

monium hydroxide was added to the filtrate. The initially-formed precipitate redissolved. After several hours 1.42 g. of solid separated. It was recrystallized from dilute acetic acid, using Norit, to yield 0.70 g. of 5-mercapto-2-acetamidothiazole, m. p. 255-257°. It decolorized iodine in warm acetic acid solution.

Anal. Calcd. for $C_8H_8N_2OS_2$: C, 34.46; H, 3.47; N, 16.08. Found: C, 34.61; H, 3.17; N, 16.11.

5-Mercapto-4-methyl-2-acetamidothiazole.—The synthesis was essentially by the above procedure. The yield of crude product was 1.15 g. from 2 g. It melted at 252-253° (dec.) after several crystallizations from acetic acid. It also decolorized iodine. Reduction with hot aqueous potassium sulfite also yielded the same product.

Anal. Calcd. for $C_9H_{10}N_2OS_2$: C, 38.07; H, 4.26. Found: C, 38.15; H, 3.94.

S-*p*-Chlorobenzylisothiuronium Sulfate.—This compound was obtained by adding an excess of an alcoholic solution of S-*p*-chlorobenzylisothiuronium chloride to aqueous sulfuric acid. The sulfate crystallized readily on cooling. It may be crystallized from water; m. p. 223-224° (dec.).

Anal. Calcd. for $C_{10}H_{10}Cl_2N_4O_4S_3$: N, 11.22. Found: N, 11.20.

Oxidation of the Thiocyanates to Sulfate Ion.—Heating of 2 g. of 5-thiocyanato-4-methyl-2-acetamidothiazole for one hour at 100° with 50 ml. of water and 10 ml. of concd.

nitric acid produced a clear yellow solution. It was evaporated to dryness. A yellow oil remained. A test portion precipitated strongly with barium chloride solution. The bulk of the oil, dissolved in 15 ml. of water, was filtered and treated with 15 ml. of a 15% solution of S-*p*-chlorobenzylisothiuronium chloride in alcohol. There was formed 0.7 g. of S-*p*-chlorobenzylisothiuronium sulfate, m. p. 221-223°, or 223-224° after recrystallization from water. The mixed m. p. was also 223-224°.

Acknowledgments.—The several combustion analyses were performed by Misses J. Anderson, N. Mold, V. Hobbs and M. Hines.

Summary

Several 2-aminothiazoles and 2-acetamidothiazoles were prepared. Reactions of mercuration, halogenation, nitration and thiocyanation are reported. The bromine in 5-bromo-2-acetamidothiazole is replaced by nitro during nitration. Reduction of the 5-thiocyanato derivatives produces the 5-mercapto derivatives, but oxidation caused cleavage to sulfuric acid. S-*p*-Chlorobenzylisothiuronium sulfate is a new derivative of sulfuric acid.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Derivatives of Thianaphthene. III¹

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It was reported in a previous communication³ that when thianaphthene-2-carboxylic, thianaphthene-2-acetic and thianaphthene-3-acetic acids were heated, in sodium carbonate solution, with Raney nickel for a short time, they were transformed into β -phenylpropionic (93%), γ -phenylbutyric (85%) and β -phenylbutyric acid (98%), respectively. These conversions offer simple, direct and conclusive proof of the structures of the original acids.

During this investigation we determined the suitability of this process for the determination of the structures of other derivatives of thianaphthene, thiophene and dibenzothiophene. The products obtained by the Raney nickel degradation are shown in Table I.

Compounds which contained a carboxyl group were dissolved in sodium carbonate solution, and then treated with Raney nickel. In other instances, methanol or ethanol was found to be a satisfactory solvent although methanol formed an azeotrope with one degradation product, namely, ethylbenzene.

The procedure was used to determine the structure of a product which had been obtained by Ancizar-Sordo and Bistrzycki⁴ from the conden-

(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.

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(3) Blicke and Sheets, *THIS JOURNAL*, **70**, 3768 (1948).

(4) Ancizar-Sordo and Bistrzycki, *Helv. Chim. Acta*, **14**, 141 (1931).

