sodium ethylate. For the alkylation, the following proportions were used, *viz.*, 15 g. of the 2-mercaptopyrimidine, 2.4 g. of sodium, 14 g. of allylbromide and 75–100 cc. of absolute alcohol. After the reaction was complete the sodium bromide was filtered off and the excess of alcohol removed in the usual manner, when we obtained the allyl derivative as a yellow oil. This was extracted with ether dried over potassium carbonate and then further purified by distillation under diminished pressure. It practically all boiled at 160–164° at 17 mm. A nitrogen determination (Kjeldahl) gave:

Calc. for $C_9H_{12}ON_2S$: N = 14.2; found: N = 14.3.

The constitution of this mercaptopyrimidine was established by its behavior on hydrolysis. It was converted smoothly into 4-methyluracil by digestion with hydrochloric acid. This was purified by crystallization from hot water and did not melt or decompose below 300°. Analysis (Kjeldahl):

Calc. for $C_5H_6O_2N_2$: N = 22.2; found: N = 22.2.

NEW HAVEN, CONN.

ON 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYLSULFINIC ACID AND 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYLMETHYLSULFONE.

[EIGHTEENTH[1] COMMUNICATION ON URAZOLES.]

BY E. W. ESSLINGER AND S. F. ACREE.

Received November 14, 1914.

In developing the study of tautomerism as illustrated in the urazoles, it has been found[2] that 1-phenyl-3-thiourazole (I) apparently gives only one mono-alkyl derivative (II) when treated with an alkyl halide, diazomethane or alcoholic hydrochloric acid, or when its salts are treated with an alkyl halide or sulfate. It will be recalled that the corresponding 3-oxyurazole always yields a mixture of the 2-N-ester (V) and 3-O-ester (VI) under these conditions, the yields varying widely with the different salts and alkyl halides used. A mathematical development of our theory[3] showed that the facts can be interpreted consistently on the idea that the salts of the 3,5-dioxyurazoles exist in two tautomeric[4] forms (III) and (IV),

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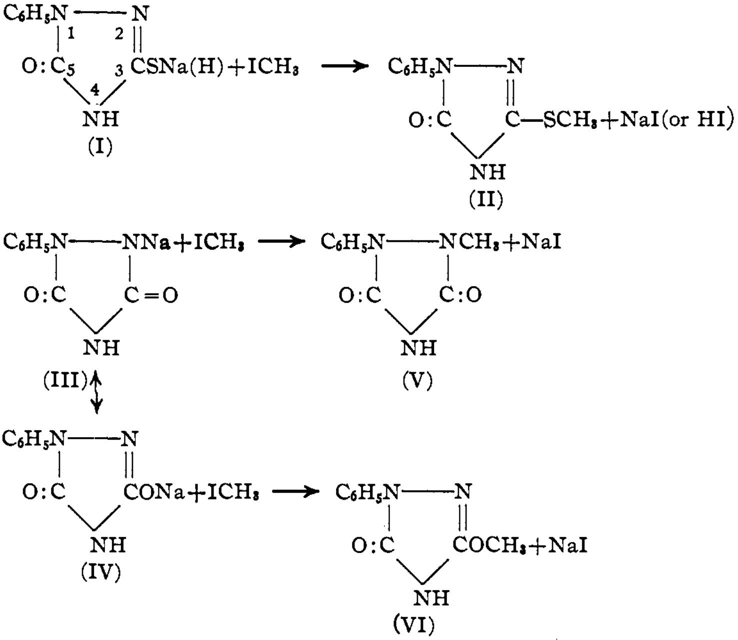
[1] This work was presented in June, 1912, by E. W. Esslinger as a partial fulfillment of the requirements for the degree of Master of Arts in the Johns Hopkins University. For previous work see *Ber.*, **33**, 1530 (1900); **35**, 553 (1902); **36**, 3139 (1903); **37**, 184, 618 (1904); **41**, 3199 (1908); *Science*, 30, 617 (1909); *Am. Chem. J.*, **27**, 118 (1902); **31**, 185 (1904); **32**, 606 (1904); **37**, 71, 361 (1907); **38**, 1 (1907); **39**, 124, 226 (1908); **43**, 358 (1910); **44**, 219 (1910); **49**, 116 (1913). [We are indebted to the Carnegie Institution of Washington for aid in these researches.]

[2] *Ber.*, **36**, 3152 (1903).

