学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 分子化学コース　　博士（理　学）　氏　名 張 四成

学 位 論 文 題 名

Development of Synthetic Methods for Two-Dimensional Acenes from Acenes

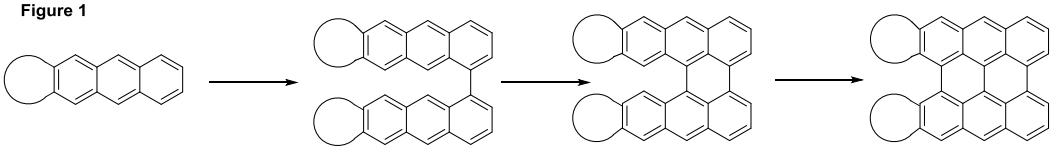
（アセンを出発物質とした二次元アセンの合成法開発）

1. Introduction

Linear acenes have been extensively explored due to their remarkable potential as organic material. Our group has developed zirconium-mediated homologation, double homologation and coupling methods for synthesis of linear acenes. Recently, we turned our attention from linear acenes to two-dimensional acenes. To synthesize two-dimensional acenes from acenes, some methods are reported. Most of them combined C-C bonds between two acenes from the inner ring to outer ring. However, these methods did not applicable for higher acenes than anthracene.

In my study, conceptly new method of combining C-C bonds between two acenes fragments from one side to the other was developed (Figure 1). It is well known that dimerization of naphtha-2-ol can produce the BINOL. Illuminated by this idea, hydroxyl group was firstly introduced to the C_2 position of one side ring of acenes. Therefore, oxidative dimerization of such acenes will produce the corresponding acenes side ring dimers. Furthermore, two hydroxyl groups of the hydroxyacene dimer can be eliminated to acene dimers in high yields. Further C-C bonds formation of these acenes dimer was successfully proceeded by choosing the proper Scholl reaction conditions.

Figure 1

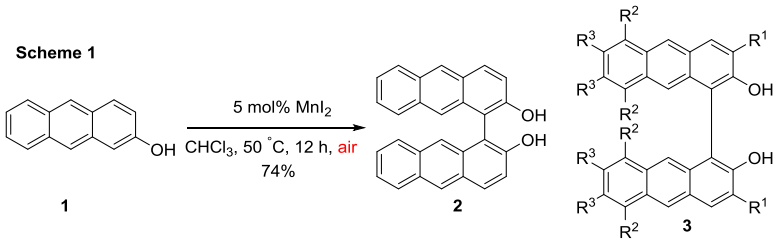


2. Results and Discussion

2.1 MnI_2- catalyzed dimerization of 2-hydroxyanthracene and further functionalization of anthracene dimer [1]

Dimerization of 2-hydroxyanthracene was investigated with 5 mol% of various catalysts. Although oxidative dimerization of 2-naphthol has been well studied, reactivity of 2-hydroxyanthracene is quite different. $Mn(acac)_3$ and $Mn(acac)_2$ were efficient catalysts for the dimerization of 2-naphthol. However both did not give the satisfactory results for 2-hydroxyanthracene.(Scheme 1) Instead MnI_2 afforded dimer **2** in good yield. However MnI_2 gave only trace amount of dimerization product in 2-naphthol under. This method was then successfully applied for a series of substituted 2-hydroxyanthracenes. Further functionalization gave various substituted anthracene side dimers and dianthrafuran derivatives.

