the caproic acid by steam distillation from acid solution and removing any dinitronaphthol by digestion with sodium carbonate solution. There was obtained 3.1 g. (73%) of crude product melting at 95–110°.

3,5-Dinitrobenzoic Acid from 4-Chloro-3,5-dinitrobenzoic Acid.—To a gently boiling solution of 6 g. (0.024 mole) of 4-chloro-3,5-dinitrobenzoic acid in 40 ml. of nitrobenzene was added 5 g. of copper powder in several portions. After all the copper had been added, the reaction mixture was heated for fifteen minutes and then filtered while hot. The insoluble material was washed with a few milliliters of petroleum ether (b. p. 60–70°). The filtrate and washings were combined and cooled. The brick-red solid which formed was removed by filtration and washed with petroleum ether. It weighed 4.5 g. Treatment with dilute hydrochloric acid and extraction with ethyl acetate gave 3,5-dinitrobenzoic acid, m. p. 197–200° (uncor.); identified by mixed m. p. with authentic sample and by preparation of the methyl ester, m. p. 106–107° (lit. 107°).

Dehalogenation of Chloronitrobenzenes: *o*-**Chloronitrobenzene.**—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 6.3 g. (0.04 mole) of *o*-chloronitrobenzene (at 150–200°) was added 10 g. of copper powder in several portions over a period of five minutes. The mixture was allowed to solidify, and was then taken up in 50 ml. of 20% sodium carbonate solution. The alkaline mixture was steam distilled until the distillate was of a clear yellow color. From the distillate there was separated 2.4 ml. (2.9 g. or 59%) of nitrobenzene, m. p. 3.5–4.5°.

m-**Chloronitrobenzene.**—The procedure was carried out substituting *m*-chloronitrobenzene for the ortho-isomer. The steam distillate contained 5.4 g. of oily solid which after melting starts to solidify at about 36°. *m*-Chloronitrobenzene containing 17% nitrobenzene starts to solidify at 34°. Assuming that the product obtained from the steam distillate was a mixture of *m*-chloronitrobenzene and nitrobenzene, less than 17% of nitrobenzene was formed in the reaction.

p-**Chloronitrobenzene.**—The procedure for *o*-isomer was repeated using *p*-chloronitrobenzene. From the steam distillate there was obtained 4.3 g. of *p*-chloronitrobenzene.

2,4-Dinitrochlorobenzene.—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 8.1 g. (0.04 mole) of 2,4-dinitrochlorobenzene (Eastman Kodak Co. practical grade) was added 10 g. of copper powder in several portions over a period of five minutes. Temperature of melt was 150–180° until about one-half of the copper had been added, at which point the reaction became quite vigorous. Heating was stopped but temperature rose to 235°. The remainder of the copper was added while temperature was above 200°. The mixture was cooled, treated with 50 ml. of 20% sodium carbonate solution and steam distilled to give 3.5 g. (52%) of 1,3-dinitrobenzene, m. p. 87–88°.

1,3,5-Trinitrobenzene.—To a gently boiling solution of 3 g. (0.025 mole) of benzoic acid and 6 g. (0.024 mole) of picryl chloride in 40 ml. of nitrobenzene was added 4.3 g. of copper powder in several small portions. The solution was heated for ten minutes after all the copper had been added, then filtered while warm and taken up in 80 ml. of ethyl acetate. The ethyl acetate solution was treated first with 10% hydrochloric acid and then with 10% sodium hydroxide solution to convert copper benzoate to benzoic acid and then to sodium benzoate. The resulting mixture was steam distilled. The insoluble material in the steam distillation residue was removed by filtration, taken up in acetone, treated with activated carbon and diluted with water to give 1 g. (20%) of 1,3,5-trinitrobenzene, m. p. 120–121°; mixed melting point with an authentic sample 120–121°, with picryl chloride *ca.* 100°.

