XXIX.—*On Condensations of Compounds which contain the Dicarbonyl-group with Aldehydes and Ammonia.*

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IN a former communication (this Journal, 1883, Trans., 9; more fully *Ber.*, **15**, 2410) I developed at some length my interpretation of the above series of condensations, the experimental details of the study of which are contained in various papers published in this Journal during the last two years by myself in conjunction with others. I pointed out the bearing of this interpretation upon the question of the constitution of lophine, glyoxaline, and allied compounds. I further showed that the interpretation which Radziszewski (*Ber.*, **15**, 1493) sought to substitute for mine, though plausible enough when Radziszewski's reactions alone are considered, is hardly tenable when these are taken in conjunction with other reactions of the same class described by me.

Radziszewski has since described (*Ber.*, **15**, 2706) a new synthesis of Wallach and Schulze's paraoxalmethyline by the condensation of glyoxal with acetaldehyde and ammonia:—

The author had not, at the time of sending in his communication, seen my paper on the interpretation of the above class of condensations,* a class to which this reaction belongs. In that paper (*Ber.*, 15, 2420) I made some suggestions concerning the constitution of the oxalines. As I consider that the experimental result obtained by Radziszewski furnishes a confirmation of the views there expressed, I desire to develop these somewhat more fully, and to point out that by adopting the formulæ for glyoxaline and oxalmethylene (methylglyoxaline) proposed by me, the constitution of the whole of the important compounds discovered by Wallach admits of explanation.

Starting therefore with the formula of oxalmethylene given by me in the above paper, and formulating oxalethyline on the same type,† we arrive at the two formulæ:—

The most probable formula for paraoxalmethylene, a compound which, as Wallach and Schulze have shown, is formed from the first of these by intramolecular change, from the second by elimination of ethylene, would be—

and this, if my views concerning the above class of condensations are correct, is the formula of a compound which would be formed by the action of acetaldehyde and ammonia upon glyoxal.‡

* I take for granted that my reservation of the further study of these condensations (this Journal, 1882, 329) has escaped Radziszewski's notice.

† The general formula of an oxaline obtained from a di-substituted oxamide of the formula $\begin{array}{c} \text{CONH}(\text{C}_n\text{H}_{2n+1}) \\ | \\ \text{CONH}(\text{C}_n\text{H}_{2n+1}) \end{array}$, in which *at least one* of the alcohol-radicles must be primary, would be $\begin{array}{c} \text{CH}-\text{N}(\text{C}_n\text{H}_{2n+1}) \\ \parallel \quad \diagup \\ \text{CH} \quad \text{N}=\text{C}-\text{C}_{(n-1)}\text{H}_{2(n-1)+1}. \end{array}$

‡ Radziszewski (*loc. cit.*) attributes to paraoxalmethylene the constitution —

The whole question between my *anhydro-base formulæ* (cf. this Journal, 1883, Trans., 9) and Radziszewski's *symmetrical formulæ* for compounds of this class (the oxalines, lophine, &c.) resolves itself into the simple question whether glyoxaline, the lowest member of the series, contains a replaceable hydrogen-atom directly attached to nitrogen. A proof that this is the case would decide in favour of the anhydro-base formula. Now from the experimental evidence adduced by Wallach and by Radziszewski, there can be little doubt that the oxalines are nothing more than glyoxaline in which one or more hydrogen-atoms have been replaced by alcohol-radicles, and I think there are experimental facts which show that in some of these compounds the radicle is directly attached to nitrogen. One such fact, which is absolutely conclusive as regards the compound in question, is that Wallach and Schulze obtained ethyloxamide by the oxidation of chloroxaethyline. The boiling point of methylglyoxaline (a compound obtained by the action of methyl iodide upon glyoxaline) also renders it probable that this compound is derived from glyoxaline by the replacement of imidic hydrogen by methyl; for whilst paraxalmethyline, as a homologue of glyoxaline in which the methyl-group is attached to carbon, boils 13° higher than glyoxaline, methylglyoxaline boils 58° lower. This lowering of the boiling point in the conversion of a secondary into a tertiary amine- or amide-group has been observed before in the case of diamines and diamides (cf. E. Fischer, *Annalen*, **190**, 155; Michler, *Ber.*, **8**, 1665). Radziszewski's argument that glyoxaline and lophine do not contain an NH-group because they do not react with acid chlorides and anhydrides, has been refuted by anticipation in my previous paper (*Ber.*, **15**, 2420). Lophine and glyoxaline behave in this respect exactly like the class of compounds to which they belong—the anhydro-bases of Hübner. Anhydrobenzdiamidobenzene may, as Hübner has shown, be heated with benzoyl chloride to 260° without alteration.

In the above connection I would call attention to the evidence afforded by the work of Ladenburg and Rügheimer on condensations of orthotolylenediamine (*Ber.*, **12**, 952) of the ease with which the symmetrical complex—

passes, under the influence of heat, into the unsymmetrical anhydro-complex—

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This is the change which I have represented as occurring when amarine is transformed by heating into lophine (*Ber.*, **15**, 1270).*