

On the other hand, it is also not to be supposed that mercury would be *separated* in the metallic condition, as the reaction with HgCl_2 is rapid enough so that even the slight solubility of mercury in water is not exceeded.

In general we may represent the reduction of mercuric compounds as going first to mercury, or some substance which behaves like mercury, and then, if conditions permit, to mercurous compounds. This manner of representing the reaction accounts for the fact that it is *bimolecular*, so far as concerns kinetics, and does away with the necessity for specific explanations for each different reducing agent.

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[CONTRIBUTION FROM JOHNS HOPKINS UNIVERSITY.]

COMMUNICATION ON TAUTOMERISM. ON THE TAUTOMERIC REACTIONS OF 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYL METHYL SULFONE AND ITS SALTS WITH DIAZOMETHANE AND WITH ALKYL HALIDES.¹

By H. A. LUBS AND S. F. ACREE.

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Various theories have been proposed to account for the phenomenon of tautomerism, and among them are those of Comstock,² Wheeler,³ Nef,⁴ and Michael.⁵ One of the facts which these theories try to explain is how two or more stable isomeric products can be obtained by the action of a reagent upon a tautomeric substance. Though these theories have been shown to fit in with the facts excellently in certain cases, yet a large amount of experimental evidence obtained in this laboratory has shown that these theories do not fully correlate the quantitative data obtained with the urazoles.

According to our theory of tautomerism, when urazoles, their salts, and derivatives give two or more stable products as a result of the reaction, they do so because they exist (a) in one tautomeric form alone which yields two or more derivatives through independent side reactions,⁶ or (b) in two or more forms in equilibrium, each of which gives its own derivatives through an independent reaction. The urazole salts or acids could react through their anions or nonionized molecules, or both.

¹ We have been aided in this work by the Carnegie Institution of Washington.

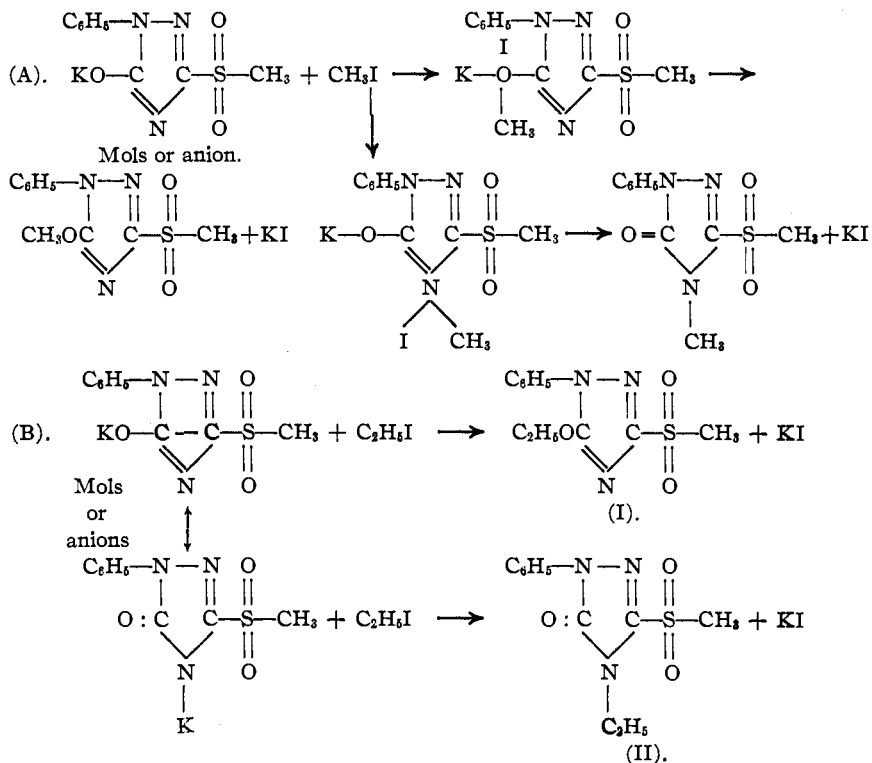
² *Ber.*, 23, 2274 (1890); *Am. Chem. J.*, 12, 493 (1890); 13, 514, 525 (1891).

