

SOME REACTIONS OF THE UREAS.

A thesis submitted to the Department of Chemistry
and the Faculty of the Graduate School in partial fulfillment
of the requirements for the Master's degree.

By

Harry A. Geauque

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B I B L I O G R A P H Y .

J. Chem. Soc., 21, 181; 22, 181.

Berichte, 31, 138; 14, 1490;

Ann., 195, 159; 206, 30.

J. pr., (2) 32, 21; (2) 49, 35.

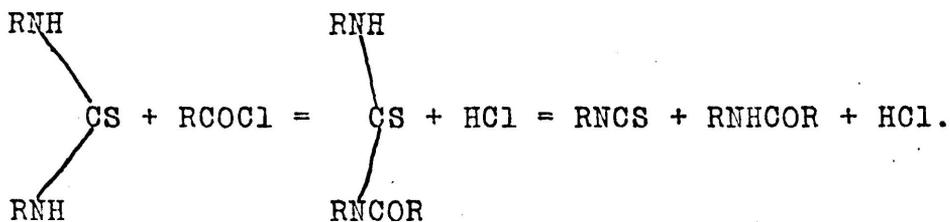
Ph. Ch., 16, 715.

Berichte, 2, 688; 43, 3214.

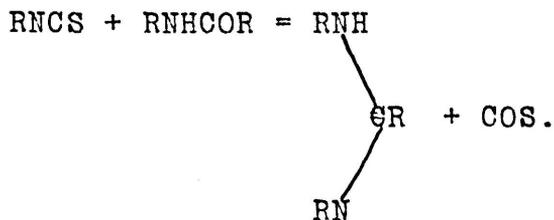
Berichte, 12, 1436; 14, 343.

The object of the work described in this paper to find out the reactions involved in treatment of ureas and substituted ureas with certain reagents containing halogens.

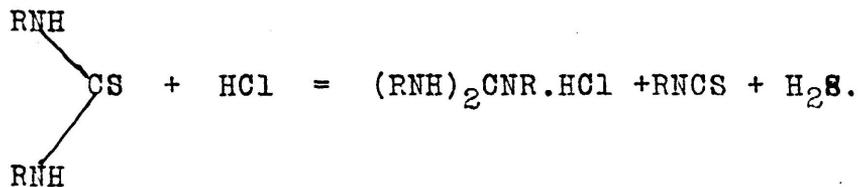
In a paper⁺, Doctor F. B. Dains gives some interesting results obtained by the action of acid chlorides on ureas, which can be formulated as follows:-



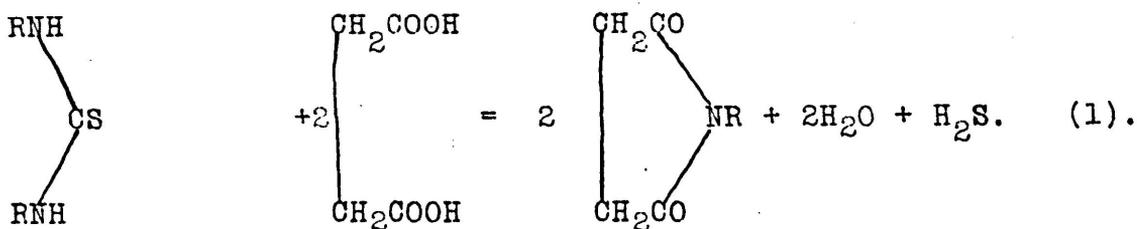
Mustard oil and an acyl anilide were the main products, while occasionally small quantities of an amidine base was formed.



