Tetrahedron Letters 50 (2009) 2722–2726

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of acenes via coupling of 1,4-dilithiobutadienes with diiodoarenes in the presence of CuCl

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ARTICLE INFO

Article history:
Received 28 January 2009
Revised 24 February 2009
Accepted 26 February 2009
Available online 1 March 2009

ABSTRACT

Dilithiobutadienes prepared from diiodobutadienes reacted with diiodobenzene or diiodonaphthalene to afford substituted naphthalene, anthracene, dihydronaphthacene, and dihydropentacene derivatives in the presence of CuCl and DMPU. Dihydronaphthacene and dihydropentacene derivatives were converted into the corresponding naphthacene and pentacene derivatives.

Linearly fused polycyclic aromatic compounds have been attractive as organic materials, since Jackson reported that pentacene showed comparable or higher charge-carrier mobility than amorphous silicon in 1997.[1] Since then the area of pentacene has been rapidly developing. Unfortunately pentacene is not soluble in organic solvent at ambient conditions. Therefore, we proposed that soluble substituted pentacenes were important.[2a]

Before our proposal, there were only two reports for the formation of substituted pentacenes.[3,4] After that substituted acenes have been reported,[5] however the preparative method of substituted acenes is still limited.

We developed two methods for the preparation of substituted acene derivatives. One is a homologation method using diynes or tetraynes with transition metals stoichiometrically or catalytically.[2] The other is a coupling method.[6] The coupling method involves reactions of zirconacyclopentadienes, which can be conveniently prepared from diynes, with diiodobenzene derivatives.

The coupling method provides a direct ring extension reaction from diiodoaromatic compounds such as diiodobenzene and diiodonaphthalene. This reaction proceeded in the presence of CuCl and DMPU. However, unfortunately trimethylsilyl-substituted zirconacyclopentadienes did not show any coupling reaction as shown in Scheme 1. This prompted us to develop more general method for the ring extension reaction from diiodobenzenes.

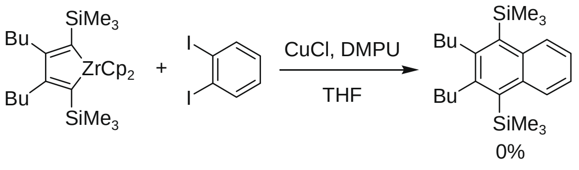
It has been believed that treatment of zirconacyclopentadienes with CuCl afforded the corresponding dicopper dienes as an active species, although the structure of such species has not been determined yet. Probably, the efficiency of the transmetalation would be affected by substituents on the 2,5-positions of zirconacyclopentadienes. We carried out the stepwise preparation of such dicopper diene species via diiodobutadiene and dilithiobutadiene derivatives as shown in Scheme 2. Diiodobutadiene derivatives were isolated and purified in high yields.[7] Dilithiobutadiene derivatives were prepared in situ and they were used for the coupling with diiodobenzene in the presence of CuCl.

Surprisingly, the corresponding naphthalene derivative **2d** was obtained in 86% GC yield. The coupling method was improved by this method via diiodobutadiene derivatives.

Similarly, a *t*-butyl-substituted zirconacyclopentadiene did not afford the coupling product at all with diiodobenzene in the presence of CuCl and DMPU. This reaction can also be circumvented via isolation of diiodobutadiene and dilithiobutadiene derivatives as shown in Scheme 3. In the presence of CuCl and DMPU, the desired product **2g** was obtained in 51% yield.

As shown above, stepwise preparation improved the situation of trimethylsilyl- or *t*-Bu-substituted zirconacyclopentadienes. In order to investigate the scope and limitation of this method, we carried out the coupling reactions using usual alkyl- or aryl-substituted diiodobutadienes (Scheme 4). Table 1 shows the result of various substituted diiodobutadienes including trimethylsilyl and *t*-butyl cases for the reaction with 1,2-diiodobenzene.

Alkyl-substituted diiodobutadienes (entries 1–3, and 5) gave the corresponding naphthalenes in yields that are comparable to those obtained from the direct coupling of zirconacyclopentadienes. Alkyl-substituted diiodobutadienes with bicyclic system



Scheme 1.

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E-mail address: tamotsu@cat.hokudai.ac.jp (T. Takahashi).

