

chiefly ammonia, hydrogen cyanide, ethylene, and a substance which is probably acetonitrile, together with smaller quantities of hydrogen and nitrogen. At 700° it gives more ethylene, less carbon and no hydrogen cyanide.

At 1000° the chief products are the elements, although traces of ethylene and probably acetonitrile were found.

Propylene at 700° gives chiefly a nitrile, ammonia, carbon and hydrocarbons, together with smaller quantities of hydrocyanic acid and the elements.

The modes of formation of the decomposition products are discussed.

LINCOLN, NEBRASKA

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

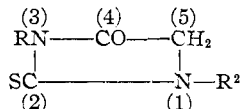
THE REACTIONS OF THE FORMAMIDINES.

X. THE THIO-IMIDAZOLONES

By F. B. DAINS, RUTH THOMPSON AND W. F. ASENDORF¹

Received June 27, 1922

Previous investigations have shown that compounds containing methylene hydrogen, $>CH_2$, reacted with the substituted formamidines, yielding derivatives as follows: $\begin{matrix} X \\ \diagup \\ Y \end{matrix} > CH_2 + RHNHCHNR = \begin{matrix} X \\ \diagup \\ Y \end{matrix} > C = CHNHR + RNH_2$. This was found to be true not only in the case of the acetyl-acetone and aceto-acetic ester type but also with certain ring compounds, such as the pyrazolones, isoxazolones and the thiazolidones.² The study of this general reaction has been now extended to the thio-imidazolones, which contain the same methylene grouping, and it has been found that the methylene hydrogen in these derivatives can be replaced with equal ease, giving the 5-amino-methylene-thio-imidazolones.³ Thus



These compounds showed a close analogy to the corresponding aldehyde substitution products investigated by Wheeler, and Johnson, and their co-workers, not only in their general properties, but also in the ability of the monosubstituted imidazolones to form thio-ethers.⁴

¹ The authors wish to thank the Research Committee of the University of Kansas for a grant which was of aid in this study.

² *Ber.*, **35**, 2509 (1902). *THIS JOURNAL*, **31**, 1148 (1909); **35**, 959, 970 (1913); **38**, 1841 (1916); **40**, 562 (1918); **43**, 613, 1200 (1921).

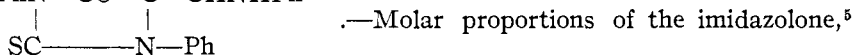
³ The numbering of the ring is that used in *Chemical Abstracts*. In some of the literature these imidazoles are regarded as 5-keto derivatives.

⁴ (a) Wheeler and Brautlecht, *Am. Chem. J.*, **45**, 447 (1911). (b) Johnson and Nicolet, *THIS JOURNAL*, **33**, 1978 (1911).

Experimental

Disubstituted Thio-imidazolones and their Amino-methylene Derivatives. 1,3-Diphenyl-2-thio-5-anilinomethylene-4-imidazolone,

$$\text{PhN}-\text{CO}-\text{C}=\text{CHNHPH}$$



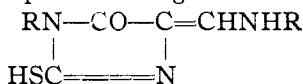
and diphenyl formamidine were heated in a flask with an air condenser at 135–140° for 20 minutes. The mixture turned red and partially solidified when cold. On the addition of alcohol, the condensation product separated as a yellow solid which was purified by recrystallization from hot alcohol. It melted at 175° and was difficultly soluble in organic solvents, but insoluble in potassium hydroxide solution.

Calc. for $\text{C}_{22}\text{H}_{17}\text{ON}_3\text{S}$: N, 11.32. Found: 11.00.

1-Phenyl-3-*p*-tolyl-2-thio-5-anilinomethylene-4-imidazolone.—The yellow needles from alcohol melted at 197–198°.

Calc. for $\text{C}_{23}\text{H}_{19}\text{ON}_3\text{S}$: N, 10.93. Found: 11.08.

Monosubstituted Imidazolones.—The preceding method of preparation was used, with the exception that the di-*p*-bromophenyl and the di- α -naphthyl-formamidines required heating at 200–220°, before reaction occurred.



These compounds were readily soluble in potassium hydroxide solution and were precipitated unchanged on acidifying, a property possessed by all imidazolones containing an NH group.