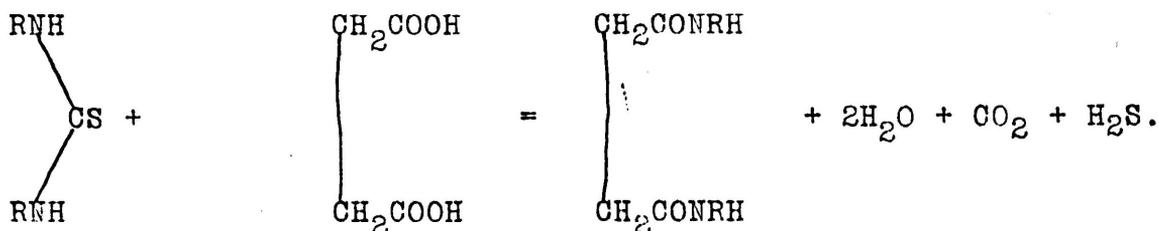
The question whether the reaction would go the same way if diphenyl urea chloride was used instead of the acyl chloride. This was tried but product was principally guanidines and mustard oil, and decomposition took place to a large extent.



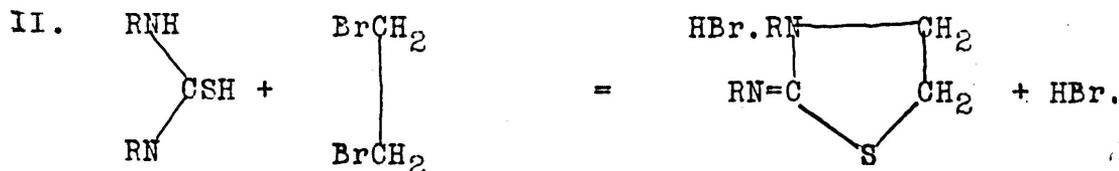
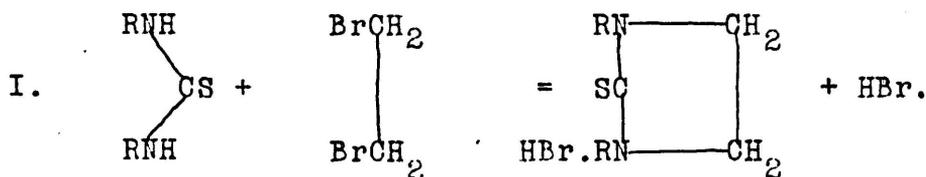
In the same paper⁺, Dr. Dains gives a general equation for the reaction with dibasic acids as follows:-



+Jour. Amer. Chem. Soc., XXII, 181.



If reagents were used which contained a halogen in place of the carboxyl group, then the reaction might go in the same way and the acid of the halide be formed in place of water. The reactions that might take place can be formulated as follows:-



In the case of ethylenbromide the reaction goes according to reaction II, but in the case of oxalchloride the reaction goes according to reaction I. A number of reagents, which, it was thought should react in the same way, were heated with substituted ureas, but decomposition and the action of the

acid given off evidently prevented such action.

The reactions with ethylenbromide and oxalchloride were the only ones that seemed to go quantitatively. The melting points were taken with ordinary laboratory thermometers and were not corrected, and in some cases were three or four degrees off, but in these cases the readings were checked by the readings taken with pure substances on hand in the laboratory. The reagents used were Kahlbaum standard reagents. Liquid reagents were in each case fractionated and redistilled before use.

DI-METAXYLYL THIOUREA and DIPHENYL UREA CHLORIDE.

10 grams of dimetaxylyl thiourea were mixed with 8.2 grams of diphenyl urea chloride and heated in a flask with reflux condenser on an oil-bath, to 110° for about three hours. A gas was given off which gave an acid reaction.

The product was distilled with steam and xylyl mustard oil was distilled over. The residue was heated with dilute HCl and filtered, and then made alkaline with NaOH solution. A base was precipitated which was filtered off and recrystallised several times from alcohol. m.p. 235° -xylyl guanidine. The residue was extracted with cold alcohol but no crystalline product could be obtained from this solution.

The residue which melted at 88° was unchanged diphenyl urea chloride.

