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Novel Synthesis of Biphenylene and Its Derivatives Using Intramolecular Coupling of Zincacyclopentadienes

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Abstract:

Biphenylene and its derivatives were synthesized using the intramolecular coupling of benzoannelated zincacyclopentadiene intermediates prepared from 2,2'-dilithiobiaryls with $ZnCl_2$. The reaction proceeded smoothly and selectively to give the desired biphenylenes in moderate to good yields. © 1998 Elsevier Science Ltd. All rights reserved.

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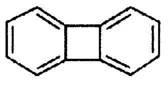
Biphenylene (**1**) has received considerable attention from both theorists and experimentalists [1], because **1** can be anticipated as a unit of new carbon allotropes [2,3], and because **1** and its derivatives can be used as spacers and building blocks for functionalized organic materials [4-8]. Many synthetic methods, such as dimerization of benzyne [9], the Ullmann coupling of 2,2'-diiodobiphenyl with Cu_2O or Cu [10,11], and the Vollhardt method using cobalt-catalyzed cyclization [12], have been employed for the preparation of **1** and [n]phenyl-



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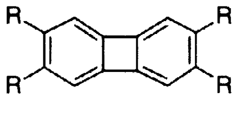
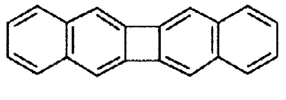


2: R = Me
3: R = F



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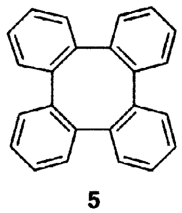

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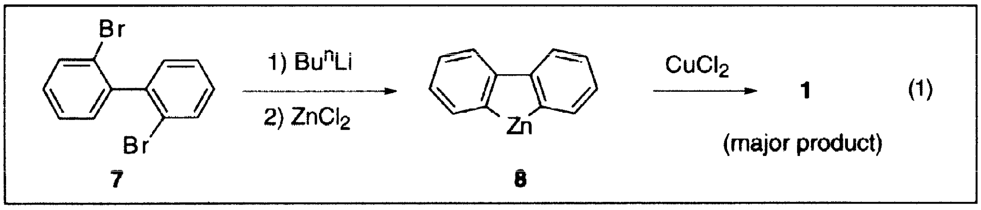

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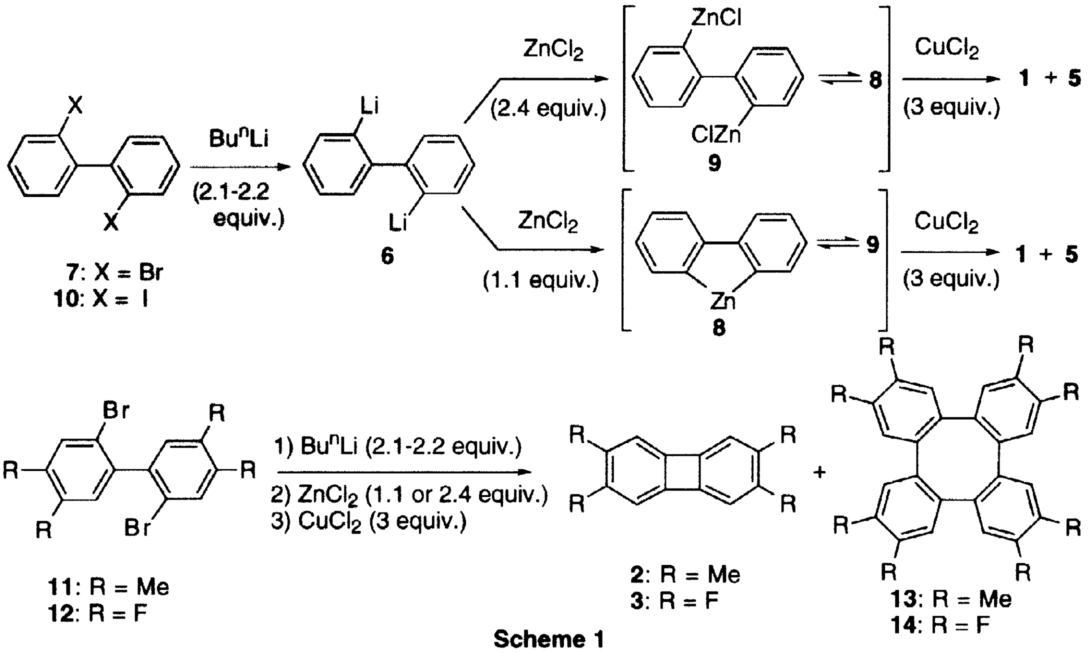
enes. However, only limited methods are known for the construction of functionalized biphenylenes with methyl and fluoro groups (**2** and **3**) [13-15]. It is known that the copper-catalyzed coupling of 2,2'-dilithiobiphenyl **6** leads to tetraphenylene **5** (53%) with a small amount of **1** (3%) [16,17]. Recently, we have found that the copper-catalyzed coupling of the organozinc compound **8** produces biphenylene **1** and its derivatives selectively as shown in eq. 1.

