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Synthetic Methodology of Manganese Corroles: Recent Developments

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ABSTRACT

Let Un be the set of unicyclic molecular graphs with 3 ≤ n ≤ 8 vertices. We show that the cycle Cn has maximal Laplacian-energy-like invariant (LEL) in Un. The authors partially proving that the conjecture hold for any unicyclic molecular graph in Un, where 3 ≤ n ≤ 8 Moreover, we show that Cn has maximal energy (E) in Un for 3 ≤ n ≤ 7, but for n=8 this is not true.

Keywords: Molecular graphs, Laplacian energy-like invariant, Energy

INTRODUCTION

Corrole is trianionic tetrapyrrolic macrocycle containing an eighteen pi-electron having a direct link between both pyrrole–pyrrole units [1,2]. The structure of corrolazine, corrine and porphyrine is in close resemble to corrole. Porphyrin has a larger cavity and higher symmetry than corrole due to direct pyrrole-pyrrole link. Therefore corrole has C_{2v} symmetry [3]. The most interesting properties of the corroles is the trianionic nature due to this properties corrrole stabiles metal ions in higher oxidation (+4 to +6) state [4-7]. These ultimate properties are responsible for the huge utility of manganese and iron corroles for great important aspects compatible to medicine and energy , because they initiate the molecules as like: O_2 [8], H_2O_2 [9], HOONO [10],CO_2, [11], H^+[12] and more. Metallocorroles already reported as catalysts for many applications such as transfer of oxygen atom, CO_2 and reduction of protons [12-22]. Application of manganese corroles reported in catalysis [23-27], ion-selective electrodes [28], Langmuir–blodgett films [29,30], single-chain magnets [31] and medicinal research [32,33]. Gross et al. reported the synthesis of tris(pentaflurophenyle)corrole in good yield using solvent free metthod [28-30]. Furthermore, the synthesis of corrole macrocycle reported by Kumar [31] and Paolesse et al. [32] by condensation of dipyrromethane (DPM) with aromatic aldehyde, and by the Rothemund reaction respectively. This synthetic achievement has expedited the study of macrocycle of the corrole a new branch of porphyrin chemistry. It has been clearly seen that in area of corrole chemistry increased exponentially a huge publication till now [33-44]. This review is mainly accommodates all synthetic aspect in manganese corrole chemistry from 1999 to 2018.

RESULTS AND DISCUSSION

Recently, few general approaches for the synthesis of manganese corroles were reported. First, use of manganese salt to cyclize tetrapyrrolic precursor and the second, is the reaction of manganese salt with free base corrole. The third report recently reported by Yadav et al. by using manganese salt with bilane to yield metallocorroles through difficult C-C bond formations. In the first methodology, cyclization of 1,19-dideoxybiladiene-ac in methanol and basic condition using manganese(II) acetate tetrahydrate as template to yield octamethylcorrolato manganese(III)s in good yield 50%-60% [45,46] has been reported (**Figure 1**).

In second methodology, as shown in **Figure 2**, using two equivalent of Mn(II) acetate and molecular oxygen in boiling DMF to cyclize tetrapyrrolic precursor of 2,2'/-Bisdipyrrin to give 18% yield of octaethylcorrolatomanganese(III). In the series of facile synthetic protocol corroles, an another alternative most convenient method is reaction between free base corrole and manganese(II) acetate tetrahydrate to obtain Mn(III) corrole [8-11] in 90%-98% yield in presence

of polar solvent such as dimethylformaamide, methanol or pyridine [45-50]. Corroles have better solubility in polar solvents in comparison to other porphyrinoid systems. Ionic corroles form metal complexes easily with manganese by the same method [51-55]. And in the last not but least recently Yadav et al. reported compound 12 to 14, new C-C coupling between both pyrroles in bilane using manganese(II) acetate tetrahydrate as template in the presence of molecular oxygen in DMF to obtain 30%-35% yield of manganese (III) corrole as shown in **Figure 3**.

