[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 110.]

THE CONDENSATION OF SUCCINYLOSUCCINIC ACID DIETHYL ESTER WITH ACETAMIDINE: 2,6-DIMETHYL-4,8-DIHYDROXY-9,10-DIHYDRO-1,3,5,7-NAPHTOTETRAZINE.[1]

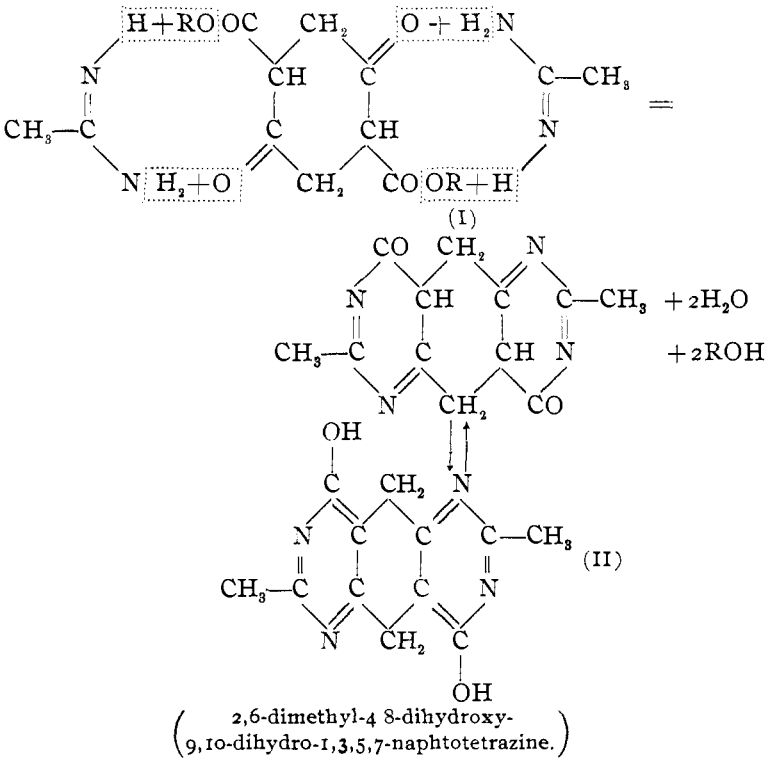
BY MARSTON TAYLOR BOGERT AND ARTHUR WAYLAND DOX.

Received August 10, 1905.

IN a previous paper,[2] we have described the preparation of a naphtotetrazine from succinylosuccinic ester and guanidine.

As the condensation there described depends upon the amidine structure of guanidine, it was expected that other amidines would react similarly, and we have found that acetamidine and succinylosuccinic ester condense smoothly to a naphtotetrazine.

The condensation may be represented thus:

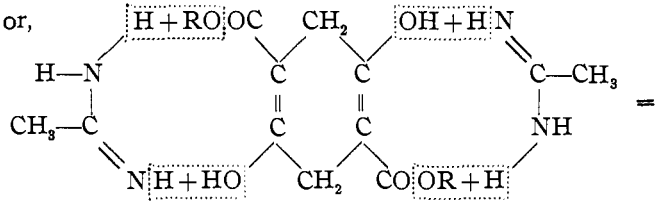


(2,6-dimethyl-4 8-dihydroxy-9,10-dihydro-1,3,5,7-naphtotetrazine.)

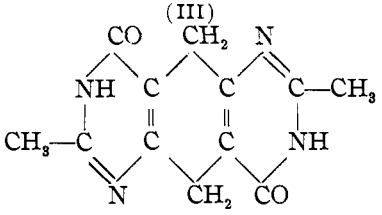
[1] Read at the General Meeting of the American Chemical Society, June 22, 1905.

[2] This Journal, **27**, 1127.

or,

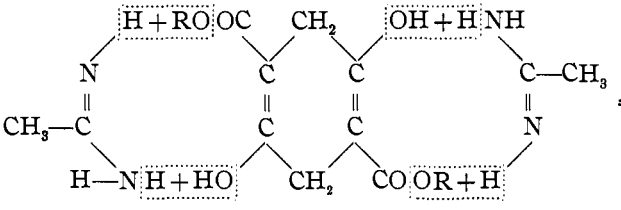


(III)

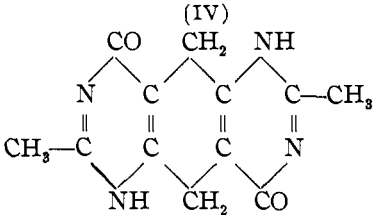


$+2H_2O+2ROH.$

There is another possibility:



(IV)



$+2H_2O$

$+2ROH,$

but this appears much less probable, in view of the ready solubility of the product in alkali.

