[Contribution from the Central Research Department,
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SOME 2-ACETYLTHIOPHENE DERIVATIVES AND RELATED ACETOPHENONE ANALOGS

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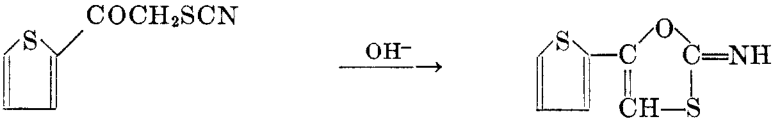
2-Acetylthiophene has been prepared in 86% yield by treating thiophene with acetic anhydride in the presence of iodine (1), in 79–83% yield from thiophene, acetyl chloride, and stannic chloride (2), and in 75% yield from thiophene, acetyl chloride, and aluminum chloride by the Perrier technique (3). More recently thiophene has been acetylated in yields up to 94% by means of acetic anhydride in the presence of such catalysts as zinc chloride (4), activated clays (5, 6), and inorganic oxyacids (7), and in 45% yield by means of acetic acid and phosphorus pentoxide (8). With 2-chlorothiophene, acetic anhydride, and phosphoric acid, the yield of 2-acetyl-5-chlorothiophene was 70% (7). Starting with 2-chlorothiophene we have prepared 2-acetyl-5-chlorothiophene in 71% conversion and 84% yield by the acetic anhydride method (1) and in 94% yield by the Perrier method (3). By the latter method 2-bromothiophene yielded 2-acetyl-5-bromothiophene in 77% conversion and quantitative yield.

Chlorination of 2-acetylthiophene gave 2-(chloroacetyl)thiophene in 41% conversion and 77% yield. Under the same conditions 2-acetyl-5-chlorothiophene gave 5-chloro-2-(chloroacetyl)thiophene in 62% yield. The compound also was prepared in 59% conversion and 73% yield from 2-chlorothiophene, chloroacetyl chloride, and aluminum chloride. 2-(Chloroacetyl)thiophene and 5-chloro-2-(chloroacetyl)thiophene reacted with potassium cyanide in aqueous ethanol to give the corresponding nitriles in 60% and 73% yields, respectively.

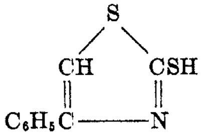
Treatment of 2-(chloroacetyl)thiophene with ammonium thiocyanate in ethanol gave 87% of 2-(thiocyanoacetyl)thiophene. Infra-red absorption spectra measurements on this compound showed bands at 6.14 microns and at 4.62 microns, which indicated the presence of a carbonyl and a thiocyano group, respectively. This compound liberated ammonia when boiled with aqueous sodium hydroxide and gave a negative chemical test for both the thiocyanate (9) and isothiocyanate (10) groups. It did not react with acetic anhydride or semicarbazide, but reacted slowly with 2,4-dinitrophenylhydrazine to give the corresponding 2,4-dinitrophenylhydrazone, which gave a positive test for the thiocyanate group.

Evidently under the influence of weak bases or heat the 2-(thiocyanoacetyl)-thiophene cyclized to give 2-imino-5-(2′-thienyl)-1,3-oxathiole, so that, except in the case of the strongly acid 2,4-dinitrophenylhydrazine reagent, the chemical reactions observed were those of the oxathiole.

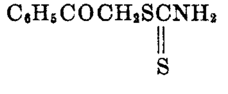


Under similar conditions thiocyanoacetone gives 2-imino-5-methyl-1,3-oxathiole (11). 5-Chloro-2-(chloroacetyl)thiophene reacted with ammonium thiocyanate to give 90% of 5-chloro-2-(thiocyanoacetyl)thiophene. The structure of this last compound is formulated by analogy to 2-(thiocyanoacetyl)thiophene.