The reaction of 2,2'-dibromobiphenyl **7** in THF with 2.2 equiv. of butyllithium in hexane produced 2,2'-dilithiobiphenyl **6** which was treated with 2.4 equiv. of $ZnCl_2$ to give the arylzinc chloride derivative **9** in a good yield.[1] The reaction of **9** with 3 equiv. of $CuCl_2$ produced biphenylene **1** (67%), together with a trace amount of tetraphenylene **5** (Table 1, entry 1). However, the yield of **1** was increased to 80% when **8**, prepared from **6** with 1.1 equiv. of $ZnCl_2$, was treated with 3 equiv. of $CuCl_2$ (entry 2). In addition, tetraphenylene (**5**) was isolated in 6% yield. Similar results were obtained from the reaction of 2,2'-diiodobiphenyl **10**[2] (entries 3 and 4). Thus, the reaction of **9**, prepared from **10**, with 3 equiv. of $CuCl_2$ gave **1** (69%) with a trace amount of **5** (entry 3), whereas the reaction of **8** with 3 equiv. of $CuCl_2$ produced **1** (81%) together with **5** (5%) (entry 4). The intramolecular coupling reaction of dibenzozincacyclopentadiene **8** with $CuCl_2$ can be applied for the synthesis of 2,3,6,7-tetrasubstituted biphenylenes (**2** and **3**). The successive treatments of **11**[2] and **12** with 2.1 equiv. of butyllithium and 1.1 equiv. of $ZnCl_2$ produced zincacyclopentadiene intermediates which were reacted with 3 equiv. of $CuCl_2$ to produce **2** (70%)



Scheme 1

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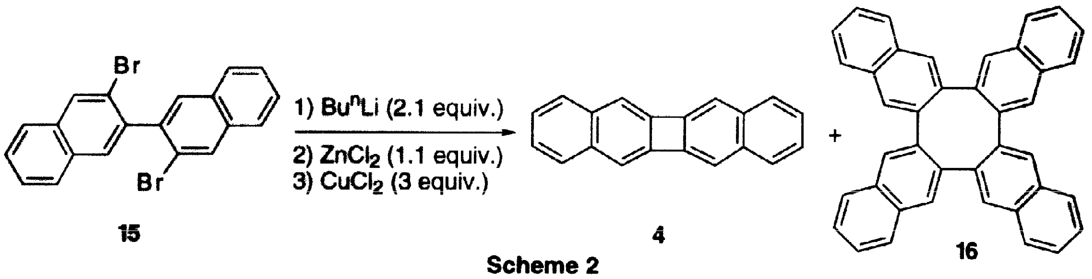
[1] The zinc compounds (**8** and **9**) may exist as an equilibrium mixture. A quenching experiment of the solution, which was prepared from **6** with 2.4 equiv. of $ZnCl_2$, with CF_3COOH in THF at -78 °C produced biphenyl in 80% yield.

