precipitated (0.25 g.) was filtered, dissolved in hexane and treated with bromine, after filtration of the solution. On chilling, 0.15 g. of dibromide crystallized. After crystallization from hexane, this was found to contain 4.01 μc. of C^{14}/mmole (calcd. for complete equilibrium (eq. 1), 3.96 μc. of C^{14}/mmole). The aqueous filtrate obtained above was mixed with a saturated aqueous dimedon solution. The precipitated formaldehyde derivative was found to contain 3.99 μc. of C^{14}/mmole.

OAK RIDGE, TENNESSEE RECEIVED OCTOBER 5, 1951

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

Reactions of 3-Thiocyano-2-butanone. I. The Preparation of 2-Substituted-4,5-dimethylthiazoles

BY JAMES T. GREGORY AND ROGER A. MATHES

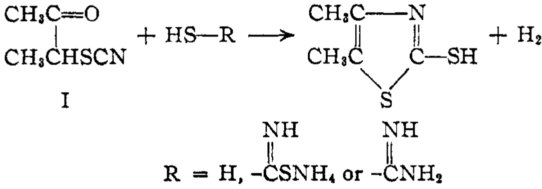
3-Thiocyano-2-butanone has been prepared and was found to react with water, hydrogen chloride, hydrogen sulfide, ammonium chloride, ammonium dithiocarbamate and thiourea to form 2-substituted-4,5-dimethylthiazoles.

Thiazoles containing substituents, other than hydrocarbon radicals, in the 2-position have been prepared from α-thiocyanoketones only in a limited number of examples. 2-Aminothiazoles have been prepared by the reaction of thiocyanoacetone with ammonia,[1a,b] ammonium thiocyanate[1a] and amines.[1a,b] The 2-hydroxy compound has been prepared by treating the α-thiocyanoketones with acidic[1a,2,3] or basic[2a] reagents and the 2-chloro compound results when dry hydrogen chloride[2a] is used.

3-Thiocyano-2-butanone (I) was prepared by treating 3-chloro-2-butanone with aqueous sodium thiocyanate and its reactions with ammonium chloride, hydrogen sulfide, hydrogen chloride, ammonium dithiocarbamate and thiourea have been investigated.

Infrared measurements[4] on I showed the presence of sharp peaks at 4.63 and 5.89μ which has been reported[5] as characteristic of an α-thiocyanoketone.

Thiourea, ammonium dithiocarbamate and hydrogen sulfide reacted with I to form 2-mercapto-4,5-dimethylthiazole (equation 1).

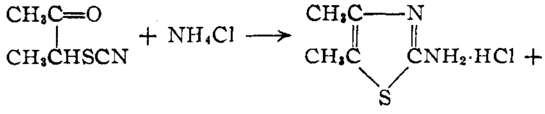


$$\begin{array}{l}CH_3C{=}O\\ \quad|\\ CH_3CHSCN\\ \quad\text{I}\end{array} + HS{-}R \longrightarrow \begin{array}{c}CH_3C{-\!-}N\\ \|\qquad\|\\ CH_3C\quad C{-}SH\\ \diagdown\;\diagup\\ S\end{array} + H_2O \qquad (1)$$

$$R = H,\ {-}\overset{\overset{NH}{\|}}{C}SNH_4 \text{ or } {-}\overset{\overset{NH}{\|}}{C}NH_2$$

The reaction with hydrogen chloride gave 2-hydroxy- and 2-chloro-4,5-dimethylthiazole as coproducts while with aqueous hydrogen chloride only 2-hydroxy-4,5-dimethylthiazole was isolated.

The reaction of I with aqueous ammonium chloride resulted in the formation of the hydrochloride of 2-amino-4,5-dimethylthiazole (equation 2). The ultraviolet absorption spectra have been determined[6] and are given in Fig. 1.



$$\begin{array}{l}CH_3C{=}O\\ \quad|\\ CH_3CHSCN\end{array} + NH_4Cl \longrightarrow \begin{array}{c}CH_3C{-\!-}N\\ \|\qquad\|\\ CH_3C\quad CNH_2{\cdot}HCl\\ \diagdown\;\diagup\\ S\end{array} + H_2O \qquad (2)$$

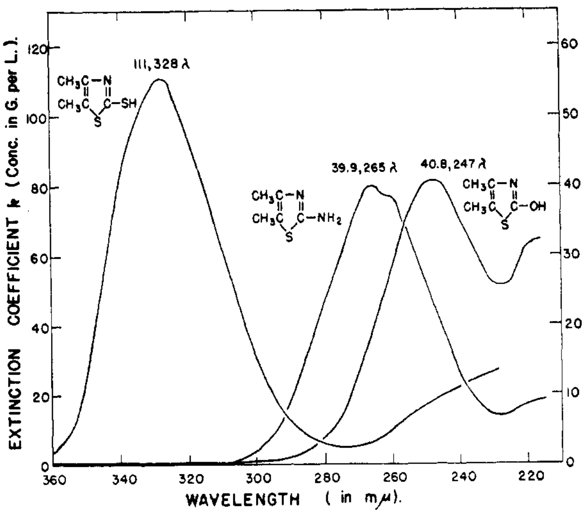


Fig. 1.