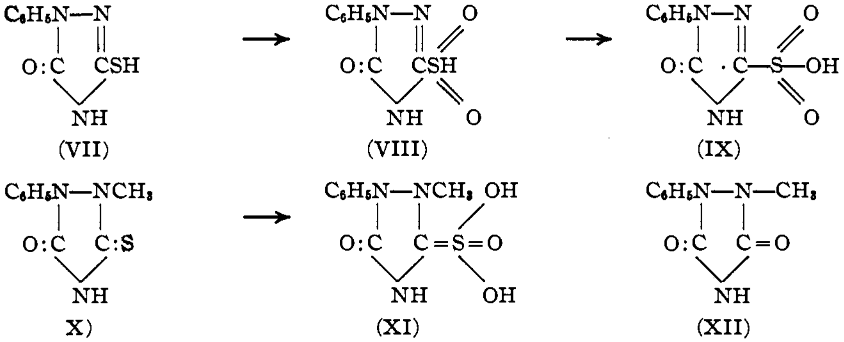
[3] *Ibid.*, **41**, 3199 (1908); *Am. Chem. J.*, **43**, 505 (1910).

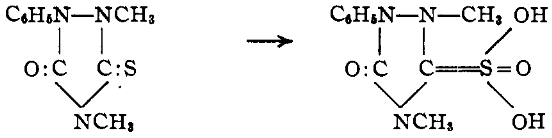
[4] *Ibid.*, **37**, 70 (1907); **38**, 1 (1907); **43**, 505 (1910); **44**, 219 (1910); **49**, 116 (1913).

whose molecules and anions are in equilibrium and react with the molecular alkyl halide to give the esters (V) and (VI). Since 1-phenyl-3-thiourazole (I) yields only one ester (II), it seemed probable that very little of the tautomeric form corresponding to (III) enters into the reaction.

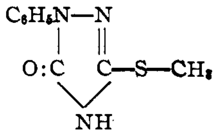

(I) (II) (III) (V) (IV) (VI)

On account of the difficulties involved and the expense of the necessary materials the 2-N-esters (X) of 1-phenyl-3-thiourazole have never been synthesized and we have not, therefore, obtained the direct evidence excluding the possibility that the esters obtained by alkylation are 2-N-esters (X) instead of 3-S-esters (II). Likewise we have not yet synthesized the dialkyl esters (XIII) and shown them to be different from the dialkyl esters (XVII) obtained by the direct alkylation of 1-phenyl-3-thiourazole.

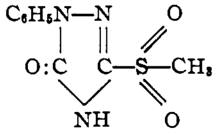

(VII) (VIII) (IX) X) (XI) (XII)



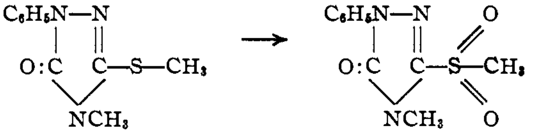
(XIII) (XIV)



(XV)



(XVI)



(XVII) (XVIII)

It has seemed to us wise, therefore, to submit the esters assumed to have the constitutions (II) and (XVII) to a number of reactions in order to secure more light on this important question. The first transformation carried out is the oxidation of 1-phenyl-3-thiourazole (VII), 1-phenyl-3-thiomethylurazole (XV), and 1-phenyl-3-thiomethyl-4-methylurazole (XVII). If 1-phenyl-3-thiourazole behaves normally on oxidation with potassium permanganate or hydrogen peroxide we should expect the formation first of a sulfinic acid (VIII) and then of a sulfonic derivative (IX), or even a derivative of sulfuric acid as described by Dr. H. A. Lubs in an article which will appear later. This particular reaction seems to be rather complicated, but Esslinger has isolated a very soluble substance which seems to be a sulfinic acid, and to which we have tentatively assigned the structure (VIII). A silver salt was made which seemed to possess the corresponding formula. Furthermore, Lubs has oxidized (VII) still further and also oxidized the 1-phenyl-3-thio-4-methylurazole corresponding to (VII) and shown definitely that, *when the sulfur at -3- has no alkyl on it, the urazole can be readily oxidized to a corresponding very soluble acid.* This evidence, though preliminary, is of great importance in the following reactions:

