

(CH₃).NH₂.—This transformation was accomplished by reduction with sodium and alcohol. The hydrochloride of the diamine was obtained in the form of plates melting at 223°. It was purified by crystallization from absolute alcohol. The salt is very soluble in water, moderately soluble in absolute alcohol and insoluble in ether and benzene.

Calc. for C₈H₁₄N₂.HCl: N, 20.2. Found: N, 20.5, 20.2.

Reduction of 2-Thio-4-methyl-6-oxypyrimidine. The Formation of 1,3-Diaminobutane, NH₂.CH₂.CH₂.CH(CH₃).NH₂.—The thiopyrimidine was prepared according to the directions of List.¹ Five grams of the pyrimidine were suspended in 100 cc. of absolute alcohol and 20 g. of sodium gradually added. Ammonia was evolved and 150 cc. of alcohol were finally added to complete the solution of the sodium. The amine was removed by distillation with steam and converted into its hydrochloride. We obtained 1.9 g. of the salt melting at 165–167°. A mixture of this with some pure hydrochloride of 1,3-diaminobutane melted at the same temperature. The hot alkaline solution remaining after the steam distillation was filtered and neutralized with hydrochloric acid. On cooling, 2 g. of unaltered 2-thio-4-methyluracil were recovered.

Diurea of 1,3-Diaminobutane, NH₂CONH.CH₂.CH(CH₃).CH₂.NH.CO.NH₂.—One-half gram of the hydrochloride of 1,3-diaminoisobutane was dissolved in 10 cc. of water and one gram of silver cyanate added. The mixture was then digested on the steam bath for 15–20 minutes and the silver chloride separated by filtration. The urea was obtained by evaporation to dryness and purified by crystallization from alcohol. It separated in the form of clusters of distorted needles melting at 172°.

Calc. for C₆H₁₄O₂N₄: N, 32.16. Found: N, 32.09.

Picrate of 1,3-Diaminobutane.—This salt crystallizes from hot water in the form of yellow needles which melt at 240–245° with decomposition.

Calc. for C₄H₁₂N₂(C₆H₃O₇N₃)₂: N, 20.51. Found: N, 20.24.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

**RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES. X.
THE UTILIZATION OF TETRACHLOROMETHYLMER-
CAPTAN FOR THE PREPARATION OF
ALKYL ISOTHIOCYANATES.²**

BY TREAT B. JOHNSON AND E. HEATON HEMINGWAY.

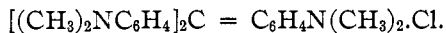
Received July 7, 1916.

Tetrachloromethylmercaptan VI, and amines combine to give representatives of an interesting class of compounds which have not been

¹ *Loc. cit.*

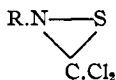
² This paper and also that entitled "Ethyl Isothiocyanacetate" (THIS JOURNAL, 38, 1550) were constructed from a dissertation presented by Earl Heaton Hemingway to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

very thoroughly investigated. The chlorine attached to sulfur is the reactive halogen atom of the mercaptan, and is removed by the action of amines, giving hydrochloric acid and almost quantitative yields of sulfamides. The anilide represented by Formula VII, is a representative of the type of compounds formed. This reaction was discovered by Rathke¹ in 1870 and later applied by him successfully for the preparation of the sulfanilide, VII, and the corresponding *o*- and *p*-sulftoluides. No analyses, however, were reported. With dimethylaniline, tetrachloromethylmercaptan interacts with formation of methylviolet,²

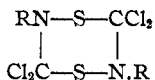


This process was patented in 1885³ and the reaction applied with eleven different tertiary amines.

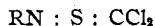
According to Rathke the sulfur combinations represented by Formula VII, are characterized by their behavior on heating and their action on alkalis. When subjected to the action of potash in alcoholic solution they lose a molecule of hydrochloric acid and are converted smoothly into unstable substances whose structure has never been established with certainty. Rathke suggested the two Formulas I and II, while Beilstein⁴ expresses the constitution of these compounds according to both Formulas I and III. The second characteristic reaction is that which



(I).



(II).



(III).

takes place by application of heat. Under such conditions Rathke states that the sulfanilides break down with formation of volatile products and sulfur combinations possessing the odor of mustard oils. These latter compounds were never identified by him and, so far as we are aware, no one has established experimentally the correctness of Rathke's assumptions. The primary object of our work was to reinvestigate this reaction and determine whether sulfanilides actually undergo such an unique rearrangement.

