[11] See also E. Negishi in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon, Oxford, **1991**, p. 1163.

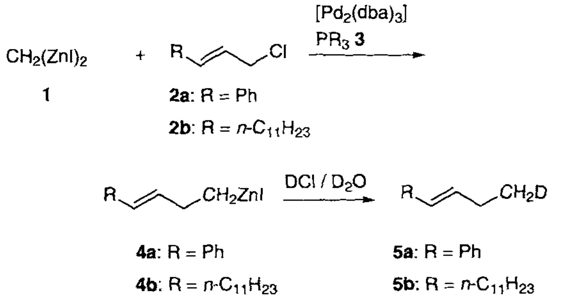
[12] A couple of reports dealing with cobalt-mediated synthetic organic reactions in aqueous media deal mainly with hydroformylations and carbonylations mediated by the $Co(CO)_4^-$ ion produced by a reaction of $[Co_2(CO)_8]$ with $H_2O$ or $HO^-$. a) F. Francalanci, M. Foá, *J. Organomet. Chem.* **1982**, *232*, 59; b) P. Eilbracht, E. Balb, M. Acker, *Tetrahedron Lett.* **1984**, *25*, 1131; c) M. Miura, F. Akase, M. Nomura, *J. Org. Chem.* **1987**, *52*, 2623; d) C. Zucchi, G. Pályi, V. Galamb, E. Sámpár-Szerencsés, L. Markó, P. Li, H. Alper, *Organometallics* **1996**, *15*, 3222.

# Stepwise Reaction of Bis(iodozincio)methane with Two Different Electrophiles[**]

Kiitiro Utimoto,[*] Narihiro Toda, Takeshi Mizuno, Masami Kobata, and Seijiro Matsubara

Geminal dimetallic reagents have attracted considerable attention as versatile reagents in organic synthesis,[1] and consequently their preparation has been extensively studied.[2] Application of the reagents has focused on regioselective olefination of carbonyl compounds[3] and coupling with two different electrophilic building blocks.[4] We have developed a method for preparing *gem*-bis(halozincio)alkanes from the corresponding dihalides and have used the organozinc compounds for the olefination of aldehydes and ketones.[5] We have also observed that one of the two C–Zn bonds of bis(iodozincio)methane is much more reactive than the other in the reaction with water or iodine.[5b] These results suggested that the two C–Zn bonds could be used separately. We describe here a stepwise reaction of *gem*-dizinc compounds with two different electrophiles under palladium catalysis.

We initially examined the Pd-catalyzed coupling of bis(iodozincio)methane (**1**) with allyl chlorides. As shown in Equation (1), an allyl chloride **2** (1.0 mmol) was treated with **1** (1.0 mmol) in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.025 mmol) and a phosphane **3** (0.1 mmol) as a ligand in THF (dba = dibenzylideneacetone). After 30 min the resulting mixture was quenched with $DCl–D_2O$ to give the deuterated product **5**. Combinations of allyl chlorides and ligands, as well as yields of coupling products **5** are summarized in Table 1. Excellent results were obtained by ligand tuning; phosphane ligands with electron-withdrawing groups such as tris[3,5-bis(trifluoromethyl)phenyl]phosphane (**3c**) and tris(2-furanyl)phosphane (**3d**) afforded the coupling products in good-to-excellent yields. Quantitative formation of iodozinciomethylated products **4a** was confirmed by $^1H$ NMR spectroscopy in $[D_8]THF$; the spectra showed the exclusive formation of (*E*)-4-phenyl-3-butenylzinc iodide when **3d** is employed as a ligand.



**1**

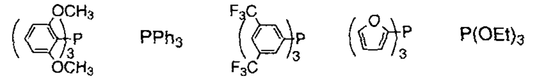
**2a**: R = Ph
**2b**: R = *n*-$C_{11}H_{23}$

**4a**: R = Ph
**4b**: R = *n*-$C_{11}H_{23}$

**5a**: R = Ph
**5b**: R = *n*-$C_{11}H_{23}$

(1)

Table 1. Yields [%] of the products **5** obtained by Pd-catalyzed coupling of **1** with allyl chlorides **2** depending on the phosphane **3**.



