a good yield of a white flaky condensation product. Recrystallized from ether it melts at 129.5° (corr.). It is soluble in acetone, chloroform, benzene and ether and but slightly soluble in water, alcohol and ethyl acetate.

Analyses. Calc. for $C_{13}H_{21}N_3S$: S, 12.75; N, 16.74. Found: S(Carius) 12.45, 12.45; N, (Dumas) 16.73.

In addition to the compounds studied and analyzed the potassium cyanate and the phenyl-isocyanate condensation products and the oxalic acid salt are obtained as well crystallizing compounds, while the benzoyl compound shows no tendency to crystallize.

Summary.[24]

1. Dimethyl-ketazine is reduced to the symmetrical di*iso*propyl-hydrazine by means of the Skita method of catalytic reduction.

2. The properties of the hydrazine and of some of its salts and derivatives are described.

3. Other derivatives and their reactions are being studied and are to be reported on in a later article.

AUSTIN, TEXAS; AND URBANA, ILLINOIS.

RESEARCHES ON PYRIMIDINES. XCI. ALKYLATION OF 2-MERCAPTO-PYRIMIDINES.

BY WILLIAM J. HORN.[1]

When a 2-mercapto-6-oxypyrimidine combination is subjected to alkylation in alkaline solution, it is susceptible to attack in three different positions and, at the present time, we have no law, or rule, which will permit one to predict the configuration most likely to be formed.

$$\begin{array}{cc} NH\!-\!\!CO \\ |\qquad | \\ RSC\quad CH \\ \|\qquad \| \\ N\!-\!\!CH \end{array}$$
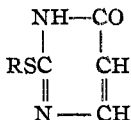
In most of the cases so far examined[2] where the radical, R, of the 2-mer-

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[24] The preparation of symmetrical di*iso*propyl hydrazine was effected by Bailey and Lochte at the University of Texas and the work was transferred later by Mr. Lochte to the University of Illinois. Professor Bailey prefers the name 2-hydrazo-propane.

[1] This paper was constructed from a dissertation presented by William John Horn to the Faculty of the Graduate School of Yale University, in June, 1921, in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson).

[2] Johnson and Clapp, *J. Biol. Chem.*, 5, 51 (1908); Johnson and Heyl, *Am. Chem. J.*, 37, 628 (1907); Wheeler and Johnson, *ibid.*, 42, 30 (1909); Johnson and Jones, *ibid.*, 40, 538 (1908); Johnson and Derby, *ibid.*, 40, 444 (1908); Wheeler and McFarland, *ibid.*, 42, 101 (1909); Wheeler and Liddle, THIS JOURNAL, 30, 1152 (1908); Johnson and Zee, *Am. Chem. J.*, 49, 287 (1913).

