

trimethyl derivative with triphenylchloromethane. Accordingly, 2.5 g. of the sirup was treated with 3.0 g. of triphenylchloromethane in 12 cc. of pyridine solution at room temperature for two days. The reaction mixture was then triturated with a small quantity of water to dissolve pyridine hydrochloride and the solution poured into an excess of rapidly stirred ice-water. The insoluble trityl derivative settled out as a gum along with residual reactant. After standing in the icebox with occasional stirring, the solution (A) was decanted from the granular residue. The latter, washed with fresh ice-water, dissolved in acetone, dried over magnesium sulfate, decolorized with norite, filtered and evaporated to a thin sirup, deposited crystals of triphenylcarbinol. The mother liquor, upon evaporation to a sirup (0.9 g.) and treatment with aniline (0.4 g.) in absolute ethanol under reflux for three hours, crystallized upon removal of solvent. Recrystallization from absolute ethanol gave the anilide of 2,3,4-trimethyl-6-trityl-galactose; yield, 0.7 g., m. p. 152°. (Found: OMe, 17.1. Calcd. for $C_{31}H_{37}O_5N$; OMe, 17.2).

The solution (A) containing unreacted 2,4,6-trimethyl-galactose was neutralized with silver carbonate and filtered. Silver ion was removed with hydrogen sulfide, and, after filtering, decolorizing with norite, and evaporating excess solvent, a sirupy residue was obtained; yield, 1.0 g. (Found: OMe, 52.2. Calcd. for $C_9H_{18}O_6$: MeO, 52.5).

The sirup, upon treatment with aniline (0.5 g.) in the usual manner crystallized upon removal of solvent. Re-

crystallization from ether-alcohol solution gave 2,4,6-trimethyl-galactose anilide; yield, 0.9 g., m. p. 178°. (Found: OMe, 31.4. Calcd. for $C_{15}H_{21}O_5N$: OMe, 31.4.)

Summary

1. Fractional distillation of the glycosidic sirup obtained upon methanolysis of arabo-galactan methyl ether yields three main fractions. These are, respectively, dimethyl-methyl-galactoside, trimethyl-methyl-galactoside, and a mixture of tetramethyl-methyl-galactoside and trimethyl-methyl-arabinoside.

2. Based upon the 6:1 molecular ratio of galactose to arabinose in the original polysaccharide, the molecular ratio of the glycosidic components is 3:1:2:1, respectively.

3. The arabinose component of arabo-galactan is joined to a tri-linked galactose residue.

4. The position of such linkage is through the 1 position of the arabinose component to the 6 position of the galactose residue.

(1) McCreath and Smith, *J. Chem. Soc.*, 390 (1939).

MOSCOW, IDAHO

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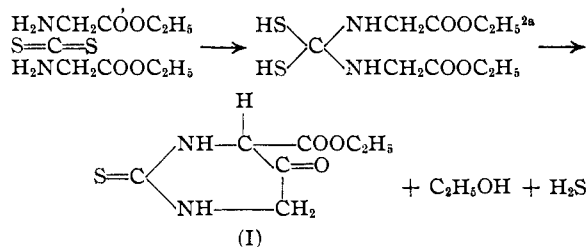
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine and Related Compounds

BY JOHN H. YOE AND GEORGE R. BOYD, JR.

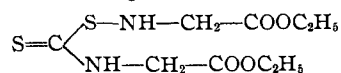
Sheppard and Brigham¹ described the preparation of a heterocyclic compound which gave a deep purple colored precipitate in the presence of silver ions and suggested that it might be used as a sensitive reagent for silver. Recently Yoe and Overholser² have employed this compound for the colorimetric determination of silver.

The compound, 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine, was prepared by the action of carbon disulfide on the ethyl ester of glycine. An intermediate product was formed, diethylaminoacetate dithiocarbamate, which upon further treatment with carbon disulfide eliminated hydrogen sulfide and ethyl alcohol, closing the ring and forming the desired product. The reaction as outlined by Sheppard and Brigham¹ is as follows



M. L. Huggins prefers to regard the structure (I) not as a closed heterocyclic ring, but as a chain which is chelated through a hydrogen bridge,³ thus

(2a) Sheppard and Brigham wrote the formula of this intermediate product with the following structure

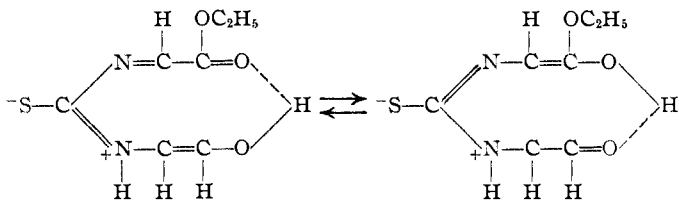


Consideration of the arrangement of the electrons about the atoms, however, suggests that the structure first given is more likely.

(3) Private communication to the authors from Dr. S. E. Sheppard, Eastman Kodak Company.

