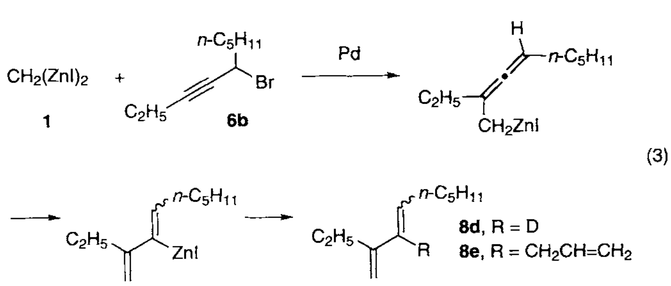
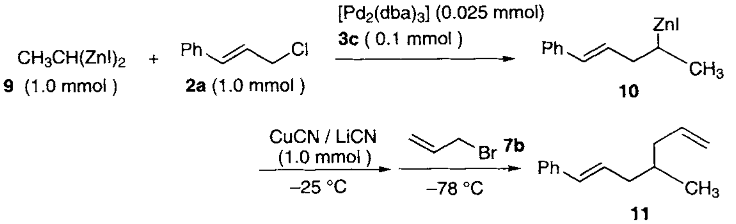


(3)

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 $[Pd_2(dba)_3]\cdot CHCl_3$ (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_2SO_4. Purification by column chromatography (silica gel) gave 1-phenyl-1,6-heptadiene (**8a**) in 87% yield.

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

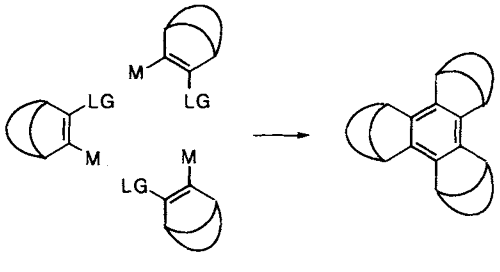
Trisannelated Benzenes by Cyclotrimerization of Bromostannylalkenes[**]

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 $Cu(NO_3)_2\cdot 3H_2O$ (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.

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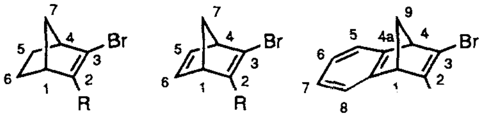
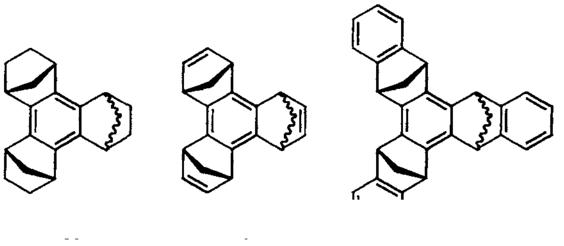
ring-containing compounds would be precursors for fullerene substructures if the cyclotrimers could be properly rearranged.

Bromo(stannyl) derivatives **1a–c**[8] were obtained in high yield under standard conditions from dibromo compounds **2a–c**[9] by metal–halogen exchange with *n*-butyllithium in THF followed by treatment with trimethyltin chloride. When a THF solution of **1a–c** was added to an equimolar amount of $Cu(NO_3)_2 \cdot 3H_2O$ in THF, a rapid reaction occurred, as shown by a color change from blue to brown. Cyclotrimerized products **5a–c**[10] were obtained as a statistical (3:1) mixture of the *anti* and *syn* isomers in yields up to 80%.