[2] The compounds (**10**, **11** and **15**) were prepared in 80%, 75%, and 60% yields, respectively, by the reaction of the corresponding 1,2-dihaloarenes with 0.5 equiv. of butyllithium [18].



Scheme 2

Table 1. Copper-catalyzed coupling of organozinc compounds derived from **7**, **10-12**, and **15**.[a]

Entry	Compound	Conditions Bu^{n}Li (equiv.)	 ZnCl$_2$ (equiv.)	Yields[b] Biphenylene	 Tetraphenylene
1	**7**	2.2	2.4	**1** (67%)	**5** (trace)
2	**7**	2.1	1.1	**1** (80%)	**5** (6%)
3	**10**	2.2	2.4	**1** (69%)	**5** (trace)
4	**10**	2.1	1.1	**1** (81%)	**5** (5%)
5	**11**	2.2	2.4	**2** (59%)	**13** (trace)
6	**11**	2.1	1.1	**2** (70%)	**13** (7%)
7	**12**	2.1	1.1	**3** (46%)	**14** (10%)
8	**15**	2.1	1.1	**4** (70%)	**16** (15%)

[a]2,2'-Dihalobiphenyl (1 mmol) in THF (20 ml) is reacted with *n*-butyllithium (2.1-2.2 mmol) in hexane (1.4 ml) at -78 °C to produce the dilithiated compound which is treated with ZnCl$_2$ (1.1-2.4 mmol) in THF (10 ml) at -50 °C, followed by CuCl$_2$ (3 mmol) at -78 °C. After stirring at -78 °C for 2 h and then at r.t. overnight, the products were separated by column chromatography on silica gel. [b]Isolated yields.

and **3** (46%) together with **13** (7%) and **14** (10%), respectively (entries 6 and 7).[3] Although 2,3:6,7-dibenzobiphenylene (**4**) was synthesized in 1% yield by the reaction of 2-bromo-3-iodo- or 2,3-diiodonaphthalene with copper bronze in DMF [19,20], the successive treatment of **15**[2] with 2.1 equiv. of butyllithium, 1.1 equiv. of ZnCl$_2$ and 3 equiv. of CuCl$_2$ produced **4** (70%) together with **16** (15%) (entry 8).[3] The results presented in Table 1 show that our method reported here can be employed widely for the synthesis of biphenylene (**1**) and its derivatives.

Although the planar structure of biphenylene (**1**) containing a [4]radialene framework was revealed by X-ray analysis [21], the nonplanarity of tetraphenylene (**5**) was deduced from an electron diffraction study [22]. In order to get further information regarding the nonplanar structure of tetraphenylenes, the structure of **16** was determined by X-ray analysis.[4] A single

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3) All new compounds descrived in this communication were fully characterized by spectroscopic analyses. Selected data were as follows. **2**: pale yellow cryst., mp 223-224 °C (lit. mp 224-225 °C [13]), MS (*m/z*) 208 (M^+); ^1H NMR ($CDCl_3$) δ 2.07 (s, 12H), 6.40 (s, 4H). **3**: colorless cryst., mp 107-108 °C, MS (*m/z*) 224 (M^+); ^1H NMR ($CDCl_3$) δ 6.49 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 109.8, 144.1, 150.5 (dd, J = 249.9, 13.4 Hz). **4**: pale yellow cryst., mp ca. 345 °C sublimed (lit. mp (sealed tube) 376 °C [20]), MS (*m/z*) 252 (M^+); ^1H NMR ($CDCl_3$) δ 7.17 (s, 4H), 7.26 (AA' part of AA'XX', 4H), 7.51 (XX' part of AA'XX', 4H). **13**: colorless cryst., mp 85-86 °C, MS (*m/z*) 416 (M^+); ^1H NMR ($CDCl_3$) δ 2.21 (s, 24H), 6.91 (s, 8H). **14**: colorless cryst., mp 57-58 °C, MS (*m/z*) 448 (M^+); ^1H NMR ($CDCl_3$) δ 6.98 (m, 8H). **16**: colorless cryst., mp 233-234 °C, MS (*m/z*) 504 (M^+); ^1H NMR ($CDCl_3$) δ 7.43 (AA' part of AA'XX', 8H), 7.76 (s, 8H), 7.79 (XX' part of AA'XX', 8H).