TABLE I

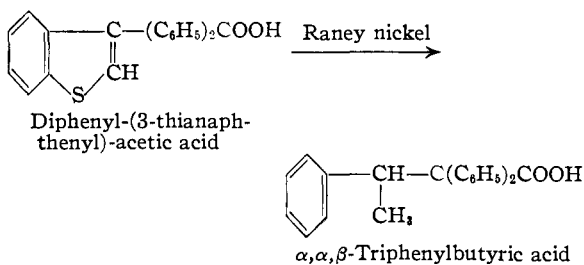
DEGRADATION PRODUCTS OF DERIVATIVES OF THIANAPHTHENE, THIOPHENE AND DIBENZOTHIOPHENE

	Degradation product	Yield, %
Thianaphthene	Ethylbenzene	75.0
3-Hydroxythianaphthene	Ethylbenzene	86.0
Thianaphthene-3-carboxylic acid	α -Phenylpropionic acid	93.4
Diphenyl-(3-thianaphthenyl)-acetic acid	α, α, β -Triphenylbutyric acid	82.5
Thiophene-2-carboxylic acid	Valeric acid	70.0
2-Benzoylthiophene	Valerophenone	75.0
Dibenzothiophene	Biphenyl	97.5
Methylphenylcarbinol	Ethylbenzene	95.3
Acetophenone	Ethylbenzene	93.0

sation of thianaphthene with benzilic acid. Although it might be expected that a 3-thianaphthenyl derivative would have been formed, at least one instance is known in which a substituent, other than a metal, entered the thianaphthene ring at the 2 position.⁵ It was found that the condensation product was diphenyl-(3-thianaphthenyl)-acetic acid since, after degradation, α, α, β -triphenylbutyric acid was obtained.

From 3-hydroxythianaphthene (3-keto-2,3-dihydrothianaphthene) we expected to obtain either

(5) Thianaphthene and phthalic anhydride condense, in the presence of aluminum chloride, to form 2-(*o*-carboxybenzyl)-thianaphthene (Mayer, Mombour, Lassmann, Werner, Landmann and Schneider, *Ann.*, **488**, 259 (1931)).



methylphenylcarbinol or acetophenone. The reaction product proved to be ethylbenzene. In separate experiments it was shown that, under the conditions employed, the carbinol, as well as the ketone, was converted into ethylbenzene. Mozingo, *et al.*,⁶ found that benzaldehyde, under very similar experimental conditions, was reduced to toluene.

Experimental Part

Ethylbenzene from Thianaphthene, 3-Hydroxythianaphthene, Methylphenylcarbinol and Acetophenone.—A solution of 4.0 g. (0.03 mole) of thianaphthene in 250 cc. of methanol was refluxed for one-half hour with 45 g. of Raney nickel.⁷ The cold mixture was filtered, and the catalyst washed with methanol. The filtrate and washings were diluted with 1.5 liters of water and extracted with three 100-cc. portions of chloroform. The chloroform extract was dried and fractionated. There was obtained 2.4 g. of ethylbenzene, b. p. 133–135°.⁸

The ethylbenzene was identified as *p*-ethylbenzenesulfonamide, m. p. and mixed m. p. 109°⁹ after recrystallization from water.

Ethylbenzene was obtained from 3-hydroxythianaphthene, methylphenylcarbinol and acetophenone by the process described above, and, in each case, it was identified by the boiling point and by the melting point of the *p*-ethylbenzenesulfonamide. However, for the reduction of 0.04 mole of the carbinol and also of the ketone, only 35 g. of Raney nickel was used.

α-Phenylpropionic Acid from Thianaphthene-3-carboxylic Acid.—By the use of the procedure described previously³ for the removal of sulfur from thianaphthene-2-carboxylic acid, 1.8 g. (0.01 mole) of thianaphthene-3-carboxylic acid was converted into 1.4 g. of α-phenylpropionic acid.

Anal. Calcd. for C₉H₁₀O₂: neut. equiv., 150.2. Found: neut. equiv., 150.0.

The amide, prepared by interaction of the acid chloride with ammonia water, melted at 91–92°¹⁰ after recrystallization from dilute alcohol.