Summary

Aromatic nitrochloro compounds containing a nitro group ortho to the chlorine undergo dechlorination when heated with copper powder and an organic acid at 150–200°. A new synthesis of 1,3-dinitronaphthalene is described.

Iowa City, Iowa Received March 28, 1949

[Contribution from the College of Pharmacy, University of Michigan]

Derivatives of Thianaphthene. II[1]

By F. F. Blicke and Don G. Sheets[2]

During the continuation of our studies of preparative procedures for thianaphthene derivatives, and their use for the synthesis of products of possible therapeutic value, we found that 2-hydroxymethylthianaphthene was obtained in 99% yield by reduction of thianaphthene-2-carboxylic acid[3] with lithium aluminum hydride, and in 56% yield by interaction of 2-thianaphthenyl sodium[3] and formaldehyde. The 2-hydroxymethyl derivative reacted with thionyl chloride to form the 2-chloromethyl compound which, in turn, was converted by potassium cyanide into 2-cyanomethylthianaphthene. Thianaphthene-2-acetic acid[4] was obtained in 93% yield by hydrolysis of the 2-cyanomethyl derivative.

2-Thianaphthenylmethyl benzoate was prepared by interaction of 2-chloromethylthianaphthene and sodium benzoate, and also by reaction between 2-hydroxymethylthianaphthene and benzoyl chloride.

In order to obtain N,N-dimethyl-N′-phenyl-N′-(2-thianaphthenylmethyl)-ethylenediamine, N,N-dimethyl-N′-phenylethylenediamine[5] was allowed to react with sodamide and then with 2-chloromethylthianaphthene. N,N-Dimethyl-N′-(2-pyridyl)-N′-(2-thianaphthenylmethyl)-ethylenediamine was prepared in an analogous manner from N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine[6] and 2-chloromethylthianaphthene.

Reduction of thianaphthene-3-carboxylic acid[7] with lithium aluminum hydride produced 3-

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(1) This paper represents part of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Monsanto Chemical Company Fellow.

(3) Schönberg, Petersen and Kaltschmitt, *Ber.*, **66**, 233 (1933).

(4) Blicke and Sheets, This Journal, **70**, 3768 (1948).

(5) Leonard and Solmssen, *ibid.*, **70**, 2066 (1948).

(6) Huttrer, Djerassi, Beears, Mayer and Scholz, *ibid.*, **68**, 2001 (1946).

(7) Komppa and Weckman, *J. prakt. Chem.*, **138**, 109 (1933).

hydroxymethylthianaphthene in 96% yield. The thianaphthenylmethyl benzoate obtained from the latter compound and benzoyl chloride was identical with the benzoate prepared from 3-chloromethylthianaphthene and sodium benzoate.

3-Hydroxythianaphthene[8] reacted with methyl chloroacetate to form methyl 3-thianaphthenyloxyacetate which was hydrolyzed to 3-thianaphthenyloxyacetic acid. Interaction of 3-hydroxythianaphthene with β-diethylaminoethyl chloride hydrochloride and sodium methylate produced 3-(β-diethylaminoethoxy)-thianaphthene.

It was found that 3-acetylthianaphthene[9] undergoes a Mannich reaction, when treated with paraformaldehyde and dimethylamine hydrochloride, to produce 3-(β-dimethylaminopropionyl)-thianaphthene hydrochloride.

When 3-chloromethylthianaphthene[4] was allowed to react with N,N-dimethyl-N′-phenylethylenediamine[5] and sodamide, N,N-dimethyl-N′-phenyl-N′-(3-thianaphthenylmethyl)-ethylenediamine was formed. Similarly, N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine,[6] sodamide and 3-chloromethylthianaphthene yielded N,N-dimethyl-N′-(2-pyridyl)-N′-(3-thianaphthenylmethyl)-ethylenediamine.[4]

3-(β-Diethylaminoethoxy)-thianaphthene and the substituted ethylenediamines are to be tested for their possible antihistaminic effects, and 3-thianaphthenyloxyacetic acid for its action as a plant growth hormone.