The three sulfanilides described by Rathke were prepared by us and the sulfanilide, (VII), and *o*-sulftoluide obtained as oils, which refused to solidify. The *p*-sulftoluide was a solid which could be purified by crystallization without decomposition. We now find that all three of these compounds are exceedingly unstable and break down, when heated at

¹ *Ber.*, 3, 858 (1870); 19, 395 (1886); *Ann.*, 167, 211 (1873); *Zentralblatt*, 1872, 547.

² Rathke, *Ber.*, 19, 397 (1886).

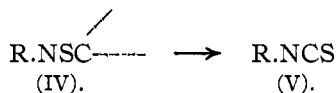
³ *Farbenfabriken vorm Bayer and Co.*, *Ber.*, 18, Ref. 679; *R. P.*, 32,829 (1885); *Wagner's Chem. Tech.*, 31, 498 (1885).

⁴ *Vol. II*, 426, 468, 504.

130–140°, with formation respectively, of two characteristic sulfur derivatives, namely, a *mustard oil*, (XII), and apparently a polymeric modification of the mustard oil, which we have represented provisionally by Formula XI. These latter products were obtained as brown, amorphous powders, which were practically insoluble in the common solvents. It is not improbable that the polymeric modification of benzoylisothiocyanate, C_6H_5CONCS , which was first described by Miquel,¹ is a representative of the same type of compounds and is to be represented by Formula X. Miquel writes as follows regarding this compound:

“Dersèche à l'étuve à 100 degrés, cette substance se présente sous la forme d'une poudre jaune amorphe, insipide d'une odeur faible et aromatique.”

In the case of *p*-sulftoluide we obtained by heating this substance at 140° a yield of *p*-tolylisothiocyanate corresponding to 33% of the theoretical. In other words, we are dealing here with an unique rearrangement involving a transformation of the sulfide grouping IV, into that corresponding to a mustard oil (V).



So far as the writer is aware, combinations containing the unsaturated radical—NSC have never been prepared.

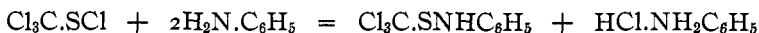
Our observation that a mustard oil (XII) is formed along with its corresponding polymeric modification (XI), when sulfanilides are heated, furnishes ample justification for certain assumptions regarding the mechanism of this interesting transformation. In the first place it seems probable that the change involves the formation of an unstable, intermediate compound which is highly unsaturated and secondly, that this combination is capable of transformation into either one of the end products of the reaction. Since this rearrangement involves a dissociation of the grouping —N.C.S— between S and N and a coupling of the N with C, it is evident that the intermediate compound must be cyclic in character.

The simplest expression which meets these conditions is that represented by the cycle (VIII). This compound is the same product that is formed by the interaction of a sulfanilide (VII) with alkali. An intermediate combination of this structure would be expected to be unstable at high temperatures and break down into chlorine and the free radical (IX). This then could undergo theoretically two fundamental changes, namely, either condense as a true methylene compound ($CH_2=$) giving the polymer (XI), or undergo transformation directly into a mustard oil (XII) with rupture of the linking between nitrogen and sulfur. Such an explanation seems logical and the various changes are expressed by the following formulas:

¹ *Ann. chim. phys.*, [5] **11**, 303 (1877).

Experimental Part.

The Action of Aromatic Amines on Tetrachloromethylmercaptan.—According to Rathke,¹ tetrachloromethylmercaptan interacts with aniline, *p*- and *o*-toluidine at low temperature with formation of sulfanilides. The aniline and *o*-toluidine compounds were obtained as



oils and the *p*-toluidide described as a solid. No attempt was made to purify the compounds, however, and no analytical data were given confirming their constitution.

We have prepared these three compounds according to a common procedure which was as follows: Thirty grams of the tetrachloromethylmercaptan were dissolved in 300 cc. of ether and the mixture cooled with ice-water. Two molecular proportions of aniline (or the toluidines) were then slowly added and the mixture agitated after each addition. Aniline hydrochloride separated at once and the ether assumed a red color. After the final addition of the amine the mixture was then allowed to stand at ordinary temperature for one hour and the aniline hydrochloride separated by filtration. The ether solution was then dried over calcium chloride and the solvent finally allowed to evaporate spontaneously. When aniline was used we obtained 33 g. of the *trichloromethylsulfanilide*, $\text{Cl}_3\text{C.SNHC}_6\text{H}_5$, or 85% of a theoretical yield. This compound was obtained as an oil which did not solidify on standing. It cannot be purified by distillation. *Trichloromethyl-o-sulfotoluide*, $\text{Cl}_3\text{CSNHC}_6\text{H}_4\text{CH}_3$, was prepared and also obtained as an oil which could not be distilled without decomposition. The yield in this case was 87% of the theoretical.