**3a** **3b** **3c** **3d** **3e**

| | 3a | 3b | 3c | 3d | 3e |
|---|---|---|---|---|---|
| **2a**[a] | < 1 | 16 | 88 | 97 | 14 |
| **2b**[a] | < 1 | < 1 | 82 | 91 | < 1 |

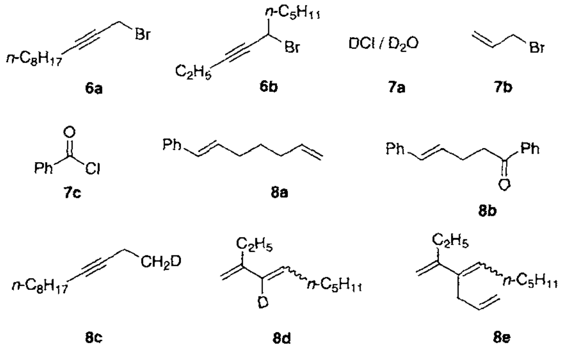
[a] Reaction mixture was treated with $DCl–D_2O$. The D contents of the products were determined by $^1H$ NMR spectroscopy ( > 95 %).

The intermediary organozinc compounds **4a** and **4b** reacted with other electrophiles such as allyl or acyl halides under the same palladium catalysis as shown in Equation (1).[6,7] This reaction permits a sequential coupling of bis(iodozincio)methane with two different electrophiles [Eq. (2)]

$$\underset{\mathbf{1}}{CH_2(ZnI)_2} + \underset{\mathbf{2/6}}{RX} \xrightarrow[2)\ EX\ \mathbf{7}]{1)\ [Pd_2(dba)_3]/\mathbf{3d}} \underset{\mathbf{8}}{RCH_2E} \qquad (2)$$

to give the three-component-coupling products in excellent yields. The results of such sequential reactions are shown in Table 2. The formation of **8d** and **8e** can be explained by Equation (3).

Table 2. Stepwise reaction of bis(iodozincio)methane with two electrophiles.



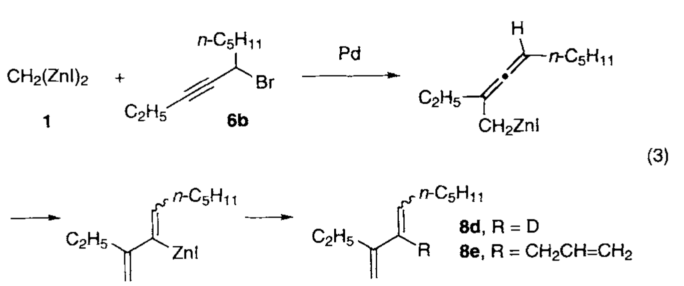
| Entry | RX | EX | Product | Yield [%][a] |
|---|---|---|---|---|
| 1 | **2a** | **7b** | **8a** | 87 |
| 2 | **2a** | **7c** | **8b** | 78 |
| 3 | **6a** | **7a** | **8c** | 55[b] |
| 4 | **6b** | **7a** | **8d** | 80[b,c] |
| 5 | **6b** | **7b** | **8e** | 70[c] |

[a] Yield of isolated product. [b] > 95% D. [c] Isolated as a diastereomeric mixture.

