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Efficient and General Synthetic Approach to Pentasubstituted Conjugated Dienes Using Site-Selective Coupling of Cuprates with 1,4-Diiodo-1,3-alkadienes as the Key Reaction**

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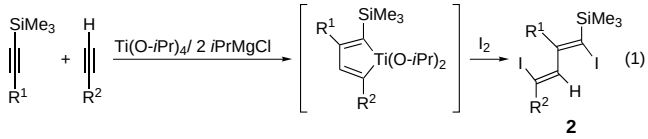
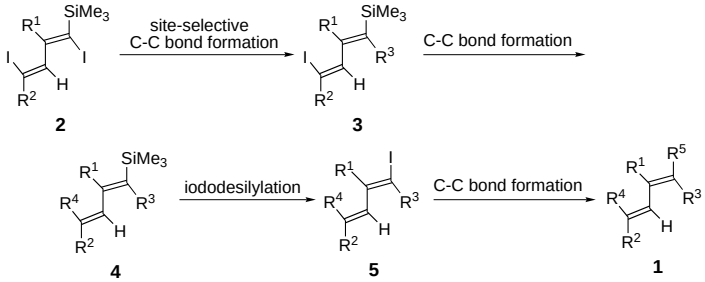
Selective preparation of polysubstituted conjugated dienes is an important transformation, because such dienes are useful intermediates and/or important structural constituents in natural product chemistry and materials science. When the regio- and stereoselective alignment of the substituents on the diene skeleton are considered, their synthesis is not necessarily an easy process, and the synthetic difficulty becomes more and more marked with an increase in the number of substituents. We report herein a general method for preparing 1,1,2,4,4-pentasubstituted 1,3-butadienes **1**.

Recently, we developed a highly efficient method for synthesizing titanacyclopentadienes by regioselective coupling of 1-trimethylsilyl-1-alkynes and terminal acetylenes, mediated by a divalent titanium reagent $Ti(O\text{-}iPr)_4$/ 2 *i*PrMgCl.[1,2] Treatment of the titanacyclopentadienes thus generated in situ with iodine furnishes 1,4-diiodo-1,3-alkadienes **2** in high yields [Eq. (1)].[1,3]



With an efficient and practical entry to **2** in hand, we planned the preparation of **1** from **2**, according to the reaction pathway shown in Scheme 1. If the reaction proceeded as we expected, quite a number of dienes **1** with a variety of substituents could be prepared. For the success of our synthetic plan, the following two transformations hold the key, as other transformations were expected to occur readily by using established reactions. One transformation is the conversion of **2** into the monoiodides **3** by the site-selective carbon–carbon bond formation at one of the two vinyliodo moieties in **2**. The other transformation is the stereoselective conversion of **4** into **5** because, although there are many precedents for converting vinylsilanes into isomerically pure vinyl iodides, there are few reports for the conversion of dienylsilanes into dienyl iodides.



Scheme 1. Synthetic plan of 1,1,2,4,4-pentasubstituted 1,3-butadienes **1** from 1,4-diiodo-1,3-alkadienes **2**.

For the transformation of **2** into **3**, we anticipated that the reaction with organocuprates might occur selectively at the α-silyl vinyliodide moiety, because it was reported that the presence of a silyl group in the α position of vinyl bromides causes acceleration of their coupling reaction with organocuprates.[4] The reaction of **2a**, prepared from 1-trimethylsilyl-1-octyne and 1-octyne, with three equivalents of Me_2CuLi in diethyl ether at −50 °C for 3 h provided monomethylated product **3aa** exclusively in 90 % yield, as shown in Equation (2) (for R′ see Table 1).

It is noteworthy that no possible monomethylated and/or dimethylated product was produced in more than 1 % yield,

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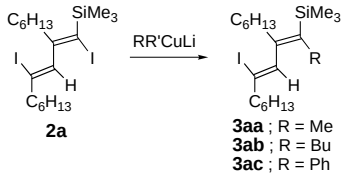
[**] C.D. would like to thank the Japan Society for the Promotion of Science (JSPS) for financial support.

