Palladium-Catalyzed Coupling of 2,2'-Dihalobiaryls with Metallated Cyclopentenes. An Easy Synthesis for Spiro[Cyclopentene-1,9'-[9H]Fluorene]s

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Abstract: In the presence of palladium catalysts, one of the two carbons attached to halogen in 2,2'-diiodobiphenyl couples with unsaturated organometallics, after which the other adds to the newly incorporated double bond. Spiro[cyclopentene-1,9'-[9H]fluorene]s can be synthesized in this way.

Since the combination of aryl (or vinyl) halides both with unsaturated organometallics by coupling¹ and with alkenes by addition and elimination (the Heck Reaction)² are catalyzed by palladium reagents, it should be possible to prepare cyclic structures by using the former reaction to generate the substrate for the latter. Equations 1-4, which we report here, are the first examples of this sequence.³ We assume, using eq 1 as an illustration, that the key steps are those outlined in Scheme I. (Two moles of alkenylzinc chloride were used in eqs 1-3, and HI is probably consumed by the excess.)

The synthesis in eq 1, for which the zinc halide derivative was used because of its efficacy in couplings previously described,^{1b,4} is considerably shorter than the classical sequence recently used to prepare the same structure.⁵ It is also notable that the even though its formation causes benzene rings to clash, the same kind of product is formed by the analogous binaphthyl (eq 2).

That the rings formed in Heck reactions are five-membered when the double bond is five atoms from the palladium (as in Scheme I and eqs 1-3), and six-membered when the double bond is six atoms from the palladium (as in eq 4), is well documented,^{6,7} as are couplings with organotin compounds like that giving the minor product (5) of eq 4.⁸

Scheme I

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Products.

1—The ^1H NMR spectrum is the same as that published (ref 5); ^{13}C NMR (75 MHz, CDCl_3): δ 33.22 (CH_2), 37.45 (CH_2), 63.73 (C), 119.62 (CH), 123.71 (CH), 127.15 (CH), 127.41 (CH), 132.89 (CH), 136.33 (CH), 139.78 (C), 152.00 ppm (C); MS (EI) m/z 218 (M^+ , 100%). The ^{13}C NMR spectrum is identical to one measured by Ohwada using a sample prepared by his method (ref 5).

2— ^1H NMR (200 MHz, CDCl_3): δ 2.49 (t, 2H), 2.93 (m, 2H), 5.45 (td, 1H), 6.30 (td, 1H), 7.55 (m, 4H), 7.92

(m, 4H), 8.71 ppm (d, 2H)—this spectrum is appropriately similar to that of **1**; MS (CI, CH₄) *m/z* 319 (M⁺ + 1, 100%), 347 (M⁺ + 29, 25%).

3a—¹H NMR (250 MHz, CDCl₃): δ 3.28 (t, 2H), 6.10 (td, 1H), 6.68 (td, 1H), 7.25 (m, 4H), 7.40 (m, 2H), 7.77 ppm (d, 2H); ¹³C NMR (62.5 MHz, CDCl₃): δ 42.6 (CH₂), 69.2 (C), 120.4, 123.6, 127.6, 128.3, 130.4, 135.0, 141.7, 145.1 (aromatic and vinyl C's), 214.2 ppm (C=O); MS (EI): *m/z* 232 (M⁺, 47%), 203 (M⁺ – 29, 100%); Anal. Calcd for C₁₇H₁₂O; C, 87.91; H, 5.21. Found: C, 87.90; H, 5.28.

3b—¹H NMR (250 MHz, CDCl₃): δ 3.34 (t, 2H), 6.50 (td, 1H), 7.25 (m, 4H), 7.38 (m, 2H), 7.75 (d, 2H), 8.18 ppm (td, 1H); ¹³C NMR (62.5 MHz, CDCl₃): δ 42.6 (CH₂), 62.3 (C), 120.3, 122.1, 127.7, 127.9, 133.9, 141.6, 146.6, 164.4 (aromatic & vinyl C's), 207.4 ppm (C=O); MS (EI): *m/z* 232 (M⁺, 100%), 203 (M⁺ – 29, 87%); Anal. Calcd for C₁₇H₁₂O; C, 87.91; H, 5.21. Found: C, 87.93; H, 5.25. The structure was analyzed by X-ray diffraction. Details of the X-Ray diffraction analysis can be obtained from the Fachinformationszentrum, Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depositary number CSD-57109, the names of the authors, and the journal citation.

4—¹H NMR (250 MHz, CDCl₃): δ 4.18 (s, 2H), 7.31–8.8 (m, 12H); MS (EI): *m/z* 266 (M⁺); Anal. Calcd for C₂₁H₁₄; C, 94.70; H, 5.30. Found: C, 94.33; H, 5.41; m.p. 157–159 °C.

5—¹H NMR (250 MHz, CDCl₃): δ 3.1 (s, 1H), 4.3 (m, 2H), 4.6 (dd, 1H), 4.7 (m, 1H), 6.1 (m, 2H), 6.9 (t, 1H), 7.1–7.8 (m, 14 H); MS (EI): *m/z* 382 (M⁺); Anal. Calcd for C₃₀H₂₂; C, 94.20; H, 5.80. Found: C, 94.18; H, 5.87. The structure was analyzed by X-ray diffraction. If another diastereomer formed, it was removed during crystallization. Details of the diffraction analysis can be obtained as described for **3b**.

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