The oxidation of (XV) and (XVII), however, is very simple, as they seem to behave like thioethers and yield sulfones. If the methyl derivative, m. p. 175–6°, obtained by the alkylation of 1-phenyl-3-thiourazole or its monobasic salt, had the sulfur free from a methyl group, as in (X), we should expect to get by the final oxidation, just as with (VII), an acid having an oxidized sulfur grouping like (VIII) or (XI). Such an acid should be *very soluble*, at least dibasic and should have at least four oxygen atoms. As a matter of fact the substance obtained *is very insoluble*, behaves like a sulfone, has only three oxygens, is a monobasic acid, forms a mono-silver salt, and behaves in every respect as if it has the structure (XVI). We must conclude, therefore, that the methyl derivative obtained by alkylating 1-phenyl-3-thiourazole, and melting at 175–6°, has the structure (XV) and is a derivative of (I) or (VII). When the sodium salt of (XVI) is alkylated with methyl iodide a neutral substance is obtained which corresponds in all respects to (XVIII). This same substance is formed by oxidizing the dimethyl derivative (XVII) obtained by methylating 1-phenyl-3-thiourazole (VII) and having the m. p. 95–6°. That this dimethylurazole has the structure (XVII) and not (XIII) is shown by the above reasoning and the fact that one methyl is surely[1] already known to be at -4-. If the other methyl were at -2-, as in (XIII), and the sulfur were free from alkyls, oxidation should give us a *very soluble acid* like (XIV) instead of the *insoluble neutral substance* obtained (XVIII).

It must be decided at present, therefore, that 1-phenyl-3-thiourazole reacts in the enol form (VII) and yields on alkylation the mono- and dialkyl derivatives, (XV) and (XVII), having one methyl on the sulfur at (III) instead of on the nitrogen at -2-. We are planning further experiments to remove the -SCH_3 and -SO_2CH_3 groups from these urazoles, in order to obtain the corresponding oxyurazoles which have been synthesized by other methods, leaving no doubt as to their constitution.

Experimental.

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic Acid (VIII).—This compound was made by oxidizing the sodium salt of 1-phenyl-3-thiourazole, either by means of an alkaline solution of potassium permanganate or with a 30% solution of hydrogen peroxide. Both methods gave the same substance which melted at 174–178°.

I. The sodium salt of 1-phenyl-3-thiourazole in a slightly alkaline solution was treated with sufficient potassium permanganate to furnish two oxygen atoms. After all the potassium permanganate had been added, the solution was boiled, then filtered to remove the manganese hydroxide, after which it was evaporated to a small volume and acidified. On cooling 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic acid crystallized out.

II. A slightly alkaline solution of the sodium salt of 1-phenyl-3-thiourazole was placed with a smaller sealed tube of 30% hydrogen peroxide in a thick walled glass tube, which was then sealed. By violent shaking the thin walled tube containing the hydrogen peroxide was broken and the two solutions were thoroughly mixed. Hydrogen peroxide in an alkaline solution decomposes rapidly, liberating a large quantity of oxygen which in this case is the active agent. After standing two days the tube was opened and no unchanged 1-phenyl-3-thiourazole was found on the addition of a slight excess of sulfuric acid. The solution was evaporated to a small volume and the same 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic acid was obtained as above.

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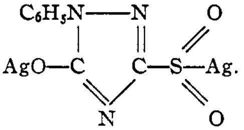
[1] *Ber.*, 36, 3154 (1903).

Di-silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic Acid,



This compound was made by adding silver nitrate to an aqueous solution of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic acid. The silver salt precipitated out as a white powder that soon turned gray and when dry was dark brown.

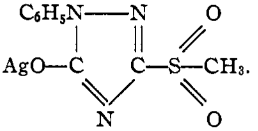
0.3221 g. substance lost 0.0120 g. H_2O at 110°; 0.5159 g. substance gave 0.2419 g. Ag. Calc. for $C_8H_6N_3SO_3Ag_2$: H_2O (1 mol), 3.94; Ag_2, 47.17; found: 3.72 and 46.88.

It is not intended by the use of the above formulas to indicate whether the water lost on heating the substance is water of crystallization or of constitution.

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone (XVI). — This compound was made by oxidizing 1-phenyl-3-thiomethylurazole by means of potassium permanganate as described under the preparation of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic acid. This substance differs from 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfinic acid in that it separates from the oxidizing mixture on the addition of sulfuric acid. It was easily purified by dissolving it in dilute alkali and precipitating it with sulfuric acid. When pure it melts at 206–207°.

1.100 g. substance required 23.1 cc. $N/5$ NaOH; calc., 22.9 cc.

Silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone,



This silver salt was made by adding silver nitrate to the neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone. The silver salt precipitated out as a white powder, which remained unchanged when dry.