capto group has been strongly positive in nature, the alkylation reactions have been productive quite generally of isomeric 1- and 3-nitrogen substituted pyrimidines, and there seems to be no regularity in the proportion in which such isomers are produced. Regarding the mechanism of these reactions we have no very positive evidence, but it has been assumed as very probable, that all these changes take place primarily by addition of the alkyl halide to the sodium salt of the pyrimidine, which is followed by dissociation of the resulting polymolecular combination giving the alkylated pyrimidine as the final product of reaction. The configuration obtained will depend entirely upon the constitution of the primary addition product.
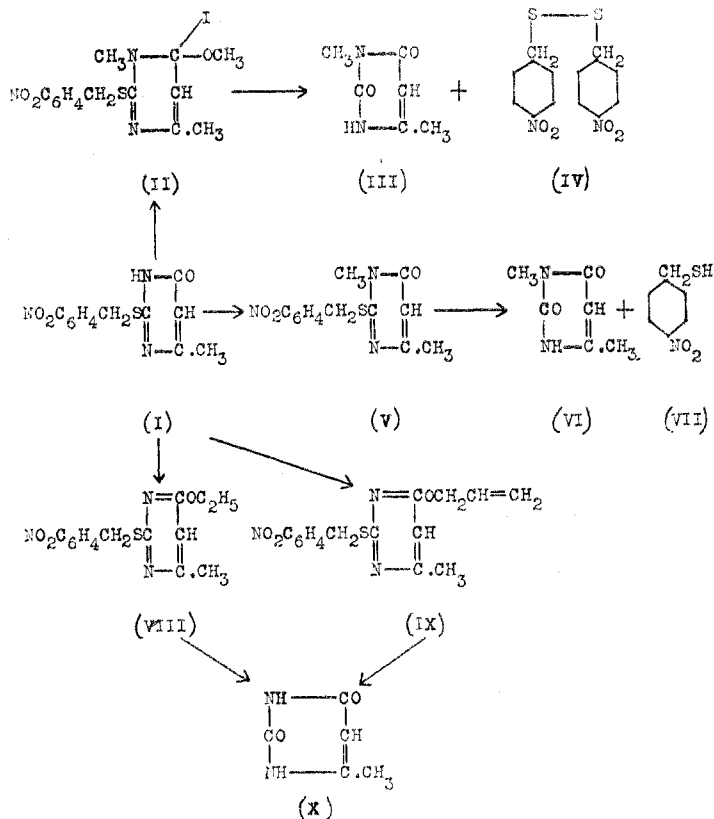
In some cases, however, it has been observed,[3,4] especially when the radical R of the 2-mercapto group is negative in character, that the product of alkylation is not a nitrogen pyrimidine derivative, but one in which the substitution of the alkyl group has taken place on oxygen in the 6-position of the pyrimidine cycle with formation of an alkoxyl or imido ester combination. Such transformations may be interpreted as taking place through direct substitution, although it is not improbable that the addition theory of reaction may apply also in these cases. In fact, the results obtained by Johnson and Moran[4] on pyrimidine alkylations, where alcoholysis of imido ester combinations was observed to take place, would seem to be very strong evidence in support of the fact that we have to deal with intermediate addition products in this type of change also.

We now describe in this paper another series of alkylation experiments which have revealed further abnormalities in chemical behavior during the process of alkylation. We have substituted the negative radical, p-nitrobenzyl, $NO_2C_6H_4CH_2$ for R and synthesized the mercapto-pyrimidine represented by Formula I. This compound is easily prepared by the action of p-nitrobenzyl chloride on the sodium salt of 2-thio-4-methyluracil.

Alkylation of this 2-mercapto-pyrimidine (I) with methyl iodide leads to the formation of two products which are not isomeric. The data thus far obtained indicate that the methyl group substitutes in methyl alcohol solution to give only one product, namely, 1,4-dimethyl-2-p-nitrobenzyl-mercapto-6-oxypyrimidine, (V). The structure of this compound was established by its behavior on hydrolysis when it was found to be transformed smoothly into p-nitrobenzyl mercaptan (VII) and 1,4-dimethyluracil (VI). We obtained no evidence of the formation of an isomeric, 3,4-dimethyl-2-p-nitrobenzyl-mercapto-6-oxypyrimidine or an imido ester combination resulting from substitution on oxygen in the 6-position of the ring.

³ Johnson and Haggard, This Journal, 37, 177 (1915).

⁴ Johnson and Moran, ibid., 37, 2591 (1915).

$$
\begin{array}{ccc}
\underset{\text{(II)}}{\overset{\displaystyle\text{I}}{\underset{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}}{\text{CH}_3\text{N}-\text{C}-\text{OCH}_3}}} & \longrightarrow & \underset{\text{(III)}}{\underset{\text{HN}-\text{C.CH}_3}{\text{CH}_3\text{N}-\text{CO}}} + \underset{\text{(IV)}}{\text{two rings}}
\end{array}
$$

(II)   (III)   (IV)

$$
\underset{\text{(I)}}{\underset{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}}{\text{HN}-\text{CO}}} \longrightarrow \underset{\text{(V)}}{\underset{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}}{\text{CH}_3\text{N}-\text{CO}}} \longrightarrow \underset{\text{(VI)}}{\text{CH}_3\text{N}-\text{CO}} + \underset{\text{(VII)}}{\text{CH}_2\text{SH ring}}
$$