Before attempting the preparation of mercaptothienylthiazoles, the preparation of mercaptophenylthiazoles was examined. Miolati (12) condensed ω-bromoacetophenone with ammonium dithiocarbamate and obtained 2-mercapto-4-phenylthiazole (I). He found it desirable to treat his crude product with hydrogen chloride in boiling benzene to cyclize any S-phenacyldithiourethan (II). He also isolated a small amount of a by-product which he thought was phenacyldithiourethan. By operating at room temperature in ether solution Levi (13) prepared this dithiourethan and showed that on heating to 135° it lost water to give the mercaptothiazole. Ubaldini and Fiorenza (14) repeated Levi's work and obtained 70% of the phenacyldithiourethan and 30% of Miolati's by-product. When the reactants were allowed to stand for sixteen hours, 55% of the mercaptothiazole was obtained together with 45% of the by-product, which was shown to be phenacyl 4-phenyl-2-thiazolyl sulfide (III).

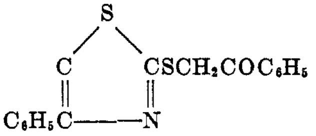


I



$C_6H_5COCH_2S\underset{\underset{S}{\|}}{C}NH_2$

II



III

Mathes (15) reported a 95% yield of 2-mercapto-4-phenylthiazole by treating ω-chloroacetophenone with ammonium dithiocarbamate in aqueous solution.

We have found that by using ω-chloroacetophenone, which is less reactive than ω-bromoacetophenone, in any solvent such as ethanol, methanol, water, or ethylene glycol, in which ammonium dithiocarbamate is somewhat soluble, yields of 81–86% of 2-mercapto-4-phenylthiazole can be obtained. While our yields were somewhat lower than that obtained by Mathes (15), our crude product had an appreciably higher melting point. It was found desirable to boil the crude product with benzene to cyclize any phenacyldithiourethan. When this was not done, a small amount of its hydrolysis product, phenacyl mercaptan, appeared as a by-product. It probably was formed when the crude reaction product was treated with alkali to separate the mercaptan. With ω-bromoacetophenone more phenacyl 4-phenyl-2-thiazolyl sulfide was obtained than mercaptothiazole.

In ethanol solution 2-(chloroacetyl)thiophene reacted with ammonium dithiocarbamate to give 86% of 2-mercapto-4-(2′-thienyl)thiazole. Under the same conditions 5-chloro-2-(chloroacetyl)thiophene gave 91% of 4-(5′-chloro-2′-thienyl)-2-mercaptothiazole. With ether as the reaction medium, in which ammonium dithiocarbamate is insoluble, some of the corresponding sulfide was obtained in each case.

The authors are grateful to Mr. D. R. Beasecker and Mr. W. Noetling of this laboratory for the measurement and interpretation of the absorption spectra.

EXPERIMENTAL[1]

2-Acetylthiophene was prepared by the method of Hartough and Kosak (1) in which thiophene and acetic anhydride were caused to react in the presence of a small amount of iodine. The yield was 86%, b.p. 89–91°/11 mm., (77–78°/4 mm.) (1), n_D^{25} 1.5644–1.5648 (n_D^{20} 1.5666) (1).

The semicarbazone was prepared by the method of Shriner and Fuson (16) in 93% yield. After one crystallization from 60% ethanol it melted at 188–189° (191–192°) (1).

2-Acetyl-5-chlorothiophene was prepared from 2-chlorothiophene, acetyl chloride, and aluminum chloride by a method previously described for 2-acetylthiophene (3). The yield of 2-acetyl-5-chlorothiophene was 94%, b.p. 117–118°/17 mm. A sample was crystallized twice from ethanol, m.p. 47° (52°) (17).

By the method of Hartough and Kosak (1) using equimolar quantities of 2-chlorothiophene and acetic anhydride in the presence of iodine, 2-acetyl-5-chlorothiophene was obtained in 71% conversion and 84% yield, b.p. 120–123°/21 mm.