Experimental Part

2-Hydroxymethylthianaphthene.—(a) A solution of 11.4 g. (0.30 mole) of lithium aluminum hydride in 700 cc. of anhydrous ether was prepared in a liter flask to which a Soxhlet extractor was attached. Thianaphthene-2-carboxylic acid[3] (35.6 g., 0.20 mole) was placed in the extractor thimble, and the ether refluxed for twenty-four hours. After the careful addition of water, 30 cc. of concd. sulfuric acid in 300 cc. of water was added to the mixture. The layers were separated, and the water layer extracted with ether. The combined ether solutions were washed successively with water, sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and fractionated; yield 32.6 g. (99%); b. p. 123–125° (1.5 mm.); m. p. 99–100° after recrystallization from petroleum ether (90–100°).

Anal. Calcd. for C_9H_8OS: S, 19.52. Found: S, 19.45.

(b) A solution of 26.8 g. (0.20 mole) of thianaphthene in 900 cc. of anhydrous ether was allowed to react with 25.0 g. of powdered sodium for forty-eight hours. The reaction mixture was cooled in an ice-bath, and formaldehyde, generated by heating 20.0 g. (0.67 mole) of paraformaldehyde at 180°, was passed into the reaction flask during a period of one hour. The ether suspension of the sodium alcoholate was decanted from the excess sodium, a small amount of alcohol was added to destroy any unchanged sodium, and water was then added cautiously. The mixture was acidified and the layers were separated. The water layer was extracted with ether, and the combined ether solutions washed with water, dried over anhydrous magnesium sulfate, and the solvent removed. From the residue there were obtained 7.9 g. of thianaphthene and 13.1 g. of 2-hydroxymethylthianaphthene; b. p. 123–125° (1.5 mm.); m. p. 99–100° after recrystallization from petroleum ether (90–100°); mixed m. p. 99–100°; yield 56.5% based on the thianaphthene which had reacted.

2-Chloromethylthianaphthene.—A mixture of 32.8 g. (0.20 mole) of 2-hydroxymethylthianaphthene and 29.7 g. (0.25 mole) of thionyl chloride was refluxed for one and one-half hours and then distilled. There was obtained 29.0 g. (79.4%) of 2-chloromethylthianaphthene; b. p. 124–126° (2 mm.); m. p. 55–56° after recrystallization from petroleum ether (40–60°).

Anal. Calcd. for C_9H_7ClS: Cl, 19.41. Found: Cl, 19.43.

2-Cyanomethylthianaphthene.—A mixture of 14.0 g. (0.076 mole) of the chloromethyl derivative, 7.8 g. (0.12 mole) of potassium cyanide, 125 cc. of dioxane and 65 cc. of water was stirred and refluxed for three hours. The mixture was cooled, water added, the organic layer separated, and the aqueous layer extracted with benzene. The combined organic layer and the benzene extract was washed with water, and then distilled. The product, 9.8 g., b. p. 129–134° (2 mm.), was recrystallized several times from isopropyl alcohol; yield 4.2 g. (32%); m. p. 62–64°.

Anal. Calcd. for $C_{10}H_7NS$: N, 8.09. Found: N, 7.91.

The mother liquors from the recrystallization were combined and evaporated to dryness. The residue was recrystallized from petroleum ether (30–60°). There was obtained 5.0 g. (40%) of 2-hydroxymethylthianaphthene; m. p. 99–100°; mixed m. p. 99–100°.