(6) Mozingo, Spencer and Folkers, *THIS JOURNAL*, **66**, 1859 (1944).

(7) The catalyst was prepared by the process described by Mozingo, Wolf, Harris and Folkers (*ibid.*, **65**, 1013 (1943)).

(8) Perkin (*J. Chem. Soc.*, **69**, 1192 (1896)) reported 135.5°.

(9) Sempotowski (*Ber.*, **22**, 2664 (1889)) reported the same melting point. We found it advantageous to use chlorosulfonic acid for the preparation of the sulfonamide.

(10) Janssen (*Ann.*, **250**, 136 (1889)) reported the same melting point.

α,α,β-Triphenylbutyric Acid from Diphenyl-(3-thianaphthenyl)-acetic Acid.—By the use of the described procedure,³ 3.4 g. (0.01 mole) of the diphenylthianaphthenyl-acetic acid, obtained by the method of Ancizar-Sordo and Bistrzycki,⁴ and 40 g. of Raney nickel yielded 2.6 g. of α,α,β-triphenylbutyric acid, m. p. 157–158°¹¹ after recrystallization from petroleum ether (60–75°).

Anal. Calcd. for C₂₂H₂₀O₂: neut. equiv., 316.4. Found: neut. equiv., 315.1.

Valeric Acid from Thiophene-2-carboxylic Acid.—Subjected to the same process,³ 2.6 g. (0.02 mole) of thiophene-2-carboxylic acid and 40 g. of Raney nickel yielded 1.4 g. of valeric acid, b. p. 180–186°.¹²

Anal. Calcd. for C₆H₁₀O₂: neut. equiv., 102.1. Found: neut. equiv., 104.0.

The *p*-bromoanilide, obtained from the acid chloride and *p*-bromoaniline, melted at 107–108°¹³ after recrystallization from dilute alcohol; mixed m. p. 107–108°.

Valerophenone from 2-Benzoylthiophene.—A solution of 3.8 g. (0.02 mole) of 2-benzoylthiophene in 600 cc. of ethanol was refluxed for one-half hour with 40 g. of Raney nickel catalyst. The cold mixture was filtered, and the catalyst washed with ethanol. The filtrate and washings were fractionated. There was obtained 2.4 g. of valerophenone, b. p. 117–118° (10 mm.); semicarbazone, m. p. 165–166°¹⁴ after recrystallization from dilute alcohol; 2,4-dinitrophenylhydrazone, m. p. 165–166°¹⁵ after recrystallization from ethanol.

Biphenyl from Dibenzothiophene.—A mixture of 1.8 g. (0.01 mole) of dibenzothiophene, 500 cc. of ethanol and 35 g. of Raney nickel was refluxed for one-half hour. The mixture was cooled, filtered, and the catalyst washed with ethanol. The filtrate was concentrated to a volume of about 15 cc., and water was added until the solution became slightly turbid. Crystalline biphenyl (1.5 g.) separated from the cold solution; m. p. and mixed m. p. with an authentic sample 69–70°¹⁶ after recrystallization from dilute alcohol.

Summary

It has been found that when thianaphthene, certain substituted thianaphthenes, dibenzothiophene and derivatives of thiophene are treated with Raney nickel, the nuclear sulfur atom is replaced by hydrogen, and a simple benzene derivative, which contains a saturated side chain, is formed. This process seems to represent a simple procedure for the determination of the structures of derivatives of these heterocycles.

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(11) Bergmann and Blum-Bergmann (*J. Chem. Soc.*, 727 (1938)) reported 158°. The isomeric α,α,γ-triphenylbutyric acid melts at 183.5–184° (Schlenk and Bergmann, *Ann.*, **479**, 86 (1930)).

(12) Lieben and Rossi (*ibid.*, **159**, 60 (1871)) found 184–185°.

(13) Robertson (*J. Chem. Soc.*, **115**, 1222 (1919)) reported 108°.

(14) Layroud (*Bull. soc. chim. France*, [3] **35**, 227 (1906)) found 166°.

(15) Evans (*J. Chem. Soc.*, 788 (1936)) reported 166°.

(16) Fittig (*Ann.*, **121**, 364 (1862)) found 70.5°.