The reaction seemed to be similar to the reaction of a substituted thio urea with HCl. The principal products

alcohol and finally from gasoline which gave a crystalline compound. This melted at 190° but there was very little of it, and not enough to identify.

The products were used up by continued recrystallization in an attempt to get them pure. There seemed to be considerable decomposition.

The reaction is probably very complicated. The principal products formed were:-

Phenyl mustard oil - C_6H_5NCS .

Diphenyl urea - $(C_6H_5NH)_2CO$.

Diphenyl guanidine - $(C_6H_5NH)_2C:NH$.

MONOPHENYL THIOUREA and DIPHENYL UREA CHLORIDE.

The above reaction was carried out again using 19 grams of monophenyl thiourea and 17.5 grams of diphenyl urea chloride. It was thoroughly mixed and heated as before in a flask with a reflux condenser on the oil-bath, at 110° for nearly three hours and then the temperature was raised to 140° for about 15 minutes.

The product was extracted with chloroform and filtered. The residue was extracted with gasoline and a very small amount of crystalline substance was obtained melting at 252° , this was not a sufficient quantity to identify.

The chloroform extract was steam distilled. The residue was treated with dilute HCl solution, and filtered hot. A compound separated which melted at 52° and was diphenyl amine. The solution was then made alkaline with NaOH solution. The remainder of the residue was extracted with gasoline, and a

compound was obtained which first melted at 45° and was found to be diphenyl amine the same as above. The residue was recrystallised and melted at 88° and was found to be diphenyl urea chloride.

The steam-distillate was filtered and NaOH solution added. Phenyl isocyanide was found here.

This reaction, is probably very complicated. The principal products of the reaction are:-

Diphenyl amine, diphenyl guanidine, diphenyl urea chloride and phenyl mustard oil.

MONOPHENYL THIOUREA and DIPHENYL UREA CHLORIDE.

Heated 25 grams of monophenyl thiourea and 15 grams of diphenyl urea chloride, to 120° on an oil-bath, with an air condenser until no bubbles were seen.

Gas - The gas was slightly acid and gave a slight test for sulphide. It did not give a test for CO_2 . It was probably COS.

Residue - The residue was a soft brown wax. It was steam distilled and the residue filtered and NaOH solution added. The basic compound was recrystallised from alcohol and melted at 145° . The sulphur test was negative. The compound was found to be diphenyl guanidine. The residue was then extracted with hot water and cooled. A small precipitate came down which melted at 148° and was monophenyl thiourea. The remainder of the residue was extracted with alcohol but no crystallin compound was obtained. The residue insoluble

in alcohol melted at 260° was a white powder but was obtained in very small quantities.

The steam distillate contained phenyl mustard oil. It did not give a test for diphenyl amine. It was made alkaline with NaOH solution but no solid was obtained.

This reaction was very complicated. The principal products of the reaction were:-

Diphenyl guanidine, phenyl mustard oil and monophenyl thiourea.

MONOPHENYL UREA and DIPHENYL UREA CHLORIDE.

13 grams of monophenyl urea and 15 grams of diphenyl urea chloride were heated on an oil-bath with an air condenser, for three hours at 120° . The product was extracted with water and filtered. The residue was dissolved in alcohol but no crystalline product was obtained. The water extract was made alkaline with NaOH solution. A base was obtained which melted at 58° and was recrystallised from alcohol and melted at 65° . The picrate melted at 75° .

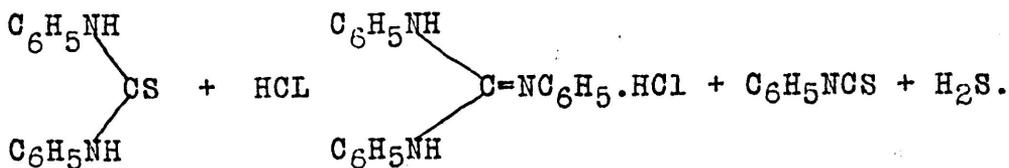
Dissolved the residue in alcohol and crystals came out on standing which melted at 175° . Extracted the crystals with HCl solution and the residue melted at 205° . The filtrate a strong diphenyl amine test. Extracted the residue with chloroform and the compound melted at 227° . Recrystallised this from alcohol and it melted at 235° and diphenyl urea.

