Acknowledgment.—The author is indebted to Mr. Samuel W. Blackman for the microanalytical results reported here.

Summary

A series of quaternary ammonium salts has been made for examination as potential curare substitutes. These were all derived from the Hantzsch pyridine synthesis employing aromatic aldehydes containing basic salt-forming groups or containing other substituents readily convertible to salt-forming groups.

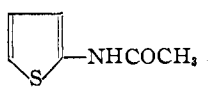
TUCKAHOE 7, NEW YORK RECEIVED MAY 16, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

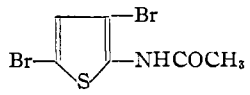
The 2-Aminothiazoles

BY CHARLES D. HURD AND H. L. WEHRMEISTER[1]

Some relationships were developed in the thiophene series, in particular with aceto-2-thiophenamide (I) and its derivatives, which were of an unexpected nature.[2] The 3,5-dibromo derivative (II), for example, underwent nitration to yield the same 3,5-dinitro derivative that was obtained by nitration of I. This substitution



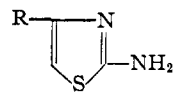
I



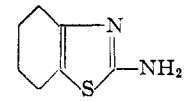
II

of bromine atoms by nitro groups is most unusual. Then again, II was found to couple readily with *p*-nitrobenzenediazonium chloride to form a dye with replacement of the 5-bromo group by azo. Coupling of I even occurred while the solution was strongly acidic. It is remarkable, as a matter of fact, that either I or II should yield azo dyes, since an amine group (not amide) is usually required to activate an aromatic molecule sufficiently for coupling.

The study of substitution reactions of amino and acetamido heterocyclic compounds now has been extended to the thiazoles. The 4-methyl- and 4-phenyl-2-aminothiazoles (III) were prepared by the reaction of thiourea with either the chloro ketone ($RCOCH_2Cl$) or with a mixture of the ketone ($RCOCH_3$) and iodine.[3] A similar procedure, using cyclohexanone, thiourea and iodine, was developed for the preparation of 2-amino-4,5,6,7-tetrahydrobenzothiazole (IV). The preparation of IV from 2-chlorocyclohexanone has been reported.[4]

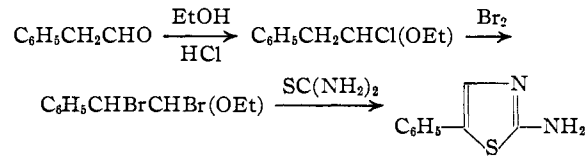


III



IV

5-Phenyl-2-aminothiazole was prepared from phenylacetaldehyde as outlined



The conventional procedure in the first step is to add the hydrogen chloride gas slowly with as little agitation as possible to avoid mixing of the water layer (formed in the reaction) with the organic layer. In the present work emulsions always were encountered, probably because of nearly identical densities of the two phases. Very dark products resulted. Some investigators[5] have designed special apparatus to perform this type of reaction so as to avoid the difficulty mentioned. In the present work, the addition of anhydrous sodium sulfate to the reaction mixture was found to be a simple solution to the problem. With this modification light colored products were obtained even when hydrogen chloride was introduced rapidly and with stirring.

Nitration of 2-acetamidothiazole is known[6] to yield 5-nitro-2-acetamidothiazole. The same compound was obtained in the present study by nitration of 5-bromo-2-acetamidothiazole, thus demonstrating that replacement of halogen does occur in the thiazole as in the thiophene series. Since the structure of the 5-bromo-2-acetamidothiazole is known,[7] the replacement reaction serves to establish the structure of the nitro compound as 5-nitro-2-acetamidothiazole.

Monomercuration of 2-acetamidothiazole occurred in position 5 with mercuric chloride in water, whereas 4,5-dimercuration took place with mercuric acetate in acetic acid. The position of the chloromercuri group in the first of these compounds (V) was established by cleavage with bromine to the known 5-bromo-2-acetamidothiazole. Conversion of V into 5-iodo-2-acetamidothiazole by reaction with iodine also proceeded

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(2) Hurd and Priestley, THIS JOURNAL, **69**, 859, 1173 (1947).