Since both I and III would pass into the same enol form (II), it is reasonably certain that this is the structure of the sodium salt. If the free base exists in the keto condition, it may then be either I or III.

The study of these new heterocycles will be continued.

EXPERIMENTAL.

The Condensation of Succinylosuccinic Ester with Acetamidine.—The condensation was at first conducted in exactly the same manner as with guanidine.[1] The yields were small, owing to the

[1] *Loc. cit.*

instability of the liberated acetamidine, most of the latter probably being decomposed before condensation with the succinylosuccinic ester occurred. By using the sodium salt of the ester, however, it was found possible not only to secure the condensation at the ordinary temperature, but also to increase the yield considerably.

The sodium salt of succinylosuccinic ester was dissolved in the smallest possible amount of cold water, the solution made slightly alkaline, and acetamidine hydrochloride added. After shaking for two or three minutes, needle-shaped crystals began to separate, and after standing for an hour the reaction was complete. The mother-liquor was reddish in color.

The free base was purified, as in the case of the guanidine condensation product, by crystallization of its sodium salt. The purified sodium salt was dissolved in hot water, and the calculated amount of acid added. The free base separated as a white precipitate, easily soluble in excess of mineral acid. It dissolves in ammonium hydroxide with a blue fluorescence, but is insoluble in the usual neutral organic solvents. When heated, it chars without melting, and without evolving any ammonia. No chlorplatinate could be formed.

The analysis of the free base resulted as follows:

	Calculated for $C_{12}H_{12}O_2N_4$.	Found.	
Carbon	59.02	58.90	
Hydrogen	4.92	4.83	
Nitrogen	22.95	23.00	23.12

Sodium Salt, $C_{12}H_{10}O_2N_4Na_2.6H_2O$.—The crude sodium salt was purified by recrystallization from caustic soda, as described for the guanidine condensation product. It forms colorless needles, which dissolve in hot water without the addition of alkali. The solution is colorless, but has a strong blue fluorescence. On heating, the salt chars, gives off ammonia, and leaves a residue of sodium carbonate. Like the corresponding guanidine condensation product, the crystals from caustic soda carry six molecules of water. The determination of the water of crystallization resulted as follows:

	Calculated for $C_{12}H_{10}O_2N_4Na_2.6H_2O$.	Found.	
		I.	II.
H_2O	27.27	27.12	27.27

Sodium was determined in the dried salt with the following results:

	Calculated for $C_{12}H_{10}O_2N_4Na_2$.	Found. I.	Found. II.
Na	15.97	15.75	15.80

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June, 1905.

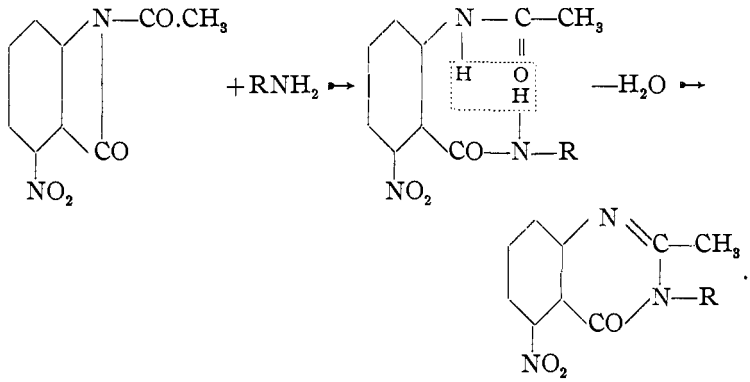
[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 111.]

THE SYNTHESIS OF 2-METHYL-5-NITRO-4-KETODIHYDROQUINAZOLINES FROM 6-NITROACETANTHRANIL AND PRIMARY AMINES.[1]

BY MARSTON TAYLOR BOGERT AND HARVEY AMBROSE SEIL.

Received August 21, 1905.

IN a previous paper,[2] Bogert and Chambers have shown that quinazolines can be readily obtained from 6-nitroacetanthranil and primary amines, the reactions involved being as follows:



They carried out this synthesis only with ammonia and with aniline. The present paper records similar syntheses with the following primary amines—methyl, ethyl, normal and isopropyl, iso- and secondary butyl, isoamyl and allyl—thus demonstrating the general applicability of the reaction to primary aliphatic amines.

We are now engaged in extending the reaction to other primary amino compounds, including the amino acids, and have already

[1] Read at the Meeting of the New York Section of the American Chemical Society, May 5, 1905.

[2] This Journal, **27**, 649 (1905).