Nothing could be obtained from the residue insoluble in alcohol which was all, or nearly so, inorganic.

The mixture was a red, wax-like fum which was very hard at room temperature. Water was added and the mixture boiled and filtered. Nothing could be obtained from the residue except a very small amount of diphenyl thiourea.

The water extract was made alkaline with NaOH solution which precipitated a base. This melted at 139° and was triphenyl guanidine.

Evidently HCl was liberated in the decomposition of the dichlorhydrin and this acted upon the diphenyl thiourea forming the guanidine. The strong disagreeable odor was partly due to the phenyl mustard oil present.



The basic compound which was obtained was analysed and found to be as stated triphenyl guanidine. The platinum salt was used for the analysis.

Analysis for $(\text{C}_{19}\text{H}_{17}\text{N}_3)_2\text{H}_2\text{PtCl}_6$.

Theoretical -----23.88% Pt.

Analysis I.-----23.83% Pt.

Analysis II.-----23.07% Pt.

ANILINE AND DICHLORHYDRIN.

14.5 grams of aniline and 10 grams of dichlorhydrin were heated on an oil-bath at 160° for about an hour. The resulting mixture was very hard gum-like, translucent red mixture. This was extracted with water and boiled.

Nothing could be obtained from the residue.

The extract was made alkaline with NaOH solution and a white precipitate came down which turned brown and then a purple shade. A rather large quantity of oil thus separated out which had an odor like that of quinoline. This was steam distilled and a clear oil came over which was aniline.

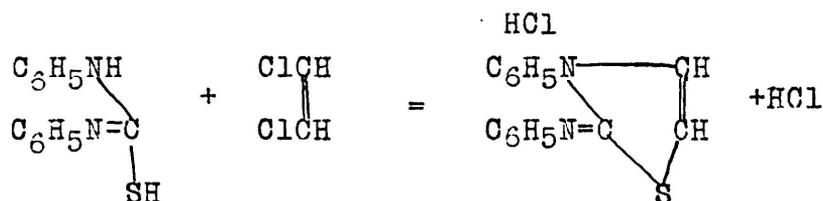
At the end of the reaction, the aniline must have been present as the hydrochloride. The only source of hydrochloric acid possible was from the dichlorhydrin. The dichlorhydrin, therefore, must have broken down liberating hydrochloric acid. As to the rest of the decomposition products nothing definite could be obtained and the product had the appearance of some carbonixation and decomposition in general.

ACETYLENDICHLORIDE AND DIPHENYL THIOUREA.

Heated 20 grams of diphenyl thiourea and enough acetylendichloride to moisten it well which was about equal weight, 20 grams, on the water bath with a reflux condenser for about two hours.

There was no change found. The mixture was insoluble in water but very soluble in hot alcohol. The compound crystallised from alcohol in shining plates which melted at 151° . A mixture with diphenyl thiourea melted at 151° . It was the original substance and evidently no change had taken place.

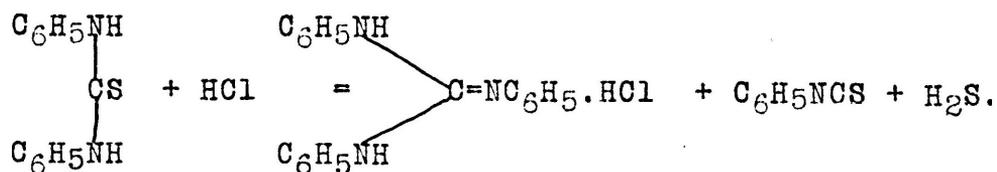
As in the experiment above the diphenyl thiourea and dichlorhydrin were heated together with the possibility that they would unite as:-



DIPHENYL THIOUREA AND ACETYLENDICHLORIDE.