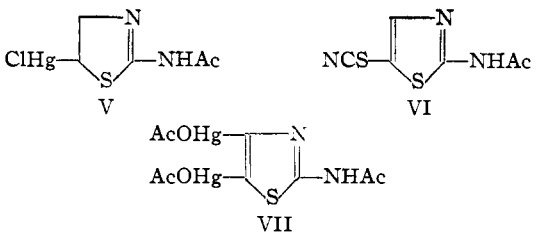
(3) Dodson and King, *ibid.*, **67**, 2242 (1945); **68**, 871 (1946).

(4) Erlenmeyer and Schoenauer, *Helv. Chim. Acta*, **24**, 172 (1941).

(5) Kok, Leendertse and Waterman, *Chem. Weekblad*, **37**, 579 (1940).

(6) Ganapathi and Venkataraman, *Proc. Indian Acad. Sci.*, **22A**, 343 (1945).

(7) Dahlbom and Ekstrand, *Svensk. Kem. Tids.*, **57**, 229 (1945).



readily.[8] Similar cleavage with thiocyanogen (sodium thiocyanate and bromine) yielded 5-thiocyanato-2-acetamidothiazole (VI). 4,5-Diiodo-2-acetamidothiazole was prepared from VII by use of iodine.

Direct thiocyanation of the 2-aminothiazoles (III, R = H, CH_3, or C_6H_5) or the corresponding acetamidothiazoles was readily achieved. Yields were highest for the 4-phenyl derivative.

That thiocyanation occurred in position 5 was established, since the compound from 2-acetamidothiazole was identical to that obtained from V. As might be expected, no product was obtained on attempted thiocyanation of 2-amino-4,5,6,7-tetrahydrobenzothiazole.

No sulfonate was obtained on oxidation of VI with either dilute nitric acid or hydrogen peroxide. Sulfate ion was identified.

Reduction of the thiocyanato group to the mercapto group (RSCN → RSH) was achieved by use of zinc and acetic acid, or of potassium sulfite. The melting point of the 5-mercapto-2-acetamidothiazole so produced differed from that reported by Faith[9] for the reduction product of the compound obtained by the action of chlorosulfonic acid on 2-acetamidothiazole. The assumption that this latter reaction yielded 2-acetamido-5-thiazolesulfonyl chloride evidently is not warranted. The similar reaction of chlorosulfonic acid with 4-methyl-2-acetamidothiazole is stated in one report[10] to yield N-acetyl-4-methyl-2-thiazolylsulfamyl chloride, while in another report[11] the product is described as 2-acetamido-4-methyl-5-thiazolesulfonyl chloride. The reported melting points are 156–157° and 159–160°, respectively. It seems possible that these two substances are identical and that the assignment of structure was in error in one of the papers. The assignment of a sulfamyl chloride was based on the hydrolysis of the compound to the known 4-methyl-2-thiazolylsulfamic acid. The assignment of the sulfonyl chloride structure was based on analogy with other electrophilic reactions (bromination, chlorination) and is probably in error.

Experimental

2-Amino-4,5,6,7-tetrahydrobenzothiazole (IV).—A mixture of 39 g. of cyclohexanone, 61 g. of thiourea, and 102 g. of iodine was heated overnight at 100°, then dissolved in 200 ml. of hot water and filtered through Celite. The filter cake was rinsed with 100 ml. of boiling water. Chilling of the combined filtrates in an ice-bath yielded 63 g. of the hydroiodide of IV. Twenty grams of this salt was heated with 150 ml. of water and the mixture was filtered through Celite. The filtrate was cooled and 20 ml. of aqueous 28% ammonia was added. The precipitated solid, after recrystallization from ligroin, appeared as white needles, m. p. 90–90.5°. It was shown to be IV by analysis. The reported[4] m. p. is 87.5–88.5°.

Anal. Calcd. for $C_7H_{10}N_2S$: N, 18.2. Found: N, 18.2.

2-Acetamido-4,5,6,7-tetrahydrobenzothiazole.—Five grams of acetic anhydride and 1.7 g. of IV, after heating for twenty minutes at 100° and diluting with 50 ml. of water, yielded a solid of m. p. 141–142°. Repeated crystallization from ligroin yielded a product melting at 144.5–145°.