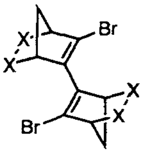


1, R = $SnMe_3$
2, R = Br
3, R = H
4, R = Cl

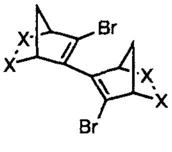


Minor differences were noticed in reactions leading to **5a–c**. Although **5a** and **5b** were obtained essentially pure from **1a** and **1b**, minor amounts of dimers **6c** and **6′c**[11] (15%) arose from **1c**. However, in contrast to other cyclotrimerization procedures, no polymeric material whatsoever was formed.[4,5]

Isomeric dimers **6c** and **6′c** form as an approximately 1:1 mixture. The centrosymmetric structure of **6c** and the C_2-symmetric structure of **6′c** prevented assignment of NMR signals by the usual methods (NOE differential spectroscopy). No crystals suitable for X-ray analysis could be grown. According to literature reports, the dimers were indeed the only products to be expected.[12]



6a-c



6′a-c

a, X-X = CH_2-CH_2
b, X-X = CH=CH
c, X-X = C_6H_4

Reaction conditions have some influence on the product composition. For example, in the case of **1c** high dilution affords predominantly the protodestannylated compounds **3c**[13] (0–10%) and a smaller amount of dimers **6c/6′c**, while high concentration favors dimers **6c/6′c** relative to the trimers. Higher temperature also favors the formation of dimers. Based on our experiments, the highest proportion of annelated compounds is obtained by adding copper(II) nitrate at room temperature to a roughly 0.1 M solution of the appropriate bromo(stannyl) compound in THF.

It is also possible to carry out the reaction in a single pot starting from the dibromo compounds **2a–c**. Sequential addition of *n*BuLi, Me_3SnCl, and $Cu(NO_3)_2 \cdot 3H_2O$ affords a 50–60% yield of trimers **5a–c**, although the product is contaminated with small amounts of the chlorobromo derivatives **4a–c** (5–15%) and the protodestannylated compounds **3a–c** (0–15%). The formation of **3a–c** is not surprising because of the presence of water in the copper salt. Formation of the chlorine-containing derivative may be a result of chloride ion liberated from trimethyltin chloride.

The reaction with other copper salts takes other paths. For example, **1b** and **1c** under similar reaction conditions afford quantitatively with $CuCl_2$ the tin-chloride substitution products **4b** and **4c**, respectively.[14] No cyclotrimers or dimers could be detected in this case. Reaction of **1c** with copper(I) chloride in DMF[15] leads quantitatively to the corresponding substitution product **4c**.[14] Iron(III) chloride gives exclusively **3a–c**, whereas Pd^0[16] under standard Stille conditions is ineffective, since only starting material was recovered from the experiments in question.[7]

The mechanism of cyclotrimer formation under the catalytic influence of copper(II) nitrate is still unclear. Based on similar experiments and literature reports[13] it is possible to conjecture tin–copper transmetalation with formation of an organocopper species that evolves into a vinyl radical. At ambient temperature the intermediate radical is sufficiently reactive to displace bromine from another molecule repeatedly until the trisannelated product **5** is formed. At lower temperature it does not possess sufficient energy, so it can only react with water or dimerize. Dimerization is further encouraged by high concentration. For maximum cyclotrimerization efficiency, the concentration of radicals along the entire reaction path must not become too high (to avoid coupling). Therefore, C–Cu bond cleavage should not occur too rapidly. The formation of chloro derivatives with $CuCl_2$ might well be accounted for by internal nucleophilic substitution by a ligand coupling mechanism[17] of the hypervalent species formed by attack of chloride ion on the tin atom.

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[8] **1a**: oil; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.95$ (1H, m, H1 or H4), 2.90 (1H, m, H4 or H1), 1.62 and 0.97 (2H, split AB system, $J(5,5') = 10.2$ Hz, H5), 1.61 and 1.17 (2H, split AB system, $J(6,6') = 11.0$ Hz, H6), 1.57 and 1.10 (2H, split AB system, $J(7,7') = 8.4$ Hz, H7), 0.22 (9H, s with tin satellites,