(I)   (V)   (VI)   (VII)

$$
\underset{\text{(VIII)}}{\underset{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}}{\text{N}=\text{COC}_2\text{H}_5}} \qquad \underset{\text{(IX)}}{\underset{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}}{\text{N}=\text{COCH}_2\text{CH}=\text{CH}_2}}
$$

(VIII)   (IX)

$$
\underset{\text{(X)}}{\underset{\text{NH}-\text{C.CH}_3}{\overset{\text{NH}-\text{CO}}{\text{CO} \quad \text{CH}}}}
$$

(X)

The second product of reaction with methyl iodide proved to be an addition compound, which we have expressed by Formula II. Not only is this interesting substance formed by direct alkylation of (I) with an excess of methyl iodide, but the same combination results also by interaction of the pyrimidine V with methyl iodide when digested in methyl alcohol. Hydrolysis of this substance with hydrochloric acid led to the formation of 1,4-dimethyluracil (VI), proving that the second methyl group does not link itself to nitrogen. The choice between the two other possible linkings, namely, addition to sulfur of the mercapto group or oxygen in the 6-position of the ring was indicated by the behavior on hydrolysis. By this treatment the mercapto group of the addition compound was replaced and identified as *p*-nitrobenzyl disulfide (IV). This sulfide is formed by oxidation of nitrobenzyl mercaptan, a change that is brought about by the influence of traces of iodine also formed as a product of hydrolytic change. In other words, we obtained no evidence of the formation by hydrolysis of the sulfide $NO_2C_6H_4CH_2SCH_3$.[5]

[5] The study of these addition compounds will receive attention in the immediate future. (T. B. J.)

This is the first case to be described where we have been able to isolate an addition product of this type, and the result indicates that such combinations have probably resulted in previous condensations and that their formation is a partial explanation of the low yields and abnormal results obtained in many cases. Johnson and Jones[6] have shown that the pyrimidine, 2-ethyl-mercapto-3-methyl-5-ethoxy-6-oxypyrimidine, combines with potassium iodide to form a characteristic addition product. Our addition product, II, was absolutely free from inorganic material.

The fact that iodine is formed by hydrolysis of the addition product (II) in acid solution is strong evidence that the alkyl halide has dissociated in the process of addition to the pyrimidine and this condition is expressed by the structural formula assigned. The identification of this addition product is strong evidence in support of the assumption that all these alkylations in the pyrimidine series probably operate through the inter- mediate formation of addition compounds.

Ethyl bromide and allyl bromide interact with the sodium salt of the mercapto-pyrimidine in an entirely different manner from methyl iodide. In neither case did we observe the formation of nitrogen-substituted derivatives, but both halides interacted to form imido ester combinations. The structures of these compounds are expressed by Formulas VIII and IX respectively. The constitution of both of these pyrimidines was established by the fact that they underwent hydrolysis with formation of 4-methyluracil and nitrobenzyl-mercaptan.

In the experimental part of this paper are recorded some new facts bear- ing on the chemistry of p-nitrobenzyl-mercaptan and its corresponding sulfide derivatives.

Experimental Part.

2-Thio-4-methyluracil and p-Nitrobenzyl Chloride.—The method employed for the preparation of 2-thio-4-methyluracil was that used by Wheeler and McFarland;[7] p-nitro-benzyl chloride was prepared according to the directions of Alway.[8]

2-p-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine. (I).—This pyrimidine was obtained in quantity by the action of p-nitrobenzyl chloride upon the sodium salt of 2-thio-4-methyl-uracil.