---

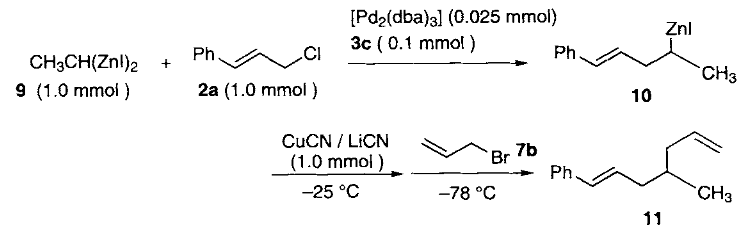
[*] Prof. K. Utimoto, N. Toda, T. Mizuno, M. Kobata, Dr. S. Matsubara
Department of Material Chemistry, Graduate School of Engineering
Kyoto University
Yoshida, Sakyo, Kyoto, 606-01 (Japan)
Fax: Int. code + (75)753 4863
e-mail: utimoto@orgrx2.kuic.kyoto-u.ac.jp

[**] This work was supported by the Ministry of Education, Science and Culture (grant in Aid nos. 06403025, 09231223, and 09238221)



(3)

1,1-Bis(iodozincio)ethane (**9**) reacted with cinnamyl chloride (**2a**) to give the organozinc intermediate **10**, which yielded the deuteriodezincated product (**10**, D in place of ZnI) in 65% yield. The direct coupling of **10** with the allyl bromide **7b** did not occur. In this case, the copper-mediated reaction[8] gave the double coupled product **11** in 66% yield [Eq. (4)].



(4)

## Experimental Section

THF (2 mL) was added to a mixture of [Pd$_2$(dba)$_3$]·CHCl$_3$ (0.025 g, 0.025 mmol) and **3d** (0.023 g, 0.1 mmol) and the mixture was stirred for 5 min at 20°C. A solution of **2a** (0.15 g, 1.0 mmol) in THF (1 mL) was added to the mixture at 20°C, then a solution of **1a** (0.5 M, 2 mL, 1.0 mmol) in THF was added at 20°C and the resulting mixture was stirred for 30 min at 20°C. Thereafter a solution of **7b** (0.15 g, 1.2 mmol) in THF (1 mL) was added at 20°C, and the resulting mixture was stirred for 2 h and then poured into 1 M HCl (20 mL) and extracted with ether. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. Purification by column chromatography (silica gel) gave 1-phenyl-1,6-heptadiene (**8a**) in 87% yield.

Received: July 22, 1997 [Z10720IE]
German version: *Angew. Chem.* **1997**, *109*, 2886–2888

**Keywords:** C–C coupling · copper · palladium · zinc

---

[1] I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241–3267; F. Bickelhaupt, *Angew. Chem.* **1987**, *99*, 1020–1035; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 990–1005; P. Knochel, J. F. Normant, *Tetrahedron Lett.* **1986**, *27*, 5727.

[2] B. J. J. Van de Heisteeg, G. Schat, M. A. G. M. Tinga, O. S. Akkerman, F. Bickelhaupt, *Tetrahedron Lett.* **1986**, *27*, 6123–6126; M. Hogenbirk, N. J. Van Eikema Hommes, G. Schat, O. S. Akkerman, F. Bickelhaupt, *ibid.* **1989**, *30*, 6195–6198.

[3] a) Cr: K. Takai, K. Nitta, K. Utimoto, *J. Am. Chem. Soc.* **1986**, *108*, 7408; T. Okazoe, K. Takai, K. Utimoto, *ibid.* **1987**, *109*, 951; D. M. Hodgson, *J. Organomet. Chem.* **1994**, *476*, 1; b) Cr–Sm: S. Matsubara, M. Horiuchi, K. Takai, K. Utimoto, *Chem. Lett.* **1995**, 259–260; c) Zn–TiCl$_4$: T. Okazoe, K. Takai, K. Oshima, K. Utimoto, *J. Org. Soc.* **1987**, *52*, 4410; K. Takai, Y. Kataoka, T. Okazoe, K. Utimoto, *Tetrahedron Lett.* **1988**, *29*, 1065–1068; K. Takai, Y. Kataoka, J. Miyai, T. Okazoe, K. Oshima, K. Utimoto, *Org. Synth.* **1996**, *73*, 73–84; L. Lombardo, *ibid.* **1987**, *65*, 81–89.