Experimental[7]

3-Thiocyano-2-butanone (I).—3-Chloro-2-butanone (319.5 g., 3.0 moles) was added dropwise to a vigorously stirred solution of sodium thiocyanate (284 g., 3.5 moles) in 600 ml. of water over a period of 3 hours during which time the temperature was maintained at 80°. After an additional hour or stirring the mixture was cooled to 25° and the water layer withdrawn. The product (a red oil) was washed twice with water (300 ml.). The unreacted chlorobutanone and dissolved water were removed by heating the crude product to 90° at a pressure of 30 mm. The product weighed 343 g. (89%). Distillation through a short column gave a light yellow liquid, b.p. 63–68° (0.5 mm.); yield 326 g. (84.2%). By careful redistillation the product can be obtained as a water-white mobile liquid, b.p. 58–59° (0.5 mm.), $n^{20}{}_D$ 1.4836, $d^{20}{}_4$ 1.1152, $d^{15}{}_4$ 1.1195; $[MR]^{20}{}_D$ 33.07 (found), 32.60 (calcd.).

2-Mercapto-4,5-dimethylthiazole. By the Reaction of I and (a) Hydrogen Sulfide.—An ethanol (200 ml.) solution of I (65 g., 0.5 mole) was placed in a stainless steel bomb (1 liter) and charged with hydrogen sulfide. The bomb was placed in a rocking mechanism and heated to 78°. The internal pressure fell from 2700 to 2100 p.s.i. The bomb was cooled and vented. The solid mush of crystals was removed and the mixture concentrated by heating the ethanolic solution. After dilution with hexane and cooling, the crystalline solid was recovered by filtration. The crude product weighed 38 g. (52.5%), m.p. 133–153°. Recrystallization from ethanol after treatment with decolorizing

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(1) (a) A. Hantzsch and J. H. Weber, *Ber.*, **20**, 3118 (1887); (b) A, Hantzsch and H. Schwaneberg, *ibid.*, **61**, 1776 (1928); (c) J. Tcherniac and T. H. Norton, *ibid.*, **16**, 345 (1883).

(2) (a) J. Tcherniac, *ibid.*, **25**, 2607 (1892); *J. Chem. Soc.*, **115**, 1071 (1919); (b) A. Hantzsch and H. Schwedler, *Ber.*, **60**, 2537 (1927).

(3) H. Andersag and K. Westphal, U. S. Patent 2,139,570.

(4) Determined by J. J. Shipman of this Laboratory.

(5) W. S. Emerson and T. M. Patrick, *J. Org. Chem.*, **13**, 722 (1948).

(6) Determined by E. Gregg and J. Efroymson of this Laboratory.

(7) All melting points are uncorrected.

carbon gave 23.5 g. (32.5%) of a yellow crystalline solid melting at 161–165°.

(b) **Thiourea.**—A solution of 15.2 g. (0.2 mole) of thiourea and 12.9 g. (0.1 mole) of I in water (200 ml.)–ethanol (50 ml.) and 42 ml. (0.5 mole) of concd. hydrochloric acid was heated at reflux (86°) for 10 hours. The solid crystalline precipitate that formed was recovered by filtration to give 9.3 g. (64.1%) of crude product melting at 158–162°. After two recrystallizations from ethanol–water (1–8) the light yellow solid melted at 161.5–164.5°. *Anal.* Calcd. for $C_5H_7NS_2$: C, 41.35; H, 4.86; N, 9.65; S, 44.15. Found: C, 41.52; H, 4.75; N, 9.64; S, 44.15.

(c) **Ammonium Dithiocarbamate.**—A 20% aqueous solution of ammonium dithiocarbamate (24 g., 0.25 mole) was added dropwise to a vigorously stirred suspension of I (25.8 g., 0.2 mole), hydrochloric acid (18.2 ml., 0.22 mole) and water (100 ml.). The temperature was maintained at 8–10° during the 1 hour period of addition. The light yellow, somewhat sticky solid which precipitated was recovered by filtration; repeated washing with hexane removed most of the impurities to give 16 g. (55%) of a white, crystalline compound melting at 157–160°. After further purification by extracting with benzene, the product melted at 160–162°.

2-Hydroxy-4,5-dimethylthiazole.—A mixture of 12.9 g. (0.1 mole) of I in water (150 ml.) and concd. hydrochloric acid (3.5 ml.) was heated at reflux (98°) for 11.5 hours. The white crystalline solid that formed when the solution was cooled was recovered by filtration. The solid (8 g.) melted at 140–146°. A further crop (1.2 g.) of slightly yellow crystals was obtained by concentrating the filtrate; yield 71.3%. Two recrystallizations from benzene gave large white crystals melting at 143–145°. *Anal.* Calcd. for C_5H_7NOS: C, 46.49; H, 5.46; N, 10.84; O, 12.39; S, 24.82. Found: C, 46.51; H, 5.46; N, 10.86; S, 24.87.