2-Acetyl-5-bromothiophene, b.p. 103°/4 mm., was prepared from acetyl chloride and 2-bromothiophene in 77% conversion and quantitative yield. The procedure was identical to that employed for the preparation of 2-acetyl-5-chlorothiophene. An analytical sample of the product, crystallized from benzene-hexane, melted at 94–95° (94°) (17).

2-(Chloroacetyl)thiophene. In a 500-cc., three-necked flask equipped with a reflux condenser, stirrer, thermometer, and gas inlet tube was placed 378 g. of 2-acetylthiophene. Chlorine was introduced while the liquid was illuminated with a 100-watt incandescent lamp. After an induction period of fifteen minutes, during which time chlorine was absorbed and the temperature rose from 20° to 65°, the evolution of hydrogen chloride commenced. The introduction of chlorine was continued at a reaction temperature of 65–75° for eighty-five minutes when a weight gain of 63 g. was observed. The reaction mixture was distilled to give 406.3 g., b.p. 101–146°/19 mm. and 21.1 g. of residue. Fractionation of the distillate gave 177.1 g. (47% recovery) of 2-acetylthiophene, b.p. 73–81°/5 mm., n_D^{25} 1.5644; 21.6 g. of intermediate, b.p. 81–111°/5 mm., n_D^{25} 1.5744; 196.9 g. (41% conversion, 77% yield) of 2-(chloroacetyl)thiophene, b.p. 111–113°/5 mm.; and 6.5 g. of residue. The product solidified in the receiver. In another experiment a small sample, dried between sheets of filter paper, melted at 47–48° (48°) (18).

5-Chloro-2-(chloroacetyl)thiophene was prepared by a method previously described for 2-acetylthiophene (3) using aluminum chloride, chloroacetyl chloride, and 2-chlorothiophene in carbon tetrachloride at 12–25°. The conversion was 59% and the yield 73%, b.p. 94–98%/1 mm., m.p. 79–81°. After recrystallization from hexane the melting point was 80–81°.

5-Chloro-2-(chloroacetyl)thiophene also was prepared by chlorinating 104.2 g. of 2-acetyl-5-chlorothiophene in 150 cc. of boiling carbon tetrachloride. A weight gain of 20 g. was observed in fifty minutes' time. A stream of dry air was then blown through the hot solution for fifteen minutes. Upon cooling, there was obtained 71.2 g. of 5-chloro-2-(chloroacetyl)thiophene, m.p. 72–77°. When the filtrate was concentrated to one-half its original volume, an additional 7.1 g. was obtained, m.p. 78–79°, total yield 62%. A sample of the first crop was twice crystallized from benzene-hexane, m.p. 80–81°.

Anal. Calc'd for $C_6H_4Cl_2OS$: Cl, 36.4. Found: Cl, 36.6.

2-Thenoylacetonitrile. To a cold solution of 13.0 g. of potassium cyanide in 40 cc. of water was added with shaking a solution of 16.1 g. of 2-(chloroacetyl)thiophene in 50 cc. of ethanol. The ketone immediately precipitated. The mixture was allowed to stand for

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[1] All melting points are corrected. The carbon-hydrogen and nitrogen analyses are micro combustions conducted by the Oakwold Laboratories, Alexandria, Virginia. Some of the sulfur determinations are by Oakwold; the remainder and the chlorine determinations are by P. J. Adams, Miss Margaret Magin and Miss Mary Neal of the Monsanto Chemical Company, Dayton 7, Ohio.

one hour with occasional shaking, during which time the maximum temperature was 33°. Water was then added to incipient turbidity followed by a few drops of 10% sodium hydroxide. After the mixture was twice extracted with small portions of benzene, Norit was added and the solution was filtered. The filtrate was cooled in ice and carefully acidified with cold 3 *N* hydrochloric acid. The precipitated 2-thenoylacetonitrile was washed with cold water and dried in a vacuum desiccator over phosphorus pentoxide. It weighed 9.0 g. (60% yield), m.p. 120–128°. An analytical sample, after several crystallizations from ethanol melted at 136–137° (137°) (19).