J(H,^{117}Sn) = 54.0 Hz, J(H,^{119}Sn) = 56.6 Hz, Me); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 147.46 (C2, J(C,^{117}Sn) = 408.8, J(C,^{119}Sn) = 427.8 Hz), 146.16 (C3, J(C,Sn) = 3.2 Hz), 52.16 (C1 or C4, J(C,Sn) = 30.5 Hz), 49.06 (C4 or C1, J(C,Sn) = 32.3 Hz), 47.79 (C7, J(C,Sn) = 19.8 Hz), 25.72 (C5, J(C,Sn) = 4.5 Hz), 24.48 (C6, J(C,Sn) = 9.7 Hz), −9.33 (Me, J(C,^{117}Sn) = 346.6 Hz, J(C,^{119}Sn) = 362.3 Hz). **1b**: oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 6.86 (1 H, dd, J = 5.2, 3.1 Hz, H5 or H6), 6.68 (1 H, dd, J = 5.2, 2.9 Hz, H6 or H5), 3.75 (1 H, bs, H1 or H4), 3.52 (1 H, br. s, H4 or H1), 2.20 (1 H, dt, J = 6.0, 1.7 Hz, H7), 1.99 (1 H. dt, J = 6.0, 1.7 Hz, H7), 0.22 (9 H, s with tin satellites, J(H,^{117}Sn) = 54.5, J(H,^{119}Sn) = 57.0 Hz, Me); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 150.72 (C3, J(C,^{117}Sn) = 414.7, J(C,^{119}Sn) = 433.9 Hz), 148.88 (C2, J(C,Sn) = 12.5 Hz), 142.57 (C5, J(C,Sn) = 4.6 Hz), 141.51 (C6, J(C,Sn) = 7.2 Hz), 73.20 (C6, J(C,Sn) = 16.6 Hz), 60.32 (C1 or C4, J(C,Sn) = 31.2 Hz), 56.99 (C4 or C1, J(C,Sn) = 33.7 Hz), −9.56 (Me, J(C,^{117}Sn) = 349.5, J(C,^{119}Sn) = 365.8 Hz). **1c**: oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.31 (1 H, m, H5 or H8), 7.14 (1 H, m, H8 or H5), 6.96 (2 H, m, H6 and H7), 4.00 (1 H, m, H1 or H4), 3.84 (1 H, m, H4 or H1), 2.52 (1 H, dt, J = 7.3, 1.6 Hz, H9), 2.25 (1 H, dt, J = 7.3, 1.5 Hz, H9), 0.21 (9 H, s with tin satellites, J(H,^{117}Sn) = 54.8, J(H,^{119}Sn) = 57.2 Hz, Me); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 152.12 (C3, J(C,^{117}Sn) = 396.1, J(C,^{119}Sn) = 414.6 Hz), 149.87 (C4a, J(C,Sn) = 3.7 Hz), 149.57 (C8a, J(C,Sn) = 7.9 Hz), 147.70 (C2, J(C,Sn) = 9.2 Hz), 124.98, 124.32, 121.93, 121.20 (C5, C6, C7, C8), 68.22 (C9, J(C,Sn) = 16.8 Hz), 60.28 (C1 or C4, J(C,Sn) = 31.0 Hz), 57.04 (C4 or C1, J(C,Sn) = 33.0 Hz), −9.30 (Me, J(C,^{117}Sn) = 349.9, J(C,^{119}Sn) = 365.8 Hz).

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[10] **5a**: quantitative yield, identical to an authentic sample (mixture of the *syn* and *anti* isomers) obtained as in P. Gassman, I. Gennick, *J. Am. Chem. Soc.* **1980**, *102*, 6863–6864. **5b**: 78%, identical to an authentic sample (mixture of the *syn* and *anti* isomers) obtained as in R. Durr, O. De Lucchi, S. Cossu, V. Lucchini, *Chem. Commun.* **1996**, 2447–2448. **5c**: 81%, identical to an authentic sample obtained as in S. Cossu, O. De Lucchi, V. Lucchini, G. Valle, M. Balci, A. Dastan, B. Demirci, *Tetrahedron Lett.* **1997**, *38*, 5319–5322.

