# Recent Advances in the Synthesis of *meso*-Substituted Corroles

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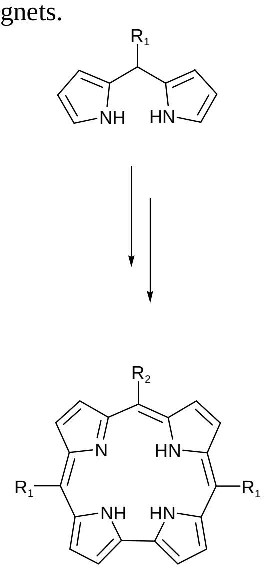
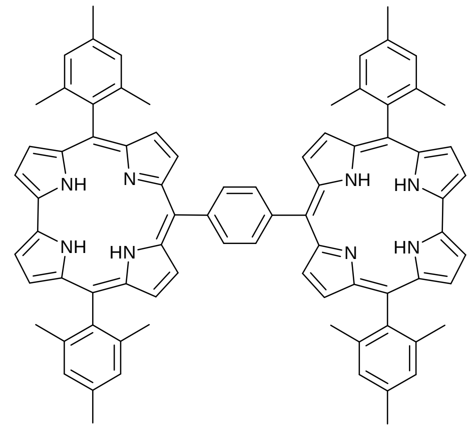
Corroles[1] are aromatic tetrapyrrole macrocycles bearing a direct pyrrole-pyrrole link, thereby constituting a bridge between porphyrins and corrins. The chemistry of corroles had its genesis with the work of Johnson and Kay in 1965.[2] Since that time corroles have been overshadowed by the easy accessibility of their porphyrin counterpart. This situation is now undergoing a highly significant change due to the breakthrough discovery of their simple syntheses made by Gross et al. [3] and by Paolesse and co-workers in 1999.[4] While all previous approaches were quite lengthy and required preparation of sophisticated precursors, Gross and Paolesse methods are one-pot procedures from commercially available reagents. Furthermore the unexpected observation that these trianionic ligands stabilize the unusually high oxidation states of metals has recently been another important impetus to the corrole chemistry. Both discoveries have generated increasing interest in this contracted macrocycle in the last few years. Some of their complexes have been examined as catalysts for epoxidation, cyclopropanation, hydroxylation and aziridination as well as molecular magnets.



We have refined a one-pot synthesis of $A_3$-corroles via condensation of an aldehyde with pyrrole followed by macrocyclization mediated by DDQ.[5] After thorough examination of various reaction parameters we have elaborated three different sets of conditions for different types of aromatic aldehydes – (highly reactive, moderately reactive and sterically hindered) which allowed us to improve yields to ~15%. We found that if a low concentration of acid and a high concentration of substrates are used in the reactions of aldehydes with dipyrromethanes, *trans*-$A_2B$-corroles can be obtained in appreciable yields.[6] An extensive modification of the conditions used for the synthesis of *trans*-$A_2B$-corroles led to the development of a comprehensive method for the preparation of *trans*-$A_2B$-corroles bearing substituents with basic nitrogen atoms at the *meso*-positions.[7] Pyridine-, quinoline- and quinoxaline-derivatized aldehydes as well as other aromatic aldehydes containing tertiary amine groups were successfully used in the condensation involving sterically hindered dipyrromethanes. Finally we have developed a new methodology that affords regioisomerically pure corroles possessing up to three different substituents at the *meso* positions. The corrole formation reaction involves the acid-catalyzed condensation of a dipyrromethane-dicarbinol with pyrrole followed by oxidation with DDQ. ABC-type corroles were synthesized for the first time according to this procedure.



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