Trichloromethyl-*p*-sulfotoluide, $\text{Cl}_3\text{C.S.NHC}_6\text{H}_4\text{CH}_3$.—From 40 g. of *p*-toluidine and 35 g. of tetrachloromethylmercaptan we obtained 47 g. of this sulfotoluide. It was purified by crystallization from petroleum ether and separated in the form of colorless crystals which melted at 72° to a yellow oil. At 145° this toluide decomposes with violent effervescence.

Calc. for $\text{C}_8\text{H}_9\text{NSCl}_3$: N, 5.4. Found: Kjeldahl, N, 5.21, 5.22.

The Action of Alcoholic Potassium Hydroxide on Trichloromethylsulfanilides: Cyclic Dichloromethylenephnylimidosulfide (VIII).—This sulfide has been described by Rathke² and its constitution established by a complete analysis. It was prepared by adding an alcoholic solution of potassium hydroxide to a cold ether solution of trichloromethylsulfanilide and separated in the form of prisms melting at 140°.

Cyclic Dichloromethylene-*p*-tolylimidosulfide.—This compound was prepared as follows: Five grams of trichloromethyl-*p*-sulfotoluide were

¹ *Loc. cit.*

² *Ber.*, 19, 395 (1886).

dissolved in ether and 1 g. of potassium hydroxide (one molecular proportion) added in alcoholic solution. Each drop of alkali added produced a deep red color which disappeared on shaking and potassium chloride deposited. After filtering from potassium chloride the ethereal solution was allowed to partly evaporate spontaneously and finally absolute alcohol was added to the residue, when this cyclic sulfide was precipitated. It was purified by crystallization from ether and separated in the form of colorless needles which decomposed with explosive violence when heated at 145° . This compound is soluble in alcohol and can be crystallized from this solvent without decomposition. On long digestion, however, it is gradually decomposed. Rathke¹ prepared this compound, but assigned to it a melting point of 138° . He did not report an analysis of his product.

Calc. for $C_8H_7NSCl_2$: N, 6.36. Found: N, 6.26, 6.00.

Cyclic Dichloromethylene-*o*-tolylimidosulfide.—This was obtained from trichloromethyl-*o*-sulftoluide by the action of potassium hydroxide. It was obtained as a solid and crystallized from ether in the form of prismatic blocks, which melted at 112° to an oil. At 145° the compound decomposes with violent evolution of gas.

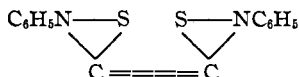
Calc. for $C_8H_7NSCl_2$: N, 6.3. Found: N, 5.90, 5.89.

The Behavior of Trichloromethylsulfanilides on Heating. The Formation of Phenylisothiocyanate from Trichloromethylsulfanilide, $Cl_3CS.NHC_6H_5 \rightarrow C_6H_5NCS$.—Thirty-three grams of trichloromethylsulfanilide were heated in an oil bath at 125 – 130° for one hour. Hydrochloric acid was evolved and the sulfanilide was transformed into a brown colored resinous mass impregnated with oil. This was subjected to a steam distillation and the operation continued as long as oil distilled over. After the operation was complete, this oil was dissolved in ether and dried over calcium chloride. On evaporating the ether we obtained 3.0 g. of phenylmustard oil. When this was combined with the required amount of aniline they interacted with evolution of heat, giving quantitatively symmetrical diphenylthiourea melting at 153° . A mixture of this compound and diphenylthiourea melted at the same temperature. The water solution, which collected during the distillation, was filtered from a brown solid left behind in the flask and evaporated to dryness. From this we obtained 2.5 g. of aniline hydrochloride.

The brown residue, which was insoluble in water, was dried and weighed 12 g. It was purified by washing several times with boiling ether to remove traces of oil and then dried for analysis at 80° . The compound was insoluble in all the common organic solvents and responded to a test for sulfur. It did not contain chlorine. When heated in a capillary tube it fused to a tar at 140° and then began to decompose as

¹ *Loc. cit.*

the temperature was raised. A nitrogen determination agreed with the calculated value for phenylisothiocyanate. Whether the following formula represents the structure of this interesting combination remains to be established.



Calc. for $(\text{C}_7\text{H}_5\text{NS})$: N, 10.37. Found: N, 10.37, 10.21.