Anal. Calc'd for C_7H_5NOS: N, 9.27. Found: N, 9.18.

2-Thenoylacetonitrile dissolved in hot 25% sodium hydroxide with the liberation of ammonia. It gave a positive test with 2,4-dinitrophenylhydrazine reagent, but gave no semicarbazone when boiled for fifteen minutes with semicarbazide in 70% ethanol and did not react with malononitrile in the presence of piperidine.

5-Chloro-2-thenoylacetonitrile. To a solution of 4.9 g. of potassium cyanide in 30 cc. of water, cooled by an ice-bath, there was added a solution of 7.0 g. of 5-chloro-2-(chloroacetyl)thiophene in 75 cc. of ethanol. The resulting suspension was removed from the ice-bath and shaken. The temperature was kept below 30° by occasional cooling. After thirty minutes, when solution was complete, the flask was placed in the refrigerator overnight. The mixture was diluted with 45 cc. of water to incipient turbidity, treated with a few drops of 10% sodium hydroxide and extracted three times with small portions of benzene. The aqueous solution was treated with Norit in the cold, filtered, and acidified with 3 *N* hydrochloric acid. The light brown crystals which precipitated were washed with cold water, and dried *in vacuo* over potassium hydroxide. This crude product weighed 4.9 g. (73% yield), m.p. 108–114°. After four recrystallizations from ethanol, in two of which the solution was treated with Norit, an analytical sample, comprising white crystals, melted at 120°.

Anal. Calc'd for C_7H_4ClNOS: Cl, 19.1. Found: Cl, 18.9.

2-(Thiocyanoacetyl)thiophene. A mixture of 32.1 g. of 2-(chloroacetyl)thiophene and 19.0 g. of ammonium thiocyanate in 300 cc. of absolute ethanol was placed in a 500-cc., three-necked flask equipped with a stirrer, thermometer, and condenser. After it had been stirred for one hour at room temperature, the mixture was heated gradually to the boiling point over a forty-five minute period. It was filtered hot and the precipitate was washed with a little hot ethanol. Upon cooling, the combined filtrate and washings deposited yellow-tan crystals of 2-(thiocyanoacetyl)thiophene. This precipitate was separated and dried, 29.5 g., m.p. 88–89°. The filtrate was evaporated nearly to dryness, cooled, and diluted with water. The gummy yellow precipitate thus obtained was recrystallized from ethanol to give an additional 2.4 g. (total yield 87%), m.p. 87–88°. An analytical sample from another preparation was crystallized three times from ethanol, m.p. 90–91° (88°) (20).

Anal. Calc'd for $C_7H_5NOS_2$: N, 7.65. Found: N, 7.92.

When boiled with 10% aqueous sodium hydroxide, 2-(thiocyanoacetyl)thiophene evolved a gas which turned moist litmus blue. The compound gave a negative test for both the thiocyanate (9) and isothiocyanate (10) groups. After standing for one-half hour with 2,4-dinitrophenylhydrazine reagent, a precipitate appeared. This was washed with ethanol, and dried. This compound gave a positive test for the thiocyanate group. An analytical sample was crystallized from a mixture of ethanol and ethyl acetate, m.p. 160–161°.

Anal. Calc'd for $C_{13}H_9N_5O_4S_2$: N, 19.3. Found: N, 19.9.

2-(Thiocyanoacetyl)thiophene was recovered unchanged when boiled for five minutes with acetic anhydride and when treated with semicarbazide in aqueous ethanol (16).

5-Chloro-2-(thiocyanoacetyl)thiophene. A mixture of 29.3 g. of 5-chloro-2-(chloroacetyl)thiophene and 15.2 g. of ammonium thiocyanate in 250 cc. of absolute ethanol was heated to 80° over a twenty-minute period and stirred at that temperature for an additional ten minutes. The precipitated ammonium chloride was washed twice with hot ethanol.