(1) S. E. Sheppard and H. R. Brigham, *THIS JOURNAL*, **58**, 1046 (1936).

(2) J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 148 (1942).



The compound prepared in this manner is an orange solid which is very soluble in aniline, phenol, thymol, and hot ethylenechlorhydrin. It is soluble in hot acetophenone and slightly soluble in acetone, acetic acid, and hot benzene. It is insoluble in carbon tetrachloride, ligroin, and water. Its melting point is 276–280°.

In an attempt to confirm the structure of this silver reagent, Sheppard and Brigham¹ attempted to synthesize it by the condensation of thiourea with α,γ -dichloroacetate, but obtained only "a red oil which could not be crystallized."

First attempts to synthesize the compound in this Laboratory were made according to the published directions of Sheppard and Brigham,¹ but as the reaction gives only very small yields (on the order of 1%) and since only small amounts of ethyl glycinate were used, it was impossible to isolate any crystalline material by this means.

In a private communication to the authors, Sheppard and Brigham revised their procedure slightly, saying that it gave somewhat higher yields than their older one. Both procedures required the use of absolute alcohol, but it has been found in this Laboratory that the presence of a small amount (1%) of water in the alcohol is essential for the preparation of the cyclic compound.

Preparation of 2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine.—The best method of synthesis was found to be as follows: 50 g. of ethyl glycinate hydrochloride was suspended in 25 ml. of water in a separatory funnel and 30 ml. of a 40% solution of sodium hydroxide was added while shaking and cooling under running water. This was saturated with anhydrous potassium carbonate and then extracted with ether, using four 25-ml. portions. The extract was allowed to dry over anhydrous potassium carbonate for twenty-four hours. At the end of this time, the potassium carbonate was filtered off and washed twice with ether that had been dried over sodium. The filtrate was cooled in ice.

Eight milliliters of carbon disulfide was added to the ether solution of ethyl glycinate while stirring and cooling in ice. The diethylaminoacetate dithiocarbamate settled out as an oil and froze to a white solid upon further cooling. The ether was decanted and poured on 50 ml. of 99% alcohol at once (the intermediate product changed into a red oil upon prolonged contact with the air); 2 ml. of carbon

disulfide was added and the solution was refluxed for forty-eight hours.⁴ At the end of this time, the solution was quite dark in color. When the solution was cooled in ice and stirred, a large amount of precipitate appeared and was filtered off. The solution from this precipitation was evaporated to about one-half of its original volume; an orange red precipitate settled out, and this was filtered off and recrystallized from ethylene chlorhydrin. The compound so formed melted at 275° and gave a very intense purple color when a 0.025% solution in acetone was treated with silver nitrate solution. The amount of the orange compound thus obtained was about 0.3 g.

Following the same procedure except for the use of absolutely dry reagents (absolute alcohol was prepared by distilling alcohol dried over lime from sodium methylate and ethyl phthalate; carbon disulfide dried over "Drierite") and with the reactions carried out in an atmosphere of nitrogen, a yellow compound was obtained. This compound was purified by recrystallizing from dioxane. The melting point was 181° and the compound gave a red color reaction with silver.

If more than 1% of water is present in the alcohol, the yield of (I) is decreased; only about 150 mg. was obtained using alcohol containing 1.5% of water.

Additional Compounds

Since the above procedures for the synthesis of the silver reagent gave, at best, only very poor yields of the desired product, several related compounds were prepared in an attempt to find some compound which would be comparable in sensitivity toward silver, but which could be more easily prepared. The starting material in every case was diaminoacetone which was synthesized from citric acid by the method of Kalischer⁵ as improved by Koessler and Hanke.⁶

The diamine, in the form of its dihydrochloride, can be purified by recrystallizing from water. *Anal.* Calcd. for $C_3H_8ON_2 \cdot 2HCl$: N, 17.39. Found: N (Dumas), 17.24; (Kjeldahl), 17.31.

Diaminoacetone is quite reactive and can be coupled with several reagents to give cyclic compounds. These were investigated as possible sensitive reagents for silver.

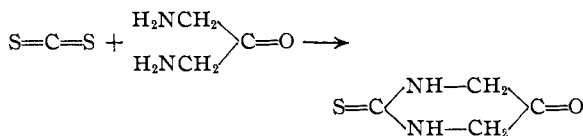
Van Alphen⁷ has shown that diamines react with carbon disulfide forming cyclic compounds, and so it was thought that diaminoacetone should react with carbon disulfide according to the scheme.

(4) S. E. Sheppard reports that the yield of 2-thio-5-keto-4-carb-ethoxy-1,3-dihydropyrimidine may be greatly increased by adding hydrogen peroxide in aqueous solution just before refluxing the alcoholic solution of diethylaminoacetate dithiocarbamate. In one experiment in which 20 ml. of 2.5% aqueous solution of hydrogen peroxide was added to 80 ml. of an alcoholic solution of the dithiocarbamate (obtained from 13 g. of ethylglycinate hydrochloride) before refluxing, a 12.6% yield of the purified orange compound was obtained. This is about a ten-fold increase in the yield previously obtained. Stronger solutions of hydrogen peroxide and also sodium peroxide are now being tried. Private communication from Dr. S. E. Sheppard.