Anal. Calcd. for $C_9H_{12}N_2OS$: N, 14.27. Found: N, 14.28.

2-Phenyl-1-chloroethyl Ethyl Ether.—Dry hydrogen chloride (11.5 g.) was introduced rapidly into a chilled, stirred mixture of phenylacetaldehyde (32.5 g.), ethanol (12.5 g.) and anhydrous sodium sulfate (30 g.). The liquid product was decanted from the solid and calcium chloride (16 g.) was added. The mixture was then maintained at 20 mm. pressure for forty-five minutes to remove excess hydrogen chloride. The yield of crude chloro ether was 47 g., or 94%.

Bromination.—Thirty-five grams of the crude ether was cooled and stirred while 30.4 g. of bromine was added during twenty minutes. The yellow crystalline solid which formed was 2-phenyl-1,2-dibromoethyl ethyl ether.

5-Phenyl-2-aminothiazole.—The above yellow solid, stirred with 50 ml. of absolute alcohol, gradually dissolved to a homogeneous, dark green solution. A suspension of 14.5 g. of thiourea in 200 ml. of absolute alcohol containing 10.3 g. of sodium methoxide was then added. The mixture was stirred for two hours and set aside overnight. Most of the solvent was distilled off, it being replaced by 200 g. of water and 20 ml. of concd. hydrochloric acid. The mixture was heated. A green oily layer appeared which was separated and further removed by extraction with ether. The aqueous layer, containing the desired thiazole salt, was cooled in an ice-bath and 100 ml. of aqueous 28% ammonia was added. The precipitate was collected, washed with water and dried; yield, 9.5 g. This crude 5-phenyl-2-aminothiazole was recrystallized thrice from dilute alcohol to yield 6 to 7 g. of product of m. p. 207.5–208.5°.

Anal. Calcd. for $C_9H_8N_2S$: N, 15.9. Found: N, 15.4.

5-Phenyl-2-acetamidothiazole.—Acetylation of the amino compound with acetic anhydride produced the amide, m. p. 244–244.5° after crystallization from alcohol.

Anal. Calcd. for $C_{11}H_{10}N_2OS$: N, 12.8. Found: N, 12.6.

5-Nitro-2-acetamidothiazole.—2-Aminothiazole was brominated and acetylated, forming 5-bromo-2-acetamidothiazole.[7] A mixture of 1.2 ml. of red fuming nitric acid (sp. gr. 1.6) and 5 g. of acetic anhydride was added to a cold solution of 3.2 g. of 5-bromo-2-acetamidothiazole in 55 g. of glacial acetic acid. A 0.3-g. precipitate was separated after ten minutes. The yellow filtrate was evaporated to dryness, taken up in 100 ml. of hot absolute alcohol, decolorized (Norit), filtered and cooled to −10°. After several hours, 0.7 g. of solid was collected, m. p. 260–262°. Recrystallization from alcohol brought the m. p. to 264–265°. Halogen was absent by test.

Anal. Calcd. for $C_5H_5N_3O_3S$: C, 32.08; H, 2.69. Found: C, 32.13; H, 2.73.

5-Nitro-2-acetamidothiazole, m. p. 262–265°, was made for purposes of comparison, by nitration[6] of 2-acetamidothiazole. The mixed m. p. was 262–265°.

(8) The preparation of several monomercurated 2-acetamidothiazoles and their conversion to iodo compounds has been reported recently by Travagli, *Gazz. chim. ital.*, **78**, 592 (1948).

(9) Faith, THIS JOURNAL, **69**, 2063 (1947).

(10) Postovskiĭ and Belaya, *Compt. rend. acad. sci. U. R. S. S.*, **40**, 326 (1943); *C. A.*, **39**, 1152 (1945).

(11) Backer and Jonge, *Rec. trav. chim.*, **62**, 163 (1943).

2-Acetamido-5-thiazolemercuric Chloride[8] **(V).**—To a hot solution of 7.1 g. of 2-acetamidothiazole in 200 ml. of water there was added 250 ml. of an aqueous solution containing 16 g. of mercuric chloride and 32 g. of sodium acetate trihydrate. The mixture was boiled for fifteen minutes, cooled and filtered. The filter cake was washed with 100 ml. of water, 50 ml. of methanol and 50 ml. of ether; yield, 16.7 g. or 88%. The material did not melt below 300°.