After the combined filtrate and washings were cooled, the white crystals were washed with water, and dried to give 22.3 g., m.p. 97–98°. Chilling of the combined filtrate and washings produced a second crop of 7.1 g., m.p. 89–92°. The total yield was 90%. An analytical sample from the first crop was crystallized twice from ethanol, m.p. 99°.

Anal. Calc'd for $C_7H_4ClNOS_2$: S, 29.5; Cl, 16.3.
Found: S, 29.0; Cl, 16.0.

2-Mercapto-4-phenylthiazole. To a suspension of 16.5 g. of ammonium dithiocarbamate in 50 cc. of absolute ethanol was added with shaking and cooling a mixture of 15.5 g. of phenacyl chloride and 100 cc. of absolute ethanol. After the initial reaction had subsided, the flask was stoppered and allowed to stand at room temperature with occasional shaking for seven days. The slurry of crystals was cooled by means of an ice-bath, diluted with 200 cc. of water and filtered. The precipitate was washed with water and dried. It was then heated under reflux with 150 cc. of benzene while the evolved water was collected in a Dean and Stark trap. The residue, obtained by evaporating the benzene, was treated with 150 cc. of 5% sodium hydroxide and filtered. The filtrate was cooled in an ice-bath and acidified with dilute hydrochloric acid. The resulting white precipitate was washed with water, and dried to give 16.5 g. (86%) of 2-mercapto-4-phenylthiazole, m.p. 167–169°. An analytical sample was crystallized from aqueous ethanol, m.p. 173–174° (170°) (13).

Anal. Calc'd for $C_9H_7NS_2$: S, 33.2; N, 7.25.
Found: S, 33.4; N, 7.45.

Yields of 81–83% of 2-mercapto-4-phenylthiazole were obtained when the reaction was conducted in water, methanol or ethylene glycol.

Phenacyl mercaptan. In a reaction similar to the above conducted in aqueous solution and in a reaction between phenacyl bromide and ammonium dithiocarbamate in ethanol, a small amount of yellow oil appeared when the alkaline solution of the mercaptothiazole was acidified. In both of these experiments the boiling with benzene was omitted. This oil was separated from the filtrate and the two samples were combined and distilled to give 3.5 g. of phenacyl mercaptan, b.p. 141–144°/14 mm. (116–122°/4 mm.), (21) n_D^{25} 1.5930.

The phenylhydrazone, prepared by the method of Shriner and Fuson (22), was crystallized three times from ethanol, m.p. 91–92° (90–91°) (21).

Phenacyl 4-phenyl-2-thiazolyl sulfide. A reaction similar to that described for the preparation of 2-mercapto-4-phenylthiazole was conducted with 16.5 g. of ammonium dithiocarbamate and 19.9 g. of phenacyl bromide in 200 cc. of water. The method for the isolation of the product was the same. The alkaline slurry, obtained by treating the product with 150 cc. of 5% sodium hydroxide, was filtered and the precipitate was washed with water. Acidification of the cooled, combined filtrate and washings with dilute hydrochloric acid precipitated crude 2-mercapto-4-phenylthiazole, which was washed with water, and dried, 3.3 g. (17% yield), m.p. 159–168°.

The residue from the filtration of the alkaline slurry was dried to give 11.8 g. (76% yield) of phenacyl 4-phenyl-2-thiazolyl sulfide, m.p. 111–116°. An analytical sample melted at 121° (115–117°) (14), after two recrystallizations from ethanol.

Anal. Calc'd for $C_{17}H_{13}NOS_2$: C, 65.6; H, 4.21; N, 4.50; S, 20.6.
Found: C, 65.4; H, 4.46; N, 5.01; S, 22.2.

When ethanol was substituted for water as the solvent for the initial condensation, the yields of 2-mercapto-4-phenylthiazole and phenacyl 4-phenyl-2-thiazolyl sulfide were 39% and 60%, respectively.