³ *Am. Chem. J.*, 21, 187 (1899); 23, 135 (1900); 30, 28 (1903).

⁴ *Ann. Chem.*, 258, 261 (1890); 266, 105 (1891); 276, 200 (1893); 277, 59, 83 (1893).

⁵ *J. prakt. Chem.*, 37, 469 (1888); 45, 580 (1892); 46, 189 (1892); *Am. Chem. J.*, 43, 322 (1910).

⁶ For mathematical discussion of this theory, see Acree, *Am. Chem. J.*, 38, 1 (1907).



It was shown in an earlier paper that both (A) and (B) led to the formation of an *O*-ester and an *N*-ester by a bimolecular reaction for each and for their sum and to a constant ratio of *O*-ester to *N*-ester for a given salt, alkyl halide, solvent, and temperature, regardless of the value of the reaction time. These ratios and reaction velocities might naturally vary with the salt, alkyl halide, solvent, and temperature, whether (A) or (B) is correct. Such facts can not then differentiate between (A) and (B). If (A), however, is correct, the urazole acid is liberated in only one form from the salt, whereas two forms of the acid are liberated from the salt if (B) is correct. Since the ratio of these two acids in (B) could possibly change it would be possible to use some very rapid physical or chemical method to tell whether only one acid is liberated as in (A) or two or more tautomeric acids as in (B).

In attempting to decide between the possibilities (A) and (B) for 1-phenyl-2-methylurazole Marshall in unpublished investigations worked at -70° with diazomethane as the alkylating agent, and found that two different ratios of esters were obtained from 1-phenyl-2-methylurazole, the results depending upon whether the urazole acid itself was alkylated or the acid is liberated from the sodium, silver or zinc salt and immedi-

ately alkylated. Even in fifteen seconds the liberated acid underwent a tautomeric or other change and gave a ratio of esters which corresponded to that obtained from the ordinary free urazole acid itself. His results were interpreted as evidence that 1-phenyl-2-methylurazole exists in two or more tautomeric forms, as in (B), as evidence for an equilibrium ratio of the two tautomeric forms of the urazole salt different from that of the two tautomeric forms of the free 1-phenyl-2-methylurazole, and as evidence for the rapidity with which equilibrium is established between the two tautomeric forms. All of the other quantitative data at hand in the urazole work harmonize with this view.

One of us¹ has shown mathematically and experimentally that the ratio of esters obtained gives only the "apparent ratio" of the two tautomers yielding the esters, and that the factors which influence the ratio of stable alkyl or other derivatives from a tautomeric compound are principally: (1) The relative reactivity of the two tautomeric forms toward the reagent; (2) the ratio between the amounts of two or more tautomeric forms when they are in constant equilibrium with each other; and (3) the rapidity of the change of each of these tautomeric forms into the other as the equilibrium is disturbed. Consideration of these possibilities makes evident the complexity of the problem, and the necessity for vastly more experimental evidence, to add to which is the purpose of this contribution.

Since in all cases we obtain both *O*-esters and *N*-esters when the urazoles or their salts are alkylated, it has been very important and is the object of this paper, to compare our work with the researches of Wheeler on the reactions of alkyl halides on amide salts. From the fact that (1) he obtained only the *O*-esters from silver salts of amides and alkyl halides at lower temperatures and only *N*-esters from sodium or silver salts at higher temperatures, and that (2) the *O*-esters and alkyl halides gave *N*-esters at higher temperatures, Wheeler logically concluded that his compounds react according to Scheme A above, salt \rightarrow *O*-ester \rightarrow *N*-ester, that all salts of amides are oxygen derivatives and that these first yield oxygen esters, which then form addition products with the alkyl halide and rearrange catalytically into nitrogen esters.