Thianaphthene-2-acetic Acid.—A mixture of 3.9 g. (0.02 mole) of 2-cyanomethylthianaphthene, 10.0 g. (0.25 mole) of sodium hydroxide, 50 cc. of water and 50 cc. of ethanol was refluxed for eighteen hours. The solution was cooled, and concd. hydrochloric acid (about 17 cc.) was added until the mixture was only weakly basic. The precipitated inorganic material, produced by the action of alkali on the flask, was filtered, and the filtrate boiled to remove the alcohol. After the addition of water, the aqueous solution was extracted with ether in order to remove unchanged nitrile and other products, treated with charcoal, and filtered. After acidification, the precipitated acid was recrystallized from carbon tetrachloride; yield 4.0 g. (93%); m. p. 141–142°; mixed m. p. 141–142° with the acid prepared by the Arndt–Eistert procedure.[4]

2-Thianaphthenylmethyl Benzoate.—(a) A mixture of 9.1 g. (0.05 mole) of 2-chloromethylthianaphthene, 7.2 g. (0.05 mole) of sodium benzoate and 0.2 g. of triethylamine was heated at 95–105° for three and one-half hours. The material was cooled, and stirred with a mixture of ether and water. The water layer was separated and extracted with ether. The combined ether solutions were washed with water, dried over anhydrous magnesium sulfate, and fractionated; yield 12.0 g. (90%); b. p. 158–160° (0.02 mm.); m. p. 70–71° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{12}O_2S$: S, 11.95. Found: S, 11.71.

(b) Benzoyl chloride (4.2 g., 0.03 mole) was dropped slowly into a solution of 3.3 g. (0.02 mole) of 2-hydroxymethylthianaphthene in 10 cc. of pyridine. The mixture was heated at 60° for fifteen minutes, cooled and poured into water. The oil was separated and the aqueous layer extracted with ether. The combined ether extract and oil was washed successively with sodium bicarbonate solution, dilute hydrochloric acid, and then with water. The ether solution was dried and the solvent removed. The benzoate was recrystallized from ethanol; yield 4.7 g. (88%); mixed m. p. 70–71°.

N,N-Dimethyl-N′-phenyl-N′-(2-thianaphthenylmethyl)-ethylenediamine Hydrochloride.—A solution of 9.1 g. (0.05 mole) of N,N-dimethyl-N′-phenylethylenediamine[5] in 50 cc. of dry toluene was stirred with 2.7 g. (0.07 mole) of powdered sodamide for two hours, and then refluxed for two hours. To the cooled reaction mixture there was

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[8] Friedländer, *Ann.*, **351**, 390 (1907). See also Smiles and Ghosh, *J. Chem. Soc.*, **107**, 1380 (1915).

[9] Komppa, *J. prakt. Chem.*, [2] **122**, 319 (1929).

added a solution of 10.0 g. (0.05 mole) of 2-chloromethylthianaphthene in 10 cc. of dry toluene. The mixture was stirred for twelve hours, refluxed for one hour, cooled, water added, the organic layer separated, and the aqueous layer extracted with ether. The combined organic layer and ether extract was washed with water, dried and distilled; yield 13.4 g. (78.5%); b. p. 185–188° (0.02 mm.). The oil was dissolved in ether, and treated with an ether solution which contained the calculated amount of hydrogen chloride. The precipitated monohydrochloride was recrystallized from isopropyl alcohol; m. p. 183–184°.

Anal. Calcd. for $C_{19}H_{23}ClN_2S$: Cl, 10.22; N, 8.08. Found: Cl, 10.19; N, 8.27.

N,N-Dimethyl-N'-(2-pyridyl)-N'-(2-thianaphthenylmethyl)-ethylenediamine Hydrochloride.—A mixture of 7.5 g. (0.04 mole) of N,N-dimethyl-N'-(2-pyridyl)-ethylenediamine,[6] 2.7 g. (0.07 mole) of sodamide, 50 cc. of toluene and 8.2 g. (0.04 mole) of 2-chloromethylthianaphthene was treated in the manner described above. The substituted ethylenediamine (6.2 g., 44%) boiled at 175–180° (0.02 mm.). The monohydrochloride melted at 149–150° after recrystallization from acetone.

Anal. Calcd. for $C_{18}H_{22}ClN_3S$: Cl, 10.19; N, 12.08. Found: Cl, 10.25; N, 11.93.