To sodium ethylate solution, prepared by dissolving a molecular proportion of sodium in absolute alcohol, finely pulverized 2-thio-4-methyl-uracil was added. On heating this mixture for two hours and shaking occasionally, the sodium salt separated and the solution became reddish-yellow in color. p-Nitrobenzyl chloride was then added and the resulting solution was heated until it became neutral. The solution, turned green at first and then dark red. After it had been heated for about 20 minutes it solidified to a white cake. At the end of the reaction, the mixture was cooled, filtered with the aid of suction and the crystalline product was treated with cold water to dis- solve the sodium chloride formed in the reaction. The yield of crude pyrimidine was

  [6] Johnson and Jones, THIS JOURNAL, 31, 590 (1909).
  [7] Wheeler and McFarland, Ref. 2.
  [8] Alway, THIS JOURNAL, 24, 1060 (1902).

93%. This compound is only slightly soluble in hot alcohol and difficultly soluble in hot water. It was purified by recrystallization from glacial acetic acid, from which it separated in the form of rosets of colorless needles. These were collected on a filter, washed, first with a little acetic acid and then with water, and dried at 115° for 10 to 15 hours. By this procedure, an 80% yield of the pure compound was obtained; it melted at 220° to give a clear yellow oil.

Analyses. Calc. for $C_{12}H_{11}O_3N_3S$: N, 15.16; S, 11.55. Found: N, 15.24, 15.6; S, 11.42.

Alkylation of 2-p-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine.
Action of Methyl Iodide.

To a sodium methylate solution, made by dissolving a molecular proportion of sodium in methyl alcohol, finely pulverized 2-p-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added and the clear greenish-yellow solution thus obtained was heated for one hour. By means of a dropping funnel, slightly more than the calculated quantity of methyl iodide was then added slowly to the warm solution of the sodium salt and the solution was heated until it became neutral. Upon removal of the alcohol by evaporation under diminished pressure, a greenish-yellow solid separated which had the odor of parsnips. This product was triturated with cold water to dissolve sodium iodide, and the insoluble material collected on a filter was dried in a vacuum desiccator over sulfuric acid for several days. This substance gave a very strong test for iodine on treatment with sulfuric acid. When the finely pulverized product was extracted in a Soxhlet apparatus with dry ether free from alcohol for 25 hours, it was separated into two distinct compounds, one of which (A) was soluble in ether and the other (B) insoluble.

(A) **1,4-Dimethyl-2-p-nitrobenzyl-mercapto-6-oxypyrimidine.** (V).—On evaporating the ether solution containing the soluble compound (A) to dryness in the air, a yellow solid was obtained which represented 71.5% of the weight of the total alkylated products. This compound was free from iodine and melted between 90° and 111°. Upon recrystallization from glacial acetic acid, it was obtained in the form of rosets of white needles which melted sharply at 136° to give a clear yellow oil. It was identified as a monomethyl derivative of the original pyrimidine.

Analyses. Calc. for $C_{13}H_{13}O_3N_3S$: N, 14.4. Found: 14.14, 14.16.

HYDROLYSIS WITH HYDROCHLORIC ACID.—The structure of this compound was established by its behavior on hydrolysis with conc. hydrochloric acid. One to three g. of the compound was digested in 100 cc. of the acid for several hours. In about 10 minutes, the boiling solution became turbid and a yellowish-brown oil separated on the surface of the liquid. At the end of the reaction period, the solution was filtered to remove the oil and the filtrate evaporated to dryness. By this procedure, a yellowish-white residue was obtained which melted at 256–258°; the yield was nearly quantitative for 1,4-dimethyluracil. After recrystallization from hot water and treatment with Norite, the substance was obtained in the form of colorless prismatic needles free from sulfur. These crystals melted sharply at 259–260° to give a clear red oil.

Analyses. Calc. for $C_6H_8O_2N_2$: N, 20.0. Found: 19.93, 19.72.

The yellowish-brown oil insoluble in water solidified as it cooled to give a pearl-white solid. Dried in a vacuum desiccator over sulfuric acid the substance was obtained in quantity corresponding very closely to the quantitative yield for p-nitrobenzyl-mercaptan. This compound is only very slightly soluble in water, but is very soluble in ether. It was purified by recrystallization from alcohol from which it separated in the form of white transparent plates melting sharply at 58° to a clear yellow oil. A molecular-weight determination was made by the freezing-point method.