2-Chloro-4,5-dimethylthiazole.—Hydrogen chloride (95 g., 2.6 moles) was added to I (129 g., 1 mole) over a period of 1 hour at 20–30° while stirring the mixture. The resulting slurry was dissolved in 350 ml. of water, the water solution extracted three times with ether (100 ml. per extraction), and the ether solution was concentrated to give 96 g. of crude product. Hexane (100 ml.) was added to the crude product to precipitate 2-hydroxy-4,5-dimethylthiazole which had formed as a second product. There was obtained on distillation 74 g. (50%) of a colorless oil boiling at 49–53° (3 mm.), $n^{20}\text{D}$ 1.5307, d^{20}_4 1.233; $[MR]^{20}\text{D}$ 36.92 (calcd.), 37.02 (found).

Anal. Calcd. for C_5H_6ClNS: C, 40.68; H, 4.07; Cl, 24.03; N, 9.49; S, 21.73. Found: C, 40.98; H, 4.09; Cl, 23.73; N, 9.37; S, 21.71.

2-Amino-4,5-dimethylthiazole Hydrochloride.—A solution of 107 g. (2.0 moles) of ammonium chloride and 32.25 g. (0.25 mole) of I in water (200 ml.)–ethanol (100 ml.) was heated at reflux (85°) for 5.5 hours. The white crystalline product that formed on cooling was isolated by filtration. After single washes with ice-cold water and acetone the product on drying weighed 41 g. (100%), m.p. 250° (dec.). Further washing with ice-cold water (twice) and acetone (once) gave 26.1 g. (63.5%) of white crystals melting at 262–263° (dec.). *Anal.* Calcd. for $C_5H_9ClN_2S$: C, 36.47; H, 5.51; Cl, 21.54; N, 17.01; S, 19.47. Found: C, 36.50; H, 5.49; Cl, 21.59; N, 17.10; S, 19.49.

Acknowledgment.—The analyses of all compounds were made by James R. Kubik, Arthur K. Kuder and Huffman Microanalytical Laboratories. Sincere appreciation is expressed to James A. Early, Martin Smilek and Paul Rohrer for their assistance with some of the experimental work reported here.

BRECKSVILLE, OHIO RECEIVED OCTOBER 1, 1951

[CONTRIBUTION FROM THE WHITMORE LABORATORY, PENNSYLVANIA STATE COLLEGE]

Urea and Thiourea Adduction of C_5–C_{42}-Hydrocarbons

BY ROBERT W. SCHIESSLER AND DAVID FLITTER

Unbranched *n*-paraffins above hexane readily form crystalline complexes with urea at 25°. If the *n*-alkyl chain is sufficiently long, terminal cyclization does not prevent urea adduction, whereas a methyl group centered on a C_{13}-chain inhibits crystalline complex formation. Hydrocarbons widely differing in structure will form crystalline complexes with thiourea at room temperature if the cross-sectional dimensions of the molecule are 5.8 ± 0.5 Å. by 6.8 ± 0.3 Å. as estimated from measurement of the Fisher–Hirschfelder models. Thiourea adduct does not form readily if the molecular dimensions are near the tolerance limits, and such an adduct will be unstable. Phenyl groups appear to interfere with the formation of urea and thiourea complexes. Normal paraffin chains, attached to otherwise suitable structures, interfere with thiourea adduction.

The formation of crystalline complexes between certain hydrocarbons and urea[1,2] or thiourea[3] has been the subject of several recent investigations.[4–11] Since better definition of the hydrocarbon structural requirements for adduct formation is important to the understanding and utility of the processes, and since a great variety of hydrocarbons covering the C_5–C_{42} range is available in this Laboratory from the work of the American Petroleum Institute Research Project 42,[12] we have investigated the tendency of the latter to form adducts at 25° with the two reagents. Certain regularities have been noted, and, in the case of thiourea, empirical treatment based on measurements of Fisher–Hirschfelder models[13] has led to a new correlation of structure and adductibility.

A standardized test procedure was employed which differed slightly for the urea and thiourea experiments.

Experimental

1. **Reagents.**—Urea, C.P. Coleman and Bell, Norwood, Ohio. Thiourea, C.P. Coleman and Bell, Norwood, Ohio. Methanol, commercial synthetic, fractionally distilled in a glass helix-packed column of 40 plates, $n^{20}\text{D}$ 1.3296. Hydrocarbons, from A.P.I. Research Project 42, this Laboratory. Benzene, anhydrous commercial, to which was added half the amount of water needed for saturation at room temperature. Methyl ethyl ketone, Shell Chemical, technical.

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(11) A. E. Smith, *J. Chem. Phys.*, **18**, 150 (1950).

(12) Advisory Committee: H. Sutherland (Chairman), E. M. Barber, J. R. Bates, L. C. Beard, Jr., G. H. Denison, L. M. Henderson, R. G. Larsen, R. F. Marschner, J. H. Ramser. Presented before the XIIth International Congress on Pure and Applied Chemistry, New York, N. Y., September, 1951.

(13) Fisher Scientific Company, Pittsburgh, Pa.