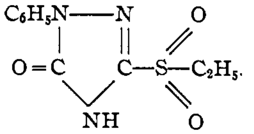
0.2317 and 0.2351 g. substance gave 0.0732 and 0.0732 g. Ag; calc. for $C_9H_8N_3O_3SAg$: Ag = 31.18; found: 31.16 and 31.13.

1-Phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone (XVIII).—This compound was made by treating the neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone with methyl iodide (CH_3I) in boiling alcoholic solution. After heating it for 2 hrs. the reaction mixture was evaporated to a small volume, made alkaline with sodium hydroxide and extracted with chloroform. The chloroform was carefully evaporated, the residue hydrolyzed with hydrochloric acid, to remove any 1-phenyl-4,5-dihydro-5-methoxy-3-triazolylmethylsulfone that was formed, then made alkaline and extracted with chloroform. The residue obtained after the evaporation of the chloroform was dissolved in a small amount of alcohol, filtered, and slowly poured into water, when the 1-phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone precipitated as a white powder. When pure, this compound melted at 94–95°.

An experiment to determine the ratio of the enol to the keto dimethyl esters gave the following results:[1]

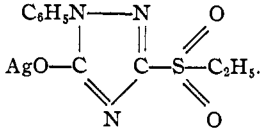
Enol (about) 60%   Keto (about) 40%

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone,



This compound was made by the same method used in the preparation of 1-phenyl-4-oxy-4,5-dihydro-3-triazolylmethylsulfone. When pure, this compound is white and melts at 199.5–200°.

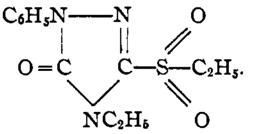
Silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone,



This salt was made by treating a neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone with silver nitrate. This salt, when dry, was stable.

0.2526 and 0.4292 g. substance gave 0.0758 and 0.1289 g. Ag; Calc. for $C_{10}H_{10}N_3SO_3Ag$: Ag, 29.96; found: 30.00 and 30.03.

1-Phenyl-5-oxy-4-ethyl-4,5-dihydro-3-triazolylethylsulfone,



This compound was made in the same manner as was used in making 1-phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone. The compound was white and melted at 74 to 75°.

The experiment made to determine the ratio of the keto to the enol di-ethyl esters gave the following results:

Enol ester (about) 60%   Keto ester (about) 40%

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[1] Method described in Marshall's Dissertation J. H. U., 1911.

Conclusions.

From the chemical and conductivity data we can conclude that 1-phenyl-3-thiourazole exists in solution chiefly as an equilibrium mixture represented below:

By means of acids at 125°, under pressure, an alkyl mercaptan can be split off from the products obtained by methylating or ethylating 1-phenyl-3-thiourazole. Hence the assumption that the alkyl group is attached to the sulfur at position 3 seems substantiated further.

Since we obtain *very soluble* acids, apparently sulfinic and sulfonic acids on oxidizing 1-phenyl-3-thiourazole, but obtain *insoluble* sulfone-like substances having two additional oxygen atoms on the oxidation of the alkylation products assumed to be 1-phenyl-3-thioalkylurazoles and 1-phenyl-3-thioalkyl-4-alkylurazoles, we may conclude that these alkyl derivatives have an alkyl on the sulfur at 3, and not on the nitrogen at 2, and that 1-phenyl-3-thiourazole is alkylated in the tautomeric thioenol forms given above.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE VALENCE OF NITROGEN IN AMMONIUM SALTS.

BY WILLIAM A. NOYES AND RALPH S. POTTER.[1]

Received November 18, 1914.

During the early years of the development of the theory of valence, many chemists held the view that each element has an unvarying valence. The apparent change of valence in nitrogen from ammonia to ammonium salts, and in phosphorus from phosphorus trichloride to phosphorus pentachloride was explained by calling the ammonium salts and the pentachloride molecular compounds, as distinguished from ammonia and the trichloride, in which the true valence of the elements was supposed to be shown. This view received support from the dissociation of ammonium salts and of phosphorus pentachloride in the gaseous state. Gradually, with the demonstration that phosphorus pentachloride volatilizes in part unchanged, that phosphorus pentafluoride, PF_5, has a vapor density corresponding to its formula and, in general, that dissociation in the gaseous

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[1] Presented in abstract before the American Philosophical Society, April 24, 1914. This paper is also an abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.