The cyclic amides, in particular the urazoles, seem to differ in the above respects from the simple amides. In the present work and in the previous work on the urazole esters, with the one possible exception of the *O*-allyl ester of 1-phenyl-4-methylurazole, no cases have been found in which either the *O*-ester or the *N*-ester rearranged under the conditions of the experiments. Further, the ratio of *O*-ester to *N*-ester does not change with time and temperature, as would certainly be the case if Wheeler's theory held in general. If the *O*-ethyl ester derived from the methyl

¹ *Am. Chem. J.*, 38, 8 (1907).

sulfone sodium salt rearranged readily enough at 60° to give about 90% *N*-ester and only 10% *O*-ester, it would be difficult to see how 97% of *O*-ester would be obtained from the *silver salt*, both at room temperature and after heating the reaction mixture, containing a large excess of alkyl halide, at 100° for six hours. That the sodium or silver salt does not yield an equilibrium mixture of *N*-ester and *O*-ester whose ratio varies for the different salts was proved quantitatively by adding known amounts of *O*-ester and *N*-ester to the reacting salt and alkyl halide and showing that the total amounts of *N*-ester and of *O*-ester isolated are simply the sums of those added and of the *N*-ester and *O*-ester formed in the usual ratio from that particular salt. Wheeler's compounds differ materially, therefore, from the urazoles in that our *O*-esters and *N*-esters are apparently formed independently in bimolecular reactions taking place according to Scheme B discussed above.

In order to solve these physical-organic problems it is necessary to have organic compounds with the physical and chemical properties needed to secure the quantitative data. Upon investigating the properties of 1-phenyl-5-oxy-4,5-dihydro-3-triazolyl methyl sulfone, it was found that this compound is extremely well adapted to the study of tautomerism. This substance can be obtained easily in pure condition and is very stable. The alkylation of the free acid or of the sodium, silver, or mercury¹ salts by diazo-methane or alkyl halides yields both *O*- and *N*-esters, which are stable white crystalline substances and are nonvolatile at the temperatures to which it is necessary to subject them.

In order to obtain information about the tautomeric properties of the methylsulfone, the free sulfone and also its salts were alkylated under varying conditions. The following tables show that these ratios of esters bear a fairly close relationship to the ratio of esters obtained by Johnson by alkylating the 1-phenyl-3-thioalkylurazoles under the same conditions.

The ratios of esters obtained by the action of diazomethane on the 1-phenyl-3-thiomethylurazole by Johnson and on the methyl sulfone by Lubs vary more widely than the ratios obtained from their corresponding salts and the alkyl halides.

From these tables it is seen that the methyl sulfone readily gives both both *O*- and *N*-esters and in particular that each is formed in sufficient amounts to handle well experimentally. It was consequently chosen for this study.

In the following pages we present the tables of data on the reactions of the methyl sulfone and its salts with diazomethane and alkyl halides. As the ratio of esters from a given salt and a given alkyl halide in a given

¹ For work on this salt see the dissertation and a forthcoming article by Dr. E. H. Wight.

Urazole.	Alkylhalide.	Tem- perature.	Per cent. N-ester.	Per cent. O-ester.
Sodium salt of methyl sulfone	Methyl iodide in 40% alcohol	100°	97.0	3.0
Sodium salt of methyl sulfone	Ethyl iodide in 40% alcohol	100°	90.4	9.6
Silver salt of methyl sulfone	Methyl iodide in ether	100°	19.0	81.0
Silver salt of methyl sulfone	Ethyl iodide in ether	100°	3.0	97.0
Sodium salt of 1-phenyl-3-thiomethyl- urazole	Ethyl iodide in 40% alcohol	60°	88.4	11.6
Silver salt of 1-phenyl-3-thiomethyl- urazole	Ethyl iodide in 40% alcohol	60°	9.0	91.0
Sodium salt of 1-phenyl-3-thioethyl- urazole	Ethyl iodide in 40% alcohol	60°	89.6	10.4
Silver salt of 1-phenyl-3-thioethyl- urazole	Ethyl iodide in 40% alcohol	60°	8.0	92.0
Silver salt of 1-phenyl-3-thio- <i>n</i> -propyl- urazole	Ethyl iodide in 40% alcohol	60°	12.1	87.9