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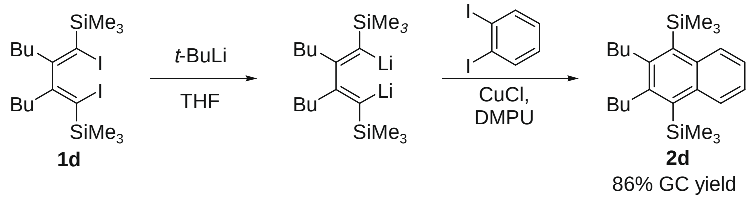
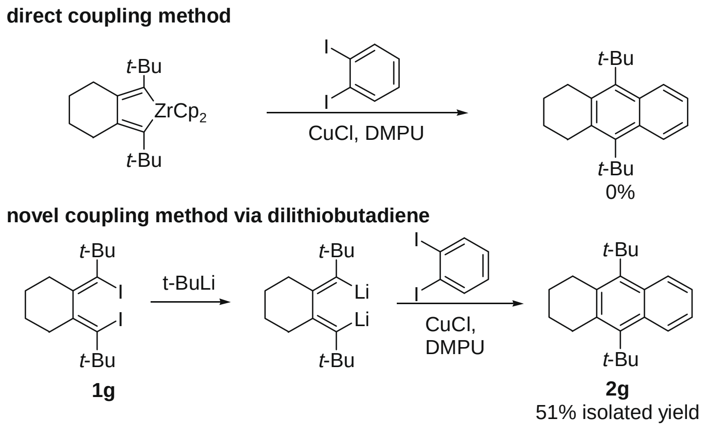
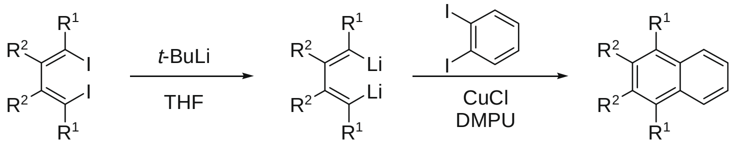
doi:10.1016/j.tetlet.2009.02.191



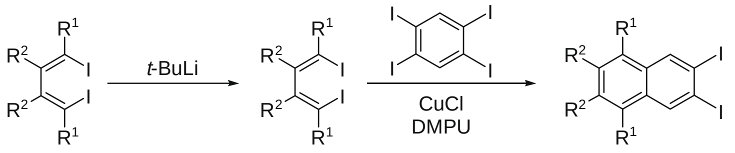
Scheme 2.



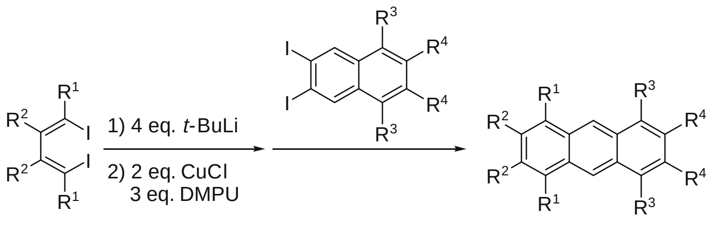
Scheme 3.



Scheme 4.



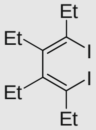
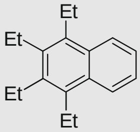
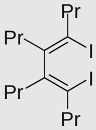
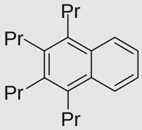
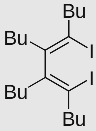
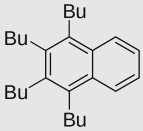
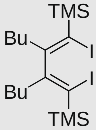
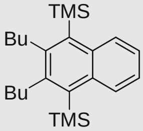
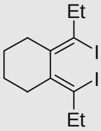
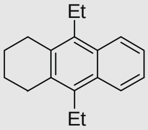
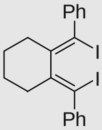
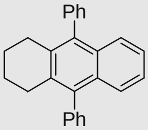
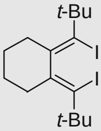
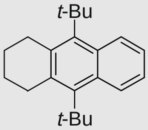
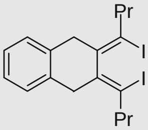
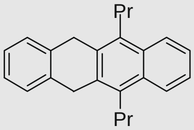
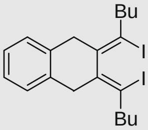
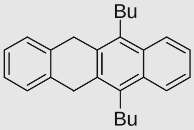
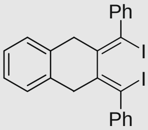
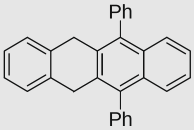
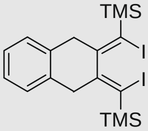
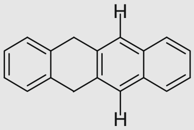
Scheme 5.