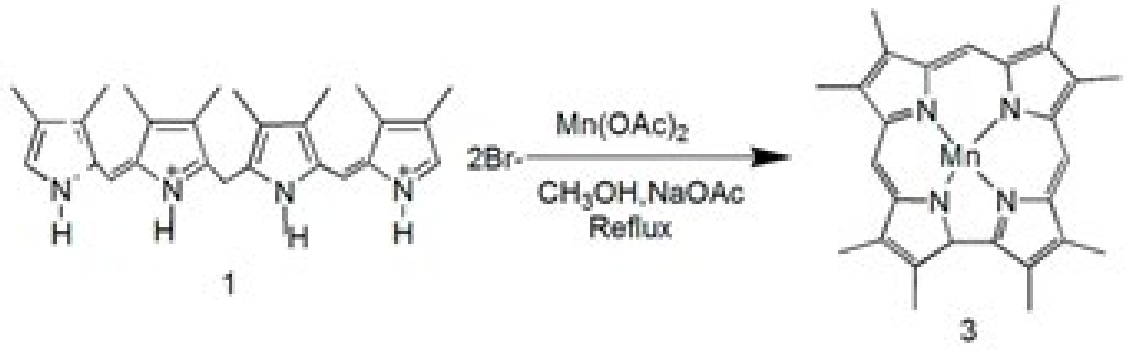

Figure 1: Cyclization of 1,19-dideoxybiladiene-ac with manganese (II) acetate tetrahydrate

Demetallation of manganese corroles

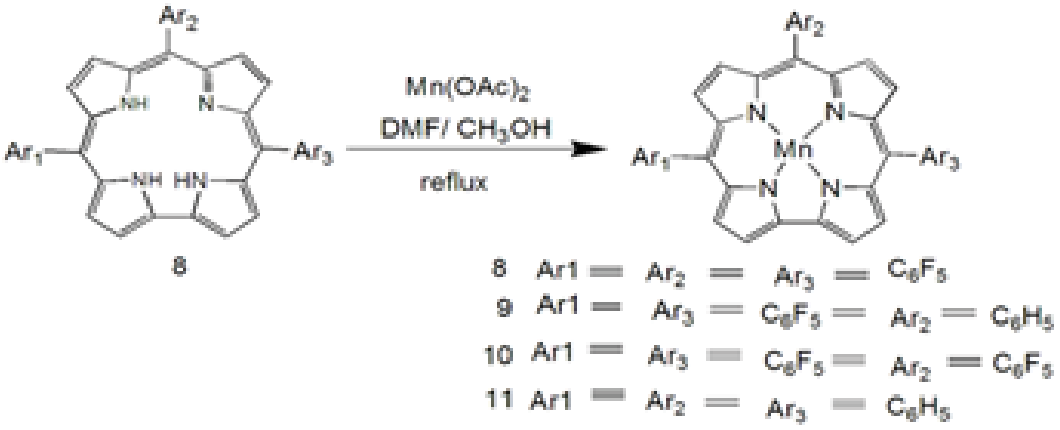

Figure 2: Cyclization of 2,2'–bisdipyrrin

The synthesis of highly electron-deficient and perhalogenated free base corrole can be achieved with the reductive demetallation of manganese corroles but did not gain much attention. Bröring et al. firstly reported by using HBr in HOAc (**Figure 4**) for demetallation of (OEC)Mn(III) 15 to yield H_3(OEC) [56]. Another method was reported by Bröring et al. [57] by using acid mixture of 10:1 volume ratio of $CHCl_3/H_2SO_4$. Demetallation of beta-octabromo-meso-triarylcorroles are possible by using concentrated H_2SO_4 with 5-200 equivalent of $FeCl_2$ or $SnCl_2$ $H_3(Br_8tpfc)$, in generally through reductive demetallation of (Br_8tpfc)Mn(III). We can be obtained in 86% yield using concentrated H_2SO_4 in the presence of $FeCl_2$ [57]. Without reductant demetallation also reported by Liu et al. in presence of HCl with $SnCl_2$ as well as in HOAc-H_2SO_4.

CONCLUSION

This short review provides the all synthetic methodology and demetallation process of manganese(III)corrole from 1999 to 2018. Furthermore, the main purpose of this review to provide information about currently reported synthetic methodology in manganese(III) corroles. The prestige of this protocol is the very simple reaction which is applicable for all type of aromatic aldehyde and aryldipyrromethane. This method also avoids the difficult steps of earlier reported by Broring et al. in compound 2 to 6. Mainly green chemistry protocol has been adopted in this methodology. The yield of the synthesized metallocorroles was plausible high and also need very short time period than earlier reported methods.