Urazole.	Diazoalkyl.	Tem- perature.	Per cent. N-ester.	Per cent. O-ester.
1-Phenyl-3-thiomethyl- urazole	0.0524 <i>N</i> diazomethane in 20 cc. ethyl alcohol plus 10 cc. ether	0°	64.4	35.6
Sodium salt of 1-phenyl- 3-thiomethylurazole	0.0524 <i>N</i> diazomethane in 20 cc. ethyl alcohol plus 10 cc. ether plus 1 mol HCl (gas)	0°	64.6	35.4
1-Phenyl-3-thiomethyl- urazole	0.0524 <i>N</i> diazomethane in ether	20°	69.8	30.2
Methyl sulfone	Diazomethane in alcohol and ether	20°	86.1	13.9

solvent is constant for different time periods and even for different temperatures it is believed that the reactions do not follow the course [salt \rightarrow O-ester \rightarrow N-ester] but can be expressed best today by Scheme B outlined on p. 951. This same reaction mechanism B is in harmony with the formation of *different* ratios of esters from *different* salts and *different* alkyl halides in *different* solvents described below.

Experimental.

Ratio of esters obtained from the sodium and silver salts of the methyl sulfone when alkylated with methyl iodide and ethyl iodide.

Preparation of the Solution of the Methyl Sulfone Sodium Salt.—The sulfone was dissolved in alcohol, and neutralized with aqueous sodium hydroxide. For example, 1.9294 g. of the sulfone required 40.57 cc. of 0.1998 *N* NaOH instead of the theoretical 40.64 cc. To this solution an excess of the alkyl halide was added. In some of the first experiments the reaction mixture was heated upon a water bath in a small flask attached to a return condenser. Later it was found more satisfactory to allow the mixture to react in a sealed tube in a water bath at 100°.

Separation of Esters Formed.—The method used to extract the esters was that suggested by one of us and used by Johnson, Nirdlinger, Marshall and Brunel. After heating the reaction mixture the necessary length of time, the volume of the solution was reduced by careful distillation, if necessary, to 5 or 10 cc.; then it was transferred directly to a small separatory funnel, which contained about 50 cc. of water. Sufficient dilute alkali was added to the aqueous layer to cause the pink color of phenolphthalein to persist after agitating the reaction mixture. This solution was extracted five times with redistilled chloroform and after each extraction the chloroform was transferred to a similar separatory funnel containing about 50 cc. of water made slightly alkaline. The chloroform solution of the esters was run into a small weighed porcelain dish after each extraction. The chloroform was evaporated off by placing the dish upon a water bath and blowing gently over the surface of the chloroform. This enables us to evaporate off the solvent below its boiling point, and further, prevents the creeping of the ester over the edge of the dish. The ester is then placed in a vacuum desiccator containing sulfuric acid, and allowed to come to constant weight. In this way, we get the weight of the total amount of ester formed.

When the esters were isolated in this way, it was found, for example, that 1.9294 g. of the sulfone and methyl iodide in 4 hrs. gave 1.2660 g. of the mixed methyl esters; 1.8110 g. of the sulfone and methyl iodide in 4 hrs. gave 0.9917 g. of the mixed methyl esters; and that 1.9905 g. of the sulfone and ethyl iodide in 4 hrs. gave 1.3739 g. of the mixed ethyl esters. Other yields are given in the tables below.

Hydrolysis of the 5-*O*-Ester.—When the mixture of esters has come to constant weight it is transferred by means of chloroform to a glass tube drawn out and sealed at the bottom, and constricted at the top. The constriction at the top facilitates the sealing of the tube. The chloroform is then evaporated off and 3 cc. of absolute alcohol saturated with hydrochloric acid gas is added. The tube is then sealed and heated at 100° for one hour. The hydrochloric acid decomposes the *O*-ester into methyl chloride and the methyl sulfone, which is soluble in alkali, whereas the *N*-ester is unattacked. By extracting the solution as described above, the alkali salt of the methyl sulfone is dissolved in the aqueous layer, and the pure methyl sulfone is obtained by acidifying the solution and is found to melt at 206°. The neutral *N*-ester is extracted by the chloroform, which is then run into a weighed dish and evaporated in the usual way. Knowing the weight of the total esters, and the weight of *N*-ester formed, by difference we know the weight of the *O*-ester.

