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| タイトル | 離散電子子の特性とその応用に関する研究  
   難燃性材料の開発とその応用に関する研究 |
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Development of Synthetic Methods for Two-Dimensional Acenes from Acenes

1. Introduction

Linear acenes have been extensively studied due to their potential applications as organic materials. Takahashi’s group has developed zirconium-mediated homologation, double homologation, and coupling methods 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. 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 C2 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 hydroxy 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](image)

2. Results and Discussion

2.1 MnI2-catalyzed dimerization of 2-hydroxyanthracene and further functionalization of anthracene dimer

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, MnI2, 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-dihdropentacen dimer 6 by FeCl₃ 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-dihdropentacen dimer 8a with DDQ in the presence of CH₃SO₃H and CH₂Cl₂ co-solvents.

**Scheme 3** Carbon-carbon bond formation of hydroxyl acene dimers

![Scheme 3](image)

### 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

![Scheme 4](image)

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/CH₃SO₃H system was found to be effective. The second C-C bond formed products 15 were obtained (Scheme 5).
Further Scholl reaction of these products 15 was studied. I found \( p-t\text{BuC}_6\text{H}_4 \) substituted 15 could not undergo Scholl reaction to give the corresponding bisanthenyl 16. Interestingly, Sc(OTf)3/DDQ in the presence of CF₃SO₂H was effective for successful Scholl reaction to give 2,4,6-trimethylphenyl substituted bisanthenyl 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 FeCl₃ 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