3-Hydroxymethylthianaphthene.—A suspension of 8.9 g. (0.05 mole) of thianaphthene-3-carboxylic acid[7] in 200 cc. of anhydrous ether was dropped slowly into a refluxing solution of 2.7 g. (0.07 mole) of lithium aluminum hydride in 200 cc. of dry ether during a period of one-half hour. The mixture was cooled, and after the careful addition of water, was treated with a solution of 10 cc. of concd. sulfuric acid in 100 cc. of water. The layers were separated, and the water layer extracted with ether. The combined ether solutions were washed with water, dried, and the ether removed. From the residue there was obtained 7.9 g. (96%) of product; b. p. 124–125° (1.5 mm.).

Anal. Calcd. for C_9H_8OS: S, 19.52. Found: S, 19.31.

3-Thianaphthenylmethyl Benzoate.—(a) This ester was prepared from 9.1 g. (0.05 mole) of 3-chloromethylthianaphthene, 7.2 g. (0.05 mole) of sodium benzoate and 0.2 g. of triethylamine by the procedure described above for 2-thianaphthenylmethyl benzoate (method (a)); yield 12.8 g. (96%); b. p. 156–158° (0.02 mm.); m. p. 92–93° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{12}O_2S$: S, 11.95. Found: S, 11.94.

(b) Interaction of 4.2 g. (0.03 mole) of benzoyl chloride and 3.3 g. (0.02 mole) of 3-hydroxymethylthianaphthene in 10 cc. of pyridine produced 4.9 g. (91%) of 3-thianaphthenylmethyl benzoate; m. p. 92–93° after recrystallization from ethanol; mixed m. p. 92–93°.

3-Thianaphthenyloxyacetic Acid and Methyl Ester.—A solution of 30.0 g. (0.20 mole) of 3-hydroxythianaphthene in 200 cc. of absolute methanol was refluxed, in a nitrogen atmosphere, and a sodium methylate solution, which had been prepared from 5.1 g. (0.22 g. atom) of sodium and 100 cc. of absolute methanol, added. After the addition of 27.1 g. (0.25 mole) of methyl chloroacetate, dissolved in 50 cc. of methanol, the mixture was refluxed for ten hours, the alcohol removed, the residue dissolved in ether, and the solution filtered. Upon fractionation of the filtrate, there were obtained 5.2 g. of unchanged 3-hydroxythianaphthene, b. p. 95–100° (1 mm.),[10] mixed m. p. 68–69°, and 20.2 g. (55%) of the methyl ester which boiled at 145° (1 mm.). The oily ester was dissolved in hot petroleum ether (60–75°); the precipitated, crystalline ester melted at 49–50°.

Anal. Calcd. for $C_{11}H_{10}O_3S$: sapon. equiv., 222.3. Found: sapon. equiv., 221.7.

To 2.2 g. of the ester, dissolved in 25 cc. of absolute ethanol, there was added a sodium ethylate solution prepared from 0.23 g. of sodium and 10 cc. of ethanol. Two drops of water were added, and the mixture was allowed to remain at room temperature for twelve hours. The precipitated sodium salt of the acid (1.9 g., 82%) was filtered, dissolved in water, and the solution acidified; the crystalline precipitate weighed 1.7 g. After recrystallization from acetone–petroleum ether (60–75°), the acid melted at 160–161°.

Anal. Calcd. for $C_{10}H_8O_3S$: S, 15.40; neut. equiv., 208.2. Found: S, 15.05; neut. equiv., 208.7.