Analyses. Calc. for $C_7H_7O_2NS$: N, 8.28; S, 18.93; Mol. wt., 169.0. Found: N, 8.13, 8.47; S, 18.54; Mol. wt., 160.2, 164.8.

A further description of this compound is given below in the section devoted to the chemistry of nitrobenzyl-mercaptan.

(*B*) **The Addition Product of Methyl Iodide and 1,4-Dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine.** (II).—The insoluble amorphous compound (*B*) which was yellowish-brown in color, was observed to turn red slowly on exposure to the air, a behavior which was due evidently to the liberation of iodine. After drying this compound in a vacuum desiccator over sulfuric acid for several days, the weight was found to correspond to 28% of the weight of the total alkylated products. In a repetition of the alkylation with methyl iodide with a quantity of the iodide greater than that previously used, as high as 50% of the insoluble addition compound was obtained in this reaction. This product did not melt sharply; the melting point ranged between 79° and 136°. It gave a very strong test for iodine when treated with sulfuric acid and left no residue when heated on platinum foil. When boiled in 50% alcohol, it was found to dissociate, and the cool solution deposited white needle-like crystals. The compound formed melted at 136° and was identified as 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine.

The addition compound was purified by dissolving it to saturation in hot 80% alcohol, filtering off any undissolved material and cooling the solution immediately in an ice-bath, with stirring. By this procedure the compound was obtained in the form of a light brown colloidal precipitate. It was collected and washed with a little 80% alcohol, and dried in a vacuum desiccator over sulfuric acid for several days. Yield, 61%. It melted between 65–75° with slight decomposition.

Analyses. Calc. for $C_{14}H_{16}O_3N_3SI$: N, 9.69. Found: 9.50, 9.39.

HYDROLYSIS WITH HYDROCHLORIC ACID.—From 1 to 5 g. of the addition compound was hydrolyzed by digestion with 50 cc. of conc. hydrochloric acid for several hours. During this operation a yellowish-brown oil separated which solidified immediately when cooled. The yellow solution was then filtered and the residue dried and saved. This compound was identified as *p*-nitrobenzyl disulfide. The yield was nearly quantitative. Two recrystallizations from alcohol gave a product which separated in the form of colorless needles melting at 126° to give a clear yellow oil. A molecular-weight determination was made by the boiling-point method.

Analyses. Calc. for $C_{14}H_{12}O_4N_2S_2$: N, 8.33; S, 19.05; Mol. wt., 336.0. Found: N, 8.02, 8.34; S, 19.02, 19.09; Mol. wt., 334.5, 346.2.

A further description of this compound and its properties is given in the section dealing with the chemistry of *p*-nitrobenzyl-mercaptan.

The yellow acid filtrate was extracted several times with ether. On evaporating the solvent a crystalline solid was obtained which was identified as free iodine.

When the filtrate from the ether extractions was evaporated to dryness, a grayish-black solid was obtained. The residue was treated with a little cold alcohol to remove traces of iodine, and then recrystallized twice from hot water and decolorized by treatment with Norite. As the solution cooled, the compound separated in the form of white prismatic needles. The melting point, 259–260°, indicated that we were dealing with dimethyluracil.

When the pyrimidine, 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine (*A*) was hydrolyzed with conc. hydrochloric acid to which a little free iodine had been added, the results were similar to those obtained by hydrolysis of the above addition compound. That is, *p*-nitrobenzyl disulfide and 1,4-dimethyluracil were formed in this reaction.

Synthesis of the Addition Product from its Components.—To synthesize the addition

compound, methyl iodide (3 moles) was added to a warm alcohol solution of 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine and the solution was boiled for 12 hours. As it cooled, yellow needle-like crystals separated. These were found to be free from iodine and after recrystallization from glacial acetic acid, melted at 136°, which corresponds to the melting point of the unaltered mercapto-pyrimidine. After the removal of the methyl alcohol and methyl iodide from the filtrate by distillation, a light brown product was obtained. This gave a very good test for iodine. Digestion with hydrochloric acid transformed it smoothly into *p*-nitrobenzyl disulfide, which melted at 135.5°, and 1,4-dimethyluracil, melting at 260°.