The Formation of *p*-Tolyliothiocyanate from Trichloromethylsulf-*p*-toluide, $\text{Cl}_3\text{CSNHC}_6\text{H}_3\text{CH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$.—Forty-seven grams of trichloromethylsulf-*p*-toluide were decomposed by heating for one hour at $110\text{--}120^\circ$. The same process of purification was then applied as in the previous preparation when *p*-tolyliothiocyanate distilled over with the steam. We obtained 9.1 g. of this reagent, corresponding to $33\frac{1}{3}\%$ of a theoretical yield. It boiled at $234\text{--}238^\circ$ and combined with aniline forming symmetrical phenyl-*p*-tolylthiourea, $\text{C}_6\text{H}_5\text{NHCSNHC}_6\text{H}_4\text{CH}_3$.¹ It was purified by crystallization from alcohol and melted at 143° .

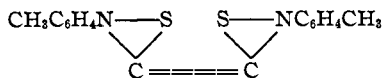
Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$: N, 11.57. Found: N, 11.57, 11.36.

The mustard oil was also combined with *p*-toluidine, when we obtained *sym*-ditolylthiourea² melting at 181° .

Calc. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{S}$: N, 10.95. Found: N, 10.70.

After steam distillation of the *p*-tolyliothiocyanate (above) a brown solid remained behind suspended in the water. This was separated by filtration and the aqueous solution evaporated to dryness, when we recovered 7.0 g. of *p*-toluidine hydrochloride.

The brown solid was ground to a fine powder, extracted thoroughly with ether and dried at 100° . It showed no signs of melting at 270° and was insoluble in the common solvents. A nitrogen determination indicated that we were dealing with a polymeric modification of *p*-tolylisothiocyanate.



Calc. for $(\text{C}_8\text{H}_7\text{NS})$: N, 9.4. Found: N, 9.0, 8.95.

The Formation of *o*-Tolyliothiocyanate from Trichloromethylsulf-*o*-toluide, $\text{Cl}_3\text{CSNHC}_6\text{H}_4\text{CH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$.—The decomposition of this toluide was effected by heating 19 g. of the compound for several hours at 128° . The very black residue which was obtained was then blown with steam as described in the two previous experiments. We obtained by this operation 3.0 g. of *o*-tolyliothiocyanate. The structure was established by the behavior of the oil towards aniline. They interacted at ordinary temperature with evolution of heat, giving *sym*-phenyl-*o*-

¹ Gebhardt, *Ber.*, 18, 3035 (1884).

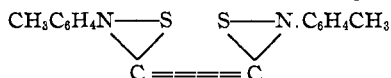
² Maly, *Jahresbericht.*, 1869, 637.

tolyl thiourea. This was purified by crystallization from alcohol and melted at 140–141°.¹

The Formation of *p*-Tolylisothiocyanate from Cyclic Dichloromethylene-*p*-tolylimidosulfide, $\text{CH}_3\text{C}_6\text{H}_4\text{N}-\text{S} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$.—The cyclic



sulfide is so explosive when heated to its melting point 145° that it is unsafe to decompose more than very small quantities at a time. Volumes of irritable gases containing chlorine are given off and a brown colored residue is left behind. Five grams of the sulfide were decomposed by heating in an oil bath at 140–145°. After the violent reaction had subsided and the mixture was cool, the residue was pulverized finely and thoroughly washed with ether and water. The ether solution was saved. The brown product was insoluble in all common organic solvents and did not melt at 270°. It was apparently identical with the product obtained by heating trichloromethylsulf-*p*-toluide. It was dried at 90°. Nitrogen determinations agreed with the calculated value for a polymer of *p*-tolylisothiocyanate. The compound contained sulfur but did not give a test for chlorine.



Calc. for $(\text{C}_8\text{H}_7\text{NS})$: N, 9.4. Found: N, 9.51, 9.50.

The ether solution obtained above was evaporated, when a small amount of oil was obtained which was *p*-tolylisothiocyanate. We did not obtain enough of this oil for distillation. When mixed with a few drops of aniline and the mixture warmed, there was an evolution of heat and a crystalline product formed which melted at 140–142°. It was identified as phenyl-*p*-tolylthiourea.

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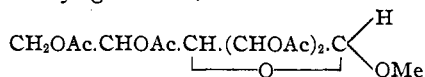
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE OPTICAL ROTATORY POWERS OF SOME ACETYLATED DERIVATIVES OF MALTOSE, CELLOSE AND LACTOSE.

By C. S. HUDSON AND RALPH SAYRE.

Received July 8, 1916.

The Rotatory Powers of the β -Heptacetates of Methyl Maltoside and Methyl Celloside.—If the molecular rotations of the alpha and beta forms of tetracetyl methyl glucoside,



are denoted by $(A + B)$ and $(-A + B)$,² respectively, the molecular

¹ Hugershoff, *Ber.*, 36, 1141 (1903).

² Hudson and Dale, *This Journal*, 37, 1264 (1915).