As an example of the use of this method, it was found that 1.2758 g. of the mixed methyl esters prepared in an open flask from the methyl sulfone sodium salt gave on hydrolysis 1.2660 g., or 99.2% of the methyl

N-ester; 1.1604 g. of the mixed methyl esters gave on hydrolysis 1.1157 g., or 96.1% of the methyl *N*-ester. When recrystallized from alcohol this methyl *N*-ester melted at 105-6° and was found to be identical in all respects with the 1-phenyl-4,5-dihydro-5-oxy-4-methyl-3-triazolyl methyl sulfone prepared in this way by Esslinger, and also made by us by the oxidation of 1-phenyl-3-thiomethyl-4-methylurazol.

Although about 15 operations involving sources of error are required to determine the ratio of esters, the total error can be reduced to within 1 to 2% by careful work. As an illustration, 0.2895 g. methyl *N*-ester on hydrolysis gave back 98.8%; when rehydrolyzed, 99.34% of the methyl *N*-ester were recovered.

ALKYLATION OF THE SODIUM SALT.

Sodium Salt of 1-Phenyl-5-Oxy-4,5-Dihydro-3-Triazolyl Methyl Sulfone and Methyl Iodide in a Mixture of Alcohol and Water, When Heated Four Hours in a Small Flask on the Water Bath.

Wt. sulfone.	Cc. methyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>N</i> -ester.
About 2 g.	4	1.2758 g.	1.2660 g.	99.2
About 2 g.	4	1.1604 g.	1.1157 g.	96.1

Average, 97.6

Sodium Salt and Methyl Iodide in a Mixture of Alcohol and Water, Heated Four Hours in a Sealed Tube at 100°.

Wt. sulfone.	Cc. methyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>N</i> -ester.
0.7639	4	0.5927 g.	0.5743 g.	96.9
0.5750 (sodium salt)	2	0.4335 g.	0.4112 g.	94.9

Average, 95.9

Sodium Salt and Ethyl Iodide in a Mixture of Alcohol and Water, Heated Four Hours in a Sealed Tube at 100°.

Wt. sulfone.	Cc. ethyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>N</i> -ester.
0.4963	4	0.1598 g.	0.1478 g.	92.5
0.4664	2	0.1418 g.	0.1281 g.	90.3
0.5167 (sodium salt)	2	0.2083 g.	0.1843 g.	88.5

Average, 90.4

Alkylation of the Silver Salt.

In alkylating the insoluble silver salt, it was suspended in ether, the alkyl halide added, and the tube sealed. In the beginning of the work these alkylations were carried on at room temperature in small flasks closed with corks. Both tubes and flasks were shaken at frequent intervals. The insoluble silver salts were filtered from the ether, washed with ether on the filter, and the ether solution was evaporated in a porcelain dish. The residue of mixed esters was dried, weighed, and transferred with chloroform to a separatory funnel and treated as described above.

Silver Salt of Methyl Sulfone and Methyl Iodide in Ether, in a Small Flask at Room Temperature for Three Days.

Wt. silver salt.	Cc. methyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>O</i> -ester.
0.5 g.*	9	0.3533 g.	0.0533 g.	85.0

Silver Salt of Methyl Sulfone and Methyl Iodide in Ether in a Sealed Tube, Six Hours at 100°.

Wt. silver salt.	Cc. methyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>O</i> -ester.
Approx. 0.5 g.	2	0.2654 g.	0.0510 g.	80.8
Approx. 0.5 g.	2	0.2741 g.	0.0515 g.	81.2

Average, 81.0

Silver Salt of Methyl Sulfone and Ethyl Iodide in Ether in a Flask at Room Temperature, Four Days.

