

TETRAHEDRON LETTERS

## 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<sub>2</sub>. 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<sub>2</sub>O or Cu [10,11], and the Vollhardt method using cobalt-catalyzed cyclization [12], have been employed for the preparation of 1 and [n]phenyl-



0040-4039/98/\$19.00 © 1998 Elsevier Science Ltd. All rights reserved. PII: S0040-4039(98)01082-X 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 coppercatalyzed 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<sub>2</sub> to give the arylzinc chloride derivative 9 in a good yield.<sup>1</sup> The reaction of 9 with 3 equiv. of CuCl<sub>2</sub> 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<sub>2</sub>, was treated with 3 equiv. of CuCl<sub>2</sub> (entry 2). In addition, tetraphenylene (5) was isolated in 6% yield. Similar results were obtained from the reaction of 2,2'-diiodobiphenyl 10<sup>2</sup> (entries 3 and 4). Thus, the reaction of 9, prepared from 10, with 3 equiv. of CuCl<sub>2</sub> gave 1 (69%) with a trace amount of 5 (entry 3), whereas the reaction of 8 with 3 equiv. of CuCl<sub>2</sub> produced 1 (81%) together with 5 (5%) (entry 4). The intramolecular coupling reaction of dibenzozincacyclopentadiene 8 with CuCl<sub>2</sub> can be applied for the synthesis of 2,3,6,7-tetrasubstituted biphenylenes (2 and 3). The successive treatments of 11<sup>2</sup> and 12 with 2.1 equiv. of butyllithium and 1.1 equiv. of ZnCl<sub>2</sub> produced 2 (70%)



<sup>1)</sup> 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<sub>2</sub>, with CF<sub>3</sub>COOH in THF at -78 °C produced biphenyl in 80% yield.

<sup>2)</sup> 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].



Table 1. Copper-catalyzed coupling of organozinc compounds derived from 7, 10-12, and 15.<sup>a</sup>

	Compound	Conditions		Yields <sup>b</sup>	
Entry		Bu <sup>n</sup> Li (equiv.)	ZnCl <sub>2</sub> (equiv.)	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%)

<sup>a</sup>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<sub>2</sub> (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. <sup>b</sup>Isolated yields.

and 3 (46%) together with 13 (7%) and 14 (10%), respectively (entries 6 and 7).<sup>3</sup> Although 2,3:6,7-dibenzobiphenylene (4) was synthesized in 1% yield by the reaction of 2-bromo-3iodo- 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<sub>2</sub> and 3 equiv. of CuCl<sub>2</sub> produced 4 (70%) together with 16 (15%) (entry 8).<sup>3</sup> 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.<sup>4</sup> A single

<sup>3)</sup> 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<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.07 (s, 12H), 6.40 (s, 4H). 3: colorless cryst., mp 107-108 °C, MS (*m*/z) 224 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.49 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 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*/2) 416 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.21 (s, 24H), 6.91 (s, 8H). 14: colorless cryst., mp 57-58 °C, MS (*m*/z) 448 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.98 (m, 8H). 16: colorless cryst., mp 233-234 °C, MS (*m*/z) 504 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.43 (AA' part of AA'XX', 8H), 7.76 (s, 8H), 7.79 (XX' part of AA'XX', 8H).

<sup>4)</sup> Crystal data for  $16 \cdot n - C_6 H_{14}$ :  $C_{40} H_{24} \cdot C_6 H_{14}$ , FW = 590.81, monoclinic, space group  $P_{2/n}$  (# 14); a = 12.617(2) Å, b = 17.077(3) Å, c = 16.236(4) Å,  $\beta = 104.46(2)^\circ$ , V = 3387(1) Å<sup>3</sup>, Z = 4,  $D_{calcd} = 1.158$  g cm<sup>-1</sup>. 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 [20  $\leq 55.0^\circ$ ,  $I > 10.0\sigma(I)$ ] measured on a Rigaku AFC7R diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å) and  $\omega - 20$  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  $66^{\circ}$  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 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<sub>2</sub> 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).



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