Scheme 6.

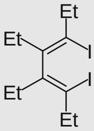
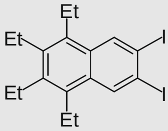
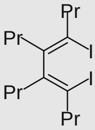
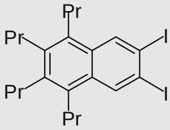
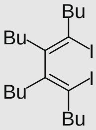
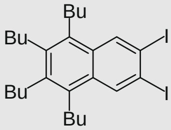
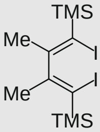
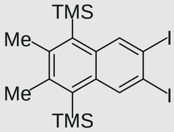
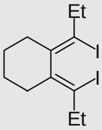
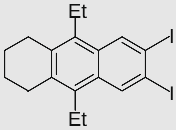
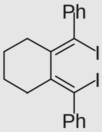
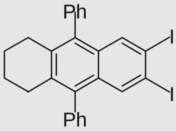
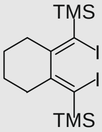
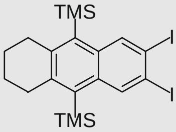
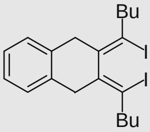
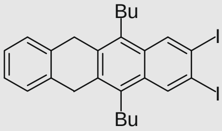
gave the products in relatively higher yields (entries 8 and 9). Phenyl-substituted diiodobutadienes also showed the similar reactivity (entries 6 and 10). Trimethylsilyl-substituted diiodobutadiene **1k** afforded the coupling product, dihydronaphthacene **2k** but during the work-up trimethylsilyl groups were eliminated (entry 11).

Table 1
Formation of substituted acenes from diiodobutadienes and 1,2-diiodobenzene[a]

Entry	Diiodobutadiene **1**	Product **2**	Yield[b] (%)
1	 **1a**	 **2a**	56 (48)
2	 **1b**	 **2b**	78 (59)
3	 **1c**	 **2c**	74 (57)
4	 **1d**	 **2d**	86 (41)
5	 **1e**	 **2e**	(57)
6	 **1f**	 **2f**	(63)
7	 **1g**	 **2g**	(51)
8	 **1h**	 **2h**	82 (57)
9	 **1i**	 **2i**	89 (61)
10	 **1j**	 **2j**	(47)
11	 **1k**	 **2k**	(54)

[a] Ratio and conditions; diiododiene **1**:*t*-BuLi:CuCl:diiodobenzene:DMPU = 1.0:4.0:2.2:2.0:3.0. The coupling was carried out at 50 °C for 3–12 h.
[b] GC yields. Isolated yields are shown in parentheses.

Table 2
Formation of substituted acenes from diiodobutadienes and 1,2,4,5-tetraiodobenzene[a]

Entry	Diiodobutadiene **1**	Product **3**	Isolated yield (%)
1	 **1a**	 **3a**	48
2	 **1b**	 **3b**	52
3	 **1c**	 **3c**	53
4	 **1l**	 **3d**	43
5	 **1e**	 **3e**	55
6	 **1f**	 **3f**	55
7	 **1m**	 **3g**	47
8	 **1i**	 **3h**	48

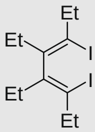
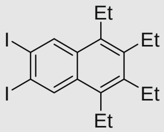
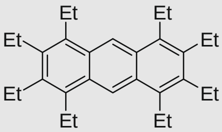
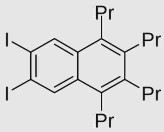
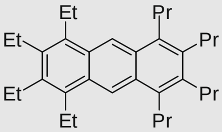
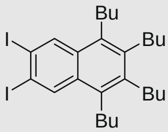
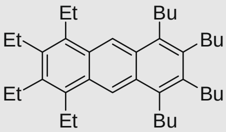
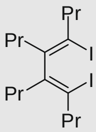
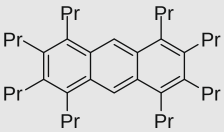
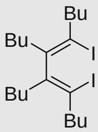
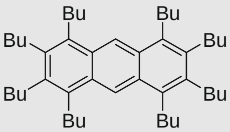
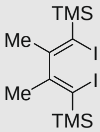
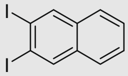
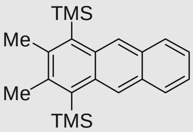
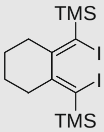
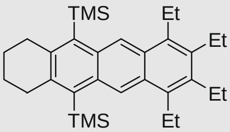
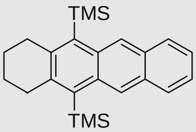
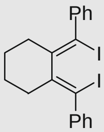
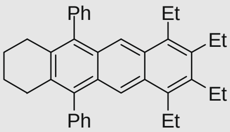
[a] Ratio and conditions; diiododiene **1**:*t*-BuLi:CuCl:tetraiodobenzene:DMPU = 1.0:4.0:2.2:2.0:3.0. The coupling was carried out at 50 °C for 3–12 h.