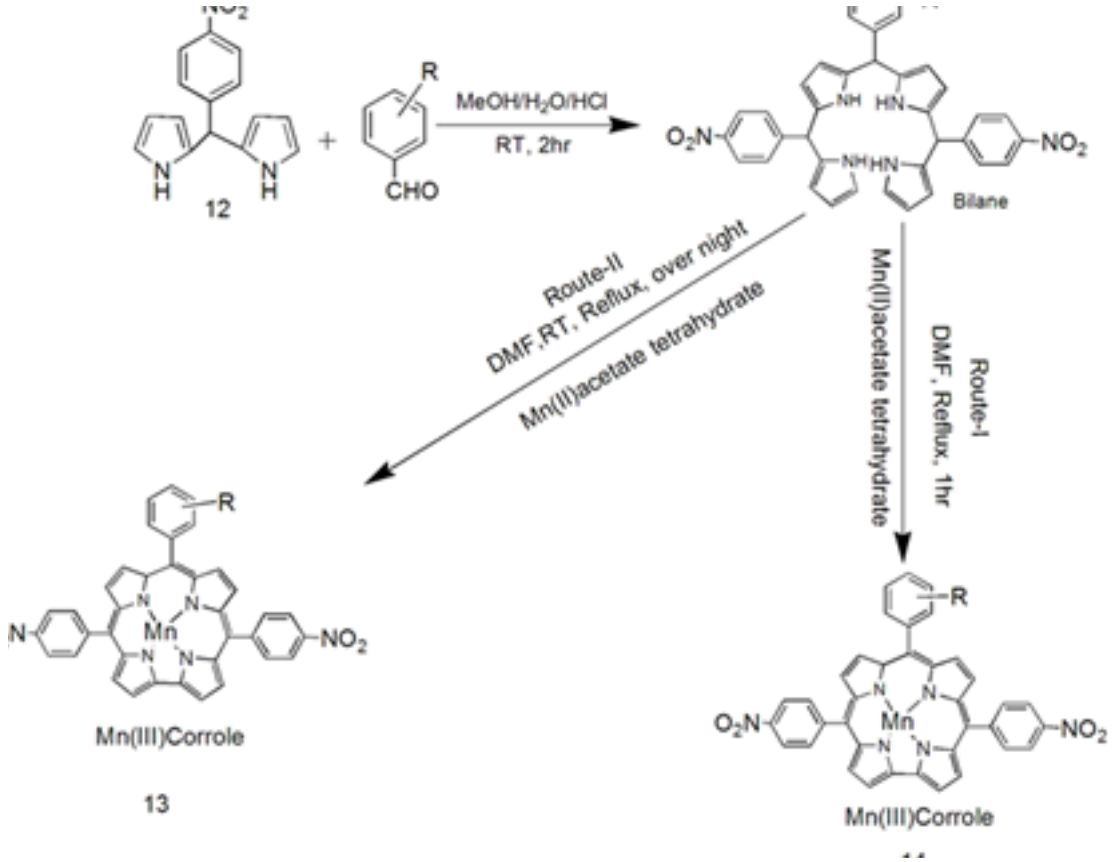

Figure 3: New synthetic methodology to yield manganese (III) corrole

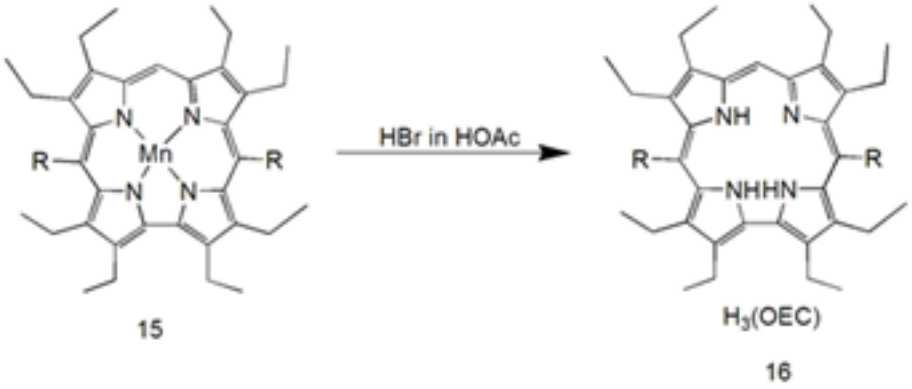

Figure 4: Demetallation of manganese corroles

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