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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 studied due to their potential applications as organic materials. Takahashi's group has developed zirconium-mediated homologation,[1a] double homologation[1b] and coupling methods[1c] for the synthesis of linear acenes. Recently, this group turned to two-dimensional acenes. To synthesize two-dimensional acenes from acenes, some methods have been reported by far. Most of them combined C-C bonds between two acenes from the central ring to outer rings to ensure the selectivity. It is obvious that the odd number ring acenes, such as tetracene or hexacene which have no central ring, are not applicable.

In my study, conceptual new method of combining C-C bonds between two acenes fragments from one side to the other was developed (Figure 1). In order to combine C-C bonds between the side rings, the hydroxyl group was introduced to the C_2 position of one side ring of acenes. This idea came from the known dimerization of naphtha-2-ol. Oxidative dimerization of such hydroxyl acenes would produce the corresponding acenes side ring dimers. Thereafter, two hydroxyl groups of the hydroxyacene dimer could be eliminated to give acene dimers. Further C-C bond formation of these acenes dimer could proceed by the proper Scholl reaction conditions.

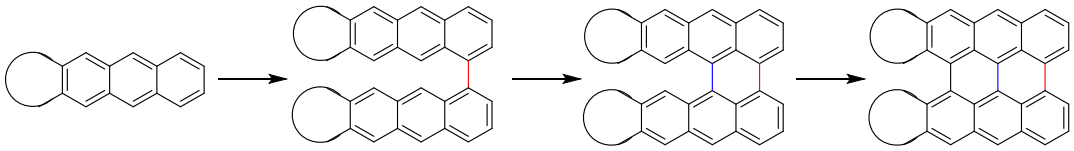


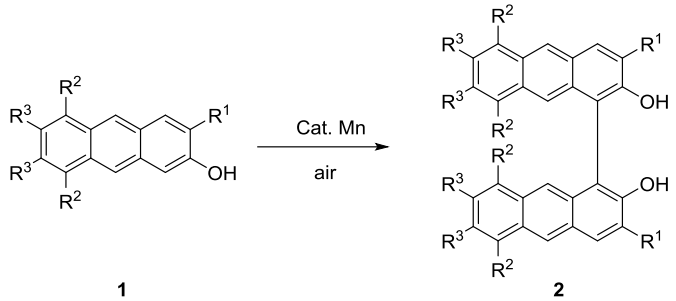
Figure 1. A strategy for the synthesis of acenes side dimer

2. Results and Discussion

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

Dimerization of 2-hydroxyanthracene was firstly investigated with 5 mol% of various catalysts which were efficient catalysts for the dimerization of 2-naphthol. Oxidative dimerization of 2-naphthol undergoes smoothly to produce the dimer. However, oxidative dimerization of 2-hydroxyanthracene was quite different. Those catalysts such as Cu(OH)Cl·TMEDA, $Mn(acac)_3$ and $Mn(acac)_2$ did not give the satisfactory results. Much to my surprise, MnI_2, which is inefficient catalyst for 2-naphthol, afforded 2,2'-dihydroxy-1,1'-dianthracene **2a** in 74% yield under the same conditions. This method was then successfully applied for substituted 2-hydroxyanthracenes.The corresponding dimers **2** were obtained in good yields.

