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Syntheses of *p*-terphenyls and 11,12-dihydroindeno[2,1-*a*]fluorene by one-pot benzannulation of Diels–Alder reactions of *trans*-1,2-dichloroethene and dienes

Jinn-Hsuan Ho *, Yu-Chen Lin, Li-Ting Chou, Ying-Zhe Chen, Wei-Qi Liu, Chao-Li Chuang

Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Road, Taipei 106, Taiwan

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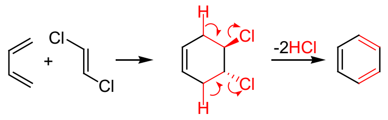
ABSTRACT

A series of substituted *p*-terphenyls and 11,12-dihydroindeno[2,1-*a*]fluorene were successfully synthesized by one-pot benzannulation of Diels–Alder reaction with 1,2-dichloroethene as an acetylene equivalent dienophile. Two chlorine atoms could be good leaving groups to easily undergo subsequent elimination reactions of Diels–Alder products at a high temperature.

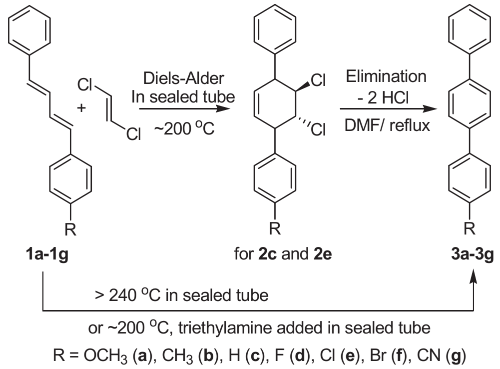
Diels–Alder reaction is a traditional way to construct a six-member ring by [4+2] annulations. But for achieving benzannulation, an additional dehydrogenation step is usually applied after Diels–Alder reaction.[1] In order to carry out one-step benzannulation of [4+2] cycloaddition, some modified synthetic methods have been developed, such as cyclization of alkynes with enynes,[2] neynals,[3] dienes containing fragmental parts[4] or polycyclic aromatics[5], and cyclization of cyclopentadienone and phenylacetylenes under sulfuric acid.[6] Although these cases showed the convenience to construct benzene rings in one-pot, they would produce specific substituents unavoidably to limit their uses.

One way to establish simple benzene without extra substituents from dienophiles is to use an acetylene equivalent dienophile in Diels–Alder reaction and other cycloadditions. These dienophiles, including phenyl vinyl sulfoxide[7] and bis-sulfonyl ethylene,[8] can construct simple benzene ring directly, but they are relatively expansive and sometimes not easily acquired. And the sulfonyl group is not a good leaving group for elimination reaction. In the case of bis-sulfonyl ethylene, even sodium amalgam was needed to eliminate sulfonyl groups.

To advance one-pot benzannulation of Diels–Alder reaction, we planned to use *trans*-1,2-dichloroethene as the acetylene equivalent dienophile, because the two chlorine atoms could be good leaving groups to easily undergo subsequent elimination reactions of Diels–Alder products (Scheme 1). In our preliminary study, heating a mixture of 1,4-diphenyl-1,3-butadiene **1c** and *trans*-1,2-dichloroethene in a high-pressure sealed glass tube at about 250 °C afforded *p*-terphenyl **3c** directly. This successful result provided a convenient way to synthesize *p*-terphenyls which is still an interesting structure for organic materials.[9] Compared



Scheme 1. Concept of one-pot benzannulation of Diels–Alder reaction.



Scheme 2. One-pot benzannulation of Diels–Alder reaction.

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* Corresponding author. Tel.: +886 2 2737 6642; fax: +886 2 2737 6644.
E-mail address: jhho@mail.ntust.edu.tw (J.-H. Ho).

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with other synthetic methods of *p*-terphenyls,[10] this approach would provide some benefits, such as one-pot, solvent-free, and metal-free reaction. Herein, we would like to report this one-pot syntheses of *p*-terphenyls.

