[CONTRIBUTION FROM JOHNS HOPKINS UNIVERSITY.]

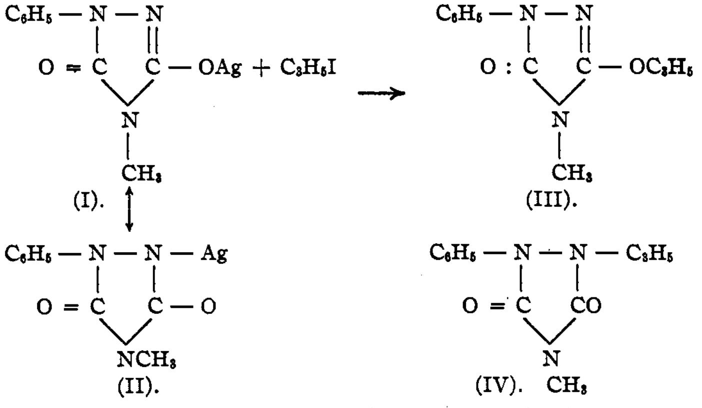
ON THE REARRANGEMENT OF 1-PHENYL-4-METHYL-3-OXY-ALLYL URAZOLE BY ALLYL IODIDE.

BY J. M. JOHNSON AND S. F. ACREE.

Received December 30, 1916.

In unpublished work on tautomerism which we completed in 1908 in our studies of cyclic amides it was shown that a large number of urazole salts and different alkyl halides undergo transformations through bi-molecular reactions. Each given urazole salt and alkyl halide gave both an *O*-ester (III) and an *N*-ester (IV) and, with one exception, these were formed in constant ratio for different time periods. All of the facts showed that these tautomeric reactions can take place because both the ions and molecules of the salt in one tautomeric form react with the molecules of the alkyl halide, or because the tautomeric salt exists in two or more forms, each of which undergoes transformations through independent side reactions, as discussed previously and in the next article by Lubs and Wilkins.

The silver and other salts gave constant ratios of esters at 60° and below.



The one exception to the above rules was noted when it was found that allyl iodide and silver 1-phenyl-4-methylurazole (I) give a much larger percentage about 98, of *N*-ester (III) at 100° than the 79% found at lower temperatures. This case reminded us of the fine work of Wheeler who had found the same evidence in his studies of the alkylation of simple amides in which he had shown that the imido-ester formed at lower temperatures was changed by the alkyl halide into the alkyl amide at higher temperatures.

$$RC(=NH)(OR) + R'I \longrightarrow RCONHR' + RI.$$

This change of ratio of the esters at the higher temperature in our case could arise because of changing temperature coefficients of the reactions, but this seemed unlikely in view of the constant ratio at all temperatures below 60° in this case and below 100° in all other cases studied. It could also happen because of the catalytic changes by the allyl iodide. It was therefore necessary to investigate this case a little more closely quantitatively to decide between these two possibilities. The evidence showed that the allyl iodide causes the change of ratio of esters because it decomposes the *O*-allyl ester (III) partially and forms more *N*-allyl ester (IV). The allyl iodide may form some hydriodic acid which decomposes the *O*-allyl ester into allyl iodide and the 1-phenyl-4-methylurazole, which then react to give more *N*-allyl ester. The change may take place in other ways, involving the formation of intermediate addition products of the allyl iodide and urazole *O*-ester.

Experimental.

The analytical method used for measuring the yields of total esters, and of the *O*-ester and *N*-ester separately, was first developed by Brunel and improved by Johnson and is described in the succeeding work by Lubs and Wilkins.

In order to learn whether allyl iodide gives a changing ratio of the *O*-allyl ester and the *N*-allyl ester in cases other than that of the silver salt, some work was done with the sodium and mercury salts of 1-phenyl-4-methylurazole.

Dr. Johnson found that the *sodium salt* of 1-phenyl-4-methylurazole and allyl iodide give a mixture of two esters in a constant ratio of about 98% *N*-allyl ester and 2% *O*-allyl ester, whatever the time or temperature, from 0° to 100°. The *mercury salt* gave about 93% *N*-allyl ester and 7% *O*-allyl ester at 60°. As the *O*-allyl ester is shown below in the case of the silver salt to be stable in the presence of allyl iodide up to 60° it is evident that below 60° none of the *N*-allyl ester is formed by the rearrangement of the *O*-allyl ester, or *vice versa*, and that only 2% of *O*-allyl ester and the entire 98% *N*-allyl ester are *each formed directly* from the sodium salt, and that the 93% *N*-allyl ester and 7% *O*-allyl ester are *each produced directly* from the mercury salt. The following tables show the data obtained:

Table I.—0.3 *N* Sodium Salt of 1-Phenyl-4-Methylurazole and 0.3 Vol. *N*-Allyl Iodide in 40 Per cent. Ethyl Alcohol at Various Temperatures.

Temperature.	Time in hours.	Total product.	Per cent. N der.
0°..............	2	0.0262	98.5
0°..............	24	0.1591	98.0
30°..............	0.25	0.1105	97.9
60°..............	0.25	0.2609	99.2
100°..............	0.16	0.2362	98.7
100°..............	0.25	0.2635	95.3

In order to learn whether a change in the ratio of the urazole ions to the urazole salt molecules produces a change in the ratio of esters, different concentrations of the sodium salt were used. There was no appreciable change of ratio in this case, but this field will be investigated to learn whether only one or both esters come from the urazole anion or from the non-ionized salt molecule, or from both.