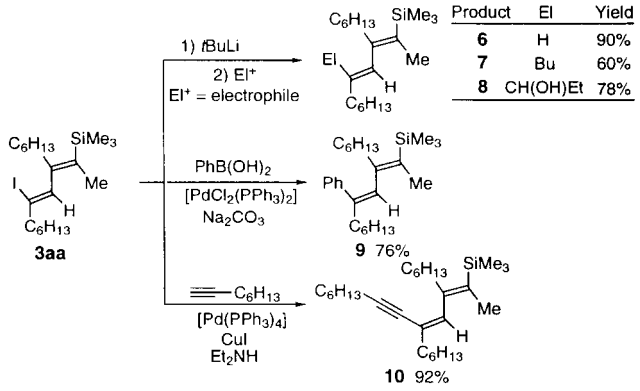
  0044-8249/02/4116-3023 $ 20.00+.50/0



(2)

even if three equivalents of the cuprate were used. The reaction of **2a** with Bu_2CuLi, which provided the expected monobutylated product **3ab**, did not proceed with satisfactory selectivity and yield; however, use of Bu(PhS)CuLi as the cuprate furnished **3ab** exclusively in 72% yield. The reaction of **2a** with Ph_2CuLi also provided monophenylated product **3ac** in 59% yield (^{1}H NMR spectroscopic analysis) but, in this case, other unseparable products, presumably including a regioisomer and a diphenylated compound, were coproduced; the selectivity was not improved by use of Ph(PhS)CuLi or Ph(CN)CuLi. These results, as well as the results of the reaction of other 1,4-diiodo-1,3-alkadienes **2b–e** with organocuprates,[5] are shown in Table 1. Although the site selectivity of the reaction is somewhat dependent on the olefinic substituents R^1 and R^2 in **2**, excellent to high selectivity was attained in every case. Thus, we now have a highly efficient approach to a variety of dienes **3**, including functionalized ones such as those in entries 4–6.

With the success of the regioselective preparation of **3** from **2**, we carried out a carbon–carbon bond-forming reaction at the vinyl iodide moiety of **3**. As shown in Scheme 2, lithiation of **3aa** with *t*BuLi followed by reaction with electrophiles such as H_2O, BuI, or EtCHO afforded the corresponding reaction products **6**, **7**, and **8**. Suzuki–Miyaura coupling[6] of **3aa** with $PhB(OH)_2$, and Sonogashira coupling[7] with 1-octyne proceeded smoothly to afford the expected products **9** and **10**, respectively.



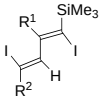
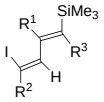
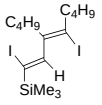
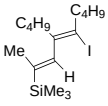
Product	El	Yield
6	H	90%
7	Bu	60%
8	CH(OH)Et	78%

Scheme 2. C–C-bond-forming coupling reactions of vinyl iodide **3aa**.

Having succeeded in synthesizing a variety of dienes of the type **4** (Scheme 1), we converted them into 1,1,2,4,4-pentasubstituted 1,3-butadienes **1** via the iodide **5**. However, the conversion of **4** into **5** did not proceed smoothly under the standard reaction conditions for converting a vinylsilyl moiety into a vinyl iodide. Thus, treatment of **7** with I_2 or ICl[8] afforded a complicated reaction mixture, and the yield of the expected product of the type **5** was less than 10% (^{1}H NMR analysis). We then carried out the reaction using $I_2/AgNO_3$,[9] and, to our satisfaction, the reaction proceeded readily with retention to afford the expected compound **11** in 82% yield.[10] The iodide **11** thus produced was finally converted into 1,1,2,4,4-pentasubstituted 1,3-butadienes **12**, **13**, **14**, and **15** using conventional reactions (Scheme 3).

In conclusion, a series of reactions (see Scheme 1) proceeded highly efficiently, thus opening up the first general method for synthesizing 1,1,2,4,4-pentasubtituted 1,3-butadienes with a variety of substitution patterns, which starts with readily available silylacetylenes and 1-alkynes. As the deiodination of **3** and/or **5** can be readily carried out by treatment with *t*BuLi and then with H_2O, this method can also allow preparation of a variety of tri- and tetrasubstituted conjugated dienes. The present method is highly practical as all the reagents used for the transformations are inexpensive and

Table 1. Results of the reaction of 1,4-diiodo-1,3-alkadienes **2** with organocuprates.