Wt. silver salt.	Cc. ethyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>O</i> -ester.
Approx. 0.5 g.	2	0.5144 g.	0.0106 g.	97.9
Approx. 0.5 g.	2	0.4185 g.	0.0103 g.	97.5
		0.1583 g.	0.0050 g.	96.8

Average, 97.4

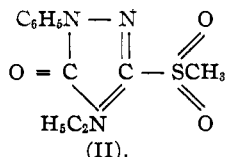
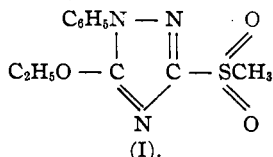
Silver Salt of Methyl Sulfone and Ethyl Iodide in Ether in a Sealed Tube at 100°, Six Hours.

Wt. silver salt.	Cc. ethyl iodide.	Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>O</i> -ester.
Approx. 0.5 g.	2	0.2030 g.	0.0078 g.	96.2
Approx. 0.7 g.	2	0.3084 g.	0.0100 g.	96.8

Average, 96.5

Since 97% of the ethyl *O*-ester is obtained by alkylating the silver salt of the methyl sulfone, this ester is obtained in practically a pure state by recrystallizing the mixture from alcohol. The corresponding *N*-ester is obtained in a pure state from the sodium salt by hydrolyzing away the *O*-ester which is formed simultaneously.

1-Phenyl-5-ethoxy-4,5-dihydro-3-triazolyl methyl sulfone (I), is a stable, white crystalline substance which melts at 97°. The isomeric *N*-ester (II), is very similar in appearance but has a different melting point, namely, 116°. By using the method described above an analysis



was made of the recrystallized *O*-ester and it was found that there was only about 1% of the *N*-ester present. Several recrystallizations would doubtless remove practically all of this small amount.

* This was one of the first ratios determined and the high ratio may possibly be due to experimental error.

Silver Salt of Methyl Sulfone and Allyl Bromide in Ether in Sealed Tubes at 0°, 25° and 100°. By Lawson Wilkins.¹

In the preceding article by Johnson and one of us it was shown that allyl iodide reacts with the silver salt of 1-phenyl-4-methylurazole and gives 79% of *N*-ester at 0°, 30°, or 60°, but at 100° a rearrangement and partial decomposition of the *O*-allyl ester takes place and about 97% of *N*-ester is found.

In studying the reactions of the methyl sulfone it seemed desirable to learn whether the *O*-ester is intermediate in the formation of the *N*-ester in any case. The following experiments were, therefore, performed in order to see whether both *O*- and *N*-allyl esters are formed from allyl bromide and the silver salt of the methyl sulfone and whether the *O*-allyl ester rearranges into the *N*-allyl ester at higher temperatures in the presence of allyl bromide. The results show that no appreciable rearrangement takes place, although large amounts of *O*-allyl ester are produced, and that a constant ratio of approximately 95.5% *O*-allyl ester and 4.5% *N*-allyl ester is formed at 0°, 25°, or 100°.

The materials were prepared as follows: 25 g. of 1-phenyl-3-thiourazole gave 23 g. of 1-phenyl-3-thiomethylurazole, melting point 172–3°, which is 87% of the theoretical yield. This methyl ester and potassium permanganate² gave a quantitative yield of 27 g. of 1-phenyl-4,5-dihydro-5-oxy-3-triazolyl methyl sulfone melting at 203–4°. Ten grams of this methyl sulfone gave 14 g., or 93% of the theoretical yield, of the pure silver salt. The allyl bromide had been washed thoroughly with water to remove hydrobromic acid and was dried over sodium sulfate.

Samples of about 0.5 g. silver salt, 2 cc. of allyl bromide and 5 cc. dry ether were sealed in small glass tubes as usual, shaken in constant temperature baths, and allowed to react during the times noted in the following table. The method used for the isolation of the esters is essentially the one described on page 955. In Expt. F the silver bromide was dissolved in aqueous potassium cyanide and the esters were extracted from the solution with chloroform, a method found very satisfactory for silver, mercury, and other heavy metal salts by Dr. E. H. Wight. The following table gives a summary of the important data.

These results show clearly that most of the silver salt, 78 to 94% has reacted. Only 4.5% of the mixed esters is the *N*-allyl derivative and 95.5% is the *O*-allyl derivative, which gives the methyl sulfone when treated

¹ All of the experimental work on the alkylation of the silver salt of the methyl sulfone in this section was performed by Mr. Lawson Wilkins, to whom we are indebted for this helpful contribution.