[4] P. Knochel, J. F. Normant, *Tetrahedron Lett.* **1986**, *27*, 4427–4430, 4431–4434; F. Chemla, I. Marek, J. F. Normant, *Synlett* **1993**, 665–668; E. Nakamura, K. Kubota, G. Sakata, *J. Am. Chem. Soc.* **1997**, *119*, 5457–5458.

[5] a) K. Takai, T. Kakiuchi, Y. Kataoka, K. Utimoto, *J. Org. Chem.* **1994**, *59*, 2668–2670; b) K. Utimoto, T. Mizuno, M. Kobata, S. Matsubara, K. Takai, unpublished results.

[6] Review on organozinc compounds under Pd catalysis: P. Knochel, R. D. Singer, *Chem. Rev.* **1993**, *93*, 2117–2188; P. Knochel, *Synlett* **1995**, 393–403.

[7] The palladium catalyst used in the first step is still active and catalyzes the reaction in the second step.

[8] Review on copper-mediated reaction of organozinc compounds with electrophiles: ref. [6].

---

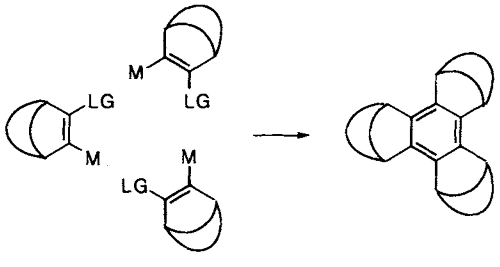
# Trisannelated Benzenes by Cyclotrimerization of Bromostannylalkenes**

Richard Durr, Sergio Cossu, Vittorio Lucchini, and Ottorino De Lucchi*

Trisannelated benzenes are enjoying growing interest both as aromatic molecules with alternating bond lengths [1] and as potential precursors of significant fullerene fragments.[2] Except for the simplest cases (triphenylene and tricycloalkyl derivatives),[3] trisannelated benzenes of polycyclic molecules are prepared by two routes: from chloroalkenes with a strong base[4] or from dibromoalkene derivatives by metal–halogen exchange reactions.[5] In both cases the yields are very low—usually 10% or less—and substantial amounts of polymers are formed. The use of metal templates such as nickel[6] also leads to unpredictable and erratic results. Because of poor yields, the real utility of these molecules as precursors to fullerene substructures and eventually to fullerenes themselves can be seriously questioned, and new reactions for the aromatic cyclotrimerization of suitable precursors have clearly become necessary for the development of routes to these molecules. Here we present a method that is readily carried out under very mild reaction conditions, and consistently and reproducibly affords high yields of trimers.

We planned to apply the Stille coupling[7] to olefins containing a suitable metal atom M at one carbon and a leaving group X at the other, in the hope that it would result in trimerization to a trisannelated aromatic product rather than uncontrolled polymerization. Eventually we found that olefins containing the trimethylstannyl group as "metal" along with bromine as a leaving group smoothly afford good yields of cyclotrimers upon reaction with Cu(NO$_3$)$_2$·3H$_2$O (Scheme 1).

The starting materials for the cyclotrimerization reactions are bromo(trimethylstannyl)alkenes. We chose the norbornene derivatives **1a–c** because such five- and six-membered



Scheme 1. Stille coupling of polycyclic olefins leading to trisannelated benzenes. M = metal, organometallic group; LG = leaving group.

---

[*] Prof. Dr. O. De Lucchi, Dr. R. Durr, Dr. S. Cossu
Dipartimento di Chimica,
Università Ca' Foscari di Venezia
Dorsoduro 2137, I-30123 Venezia (Italy)
Fax: Int. code + (41)529-8517
e-mail: delucchi@unive.it
Prof. Dr. V. Lucchini
Dipartimento di Scienze Ambientali,
Università Ca' Foscari di Venezia

[**] Work supported by C.N.R. (Rome). We thank the Regione Veneto, Dipartimento per l'Industria e l'Energia, for financial support in purchasing a Varian Unity 400 NMR spectrometer and Prof. Dr. Metin Balci for a sample of dibromobenzonorbornadiene.