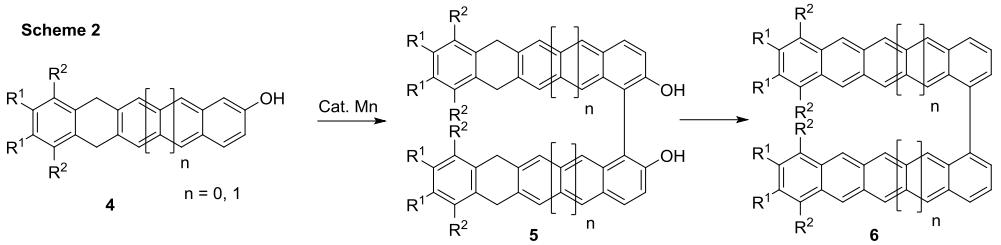
Scheme 1



2.2 Synthesis of naphthacene and pentacene side ring dimer

As a further extension, oxidative dimerization of hydroxydihydronaphthacene and hydroxydihydropentacene derivatives were studied.(Scheme 2) I found that $Mn(acac)_2$ and $Mn(acac)_3$ were effective catalysts, while MnI_2 did not work. Although the substituted dihydropentacene contains anthracene skeleton, oxidation potential value was higher than anthracene derivatives. That may be the reason why the mild catalyst MnI_2 could not work. Furthermore, removal of OH groups and subsequent aromatization of hydroxydihydropentacenes provided pentacene side ring dimers successfully.

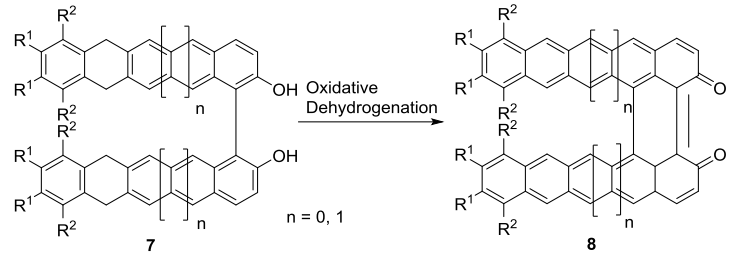
Scheme 2



2.3 Carbon-carbon bond formation of hydroxyl acene dimers

In an effort to synthesize two-dimensional acenes, further intramolecular oxidative dehydrogenation of hydroxyl acenes dimer was studied. Oxidative dehydrogenation of hydroxyldihydronaphthacene and hydroxyldihydropentacene dimers by $FeCl_3$ afforded the corresponding acene dione derivatives **8**, respectively. C-C bond between the second rings was combined together with oxidation of C-OH to C=O. Further C-C bond formation of the naphthacene dione was studied by pyrolysis in high temperature under vacuum. The C-C bond between the third rings was formed by this method.

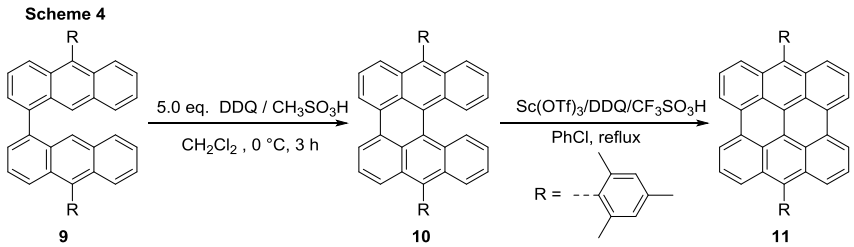
Scheme 3



2.4 Carbon-carbon bond formation of acene dimers

Characterization of dione in Scheme 3 was difficult because of the poor solubility. Moreover, further C-C bonds formation of dione toward peri-acenes was difficult due to the distorted structures. Therefore, I turned to study the acene side dimers without OH groups. (Scheme 4) C-C bond formation between two anthracene skeleton was firstly studied. Oxidative dehydrogenation of substituted anthracene side dimer successfully afford the second C-C bond formed product by DDQ/CH_3SO_3H oxidant. For further C-C bond formation, substituents of the anthracene side dimer gave remarkable effects. Finally, bulky substituents like mesityl group gave good results. Two C-C bonds combined bisanthracene was treated with $Sc(OTf)_3$/DDQ in the presence of CF_3SO_3H, a fully combined bisanthracene **11** was obtained in high yield.

Scheme 4



3. Conclusion

Oxidative dimerization of hydroxyl acenes successfully afforded the corresponding hydroxyl acenes dimers. Thus, this method provided a systematical synthesis of acene side dimer. Oxidative dehydrogenation of hydroxyl acene dimers produced acene dione with two C-C bonds connected but difficult for more C-C bonds. While, oxidative dehydrogenation of acene side dimers without OH groups was proven to be success. A fully combined bisanthracene, for an example, was successfully synthesized through forming the three C-C bonds one by one from one side.

4. References and Notes

(1) Zhang, S.; Wang, Y.; Song, Z.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2013**, *42*, 697.