(5) G. Kalischer *Ber.*, **28**, 1519 (1895).

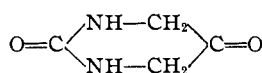
(6) K. K. Koessler and M. T. Hanke, *THIS JOURNAL*, **40**, 1716 (1918).

(7) J. Van Alphen, *Rec. trav. chim.*, **55**, 412 (1936).



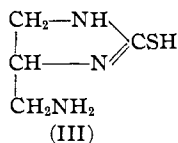
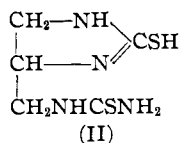
Diaminoacetone dihydrochloride was dissolved in hot alcohol and hot alcoholic sodium hydroxide then added in sufficient quantity to neutralize all hydrochloric acid. An equivalent amount of carbon disulfide was then poured into the solution, causing a vigorous reaction. A brown precipitate formed immediately, which was filtered off and dried at 110°. This compound gives a white precipitate with silver ions which decomposes into silver sulfide upon standing.⁸ The compound decomposes without melting at about 150°.

Chloroformic ester was added to a hot alkaline solution of diaminoacetone, yielding a white precipitate which Rügheimer and Mischel⁹ say is probably a derivative of urea having the formula



This compound gives a white precipitate with silver ions.

According to Pyman¹⁰ two products are obtained when diaminoacetone is treated with potassium thiocyanate



Diaminoacetone dihydrochloride was heated on a water-bath for ninety minutes with the theoretical amount of potassium thiocyanate causing the formation of a white precipitate. The two products were separated by heating

(8) Sheppard and Brigham¹ also prepared this compound by another method and report this reaction with silver.

(9) S. E. Rügheimer and E. Mischel, *Ber.*, **25**, 1562 (1892).

(10) F. L. Pyman, *J. Chem. Soc.*, **99**, 668 (1911).

with water in which most of the precipitate dissolved leaving only a small residue. This residue, which melts at 212° with decomposition, is only very slightly soluble in acetone and alcohol. In acid solution, however, it gives a yellow precipitate with silver ions. This seems to be compound (II).

If the aqueous solution is allowed to crystallize, another compound is obtained which darkens at 240° but does not melt even when heated to 350°. This compound gives a white precipitate with silver and presumably is compound (III).

It is apparent from the reactions of the various compounds with silver ions that those with simpler structures give white or light colored precipitates and that only compound (I) gives a highly colored precipitate and hence is the most sensitive reagent for silver.

Rhodanine, which is closely related to these compounds, behaves in an analogous manner. Thus, Feigl¹¹ found that the condensation product of rhodanine with *p*-dimethylaminobenzaldehyde gave a more highly colored precipitate with silver ions than did rhodanine itself.

Acknowledgment.—Our thanks are expressed to Professors Robert E. Lutz and Alfred Burger for helpful suggestions during the course of this investigation.

Summary

2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine has been prepared by a modification of the Sheppard and Brigham method. Several related compounds have also been made. The reactions of these compounds with silver ions have been studied; only the former is a sensitive reagent for silver.

(11) F. Feigl, *Z. anal. Chem.*, **74**, 380 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Adsorption of Organic Compounds. I. Adsorption of Ampholytes on an Activated Charcoal*

BY VERNON H. CHELDELIN AND ROGER J. WILLIAMS

During recent years charcoal adsorption has become an important operation in the purification of materials of biological importance. It has been especially useful in the concentration and isolation of several of the water-soluble vitamins, the wound hormone traumatin¹ and the amino acid methionine.²

Amino acids as a class might be expected to be adsorbed considerably less than the parent car-

boxylic acids, due to their salt forming properties and high water solubilities. A few experiments by Phelps and Peters³ and Bartell and Miller⁴ indicate that glycine and alanine are not adsorbed at all on Norite or sugar charcoal, and that aspartic acid and glutamic acid are only slightly adsorbed, with a maximum near the isoelectric point. Ito⁵ observed marked adsorption of the

(3) Phelps and Peters, *Proc. Roy. Soc. (London)*, **124A**, 554 (1929).

(4) Bartell and Miller, *THIS JOURNAL*, **45**, 1106 (1923).

(5) Ito, *J. Agr. Chem. Soc., Japan*, **12**, 204 (1936); through *Chemical Abstracts*, **30**, 6265² (1936).

* Original manuscript received August 5, 1941.

(1) English and Bonner, *J. Biol. Chem.*, **121**, 791 (1937).

(2) Mueller, *Proc. Soc. Exptl. Biol. Med.*, **18**, 14 (1921).