20 grams of diphenyl thiourea and 10 grams of acetylendichloride were heated in a bomb tube, at 140°, for one and 1/4 hours. The tube was then opened by heating an end and the gas evolved gave an illuminous flame, which was possibly acetylene. The material in the tube was a reddish-brown liquid H₂S was recognized by its odor. The liquid was poured off and steam distilled. The distillate contained phenyl mustard oil. The residue was filtered and made alkaline with NaOH solution and a base came down that melted at 136° and triphenyl guanidine. Considerable amount of crystalline were separated from the original liquid which melted at 155° and was the original diphenyl thiourea.

Evidently HCl is liberated and this acts upon the diphenyl thiourea as:-



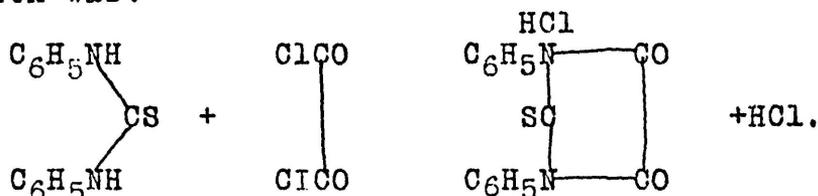
DIPARATOLYL THIOUREA AND ACETYLENDICHLORIDE.

17 grams of diparatolyl thiourea and 8 grams of acetylen-dichloride were heated in a bomb tube at 150° for one and one-half hours. Pyridine was added to take up the HCl that might be formed. The tube was opened by heat. HCl was added to dissolve the pyridine and the residue melted at 176° and

and was the original diparatolyl thiourea.

DIPHENYL THIOUREA AND OXALYLCHLORIDE.

15 grams of diphenyl thiourea and 8 grams of oxalylchloride were mixed. The reaction was immediate but not very fast. The diphenyl thiourea and oxalylchloride were both in benzene solution. The product was steam distilled to get rid of the benzene. The product was recrystallised from hot alcohol and melted at 202° . This was 2-Thiocarbonyl-,5-Dike to-1,3,-Diphenyltetrahydroimidazol#. The reaction was:-



M. V. Stojentin⁺ prepared this compound by heating together diphenyl thiourea and ethyloxalylchloride and gives this formula. Hoffman² gives the melting point as 204° .

Ber. 31,138.

+ Jour. fur Praktische Chemis, (2) 32, 1.

2 Ber. 2, 138. (688)

DIPHENYL THIOUREA and OXALYLCHLORIDE.

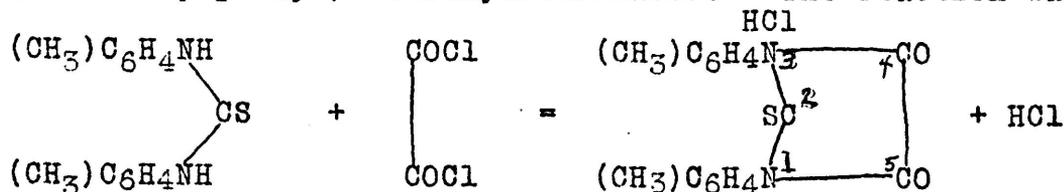
15 grams of diphenyl thourea and 8 grams of oxalylchloride in benzene solutions were mixed with two mols of pyridine. The product was then steam distilled to get rid of the benzene and pyridine. The residue was

recrystallised from alcohol. Yellow crystals were obtained which melted at 202° , the same as before.

There was a very small amount of a white residue which melted at 243° but not enough for identification.

DIPARATOLYL THIOUREA AND OXALYLCHLORIDE.