Alkylation with Ethyl Bromide.

2-*p*-Nitrobenzyl-mercapto-4-methyl-6-ethoxy-pyrimidine. (VIII).—2-*p*-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added to a sodium ethylate solution made by dissolving a molecular proportion of sodium in absolute alcohol, and the solution was heated for 3 hours. A little more than the molecular quantity of ethyl bromide was then added slowly through a dropping funnel and the solution was heated until it became neutral. The hot solution was filtered to remove sodium bromide, and as the filtrate cooled, rosets of needle-like crystals separated. After filtering and treating the residue with a little water to remove any traces of sodium bromide, the above pyrimidine was obtained; it melted between 90° and 96°. Recrystallization from alcohol gave a product which melted sharply at 104°. Yield, about 32%.

Analyses. Calc. for $C_{14}H_{15}O_3N_3S$: N, 13.77. Found: 13.70, 13.90.

HYDROLYSIS WITH HYDROCHLORIC ACID.—From 1 to 3 g. of this compound was hydrolyzed by digestion with 100 cc. of conc. hydrochloric acid for 3 hours. The solution was filtered to remove the oil which separated and evaporated to dryness, yielding a yellowish-white solid. This compound was identified as 4-methyluracil. It was obtained in the form of white prismatic needles which crystallized from water and did not melt below 300°. The yield was quantitative.

Analyses. Calc. for $C_5H_6O_2N_2$: N, 22.22. Found: 22.24, 22.38.

When the oily product formed in this reaction was cooled, it solidified to form a pearl-white solid which corresponded in quantity very closely to the calculated yield for *p*-nitrobenzyl-mercaptan. After recrystallization from alcohol, it was obtained in the form of white transparent plates melting at 57° to give a clear yellow oil. A mixture of this compound with *p*-nitrobenzyl-mercaptan obtained in a previous experiment melted at 57–58°.

Alkylation with Allyl Bromide.

2-*p*-Nitrobenzyl-mercapto-4-methyl-6-alloxy-pyrimidine. (IX).—To sodium ethylate solution made by dissolving a molecular proportion of sodium in absolute alcohol, 2-*p*-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added and the solution was heated for 2½ hours. Allyl bromide (1 mol.) was then added slowly through a dropping funnel and the resulting solution was heated until it became neutral. On removal of the alcohol by distillation, a soft, sticky, dark red solid separated. This was dried in a vacuum desiccator over sulfuric acid for several days, and then extracted in a Soxhlet apparatus with dry ether free from alcohol. By this procedure two compounds were obtained; a compound insoluble in ether, which proved on purification to be unaltered material, and a compound soluble in ether.

When ether solution of the soluble compound was evaporated to dryness in the air, a reddish-yellow residue was obtained. After two recrystallizations from ligroin the compound was isolated in the form of light yellow needles which melted at 77–78° to form a clear yellow oil.

Analyses. Calc. for $C_{15}H_{15}O_3N_3S$: N, 13.25. Found: 13.42, 13.52.

HYDROLYSIS WITH HYDROCHLORIC ACID.—A small quantity of this compound was hydrolyzed by digestion with 100 cc. of conc. hydrochloric acid for 1 $^1/_2$ hours. The hot solution was filtered to remove the oil which separated and the filtrate was evaporated to dryness. A nearly quantitative yield of 4-methyluracil was thus obtained which, on recrystallization from water, did not melt below 300°.

By recrystallization of the oily product from alcohol, white transparent plates were obtained which melted at 57° to give a clear yellow oil.

The Chemistry of *p*-Nitrobenzyl-mercaptan.