4) *Crystal data* for **16**•*n*-C_6H_{14}: $C_{40}H_{24}{\bullet}C_6H_{14}$, FW = 590.81, monoclinic, space group $P2_1/n$ (# 14); a = 12.617(2) Å, b = 17.077(3) Å, c = 16.236(4) Å, β = 104.46(2)°, V = 3387(1) Å^3, Z = 4, D_{calcd} = 1.158 g cm^{-1}. The structure was solved by direct method. Full matrix least-squares refinement yielded the final R value of 0.08 (R_W = 0.085) for 2163 independent reflections [$2\theta \leq 55.0°$, $I > 10.0\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω - 2θ scan.

crystal of **16** contains one disordered molecule of hexane per formula unit, but fairly good information regarding the structure of **16** was obtained. As shown in Figure 1, the central cyclooctatetraene ring has a tub form with an average dihedral angle of 66° which is smaller than that in **5** (ca. 70° based on the molecular models [22]). Interestingly, all bond distances in the central cyclooctatetraene ring are approximately equal to 1.46 Å, reflecting an [8]radialene structure.

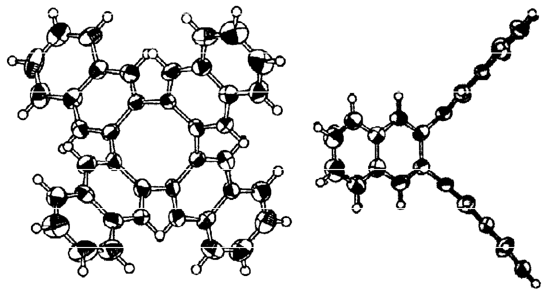
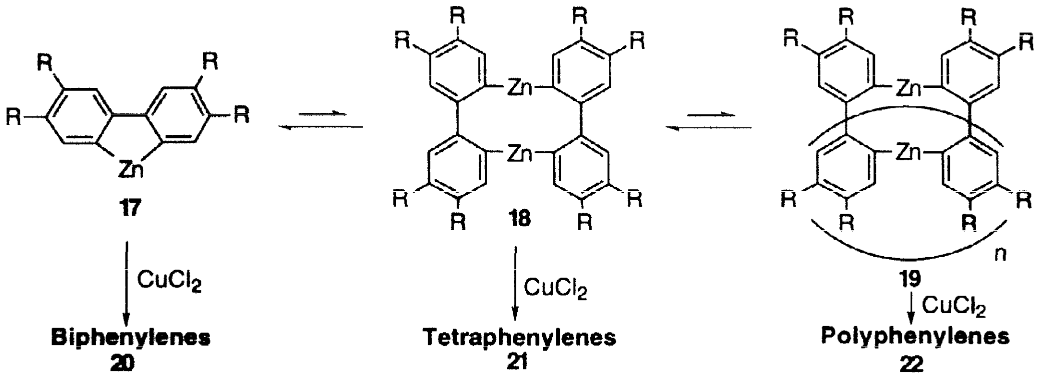

(a) (b)

Figure 1. Crystal structure of **16**.
(a) Top view. (b) Side view.

A possible mechanism for the formation of biphenylenes (**20**), tetraphenylenes (**21**) and polyphenylenes (**22**) from the diarylzinc intermediates is shown in Scheme 3. The diarylzinc species (**17**, **18** and **19**) react with $CuCl_2$ to give the corresponding **20**, **21** and **22**, respectively. Thus, the most thermodynamically stable **17** is formed predominantly in solution to lead to the preferential formation of biphenylenes (**20**).



Scheme 3

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