3-(β-Diethylaminoethoxy)-thianaphthene.—A stream of dry nitrogen was passed over a boiling solution of 30.0 g. (0.2 mole) of 3-hydroxythianaphthene[8] in 200 cc. of absolute methanol, and a solution of sodium methylate, which had been prepared from 5.1 g. (0.22 g. atom) of sodium and 100 cc. of absolute methanol, was added. The mixture was refluxed for three hours. Another sodium methylate solution was prepared from 9.2 g. (0.4 g. atom) of sodium and 100 cc. of absolute methanol. A solution of β-diethylaminoethyl chloride hydrochloride also was prepared from 68.8 g. (0.4 mole) of the salt and 100 cc. of methanol. Additional methanol was added to each solution until the volume was 130 cc. The two solutions were added simultaneously and dropwise, and at the same rate, to the boiling solution of the sodium derivative of 3-hydroxythianaphthene during the course of one hour. After the material had been refluxed for eighteen hours, the methyl alcohol was removed, the residue dissolved in dry ether, the mixture filtered, the ether removed and the residue distilled. The desired product (30.0 g., 60%) boiled at 125–127° (0.5 mm.). The hydrochloride melted at 132–135° after recrystallization from butanol–ether.

Anal. Calcd. for $C_{14}H_{20}ClNOS$: Cl, 12.41; N, 4.90. Found: Cl, 12.61; N, 5.10.

Methyl β-diethylaminoethyl ether (9.2 g.), b. p. 136° (about 740 mm.), was obtained as a by-product. The hydrochloride melted at 115–116° after recrystallization from acetone.

Anal. Calcd. for $C_7H_{18}ClNO$: Cl, 21.15; N, 8.35. Found: Cl, 21.23; N, 8.55.

3-(β-Dimethylaminopropionyl)-thianaphthene Hydrochloride.—A solution of 8.8 g. (0.05 mole) of 3-acetylthianaphthene,[9] 2.4 g. (0.08 mole) of paraformaldehyde and 6.5 g. (0.08 mole) of dimethylamine hydrochloride in 50 cc. of isoamyl alcohol was refluxed for forty-five minutes. The hydrochloride of the Mannich base precipitated when dry ether was added to the cold mixture. The crude product (12.9 g., m. p. 145–160°) was dissolved in water, the solution treated with charcoal, filtered, and the filtrate made alkaline. The base was extracted with ether, the ether solution dried with anhydrous magnesium sulfate, and treated with hydrogen chloride. The precipitated hydrochloride was recrystallized from isopropyl alcohol; yield 8.0 g. (60%); m. p. 175–176°.

Anal. Calcd. for $C_{13}H_{16}ClNOS$: Cl, 13.14; N, 5.19. Found: Cl, 13.16; N, 5.14.

N,N-Dimethyl-N'-phenyl-N'-(3-thianaphthenylmethyl)-ethylenediamine Hydrochloride.—This compound was prepared in a manner similar to that used for the substituted 2-thianaphthenylmethylethylenediamine by the interaction of 8.2 g. (0.05 mole) of N,N-dimethyl-N'-phenylethylenediamine, 2.3 g. (0.06 mole) of powdered sodamide and 9.1 g. (0.05 mole) of 3-chloromethylthianaphthene in 50 cc. of dry toluene; yield 11.6 g. (75%); b. p. 162–165° (0.01 mm.). The monohydrochloride melted at 199–200° after recrystallization from acetone–ethanol–ether.

Anal. Calcd. for $C_{19}H_{23}ClN_2S$: Cl, 10.22; N, 8.08. Found: Cl, 10.21; N, 7.93.

N,N-Dimethyl-N'-(2-pyridyl)-N'-(3-thianaphthenylmethyl)-ethylenediamine Hydrochloride.—N,N-Dimethyl-N'-(2-pyridyl)-ethylenediamine (9.4 g., 0.05 mole), 3.1 g. (0.08 mole) of powdered sodamide and 10.4 g. (0.05 mole) of 3-chloromethylthianaphthene were allowed to react in the manner described above; yield 11.2 g. (63%); b. p. 169–170° (0.01 mm.). The monohydro-

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(10) Friedländer[8] stated that 3-hydroxythianaphthene decomposed when an attempt was made to distil it at 20 mm. pressure.

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.