A series of starting butadienes, 1-aryl-4-phenyl-1,3-butadienes **1a**, **1b**, and **1d**–**1g**, were synthesized by the Wittig reactions of 3-phenylpropenal and the corresponding (4-substitutedbenzyl)-triphenylphosphonium halides (see Supplementary data). Heating compounds **1a**–**1g** and *trans*-1,2-dichloroethene in a high-pressure sealed glass tube above 240 °C for 24 h afforded a series of *p*-terphenyls (Scheme 2) and the reaction yields are listed in Table 1.

When the Diels–Alder reaction of **1c** and *trans*-1,2-dichloroethene was carried out below 240 °C, the result is quite different. There was no reaction happening between **1c** and *trans*-1,2-dichloroethene when the reaction temperature was below 180 °C. That may be because chloro substituent is not a strong electron-withdrawing group. When the reaction temperature was at around 200 °C, a common Diels–Alder product **2c**, 4,5-dichloro-3,6-diphenylcyclohexene, was obtained after 24-h reaction. During the range of 200–240 °C, a mixture of **2c** and **3c** was obtained (Scheme 2). The benzannulation product **3c** was obtained at above 240 °C because subsequently twice eliminations of hydrochloride of compound **2c** could occur under this high temperature. Beside the high temperature (>240 °C), there are still two methods able to transform **2c** into **3c**, one is to react **2c** in a general refluxing DMF solution for 20 h and the other is to heat a mixture of **1c**, *trans*-1,2-dichloroethene, and triethylamine at around 200 °C in a high-pressure sealed glass tube.[11]

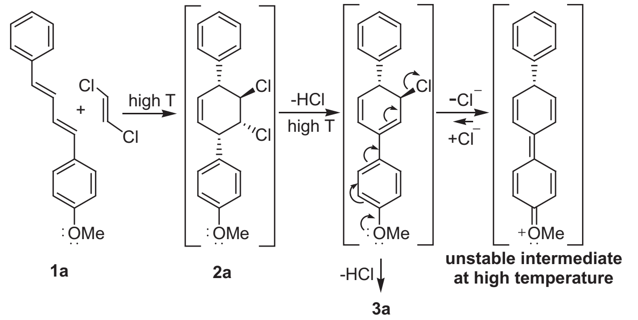
In order to figure out the reason for the low yield of **3a** (Table 1, entry 1), the reaction of **1a** and *trans*-1,2-dichloroethene at around 210 °C in a high-pressure sealed glass tube was done but few of **2a** could be obtained. Increasing the reaction temperature could only enhance the formation of **3a**. However, another comparative experiment, the reaction of **1e** and *trans*-1,2-dichloroethene at 210 °C, could apparently afford compound **2e**.[12] This meant the methoxy group, an electron-donating group, made **1a** an unfavorable diene in this Diels–Alder reaction and it also made the reaction occur at a high temperature. This high temperature may not only drive hydrochloride eliminated directly but also cause some intermediates of **1a**, only formed by the influence of methoxy group, reacted to unwanted side products, so this may be the reason for the low yield of **3a** (Scheme 3). Compared with **1a**, compound **1g** containing a cyano group, an electron-withdrawing group, underwent this Diels–Alder reaction to afford **3g** in a better yield (Table 1, entry 7). Therefore, the yields of **3a**–**3g** are roughly affected by the substitution effect.

Unlike *trans*-1,2-dichloroethene, *cis*-1,2-dichloroethene is not a good acetylene equivalent dienophile for this Diels–Alder reaction. Heating of **1c** and *cis*-1,2-dichloroethene in a high-pressure sealed glass tube above 240 °C for 24 h caused a complicated result and *p*-terphenyl **3c** was only obtained in a 8% yield after chromatography.