² Esslinger and Acree, *THIS JOURNAL*, 37, 187 (1915).

PER CENT. OF *O*-ALLYL ESTER AND *N*-ALLYL ESTER OBTAINED FROM ALLYL BROMIDE
AND THE SILVER SALT OF 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYL
METHYL SULFONE IN ETHER AT 0°, 25°, AND 100°.

No. of expt.	Wt. of salt.	Temp.	Time in hours.	Wt. mixed esters.	% yield.	Wt. N-der.	% N-der.	% O-der.
A.....	0.650	100°	1.5	0.4763	89	0.0197	4.14	95.86
B.....	0.648	100°	1	0.4170	78
E.....	0.462	100°	1	0.3525	88	0.0181	5.14	94.86
C.....	0.571	25°	15	0.4346	93	0.0235	5.41	94.59
D.....	0.580	25°	24	0.4465	94	0.0170	3.81	96.19
F.....	0.506	$\left\{ \begin{array}{l} 0^\circ \text{ for } 15 \\ \text{and} \\ 25^\circ \text{ for } 144 \end{array} \right\}$		0.3827	92	0.0137	3.86	96.14

Average % of *N*-Ester at 100°, 4.64.

Average % of *N*-Ester at 25°, 4.36.

with alcoholic hydrochloric acid. This ratio of esters is practically independent of the time and temperature of the reaction. Since a large amount of *O*-allyl ester is formed, the change of only 5% of it at 100° into the isomeric *N*-allyl ester would practically double the percentage of *N*-allyl ester obtained. Since the percentage of *N*-allyl ester formed is practically the same at 25° as at 100° it is clear that the allyl bromide does not cause any appreciable rearrangement of the *O*-allyl ester of 1-phenyl-4,5-dihydro-5-oxy-3-triazolyl methyl sulfone into the isomeric *N*-allyl compound even at 100°, and that this case is different from those of Wheeler and the single one of Johnson, who observed rearrangements of several imido esters and of one urazole *O*-ester by alkyl halides, including allyl iodide. Further experiments with allyl iodide and bromide and other alkyl halides and the urazole esters at these and still higher temperatures, and a physical chemical investigation of the laws governing these rearrangements, are in progress.

By considering the above data we see that widely different ratios of esters are obtained upon alkylating the sodium and silver salts with various alkyl halides. In this as in all previous cases, any given alkyl halide yields a higher percentage of *N*-ester from the sodium salt than from the silver salt. Any given salt yields a higher percentage of *N*-ester from methyl iodide than from ethyl iodide. From the sodium salt of the methyl sulfone and ethyl iodide, 90.4% of *nitrogen* ester is obtained, while from the silver salt and ethyl iodide 97% of *oxygen* ester is obtained. In the case of the sodium and silver salts of the methyl sulfone treated with *methyl iodide*, from the sodium salt we obtain 96.8% nitrogen ester, and from the silver salt 81% oxygen ester. These are the widest differences in ratios which we have yet obtained from the sodium and silver salts of any urazole, and these facts render possible the ready isolation of the *N*- and *O*-esters in a practically pure condition. The ratios show conclusively that both esters are formed in each case and

since the changes in temperature, time, and concentration had no appreciable effect on the ratio, the theories of Wheeler, Comstock, Nef and Michael are not applicable to these cases. If the esters rearranged under the experimental condition it would be difficult to see how 90.4% of the nitrogen ester would be obtained from the sodium salt, and 96.8% of the oxygen ester from the silver salt, especially in the light of the fact that these salts were heated in all cases with a large excess of the alkyl halide.