Derivative of 3-aryl-2-thio
R-aminomethylene-4-
imidazolone

	M. p. ° C.	Nitrogen		Properties
		Calc. %	Found %	
3-Phenyl-5-anilino $\text{C}_{15}\text{H}_{13}\text{ON}_3\text{S}$	252	14.23	14.17	Yellow needles
3- <i>p</i> -Tolyl-5-anilino $\text{C}_{17}\text{H}_{15}\text{ON}_3\text{S}$	250	13.61	13.45	Yellow plates
3- <i>o</i> -Tolyl-5-anilino $\text{C}_{17}\text{H}_{15}\text{ON}_3\text{S}$	215	13.61	13.24	Yellow crystals
3- <i>m</i> -Tolyl-5-anilino $\text{C}_{17}\text{H}_{15}\text{ON}_3\text{S}$	207–8	13.61	13.57	Yellow needles
3- <i>p</i> -Chlorophenyl-5-anilino $\text{C}_{16}\text{H}_{12}\text{ON}_3\text{S}$	274–6	12.75	12.76	Light brown crystals
3- <i>p</i> -Ethoxyphenyl-5-anilino $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3\text{S}$	227	12.39	12.36	Pale yellow crystals
3-Phenyl-5- <i>p</i> -bromophenyl anilino $\text{C}_{16}\text{H}_{12}\text{ON}_3\text{SBr}$	190	11.23	11.09	Reddish brown needles
3-Phenyl-5- α -naphthylino $\text{C}_{20}\text{H}_{15}\text{ON}_3\text{S}$	160	12.19	12.17	

In the above work the following 2 new imidazolones were used.

* Ref. 4a, p. 457.

3-*m*-Tolyl-2-thio-4-imidazolone.—This was prepared by heating at 100° for 3 hours, a mixture of *m*-tolyl-isothiocyanate (10 g.), amino-acetic acid (5.5 g.), sodium hydroxide (8 g.), water (10 cc.), and alcohol (25 cc.). After concentrating the mixture to 1/2 its volume, it was acidified with hydrochloric acid and evaporated to dryness. The sodium chloride was removed by washing with cold water and the residue, which crystallized from alcohol in fine, yellow needles, melted at 167°. The yield was 90%.

Calc. for C₁₀H₁₀ON₂S: N, 13.58. Found: 13.57, 13.66.

3-*p*-Chlorophenyl-2-thio-4-imidazolone.—This was synthesized in the same manner as was the *m*-tolyl derivative from *p*-chlorophenyl-isothiocyanate. It crystallized from alcohol in yellow needles. (M. p., 234.5°.)

Calc. for C₉H₇ON₂ClS: N, 12.36; Cl, 15.65. Found: N, 12.32, 12.41; Cl, 15.60, 15.71.

Alkyl Thio-ethers.—Wheeler and Brautlecht⁶ have found that these hydantoin condensed easily with benzaldehyde on boiling in glacial acetic acid solution with sodium acetate. Experiment showed that the same 5-benzal derivative was formed by simply heating the components at 150–170° for some time.

These aldehyde condensation products were characterized by their solubility in alkaline hydroxides, and the formation of salts which with alkyl halides gave the corresponding alkyl thio-ethers.⁷

The anilino-methylene-imidazolones have an analogous constitution and gave with equal ease, the corresponding alkyl thio-ethers of the general formula, RN—CO—C=CHNHR.



The general procedure in the synthesis of the thio-ethers was as follows. The imidazolone (1 mol.) was dissolved in an alcoholic solution of sodium ethylate (1 mol.). To this was added the alkyl iodide and the solution heated until it became neutral. The thio-ethers were precipitated with water, washed free from sodium iodide and crystallized from hot alcohol in which they were very soluble.

Benzyl Thio-ethers.—Here the method was modified in that the imidazole was dissolved in 20% potassium hydroxide solution, shaken with

Derivative of 3-aryl-2-R-thio-5-anilino-4-imidazolone	M. p. ° C.	Nitrogen		Properties
		Calc. %	Found %	
3-Phenyl-2-methylthio C ₁₇ H ₁₅ ON ₂ S	173	13.61	13.60	White crystals
3-Phenyl-2-ethylthio C ₁₈ H ₁₇ ON ₂ S	164.5	13.02	13.10	White crystals
3-Phenyl-2- <i>n</i> -butylthio C ₂₀ H ₂₁ ON ₂ S	124	11.95	11.69	Yellow needles

⁶ Ref. 4a, p. 448.