20 grams of diparatolyl thiourea and 10 grams of oxalylchloride and two mols of pyridine were added together as benzene solutions. The product was steam distilled to get rid of the benzene and pyridine. The product was then recrystallised from hot alcohol and melted at 235° . It was 2-thiocarbonyl -4,5 -oiketo - 1, 3 - di (4 - methylphenyl) tetrahydroimidazol.+ The reaction was:--



This compound is described by Rudolf Andreasch[#], who gives the melting point as 236° .

It is slightly soluble in water and alcohol and very soluble in benzene. It crystallises as bronze needles.

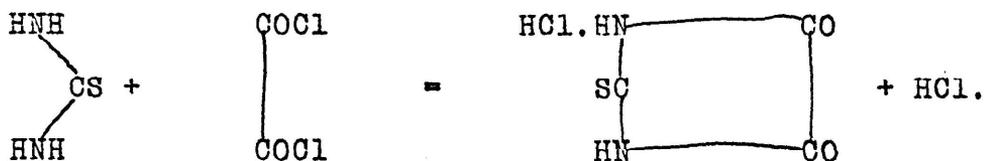
+ C 1899, II, 806.

Ber. 31, 138.

THIOUREA AND OXALYLCHLORIDE.

15 grams of thiourea were dissolved in benzene and two mols of pyridine were added. Then a benzene solution of oxalylchloride were added using 9 grams of the chloride. This was carried out in a freezing mixture. It was then steam

distilled to get rid of the benzene and pyridine. The product was then recrystallised from hot water. The melting point was 154° , and yield was small. The product was 2-thiocarbonyl-4,5-diketotetrahydroimidazol⁺. The reaction was:-

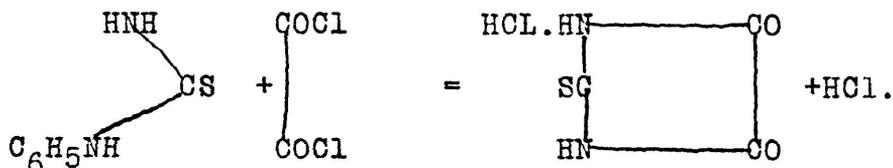


This compound has been prepared by Michael⁺, who does not describe it.

It crystallises as yellow needles.

MONOPHENYL THIOUREA and OXALYLCHLORIDE.

15 grams of monophenyl thiourea were dissolved in benzene and two mols of pyridine were added and then a benzene solution of 12 grams of oxalylchloride were added in benzene solution. This was carried out in a freezing solution. The mixture was then steam distilled to remove the benzene and the pyridine. The product was then recrystallised from hot water. The compound melted at 133° , and was 2-thiocarbonyl-4,5-diketo-1-phenyltetrahydroimidazol². The reaction was:-

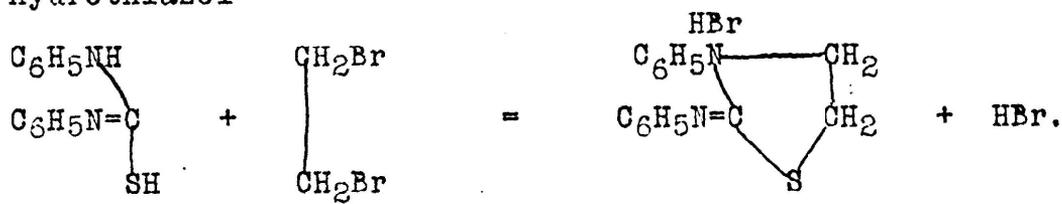


This compound was made by Hector² by treating diphenylthiourea cyanide with HCl.

It is slightly soluble in alcohol and crystallises in yellowish-golden needles.

DIPHENYL THIOUREA and ETHYLENBROMIDE.

