

On the Formation of Mauvein: Mechanistic Considerations and Preparative Results

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Dedicated to Professor Gerhard Maass on the occasion of his 60th birthday

The reaction of aniline (AH_2) with an oxidizing agent in acidic solution gives rise to the formation of a mixture of products containing, besides a variety of oligoanilines named as Aniline Black or Polyaniline, Mauvein as a deeply purple phenazine derivative. Although this Mauvein synthesis was developed by W.H. Perkin more than 150 years ago and has opened the era of industrial dyestuff chemistry, the detailed mechanism of this reaction has remained rather unclear until today. The elucidation of the mechanism of the Mauvein formation as an oxidative coupling process of AH_2 is hindered by the fact that several different types of coupling reactions occur simultaneously. Among them the *C,N*-coupling reaction is the most important one and responsible for the formation of Polyaniline and Mauvein. It gives rise to the formation of, *e. g.* 2 different aniline dimers, 7 trimers and more than 20 tetramers including Mauvein as one representative of these tetramers.

In the present study, the oxidative coupling of a mixture of AH_2 and 4-amino-4'-(*N*-anilino)-diphenylamine (T_aH_2) as one of the aniline trimers was studied in more detail. The reaction leads to the formation of Mauvein in satisfactory yields and, after some manipulations, widely free of by-products. By using simple aniline derivatives as co-reagents in the oxidative coupling with T_aH_2 , the reaction can be extended to the synthesis of different Mauvein derivatives most of which have been unknown to date.

Key words: Mauvein, Phenazine Dyes, Synthesis, Mechanism