⁷ Ref. 4a, p. 450.

3-Phenyl-2-allylthio C ₁₇ H ₁₇ ON ₃ S	218	12.56	12.45	Greenish yellow crystals
3-Phenyl-2-benzylthio C ₂₃ H ₁₉ ON ₃ S	145	10.93	10.91	Yellow needles
3- <i>o</i> -Tolyl-2-benzylthio C ₂₄ H ₂₁ ON ₃ S	148	10.53	10.57	
3- <i>m</i> -Tolyl-2-benzylthio C ₂₄ H ₂₁ ON ₃ S	154	10.53	10.57	
3- <i>p</i> -Ethoxyphenyl-2-benzylthio C ₂₅ H ₂₃ ON ₃ S	170	9.38	9.48	Yellow needles

benzyl chloride and the resulting insoluble product purified by crystallization from alcohol.

Imidazolones Containing a Benzoyl Group

1-Benzoyl-2-thio-3-phenyl-4-imidazolone.—This new type of substituted hydantoin was readily prepared by heating molar quantities of phenyl mustard oil and hippuric acid at 150° for 1½ hours. The melt was dissolved in hot alcohol and the crystals, which separated, were treated with hot water to remove any unchanged hippuric acid. On recrystallization from alcohol, white needles were obtained which melted at 177–179°.

Calc. for C₁₆H₁₂O₂N₂S: N, 9.47. Found: 9.42, 9.48.

The corresponding *m*-tolyl derivative, from *m*-tolyl-isothiocyanate and hippuric acid, melted at 197°.

Calc. for C₁₇H₁₄O₂N₂S: N, 9.04. Found: 9.03, 9.07.

1-Benzoyl-2-thio-3-*p*-ethoxyphenyl-4-imidazolone was synthesized from *p*-ethoxyphenyl-isothiocyanate and hippuric acid, following the method used in the preparation of *m*-tolyl-2-thio-imidazolone. The greenish colored crystals melted at 168°.

Calc. for C₁₈H₁₆O₃N₂S: N, 8.24. Found: 8.21, 8.35.

Aminomethylene Derivatives.—1-Benzoyl-2-thio-3-phenyl-5-anilino-methylene-4-imidazolone, occurring as white needles, melted at 184–186°.

Calc. for C₂₃H₁₇O₂N₃S: N, 10.88. Found: 10.75, 11.01.

The analogous 3-*m*-tolyl compound melted at 187°.

Calc. for C₂₄H₁₉O₂N₃S: N, 10.15. Found: 10.26, 10.01.

Derivatives of 1-benzoyl-2-thio-4-imidazolone.⁸—This compound which condenses with aldehydes, combined with diphenyl formamidine and gave the 5-anilino-methylene-imidazolone. This crystallized from alcohol in red needles, which were soluble in sodium hydroxide and melted at 164–165°.

Calc. for C₁₆H₁₃O₂N₃S: N, 13.00. Found: 13.15, 13.17.

Thio-Ethers.—The 2-benzyl thio-ether crystallized in fine, yellow needles, which melted at 165°.

Calc. for C₂₄H₁₉O₂N₃S: N, 10.14. Found: 9.99.

⁸ Ref. 4b, p. 1977.

The Unsubstituted Thio-imidazolone.—This condensed with the formamidine and gave 2-thio-5-anilino-methylene-4-imidazolone. The deep red crystals from alcohol melted at 264°.

Calc. for $C_{10}H_9ON_3S$: N, 19.19. Found: 19.22.

The compound was soluble in sodium hydroxide, but all efforts to obtain definite benzyl thio-ethers were fruitless. Only amorphous mixtures were obtained.