The reaction of various dilithiobutadienes prepared from diiodobutadienes was also applicable for the coupling with 1,2,4,5-tetraiodobenzene as shown in Scheme 5. The results are summarized in Table 2.

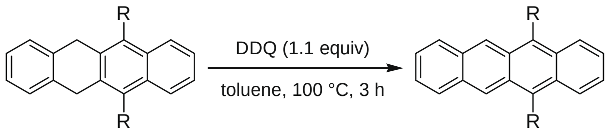
Alkyl-substituted diiodobutadienes afforded the corresponding diiodoarene derivatives in moderate yields (entries 1–3, 5, and 8). Trimethylsilyl-substituted diiodobutadienes also gave the products in yields comparable to those of alkyl substituted cases (entries 4 and 7).

Recently we have reported positive effects of phenyl substitution for the coupling reaction of zirconacyclopentadienes with

Table 3
Formation of substituted acenes from diiodobutadienes and 2,3-diiodonaphthalenes[a]

Entry	Diiodobutadiene **1**	Product **3**	Product **4**	Isolated yield (%)
1	 **1a**	 **3a**	 **4a**	(51)
2	**1a**	 **3b**	 **4b**	(56)
3	**1a**	 **3c**	 **4c**	(53)
4	 **1b**	**3b**	 **4d**	(57)
5	 **1c**	**3c**	 **4e**	(54)
6	 **1l**	 **3i**	 **4f**	(35)
7	 **1m**	**3a**	 **4g**	(32)
8	**1m**	**3i**	 **4h**	(37)
9	 **1f**	**3a**	 **4i**	(53)

[a] Ratio and conditions; diiododiene **1**:t-BuLi:CuCl:diiodonaphthalene **3**:DMPU = 1.0:4.0:2.2:2.0:3.0. The coupling was carried out at 50 °C for 3–12 h.



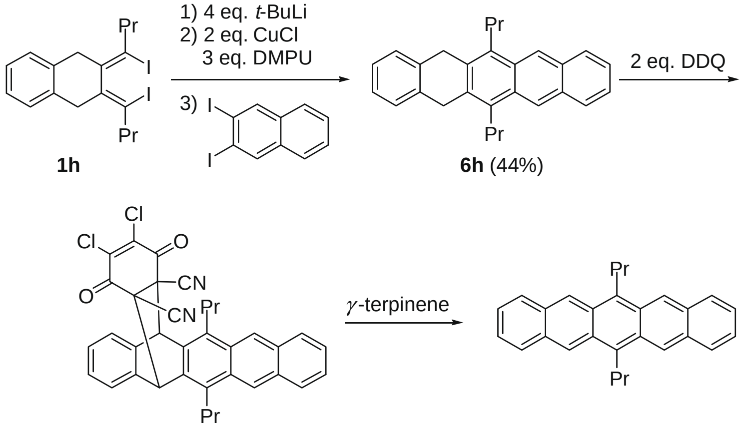
2i (R = Bu)
j (R = Ph)

5i (78%)
j (48%)

Scheme 7.

tetraiodobenzene.[6e] In the present method, however, such phenyl effects were not observed (entry 6).

Coupling reaction with 2,3-diiodonaphthalene derivatives is very useful since two rings can be extended at once. Scheme 6 shows the coupling of diiodonaphthalenes and the results are summarized in Table 3. Alkyl-substituted diiodobutadienes gave the corresponding anthracene derivatives (entries 1–5). Trimethylsilyl-substituted diiodobutadienes reacted with 2,3-diiodonaph-



Scheme 8.