Scheme 1 Synthesis of anthracene side dimer derivatives

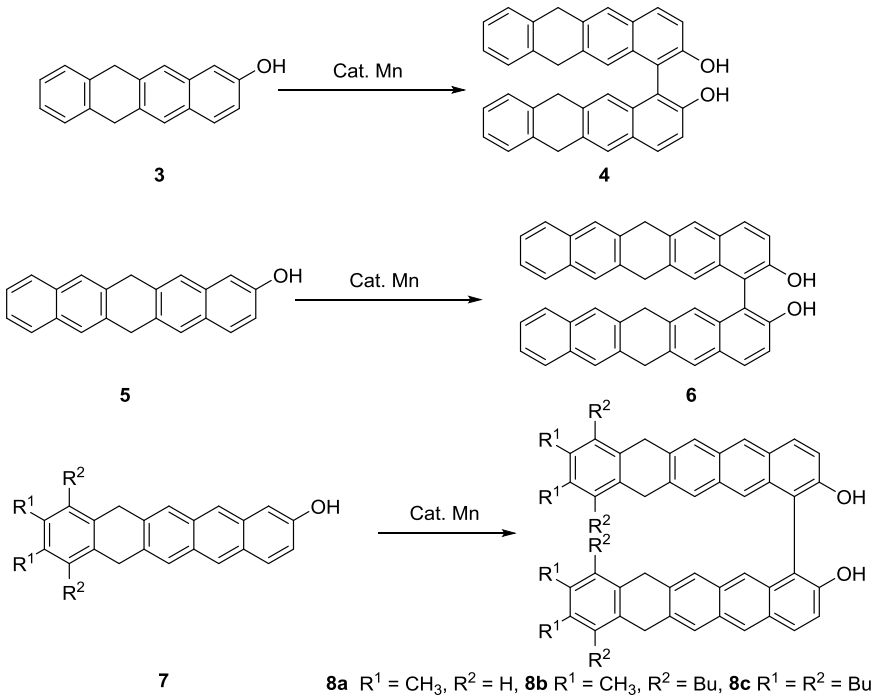


2.2 Synthesis of 2-hydroxydihydronaphthacene and 2-hydroxydihydropentacene side ring dimers

As a further extension of my research, oxidative dimerization of 2-hydroxydihydronaphthacene and 2-hydroxydihydropentacene derivatives were studied. 2-Hydroxydihydronaphthacene and 2-hydroxydihydropentacene were firstly prepared by quinone method. 2-Hydroxydihydropentacene derivatives were prepared by Zirconium-mediated homologation method.

$Mn(acac)_2$ and $Mn(acac)_3$ were both effective catalysts for oxidative dimerization of hydroxyl acenes. However, MnI_2 did not work. The substituted dihydropentacenes have higher oxidation potential than anthracene derivatives. That may be the reason why the mild catalyst MnI_2 could not work.

Scheme 2 Synthesis of naphthacene and pentacene side dimers

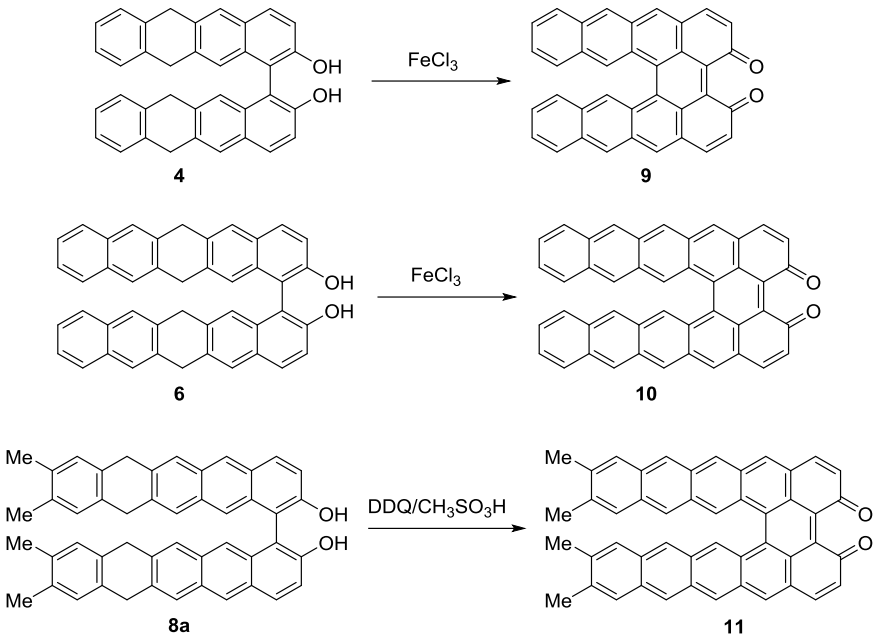


2.3 Carbon-carbon bonds formation of hydroxyl acene dimers

In order to synthesize two dimensional acenes, further oxidative dehydrogenation of hydroxyl acenes dimer was carried out. Oxidative dehydrogenation of 2-hydroxy-6,11-dihydronaphthacenl

dimer **4** and 2-hydroxy-6,13-dihydropentacen dimer **6** by $FeCl_3$ in chloroform afforded the corresponding acene dione derivatives **9** and **10**, respectively (Scheme 3). While dione **11** was obtained by treatment of 2-hydroxy-9,10-dimethyl-7,12-dihydropentacen dimer **8a** with DDQ in the presence of CH_3SO_3H and CH_2Cl_2 co-solvents.