2-Mercapto-4-(2'-thienyl)thiazole. To a suspension of 16.5 g. of ammonium dithiocarbamate in 50 cc. of absolute ethanol was added with shaking a partial solution of 16.1 g. of 2-(chloroacetyl)thiophene in 100 cc. of absolute ethanol. The mixture warmed immediately and became yellow. It was cooled in an ice-bath for fifteen minutes until the reaction had subsided, and then was allowed to stand at room temperature with occasional shaking for four days. The slurry of yellow crystals was diluted with 200 cc. of water and cooled by an ice-bath. The solid was washed with water and treated with 125 cc. of cold 5% aqueous sodium hydroxide. Nearly all the solid dissolved. The mixture was filtered and the filtrate was cooled and carefully acidified with dilute hydrochloric acid. The crude 2-mercapto-4-(2′-thienyl)thiazole was washed with water, and dried. It weighed 17.2 g. (86% yield), m.p. 173–176°. An analytical sample was crystallized from benzene and ethanol, m.p. 177°.

Anal. Calc'd for $C_7H_5NS_3$: N, 7.03; S, 48.3.
Found: N, 7.22; S, 48.4.

2′-Thenoylmethyl 4-(2″-thienyl)-2-thiazolyl sulfide. The reaction between 120.3 g. of 2-(chloroacetyl)thiophene and 82.5 g. of ammonium dithiocarbamate in 600 cc. of anhydrous ether was allowed to proceed for fifteen days at room temperature after the initial cooling. The solid was filtered and divided by treatment with 5% aqueous sodium hydroxide into 74.1 g. of alkali-soluble 2-mercapto-4-(2′-thienyl)thiazole, m.p. 176–177°, and 8.0 g. of alkali-insoluble 2′-thenoylmethyl 4-(2″-thienyl)-2-thiazolyl sulfide, m.p. 86–88°. After two crystallizations from ethanol, the first after treatment of the solution with Norit, an analytical sample of the latter compound melted at 89–90°.

Anal. Calc'd for $C_{13}H_9NOS_4$: N, 4.33; S, 39.7.
Found: N, 4.58; S, 39.7.

The ethereal filtrate was worked up similarly to obtain 4.8 g. of 2-mercapto-4-(2′-thienyl)thiazole, m.p. 164–168° after two crystallizations from aqueous ethanol (total yield 53%) and 4.2 g. of 2′-thenoylmethyl 4-(2″-thienyl)-2-thiazolyl sulfide, m.p. 88–89° after three crystallizations from ethanol (total yield 10%).

4-(5′-Chloro-2′-thienyl)-2-mercaptothiazole. To a suspension of 16.5 g. of ammonium dithiocarbamate in 50 cc. of absolute ethanol was added a mixture of 19.5 g. of 5-chloro-2-(chloroacetyl)thiophene and 100 cc. of absolute ethanol. The mixture was cooled by an ice-bath for a few minutes until the initial reaction had subsided, and then allowed to stand at room temperature with occasional shaking for seven days. The orange suspension of crystals was diluted with an equal volume of water and cooled by an ice-bath. The precipitate was washed thoroughly with water. Treatment with 175 cc. of 10% potassium hydroxide dissolved most of this solid. The alkaline mixture was filtered and the filtrate was cooled and carefully acidified with dilute hydrochloric acid. The precipitated 4-(5′-chloro-2′-thienyl)-2-mercaptothiazole was washed with water, and dried *in vacuo* over calcium chloride to give 20.7 g. (91% yield), m.p. 201°. An analytical sample was crystallized twice from ethanol, m.p. 205°.

Anal. Calc'd for $C_7H_4ClNS_3$: S, 41.2; Cl, 15.2.
Found: S, 41.4; Cl, 15.1.