Anal. Calcd. for $C_5H_5ClHgN_2OS$: N, 7.43. Found: N, 8.09.

5-Bromo-2-acetamidothiazole.—A mixture of 1 g. of V in 20 ml. of methanol saturated with sodium bromide was treated with 1 g. of bromine. After fifteen minutes some sodium sulfite was added and the mixture was heated to boiling and filtered. The filtrate was diluted with an equal volume of water and concentrated to about 5 ml. Water was added and the solid which separated was recrystallized from dilute acetic acid; yield, 0.24 g. (42%), m. p. 210–212°. Recrystallization from dilute acetic acid brought the m. p. up to 218–220°. A mixture of this product and an authentic sample of 5-bromo-2-acetamidothiazole, m. p. 225–226°, melted at 218–220°.

The authentic sample was prepared both by bromination of 2-aminothiazole[7] and of 2-acetamidothiazole.[12] The once recrystallized product melted at 218–220°. Reported melting points are 224–225°[7] and 229–231°.[12] Our samples melted at 225–226°.

2-Acetamido-4,5-thiazolebis-(mercuric Acetate) (VII).—Forty grams of mercuric acetate, 7.1 g. of 2-acetamidothiazole and 170 ml. of glacial acetic acid were heated together at 100° for eighteen hours. The hot mixture was filtered and the solid product was washed with acetic acid, water, methanol and acetone; yield 23.4 g. (74%). This material did not melt.

Anal. Calcd. for $C_9H_{10}Hg_2N_2O_5S$: N, 4.24. Found: N, 3.46.

5-Iodo-2-acetamidothiazole.—A mixture of 1 g. of V, 1.5 g. of potassium iodide, 10 g. of water and 0.5 g. of iodine was triturated and filtered. The solid was rinsed with water and treated with 30 ml. of alcohol. The mixture was filtered and the filtrate evaporated to 15 ml. On cooling, 0.4 g. (56% yield) of crystals separated; m. p. 210–212°. A constant melting point of 225–226° was achieved after five recrystallizations from dilute alcohol. The recorded m. p. for the 5-iodo-2-acetamidothiazole obtained[8] by a similar approach is 228°.

Anal. Calcd. for $C_5H_5IN_2OS$: C, 22.36; H, 1.88. Found: C, 22.42; H, 1.90.

2-Acetamido-5-thiocyanatothiazole (VI).—To a mixture of 1.2 g. of V and 0.65 g. of sodium thiocyanate in 20 ml. of acetic acid, there was added a solution of 0.58 g. of bromine in 10 ml. of acetic acid. After standing at room temperature overnight, the mixture was filtered and the solid was washed with 10 ml. of acetic acid. Approximately 35 ml. of water was added to the filtrate, and the mixture was evaporated to dryness. The solid residue was recrystallized from methanol. The product weighed 0.32 g. (50% yield) and melted at 195–198°. This material was twice recrystallized from methanol yielding 0.2 g. of a product melting at 212–214°. A mixture of this material and the product of direct thiocyanation of 2-acetamidothiazole melted at 212–214°.

2-Acetamido-4,5-diiodothiazole.—To 20.5 g. of VII there was added a solution of 15 g. of sodium chloride in 150 ml. of water. The stirred mixture was heated at 100° for five hours, cooled and filtered. The solid obtained was washed with 1 l. of water, 50 ml. of methanol and 50 ml. of acetone. The dried product weighed 18.5 g.

A mixture of 3.1 g. of this material, 7 g. of potassium iodide, 2.9 g. of iodine and 25 ml. of water was triturated for a few minutes. The solid obtained was washed with potassium iodide solution until free of iodine. This product was washed with water and dried; yield 1.6 g. A 1.2-g. portion of this material was heated with 60 ml. of 95% alcohol, decolorizing carbon was added, and the mixture was filtered through Celite. The filtrate was concentrated to 30 ml. and 20 ml. of water was added to yield a nearly saturated hot solution. On cooling, there was deposited 0.5 g. of crystalline material. This material decomposed at 222–232° when heated from 100°. When heated from 230°, the sample decomposed at 239–240°. The product was recrystallized from dilute alcohol yielding a sample which decomposed at 240° when inserted in an oil-bath at an initial temperature of 239°. Violet vapors were observed when the sample decomposed.