When we endeavored to identify *p*-nitrobenzyl mercaptan ($NO_2C_6H_4$-CH_2SH), formed in the hydrolysis of some of the 2-mercapto-pyrimidines, unexpected results were obtained. We obtained a product which melted consistently at 58°, while the melting point assigned to this compound in the literature is 140°. This marked discrepancy led us, therefore, to an investigation of the properties of this mercapto compound and its corresponding sulfide derivatives. We found that our product melting at 58° gave analytical results in complete agreement with those required for the mercaptan. When this compound was subjected to oxidation in the presence of iodine, or with potassium permanganate, or air in the presence of ammonia, it was transformed into the disulfide ($NO_2C_6H_4CH_2)_2S_2$ melting at 126.5°. Price and Twiss[9] give the melting point of this compound as 126.5°. It was prepared by these chemists by the action of sodium carbonate upon *p*-nitrobenzyl thiosulfate.

Strakosch,[10] who investigated the preparation of *p*-nitrobenzyl-mercaptan, prepared it by the action of potassium hydrosulfide and ammonium sulfide upon *p*-nitrobenzyl chloride and states that these reactions lead to the formation of *p*-nitrobenzyl-mercaptan melting at 140°. He also states that, in the case of the action of ammonium sulfide upon *p*-nitrobenzyl chloride, prolonged boiling leads to the formation of *p*-nitrobenzyl disulfide which he describes as melting at 89°. On repeating his work, with potassium hydrosulfide as a reagent, it was impossible to isolate any of the compounds which he describes. Furthermore, it was found that ammonium sulfide reacts with *p*-nitrobenzyl chloride in alcoholic solution to give only the sulfide ($NO_2C_6H_4CH_2)_2S$ melting at 158–159°.

When *p*-nitrobenzyl chloride was treated with sodium hydrosulfide in alcoholic solution, we obtained two compounds; the disulfide melting at 126°, and the sulfide melting at 158–159°. This compound corresponds to *p*-nitrobenzyl sulfide described by O. Fischer.[11]

The interesting results obtained with *p*-nitrobenzyl-mercaptan raise the question whether the corresponding *ortho* and *meta* isomers of this mercapto compound have been correctly described.

[9] Price and Twiss, *J. Chem. Soc.*, **93**, 1401 (1908).

[10] Strakosch, *Ber.*, **5**, 698 (1872).

[11] O. Fischer, *ibid.*, **28**, 1338 (1895).

Summary.

1. Methyl iodide interacts with the sodium salt of 2-p-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine to give first a nitrogen substituted derivative, which then interacts with another molecule of methyl iodide to form an addition product. The methyl group substitutes in the 1-position of the pyrimidine ring.

2. Ethyl bromide and allyl bromide interact with the mercapto-pyrimidine in a manner entirely different from that with methyl iodide. In both of these cases, an oxygen ether is formed, and no evidence was obtained of substitution of the alkyl groups on a nitrogen atom of the pyrimidine ring.

3. In the hydrolysis of 2-p-nitrobenzyl-mercapto-pyrimidines with acids, p-nitrobenzyl-mercaptan is formed melting at 57–58°. If, however, free iodine functions during hydrolysis, this mercaptan is destroyed and the disulfide, melting at 126.5°, is formed by oxidation.

4. The literature concerning p-nitrobenzyl-mercaptan is incorrect; in this paper the melting points of this compound, its disulfide and corresponding monosulfide are described correctly.

NEW HAVEN, CONNECTICUT.

PARA-CYMENE STUDIES. III. THE BROMINATION OF 2-AMINO-PARA-CYMENE.

BY ALVIN S. WHEELER AND IRA W. SMITHEY.[1]

The previous two papers dealing with p-cymene concerned (1) the production of toluene[2] by the action of aluminum chloride on a mixture of benzene and p-cymene and (2) p-cymene as a solvent.[3] This paper describes the action of bromine upon 2-amino-p-cymene and the preparation of certain derivatives of the monobromo-amino-cymene obtained. The research began with the isolation of cymene from spruce turpentine, a by-product in the manufacture of paper by the sulfite process. In addition to the steps given by one of us in the second paper of this series on the purification of p-cymene we find it necessary to shake out the cymene with a limited amount of conc. sulfuric acid. When this is not done the cymene, even though it be a fraction of narrow range in boiling point (176–178°), acquires a yellow color on standing, and fully satisfactory