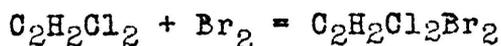
15 grams of diphenyl thiourea and 11 grams of ethylenbromide were heated on the oil-bath at 130° for one and one-half hours. Dissolved the entire product in water and made alkaline with NaOH and a base precipitated. This was recrystallises from gasoline. It was a white crystalline compound melting at 135° . This product was 2-phenylinido-3-phenyltetrahydrothiazol⁺. The reaction was:-



This compound is described by W. Will[#], who gives the melting point as 136°

DIPHENYL THIOUREA and DIBROM-DICHLOR-ETHANE

Dibromidichlorethane was prepared by adding, to 50 grams of acetylene dichloride, 93 grams of bromine. This was then fractionated.



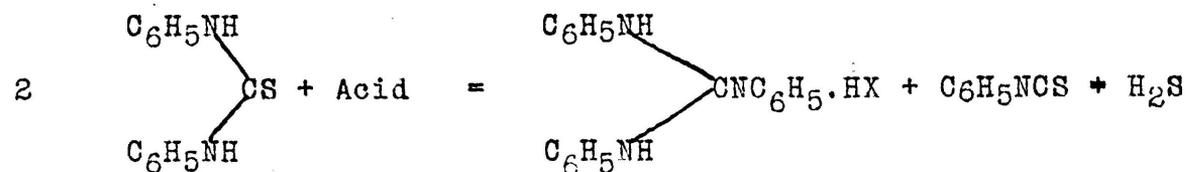
20 grams of diphenyl thiourea and 18 grams of dibrom-dichlorethane were heated at 160° , for one and one-half hours. The product was extracted with water and filtered. The product was made alkaline with NaOH solution and a base was precipitated. Recrystallises from alcohol and it melted at 143° . This was shown to be triphenyl guanidine by mixing with pure triphenyl

guanidine; the melting point did not change.

The residue was dissolved in alcohol and then recrystallised from benzene, when it melted at 152°. This was found, in the same way to be diphenyl thiourea, for when it was mixed with pure diphenyl thiourea the melting point did not change. Phenyl mustard oil was recognised by the odor.

Evidently the only change that took place was that caused by the acid liberated when the dibrom-dichlor-ethane broke down. There was indication of a little decomposition.

The chief reaction was:-



DIPHENYL THIOUREA and DIBROM PHENYL PROPIONIC ACID.

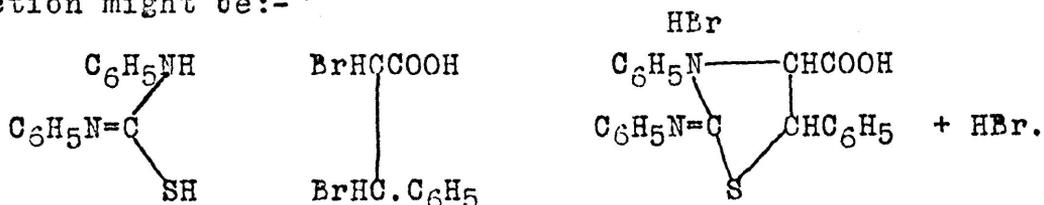
B-Dibrom-B-phenyl-propionic acid was prepared by adding 53 grams of bromine to a solution of 50 grams of cinnamic acid. They reacted rapidly and the product was recrystallised. It melted at 195°.

10 grams of diphenyl thiourea and 12 grams of the brom-acid were heated together, 160° for about two hours. The product was dissolved in water and filtered. The filtrate was made alkaline with NaOH solution and a base separated which was recrystallised and melted at 143°. This was found to be triphenyl guanidine by mixing with the pure substance and the melting point did not change.

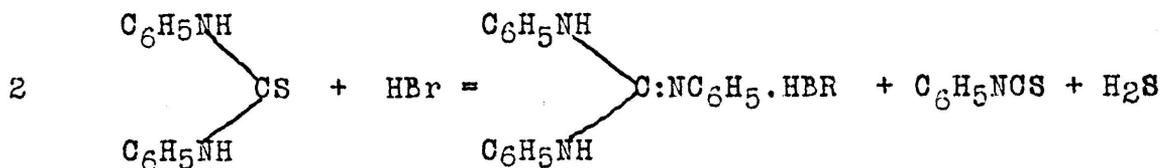
The residue was treated with NaOH solution and an acid

was obtained which melted at 133° and was found, by mixing with pure compound in the laboratory, and the melting point did not change, to be cinnamic acid. Some unchanged diphenyl thiourea was obtained also.