Anal. Calcd. for $C_5H_4I_2N_2OS$: C, 15.24; H, 1.02. Found: C, 15.20, 15.22; H, 1.08, 1.00.

5-Thiocyanato-4-phenyl-2-aminothiazole.—To a cooled (ice-bath) and stirred mixture of 2-amino-4-phenylthiazole (19 g.), sodium thiocyanate (27 g.) and methanol (100 ml.), there was added a solution of 17.3 g. of bromine in 25 ml. of methanol saturated with sodium bromide. The addition time was twelve minutes. After stirring the reaction mixture for two and one-quarter hours, it was poured onto 200 g. of crushed ice. Approximately 100 ml. of water was used to complete the transfer. A yellow solid was present. Twenty milliliters of concd. ammonium hydroxide was added and the solid was collected by suction filtration, washed with water and dried; weight 24.8 g., m. p. 168–173°.

A part of this product was dissolved in 550 ml. of boiling absolute alcohol to yield an almost saturated solution. The solution was cooled to room temperature and the precipitated solid was collected by filtration. The filtrate was used to dissolve a further portion of the product. This process was repeated a total of five times until all the material had been recrystallized. The recrystallized material weighed 19.5 g. (78% yield) and melted at 171–174°. A sample for analysis was recrystallized repeatedly from absolute alcohol to yield a product with a melting point of 186–187°.

Anal. Calcd. for $C_{10}H_7N_3S_2$: C, 51.48; H, 3.03. Found: C, 51.51; H, 3.11.

This identical procedure was used in the thiocyanation of the other 2-aminothiazoles and 2-acetamidothiazoles. Pertinent data are assembled in Table I. Yields refer to once-crystallized material. The m. p. listed in the table is for material which was crystallized two or more times to constancy. Crystallization was from ethanol, 2-propanol or benzene.

TABLE I

THIOCYANATION EXPERIMENTS

Compound formed: 5-thiocyanato deriv. of	Yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Found
2-Aminothiazole	32	142.5–143.5	$C_4H_3N_3S_2$	26.7	27.5
4-Methyl-2-aminothiazole	47	164.0–164.5	$C_5H_5N_3S_2$	24.5	24.5
4-Phenyl-2-acetamidothiazole	100	198–199	$C_{12}H_9N_3OS_2$	15.2	15.0
4-Methyl-2-acetamidothiazole	73	176–176.5	$C_7H_7N_3OS_2$	19.7	19.9
2-Acetamidothiazole	49	212–214	$C_5H_5N_3OS_2$	21.1	21.1

The acetylation of the thiocyanated 2-aminothiazoles with acetic anhydride gave the same products as were obtained by thiocyanation of the analogous 2-acetamidothiazoles. These acetamido compounds were soluble in alkali.

5-Mercapto-2-acetamidothiazole.—One and a half grams of zinc dust was added to a filtered solution of 2 g. of 5-thiocyanato-2-acetamidothiazole in 20–30 ml. of glacial acetic acid. The mixture was heated at 100° for an hour with stirring, then was cooled, poured into 100 ml. of water and evaporated to 40 ml. Then 100 ml. of glacial acetic acid and 20 ml. of water were added and the mixture was heated to 100° and filtered. The gray insoluble material was dissolved in 40 ml. of water and 10 ml. of concd. hydrochloric acid. After filtration, 40 ml. of concd. am-

(12) Backer and Buisman, *ibid.*, **63**, 226 (1944).

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 $C_5H_6N_2OS_2$: 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 $C_6H_8N_2OS_2$: 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 $C_{16}H_{20}Cl_2N_4O_4S_3$: 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.

EVANSTON, ILLINOIS RECEIVED JUNE 27, 1949

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

Derivatives of Thianaphthene. III[1]

BY F. F. BLICKE AND DON G. SHEETS[2]

It was reported in a previous communication[3] 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 Bistrzycki[4] from the condensation 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

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

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

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

(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)).