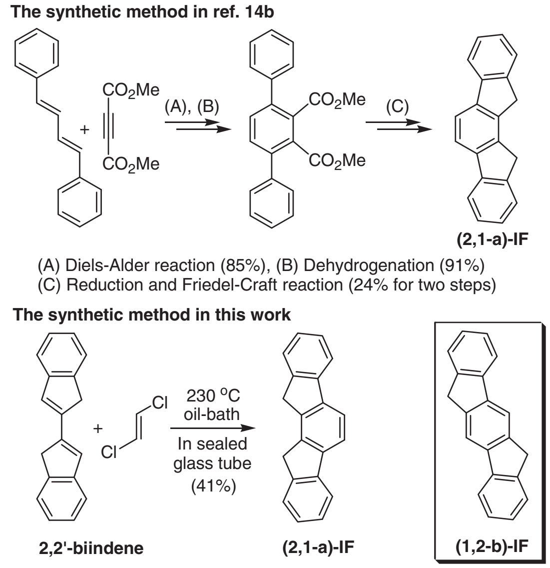
Table 1
Results of syntheses of *p*-terphenyls **3a**–**3g**

Entry	Diene	R	*p*-Terphenyl	Yield[a]
1	**1a**	OCH_3	**3a**	24
2	**1b**	CH_3	**3b**	50
3	**1c**	H	**3c**	75
4	**1d**	F	**3d**	33
5	**1e**	Cl	**3e**	65
6	**1f**	Br	**3f**	52[b]
7	**1g**	CN	**3g**	68

[a] Isolated yields.
[b] A mixture of **3e** and **3f** (ratio = 1:2.2).



Scheme 3. A possibility of the low yields of **3a**.



(A) Diels-Alder reaction (85%), (B) Dehydrogenation (91%)
(C) Reduction and Friedel-Craft reaction (24% for two steps)

Scheme 4. Synthetic methods for **(2,1-a)-IF**.

Because of the successful syntheses of *p*-terphenyls by this one-pot benzannulation of Diels–Alder reaction, it occurred to us that it might be a good synthetic method for 11,12-dihydroindeno[2,1-*a*]fluorene **(2,1-a)-IF**, an isomer of 6,12-dihydroindeno[1,2-*b*]fluorene **(1,2-b)-IF** (Scheme 4) which has been used as a core structure in many cases of optoelectronic materials.[13] Compound **(2,1-a)-IF** was not studied as much as **(1,2-b)-IF** because of its synthetic difficulty. A series of derivatives of **(2,1-a)-IF** were recently synthesized by Poriel's group,[14] and one of the synthetic pathways of **(2,1-a)-IF** they proposed was a four-step synthesis with a total yield of 18%.[14b] However, the synthesis of **(2,1-a)-IF** by our approach only need one-step reaction from 2,2′-biindene, which was synthesized by a palladium-catalyzed coupling reaction of tributyl(inden-2-yl)-stannane and 2-bromoindene,[15] and the yield of **(2,1-a)-IF** was about 41%.

It is worthy to mention that the simple workup procedure also makes this reaction more practical. In the cases of compounds **3b**–**3e**, the products with enough purity for organic synthesis were obtained only by adding a large amount of hexane into the cooled reaction mixture and then filtrating the gray precipitated solids.

In summary, a series of *p*-terphenyls **3a**–**3g** and 11,12-dihydroindeno[2,1-*a*]fluorene **(2,1-a)-IF** have been conveniently synthesized by a one-pot benzannulation of Diels–Alder reaction with 1,2-dichloroethene as a dienophile. A further study of this direct benzannulation of Diels–Alder reaction between a variety of dienes and dienophiles containing appropriate leaving groups is in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.02.002.

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11. Two comparative experiments were done to see the effect of triethylamine in this one-pot benzannulation of Diels–Alder reaction under 200 °C at the same time. The result of the reaction of **1c** and *trans*-dichloroethene is to produce **2c** as a major product but that of the reaction of **1c**, *trans*-dichloroethene, and triethylamine is only to produce **3c**.
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