Hydrolysis of Substituted Imidazolones

Johnson and Nicolet⁸ have shown that the benzoyl group was readily removed from the 1-benzoyl-2-thio-4-imidazolone, giving the unsubstituted imidazole. *In certain other cases, the present investigation has noted some interesting differences.*

Opening of the Ring

Five g. of 1-benzoyl-2-thio-3-phenyl-4-imidazolone was heated under a reflux condenser for 6 hours in a mixture of alcohol (75 cc.) and conc. hydrochloric acid (10 cc.). After evaporating the alcohol the residue was found to contain aniline, a little benzoic acid, and hippuric acid (m. p., 191°) which was identified by a mixed-melting-point determination and analysis.

Calc. for $C_9H_9O_2N$: N, 7.82. Found: 7.92, 8.01.

The ring was evidently opened and the mustard oil first formed, hydrolyzed to aniline. Similar results were noted in the case of the 5-anilino-methylene derivative of the same imidazolone.

It is possible that the combination of a 1-benzoyl and 3-phenyl group lessens the stability of the imidazole ring, since no evidence of such decomposition was obtained when 1-benzoyl-5-anilino-methylene, 3-phenyl-5-anilino-methylene and 3-phenyl-imidazolone were heated, with either hydrochloric acid or 20% aqueous sodium hydroxide solution.

Another instance of ring opening was observed in the following case. Numerous efforts were made to synthesize the benzyl thio-ether of the unsubstituted thio-imidazolone by solution in 20% aqueous sodium hydroxide and treatment with benzyl chloride. Instead of the formation of the expected ether, it was found that the thio-hydantoin was desulfurized with the formation of dibenzyl-disulfide and phenyl-carbamido acetic acid (γ -phenyl hydantoic acid), $C_6H_5NHCONHCH_2COOH$,⁹ which melted at 197°.

Calc. for $C_9H_{10}O_3N_2$: N, 14.44. Found: 14.27, 14.48.

Summary

The 2-thio-4-imidazolone and its mono- and disubstitution products have been found to react with the formamidines giving 5-R-amino-methylene derivatives.

⁹ *Ber.*, **41**, 2499 (1908). *Am. Chem. J.*, **28**, 395 (1902).

The monosubstituted thio-imidazolones, where the methylene hydrogen has been replaced, yielded in every case thio-ethers.

The hydrolysis of certain of these imidazolones has been studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

POTASSIUM AZIDO-DITHIOCARBONATE¹

BY A. W. BROWNE AND A. B. HOEL

(With Notes on Crystallography by A. C. GILL)

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In connection with an investigation of the imide character of hydronitric acid, F. Sommer² succeeded in preparing and analyzing the hydrated sodium and barium salts of a new acid, which he named azido-dithiocarbonic acid. These compounds were shown to have the formulas $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Ba}(\text{SCSN}_3)_2 \cdot 5\text{H}_2\text{O}$. When the attempt was made by Sommer to prepare the corresponding potassium salt by a similar method, the crystalline product that he obtained exploded with violence as he spread it carefully, with the aid of a porcelain spatula, upon a porous plate, thus deterring him from further work upon this compound.

The formation of potassium azido-dithiocarbonate has been shown by the authors of the present paper³ to take place slowly, even at ordinary temperatures, when carbon disulfide is brought into contact with aqueous solutions of potassium trinitride. It has, moreover, been demonstrated that an important catalytic effect is exerted by this azido-salt in the reaction between aqueous solutions of potassium trinitride and iodine in presence of carbon disulfide. In this connection it has been found necessary to prepare and analyze the azido salt, and to study certain of its properties and reactions.

Method of Preparation.—A sample of pure potassium trinitride weighing 6 g. was dissolved in 25 cc. of distilled water, and the resulting solution, in a 100cc. glass bottle, was treated with about 6 g. of pure, redistilled carbon disulfide, an amount slightly in excess of that required for the ratio $\text{KN}_3:\text{CS}_2$. The tightly corked bottle containing the reacting mixture was held at a temperature of about 40° in a water-bath, with occasional shaking, until the carbon disulfide had entirely disappeared.

A convenient test indicating the completion of this reaction consists in adding a few drops of iodine solution to a small sample of the reacting mix-

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 3 under Heckscher Grant No. 4. For Articles 1 and 2 see *THIS JOURNAL*, **44**, 2106 and 2116 (1922).

² Sommer, *Ber.*, **48**, 1833-41 (1915).

³ Browne and Hoel, *THIS JOURNAL*, **44**, 2109 (1922).