TABLE II.—0.0015 *N* Na SALT + 0.0015 *N*-ALLYL IODIDE IN DIFFERENT CONCENTRATIONS AT 60°.

Cc. 40% alcohol used as solvent.	Time in hours.	Total product.	Per cent. N der.
10	0.25	0.2577	97.7
20	0.25	0.2279	97.9
20	0.083	0.1838	99.1
20	0.166	0.2160	96.7
20	0.42	0.2437	97.6

TABLE III.—0.3 WEIGHT NORMAL MERCURY SALT + 0.3 VOLUME NORMAL ALLYL IODIDE IN 40% ALCOHOL AT 60°.

Mols Hg salt.	Mols C_3H_5I.	Time in hours.	Total product.	Per cent. reacted.	Weight N der.	Per cent.	
						N der.	O der.
0.435	1	1	0.0588	16.9	0.0552	93.9	6.1
0.435	1	4	0.0444	12.8	0.0407	91.7	8.3
					Average,	92.8	7.2

Johnson found further that a mixture of 79% *N*-allyl ester and 21% *O*-allyl ester is obtained from the silver salt of 1-phenyl-4-methylurazole and allyl iodide at 0°, 30°, or 60°. At 100° the total product decreased after a given time and the percentage of *N*-allyl ester increased up to 98% because, as the special experiments below showed, the mixed esters isolated at 60° or below are acted upon by allyl iodide at 100° and the *O*-allyl ester is partially hydrolyzed and partially changed into the *N*-allyl ester, which then corresponds to 98% of the resulting ester mixture and to 88% of the original total product, instead of 79%. Tables IV and V tables show the results obtained.

TABLE IV.—0.3 *N* SILVER 1-PHENYL-4-METHYLURAZOLE AND 0.3 VOL. *N*-ALLYL IODIDE IN 40% ALCOHOL AT VARIOUS TEMPERATURES.

Temperature.	Time in hours.	Total product.	Per cent. N der.
0°	1	0.2633	82.2
30°	0.25	0.2227	78.8
60°	0.5	0.2533	78.8
60°	2	0.2052	78.5
100°	0.25	0.2297	89.7
100°	1	0.2048	98.4

The 97.3% of *N*-ester found in Table V for the mixture of esters and allyl iodide which had been heated one hour at 100° is practically identical with the 98.4% isolated in Table IV from the products of reaction of the silver 1-phenyl-4-methylurazole and allyl iodide one hour at 100°. Since this amount of *N*-ester in Cols. 8 and 10, Table V, is actually larger than corresponds to the normal 79% (See Table IV) of the amounts in Col. 4, Table V, it follows that some *N*-ester has been generated during

the digestion with allyl iodide. As it is shown in Col. 7, Table V, that the total amount of ester recovered is smaller than that used, Col. 4, it follows that a considerable quantity of *O*-ester has been decomposed. As its normal decomposition product is 1-phenyl-4-methylurazole, with which ethyl bromide and ethyl iodide have been shown to react slowly, it would not be surprising that the much more highly reactive allyl iodide would yield some of the *N*-allyl ester. Furthermore, the allyl iodide and *O*-allyl ester may, to some extent, form an addition product which rearranges into the *N*-allyl ester. The increase in the actual amount of *N*-ester and the decrease in the amount of *O*-ester therefore raise the per cent. *N*-ester to 97.3% of the total ester isolated in Col. 8, of Table V.

TABLE V.—0.3 WEIGHT *N* SILVER SALT + 0.3 VOL. *N*-ALLYL IODIDE IN 40% ALCOHOL AT 60°; THE REACTION PRODUCT WAS THEN ISOLATED AND HEATED ONE HOUR WITH ALLYL IODIDE AT 100°.

Weight Ag salt.	Mols C_3H_5I.	Time in hours.	Total product.	Per cent. yield.	Mols C_3H_5I.	Wt. after reheating.	N ester wt. after hydrolysis.	Per cent. N der. in reheated mixture.	Per cent. of total product found as N der. in reheated mixture.
0.447	1	0.25	0.1939	55.9	10	0.1755	0.1699	96.8	87.6
0.447	1	0.33	0.1547	44.6	1	0.1388	0.1356	97.7	87.7
							Average,	97.3	87.7

Summary.

1. At 60° and below, the sodium, mercury, or silver salt of 1-phenyl-4-methylurazole gives with allyl iodide its own ratio of *N*-ester and *O*-ester which does not change with change in temperature or time.

2. It was observed that the silver salt of 1-phenyl-4-methylurazole and allyl iodide at 100° give a ratio of *N*-ester to *O*-ester, 98:2, which is considerably higher than that found at 60° and below, 79:21. It is here shown that this change is caused by an action of the allyl iodide at 100° on the *O*-allyl ester which results in its partial decomposition and the formation of some *N*-ester. This case is therefore somewhat like that of Wheeler who showed that imido esters are changed by alkyl halides into substituted amides.

MADISON, WIS.

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, U. S. DEPT. AGRICULTURE.]

THE PREPARATION OF BETA GLUCOSE.

BY A. W. MANGAM AND S. F. ACREE.[1]

Received February 24. 1917.

Because of the difference between the rate of fermentation and the reactions of the alpha and beta derivatives of different sugars, and because

---

[1] Chief, Section of Derived Products, Forest Products Laboratory, Madison, Wisconsin.