,2,3-trichloro-1-(2-thienyl)-1-butanol was prepared in 88% yield by the same procedure. The ester was obtained as a light yellow, viscous liquid, b. p. 138–142° at 3 mm.

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(1) Metcalf and Gunther, THIS JOURNAL, **69**, 2579 (1947).

(2) Truitt, Mattison and Richardson, *ibid.*, **70**, 79 (1948).

(3) Feeman, Dove and Amstutz, *ibid.*, **70**, 3136 (1948).

(4) Dean and Wolf, *ibid.*, **58**, 332 (1936).

(5) Floutz, *ibid.*, **67**, 1615 (1945).

(6) Floutz, *ibid.*, **68**, 2490 (1946).

(7) Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1943).

(8) All C and H analyses performed by Dr. Carl Tiedcke, Teaneck N. J.

Anal. Calcd. for $C_{10}H_{11}O_2SCl_3$: Cl, 35.27. Found: Cl, 35.48.

The benzoate of trichloromethyl-2-thienylcarbinol was prepared according to the usual procedures of the Schotten–Baumann reaction. In this manner there was obtained from 5 g. of the carbinol 5 g. of a highly viscous oil, b. p. 175–177° at 3 mm. After standing the product began to solidify. The solid mass, crystallized twice from ethanol, yielded a white crystalline compound, m. p. 74.5°.

In a like manner the benzoate of 2,2,3-trichloro-1-(2-thienyl)-1-butanol was prepared in 60% yield. The ester distilled as a highly viscous oil, b. p. 188–191° at 1 mm., but solidified after standing for one day. Two crystallizations from ethanol gave a white crystalline product, m. p. 102°.

Anal. Calcd. for $C_{15}H_{13}O_2SCl_3$: Cl, 29.25. Found: Cl, 29.30.

Summary

1. Chloral and butyl chloral react normally with 2-thienylmagnesium bromide.

2. The secondary alcohols trichloromethyl-2-thienylcarbinol and 2,2,3-trichloro-1-(2-thienyl)-1-butanol have been synthesized via the Grignard reaction. The acetates and benzoates of these carbinols have been prepared.

AKRON, OHIO RECEIVED APRIL 14, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Some 2-Aryl-1,3-butadienes[1a]

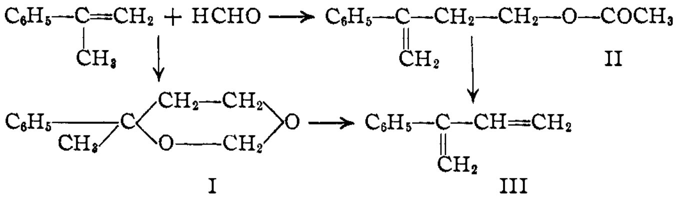
BY CHARLES C. PRICE, F. LEE BENTON AND CLAUDE J. SCHMIDLE[1b]

The synthesis of 2-phenyl-1,3-butadiene has been reported but the methods involve the use of Grignard reagents and are therefore limited in scope.[1c,2] The reaction of α-methylstyrene with formaldehyde followed by pyrolysis of the condensation products appeared to offer a more convenient and practical method of preparing 2-aryl-1,3-butadienes and the results of this investigation are herein described. While this work was in progress, Baker[3] reported that the reaction of α-methylstyrene with formaldehyde in glacial acetic acid containing 13% of sulfuric acid gave the formal of 3-phenylbutane-1,3-diol (I), the diacetate of 3-phenyl-1,3-butanediol, considerable polymeric material and an unidentified fraction.

By employing milder reaction conditions, this reaction gives fairly good yields of products which can be converted into the desired 2-phenyl-1,3-butadiene. When the amount of sulfuric acid is reduced to 0.17%, a mixture is obtained which consists chiefly of 4-phenyl-4-methyl-1,3-dioxane (I), 2-phenyl-4-acetoxy-1-butene (II) and 2-phenyl-4-acetoxy-2-butanol. In the absence of sulfuric acid, 2-phenyl-4-acetoxy-1-butene is obtained by refluxing the crude product with acetic anhydride. Substitution of orthophosphoric acid for the sulfuric acid gives 4-phenyl-4-methyl-1,3-dioxane.

2-Phenyl-1,3-butadiene (III) was obtained from the acetoxybutene by pyrolysis at 530°, by pyrolysis over a heated nichrome filament or by the action of molten potassium hydroxide and was also obtained from the dioxane by pyrolysis over a heated nichrome filament, by pyrolysis over a phosphoric acid catalyst or by heating the dioxane to 150° with sodium bisulfate. The butadiene was characterized by quantitative hydrogenation and through its Diels–Alder adduct with 1,4-naphthoquinone.

The above methods applied to *p*-methyl-α-methylstyrene and 3,4-dichloro-α-methylstyrene gave the corresponding butadienes.



Acknowledgment.—The authors are indebted to the General Tire and Rubber Company for financial assistance in the form of a fellowship (C. J. S.) and for supplying the *p*-methyl-α-methylstyrene and 3,4-dichloro-α-methylstyrene used in this investigation.

Experimental[3a]

Reactions of α-Methylstyrenes with Formaldehyde. A. Using Acetic Acid and Sulfuric Acid.—A solution of 3.6 ml. of concentrated sulfuric acid in 2250 ml. of glacial acetic acid was added to a well-stirred mixture of 330 g. of paraformaldehyde and 1180 g. of α-methylstyrene maintained at a temperature of 35–40° for three hours. The reaction mixture was poured into 3 l. of water and extracted with 2 l. of benzene. The benzene layer was washed with one l. of water, and one l. of 6 *N* sodium carbonate, 1 l. of water and then dried by azeotropic distillation. The benzene and unreacted α-methylstyrene were removed by distillation under reduced pressure and the crude product was then fractionally distilled. The fractions and some of their properties are listed in Table I. Fraction 1 crystallized upon standing at room temperature and consisted of 4-phenyl-4-methyl-1,3-dioxane. Fraction 2 was a mixture while fraction 3 con-

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[1a] Abstracted from a Ph.D. dissertation presented to the Graduate School of the University of Notre Dame by Claude J. Schmidle.

[1b] Present address: Rohm and Haas Co., Philadelphia, Pennsylvania.

[1c] Carothers and Berchet, THIS JOURNAL, **55**. 2813 (1933).

(2) Backer and Strating, *Rec. trav. chim.*, **53**, 539 (1934).

(3) Baker, *J. Chem. Soc.*, 89 (1948).

[3a] The analyses. by Micro Tech Laboratories of Skokie, Illinois. are recorded in tabular form.