The following table gives a résumé of the percentage of *N*-ester and *O*-ester obtained from the different salts of the sulfone and alkyl halides in different solvents at different temperatures:

Salt.	Alkyl halide.	Solvent.	Temperature.	Per cent. <i>N</i> -ester.	Per cent. <i>O</i> -ester.
Sodium	CH ₃ I	Alc.-water	100°	97	3
Sodium	C ₂ H ₅ I	Alc.-water	100°	90	10
Silver	CH ₃ I	Ether	22°	15	85
Silver	CH ₃ I	Ether	100°	19	81
Silver	C ₂ H ₅ I	Ether	22°	3	97
Silver	C ₂ H ₅ I	Ether	100°	3	97
Silver	C ₃ H ₅ Br	Ether	25°	4	96
Silver	C ₃ H ₅ Br	Ether	100°	5	95

These esters have now been investigated very carefully by Dr. E. H. Wight, are perfectly stable, and do not seem to rearrange into one another; if they do, the amount of change is so small that it cannot be detected in our data.

Alkylation of the Methyl Sulfone with Diazomethane.

The diazomethane was prepared by the method of Von Pechman.¹ The sulfone was dissolved in alcohol and an excess of an ethereal solution of diazomethane was added, which was indicated by the yellow color of the reaction mixture. The solvents were then carefully evaporated off and the ester formed was transferred by means of chloroform to a small separatory funnel and extracted and hydrolyzed in the usual way.

RATIO OF ESTERS FROM METHYL SULFONE AND DIAZOMETHANE.

Wt. total ester.	Wt. <i>N</i> -ester.	Per cent. <i>N</i> -ester.
0.2332	0.1981	84.9
0.3321	0.2858	86.1
0.4499	0.3930	87.3

Average, 86.1

The ratio of esters obtained by the action of diazomethane on the methyl sulfone shows that the reactions which produce the two forms of the ester are of the same apparent order; otherwise, a constant ratio

¹ *Ber.*, 27, 1888 (1894); 28, 855 (1895).

of esters for different time periods would not have been obtained. Let Equation 1 represent the rate of formation of the *O*-ester, and Equation 2 that of the *N*-ester. By division we get Equation 3 which, on integration, gives Equation 4 for this case.

$$(1) \quad dx'/dt = K'(C_{ur} - x - x')^m (C_{dm} - x - x')^n$$

$$(2) \quad dx/dt = K(C_{ur} - x - x')^o (C_{dm} - x - x')^p$$

$$(3) \quad dx'/dx = K''(C_{ur} - x - x')^{m-o} (C_{dm} - x - x')^{n-p}$$

$$(4) \quad dx'/dx = K'' = x'/x$$

If $m-o$ and $n-p$ were not zero, the ratio x'/x would vary with x , and therefore with t . Since the ratio is constant, Equation 4 must hold for the reaction and $m-o$ and $n-p$ must be zero; that is, m and o are equal, as are also n and p . In other words, the orders of the two reactions are the same with reference to both the urazole and diazomethane, as has also been found to be the case with all of the other urazoles¹ studied up to this time, and by Dr. E. K. Marshall in unpublished work.

Summary.

1. In the present investigation we have attempted to study the tautomeric reactions of alkyl halides and the salts of 1-phenyl-4,5-dihydro-5-oxy-3-triazolyl methyl sulfone in order to learn the mechanism of the formation of the isomeric *O*- and *N*-esters.

2. In all of these alkylation reactions of the free acid and its salts any salt and alkyl halide in a given solvent will give a constant ratio of esters at different time periods and different temperatures. This shows that these esters are formed by independent side reactions somewhat like Scheme B and not in accordance with the equation [salt \rightarrow *O*-ester \rightarrow *N*-ester], applying to the simple amides.

3. This interpretation of the tautomeric reactions is in harmony with the formation of *different* ratios of esters from *different* salts and *different* alkyl halides in *different* solvents and all of the other facts discovered in the urazole series.

4. Allyl bromide and the silver sulfone salt give the same ratio of esters at 25° and 100°. This case is therefore different from that of allyl iodide and silver 1-phenyl-4-methylurazole, in which it was found by Johnson that the *O*-allyl ester is converted partially into the *N*-allyl ester at 100°.

5. The action of diazomethane on the sulfone shows that the *O*-ester and *N*-ester are formed by reactions of the same apparent order.

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¹ Nirdlinger and Acree, *Am. Chem. J.*, 43, 358 (1910).