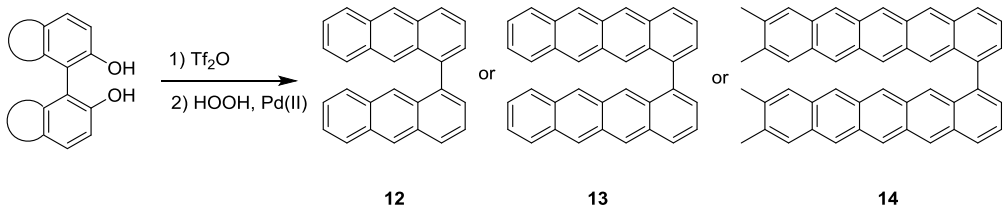
Scheme 3 Carbon-carbon bond formation of hydroxyl acene dimers



2.4 **Carbon-carbon bond formation of acene dimers**

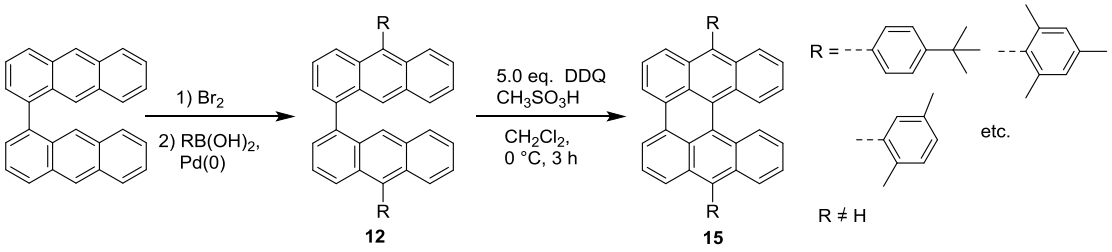
Characterization of dione was difficult due to the poor solubility. Moreover, further C-C bonds formation of dione toward peri-acenes was difficult because of the distorted structures. Therefore, I turned to oxidative dehydrogenation of acene side dimers without OH groups. For this regard, acenes side ring dimers **12-14** were firstly prepared removing hydroxyl group. (Scheme 4)

Scheme 4 Synthesis of acenes side ring dimer



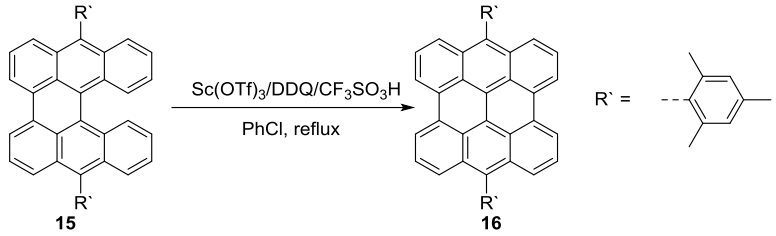
C-C bonds formation between two anthracene skeleton was then studied. Without substituents, oligomerization and oxidation were easily occurred at the outside of central ring of anthracene side dimer. In order to restrain such reaction, substituents were introduced to the outside of central ring of anthracene side dimer. Scholl reactions of substituted anthracene side dimers **12** were subsequently studied. DDQ/CH_3SO_3H system was found to be effective. The second C-C bond formed products **15** were obtained (Scheme 5).

Scheme 5 The second C-C bond formation of anthracene side ring dimer



Further Scholl reaction of these products **15** was studied. I found *p*-^{t}BuC$_6$H$_4$ substituted **15** could not undergo Scholl reaction to give the corresponding bisanthene **16**. Interestingly, Sc(OTf)$_3$/DDQ in the presence of CF_3SO_3H was effective for successful Scholl reaction to give 2,4,6-trimethylphenyl substituted bisanthene successfully. (Scheme 6)

Scheme 6 The third C-C bond formation of anthracene side ring dimer



3. Conclusion

To synthesize two-dimensional acenes from acenes, combining C-C bonds between two acenes fragments from one side to the other was developed. In the first part of this thesis, a convenient method towards the systematic synthesis of acenes side ring dimer is proposed. Oxidative dimerization of hydroxyl acenes in the presence of Mn catalysts successfully afforded the corresponding hydroxyl acenes dimers. In the second part, further C-C bonds formation of acenes dimer was studied. Oxidative dehydrogenation of hydroxyl acene dimers with $FeCl_3$ produced acene dione derivatives. The second C-C bond was formed and the OH groups was oxidized to carbonyl groups. On the other hand, hydroxyl groups were firstly eliminated to afford acene side dimers. Oxidative dehydrogenation of these dimers was conducted to combine the further bonds. Finally, a fully combined bisanthracene was successfully synthesized through forming the three C-C bonds one by one from one side. This thesis is providing a much general synthetic sequence of two-dimensional acenes from acenes.

4. References and Notes

(1) (a) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967. (b) Li, S.; Li, Z.; Nakajima, K.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2009**, *4*, 294. (c) Zhou, L.; Nakajima, K.; Kanno, K.; Takahashi, T. *Tetrahedron Lett.,* **2009**, *50*, 2722.

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