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[14] **4b**: ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 6.86–6.93 (2 H, m), 3.58–3.63 (1 H, m), 3.50–3.55 (1 H, m), 2.41–2.46 (1 H, dt, J = 6.3, 1.6 Hz), 2.16–2.21 (1 H, dt, J = 6.3, 1.6 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 144.00, 141.64, 141.06, 128.30, 71.49, 57.86, 56.87; see also ref. [9b]. **4c**: oil; ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.40–7.34, 7.05–7.00 (4 H, m), 3.90 (1 H, bs), 3.85 (1 H, s), 2.73 (1 H, dt, J = 7.6, 1.6 Hz), 2.40 (1 H, dt, J = 7.6, 1.6 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 148.16, 147.71, 144.33, 129.16, 125.52, 125.48, 122.03 (2C), 66.74, 57.98, 56.98; GC-MS: m/z = 256, 254, 221, 219, 195, 177 (100), 175, 139, 115, 99, 87, 63.

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β-Donor Bonds in Compounds Containing SiON Fragments[**]

Norbert W. Mitzel[*] and Udo Losehand

Dedicated to Professor Evelyn A. V. Ebsworth

We investigated H$_3$SiONMe$_2$ and H$_2$Si(ONMe$_2$)$_2$, which unequivocally show the formation of Si–N β-donor bonds and are probably the simplest isolable compounds containing a SiON fragment. Recently we reported (4+4) coordination at the silicon center in Si(ONMe$_2$)$_4$.[1] This compound has an Si-O-N angle that is compressed by more than 16° with respect to the Si-O-C angle in the isoelectronic Si(OCHMe$_2$)$_4$. Ab initio calculations on H$_3$SiONMe$_2$ and FH$_2$SiONMe$_2$ predicted narrow Si-O-N angles (102.5 and 90°, respectively) and short Si–N distances.[1]. So far there has been no experimental evidence for these postulated extreme bonding situations in the SiON unit. The knowledge of the formation of Si–N β-donor interactions in SiON compounds is important for understanding the effect of *O*-silylated hydroxylamines and oximes as cross-linking agents[2] and cold-curing catalysts[3] in the synthesis of silicon polymers with low molecular weights, which can be used in electronics, construction, and medical applications. Acceleration of hydrolysis and alcoholysis of Si–H bonds in the presence of catalytic amounts of R$_2$NOH-type compounds was only recently established.[4] It can be explained by this interaction, which is unusual in the chemistry of p-block elements.

Numerous attempts to prepare H$_3$SiONMe$_2$ by condensation of H$_3$SiCl or H$_3$SiBr with HONMe$_2$ in the presence of auxiliary bases as well as reactions of HONMe$_2$ with silylamines failed. Despite the high reactivity of the agents, the reaction of H$_3$SiBr with LiONMe$_2$ proved to be the best synthetic method [Eq. (1)]. H$_2$Si(ONMe$_2$)$_2$ was prepared in a similar way from dichlorosilane [Eq. (2)]. Both products are

$$\mathrm{H_3SiBr + LiONMe_2 \longrightarrow H_3SiONMe_2 + LiBr} \tag{1}$$

$$\mathrm{H_2SiCl_2 + 2\,LiONMe_2 \longrightarrow H_2Si(ONMe_2)_2 + 2\,LiBr} \tag{2}$$

extremely sensitive to moisture, but are not pyrophoric. Although isomerization of H$_3$SiONMe$_2$ and H$_2$Si(ONMe$_2$)$_2$ to the aminosilanoles is thermodynamically favored, they can be heated to about 100 °C.

The identity of the compounds was proven by ^{1}H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si NMR spectroscopy, gas-phase IR spectroscopy, and mass spectrometry. Since H$_3$SiONMe$_2$ melts at low temperatures (≈ -60 °C), a single crystal for X-ray diffraction analysis had to be grown by in situ methods.[5] The molecules contain a crystallographically imposed mirror plane with an Si-O-N angle of only 102.63(5)° and short Si$\cdots$N distances of 2.453(1) Å (Figure 1; the sum of the van der Waals radii of Si and N is 3.54 Å[6]). This is in excellent agreement with the

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