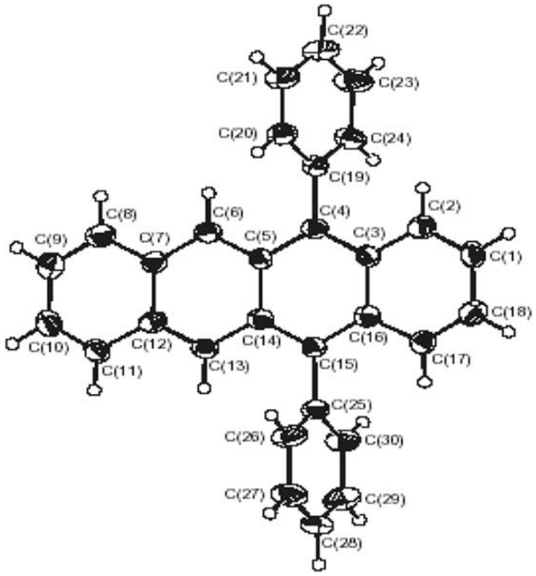


Figure 1. Structure of diphenylnaphthacene **5j**.

thalene or substituted diiodonaphthalenes to give anthracene derivatives with trimethylsilyl groups in moderate yields (entries 6–8). Phenyl-substituted one also showed the similar reactivity (entry 9).

Compounds **2i** and **2j** were aromatized with DDQ at 100 °C in toluene to afford the corresponding naphthacenes **5i** and **5j**, respectively (Scheme 7). The structure of naphthacene **5j** was determined by X-ray analysis. The structure is shown in Figure 1.

Furthermore, the present method was applied for synthesis of 6,13-dipropylpentacene as shown in Scheme 8. Bicyclic diiodobutadiene **1h** was subjected to the coupling reaction with 2,3-diiodonaphthalene to afford the corresponding dihydropentacene **6h**, which can be converted to 6,13-dipropylpentacene via the DDQ adduct as we reported recently.[6d]

In summary, we have developed a general reaction for the construction of polycyclic aromatic compounds. The 1,4-dilithiobutadiene species were demonstrated to be more reactive substrates for the coupling reaction. The present method extended the scope of polyacenes compared with the known method.

Acknowledgment

Authors thank Mr. Keiichi Kashima for his experimental assistance.

Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.191.

References and notes

1. (a) Gundlach, D. J.; Lin, Y.-Y.; Jackson, T. N.; Nelson, D. F.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87; (b) Lin, Y.-Y.; Gundlach, D. J.; Nelson, D. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606; (c) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Electron Devices* **1997**, *44*, 1325; (d) Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854; (e) Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748.
2. (a) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876; (b) Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410; (c) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967; (d) Takahashi, T.; Li, Y.; Hu, J.; Kong, F.; Nakajima, K.; Zhou, L.; Kanno, K. *Tetrahedron Lett.* **2007**, *48*, 6726; (e) Ogasawara, M.; Sakamoto, T.; Nakajima, K.; Takahashi, T. *J. Organomet. Chem.* **2007**, *692*, 55; (f) Li, S.; Zhou, L.; Song, Z.; Bao, F.; Kanno, K.; Takahashi, T. *Heterocycles* **2007**, *73*, 519; g Li, S.; Li, Z.; Nakajima, K.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2009**, *4*, 294.
3. Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253.
4. Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1969**, *34*, 1734.
5. For reviews, see: (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028; (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.
6. For coupling of zirconacyclopentadienes, see: (a) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154; (b) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576; (c) Zhou, X.; Li, Z.; Wang, H.; Kitamura, M.; Kanno, K.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2004**, *69*, 4559; (d) Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2007**, *129*, 15752; (e) Seri, T.; Qu, H.; Zhou, L.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2008**, *3*, 388.
7. For the synthesis of 1,4-dihalo-1,3-dienes, see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829; (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. K.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336; (c) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870; (d) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911; (e) Yamaguchi, S.; Jin, R.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060; (f) Xi, C.; Kotora, M.; Takahashi, T. *Tetrahedron Lett.* **1999**, *40*, 2375; (g) Xi, Z.; Liu, X.; Lu, J.; Bao, F.; Fan, H.; Li, Z.; Takahashi, T. *J. Org. Chem.* **2004**, *69*, 8547; (h) Xi, Z.; Song, Z.; Liu, G.; Liu, X.; Takahashi, T. *J. Org. Chem.* **2006**, *71*, 3154.