5′-Chloro-2′-thenoylmethyl 4-(5″-chloro-2″-thienyl)-2-thiazolyl sulfide. The reaction between 39.0 g. of 5-chloro-2-(chloroacetyl)thiophene and 33.0 g. of ammonium dithiocarbamate was allowed to proceed for four days at room temperature in 250 cc. of ether. Part of the 4-(5′-chloro-2′-thienyl)-2-mercaptothiazole was separated from the crude reaction product by treatment with 5% sodium hydroxide. The remainder of the separation was effected with hot benzene and hot ethanol. The mercaptan was fairly soluble in the ethanol and insoluble in the benzene, whereas the sulfide showed the opposite solubility. By these means there was isolated 16.3 g. (35% yield) of crude 4-(5′-chloro-2′-thienyl)-2-mercaptothiazole and 8.3 g. (21% yield) of 5′-chloro-2′-thenoylmethyl 4-(5″-chloro-2″-thienyl)-2-thiazolyl sulfide. An analytical sample of the latter compound was crystallized several times from benzene, m.p. 133–134°.

Anal. Calc'd for $C_{13}H_7Cl_2OS_4$: S, 32.7; Cl, 18.1.
Found: S, 32.7; Cl, 17.6.

SUMMARY

The preparations of 2-(chloroacetyl)thiophene and of 5-chloro-2-(chloroacetyl)thiophene, have been described and their reactions with potassium cyanide, ammonium thiocyanate and ammonium dithiocarbamate have been

examined. In connection with the ammonium dithiocarbamate reactions, the corresponding phenacyl chloride chemistry also was reëxamined.

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REFERENCES

(1) HARTOUGH AND KOSAK, *J. Am. Chem. Soc.*, **68**, 2639 (1946).

(2) JOHNSON AND MAY, *Org. Syntheses*, Coll. Vol. II, p. 8.

(3) MOWRY, RENOLL, AND HUBER, *J. Am. Chem. Soc.*, **68**, 1107 (1946).

(4) HARTOUGH AND KOSAK, *J. Am. Chem. Soc.*, **69**, 1012 (1947).

(5) HARTOUGH, KOSAK, AND SARDELLA, *J. Am. Chem. Soc.*, **69**, 1014, (1947).

(6) HARTOUGH AND SARDELLA, U. S. Patent 2,432,991.

(7) HARTOUGH AND KOSAK, *J. Am. Chem. Soc.*, **69**, 3093 (1947).

(8) HARTOUGH AND KOSAK, *J. Am. Chem. Soc.*, **69**, 3098 (1947).

(9) HAGELBERG, *Ber.*, **23**, 1083 (1890).

(10) MULLIKEN, "The Identification of Pure Organic Compounds", John Wiley and Sons, Inc., New York, **1922**, Vol. IV, p. 17.

(11) TCHERNIAC, *J. Chem. Soc.*, **115**, 1071 (1919).

(12) MIOLATI, *Gazz. chim. ital.*, **23**, 575 (1893).

(13) LEVI, *Gazz. chim. ital.*, **61**, 719 (1931).

(14) UBALDINI AND FIORENZA, *Gazz. chim. ital.*, **73**, 169 (1943).

(15) MATHES, U. S. Patent 2,186,419; *Chem. Abstr.*, **34**, 3537 (1940).

(16) SHRINER AND FUSON, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, **1940**, p. 142.

(17) GATTERMANN AND ROMER, *Ber.*, **19**, 688 (1886).

(18) STEINKOPF, *Ann.*, **413**, 343 (1916).

(19) SALVATORI, *Gazz. chim. ital.*, **21**, II, 284 (1891); *J. Chem. Soc.*, **62**, 304 (1892).

(20) BRUNSWIG, *Ber.*, **19**, 2893 (1886).

(21) GROTH, *Ark. Kem. Mineral Geol.*, **9**, No. 1 (1924); *Chem. Abstr.*, **18**, 1281 (1924).

(22) SHRINER AND FUSON, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, **1940**, p. 64.