This reaction was undertaken with the possibility that the reaction might be:-



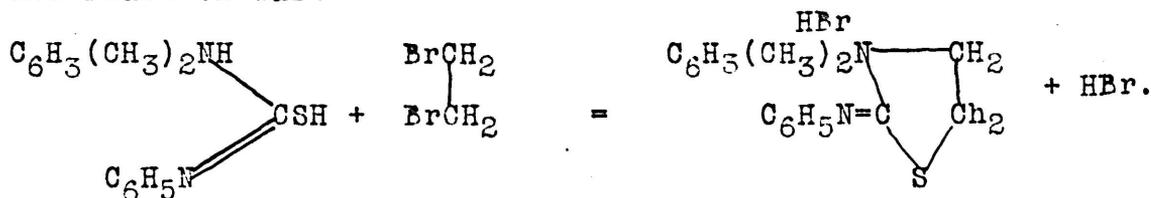
Evidently, however the reaction was that of HBr upon the diphenyl thiourea and giving cinnamic acid as one of the products.



PHENYL METAXYLYL THIOUREA and ETHYLENE BROMIDE.

12 grams of phenyl metaxylyl thiourea and 9 grams of ethylene bromide were heated on the oil-bath at 160° , for about one and one-half hours. The resulting product was dissolved in water and it nearly all dissolved. The water solution was made alkaline and a basic product was precipitated. This was recrystallised several times from alcohol and then from gasoline several times and a crystalline compound was obtained which melted at 86° . The picrate melted at 151° . It was treated with molar quantities of platonic chloride using acetic acid and then chloroform, but no crystalline compound was obtained.

The reaction was:-



This was analysed for Nitrogen (Kjeldahl). as $\text{C}_{17}\text{H}_{18}\text{N}_2\text{S}$:-

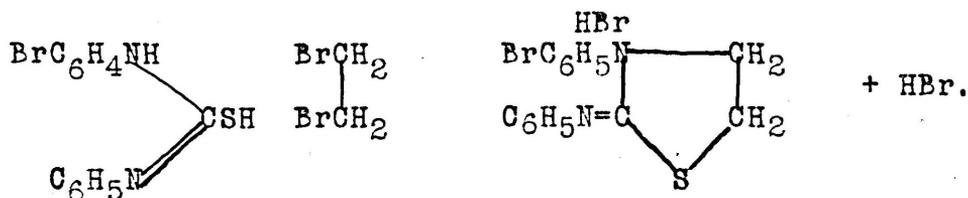
Theoretical-	9.93%
I. Found-	-10.06%
II. Found-	-10.53%

According to previous nomenclature this compound should be 2-phenylimido-3-metaxylyltetrahydrothiazol. Nothing could be found in the literature in regard to this compound. This was heated in the bomb furnaces at 140° for 3 hours. A slight test for aniline was gotten but most of the original compound was obtained from the product.

METABROM⁺DIPHENYL THIOUREA and ETHYLENE BROMIDE.

12 grams of metabrom-diphenyl thiourea and 10 of ethylene bromide were heated on the oil-bath at 120° - 130° for one and one-half hours. The product was dissolved in water and the solution made alkaline with NaOH solution. A base was precipitated which was recrystallised from gasoline, and melted at 163° .

According to the reactions above this reaction should be:-



The product should be 2-phenylimido-3 metabrom- phenyl-tetrahydrothiazol.

In conclusion, I wish to thank Doctor F. B. Dains for his many helpful suggestions during this work.

Chemical Laboratories,

University of Kansas.

May 15th., 1915.