Entry	Compound **2**[a,b]				Cuprate (3 equiv)	Conditions	Compound **3**[c]		Selectivity[d]	Yield [%][e]
										
		R^1	R^2					R^3		
1	**2a**	C_6H_{13}	C_6H_{13}	(67%)	Me_2CuLi	−50°C, 3 h	**3aa**	Me	99:1	90
2	**2a**				Bu(PhS)CuLi	−78°C, 1 h→0°C, 18 h	**3ab**	Bu	99:1	72
3	**2a**				Ph_2CuLi	0°C, 18 h	**3ac**	Ph	87:13	68[f]
4	**2b**	C_6H_{13}	C_2H_4OBn	(74%)	Me_2CuLi	−50°C, 3 h	**3ba**	Me	92:8	87[f]
5	**2c**	$CH(OEt)_2$	C_2H_4OBn	(78%)	Bu(PhS)CuLi	−78°C, 1 h→0°C, 8 h	**3cb**	Bu	—[g]	69
6	**2d**	CO_2tBu	C_6H_{13}	(84%)	Bu(PhS)CuLi	−78°C, 2 h −50°C, 4 h	**3db**	Bu	—[g]	84
7	**2e**			(63%)	Me_2CuLi				98:2[h]	84

[a] The isolated yield of **2** after the reaction in Equation (1) is shown in parentheses. [b] The iodolysis was carried out by adding excess I_2 directly to the reaction mixture at −50°C, addition of a THF solution of I_2 lowered the yield. [c] The stereochemistry was verified by NOESY or NOE experiments. [d] The ratio of **3**: other products was determined by ^{1}H NMR spectroscopic analysis of the crude product unless otherwise noted. [e] Yield of **3** after column chromatography. [f] Total yield; **3** and other product(s) could not be separated by column chromatography. [g] Not determined. [h] GC measurement.

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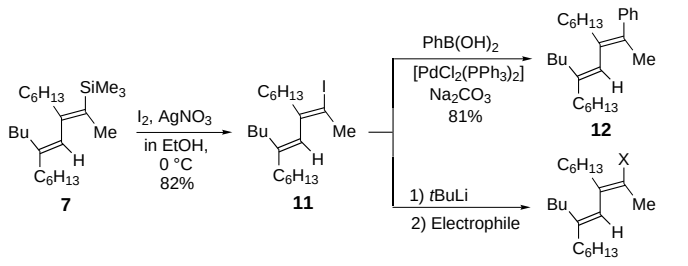

Product	Electrophile	X	Yield
13	H_2O	H	95%
14	PhCHO	CH(OH)Ph	80%
15	$HC(O)NMe_2$	CHO	73% (95% purity)

Scheme 3. Transformation of **7** to the vinyl iodide **11** and the following coupling reaction.

easily available in quantity, and the reaction operation is easy.

Experimental Section

Typical procedure for the site-selective C–C bond formation of **2** with organocuprates (preparation of **3aa**, Table 1, entry 1): To a stirred solution of CuI (1.99 g, 10.4 mmol) in Et_2O (10 mL) was added a 1.04 M solution of MeLi in ether (20.0 mL, 20.8 mmol) at 0 °C, under argon, to give a homogeneous solution. The solution was cooled to −50 °C, then **2a** (1.90 g, 3.48 mmol) was added to the solution. After stirring at −50 °C for 3 h, the reaction mixture was quenched by the addition of aqueous NH_4Cl and the organic products were extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil. Chromatography on silica gel (hexane) afforded compound **3aa** (1.35 g, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 0.85–0.90 (m, 6H), 1.25–1.60 (m, 16H), 1.65 (s, 3H), 2.18 (t, J = 8.0 Hz, 2H), 2.51 (t, J = 7.1 Hz, 2H), 6.19 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.41, 14.18, 14.21, 19.67, 22.73, 22.76, 27.94, 28.84, 29.45, 29.85, 31.63, 31.91, 36.61, 45.06, 110.59, 131.35, 136.40, 149.32 ppm.

Typical procedure for conversion of **4** into **5** (synthesis of **11**; Scheme 3): To a stirred solution of **7** (0.126 g, 0.345 mmol) in absolute ethanol (6 mL) was added $AgNO_3$ (0.088 g, 0.518 mmol) at 0 °C. The mixture was stirred for 10 min to ensure complete dissolution. Iodine (0.114 g, 0.449 mmol) was added in one portion and stirred at 0 °C for 20 min. The reaction mixture was diluted with diethyl ether, filtering through a celite pad. The filtrate was washed with sodium thiosulfate solution, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil. Chromatography on silica gel (hexane) afforded compound **11** (0.118 g, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–0.91 (m, 9H), 1.21–1.42 (m, 20H), 1.89 (t, J = 7.4 Hz, 2H), 2.05 (t, J = 7.1 Hz, 2H), 2.24 (t, J = 7.1 Hz, 2H), 2.42 (s, 3H), 5.47 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.16, 14.20, 14.23, 22.74, 22.76, 23.13, 27.94, 28.04, 29.20, 29.27, 29.61, 30.75, 31.67, 31.82, 31.86, 35.47, 43.36, 96.24, 121.60, 142.69, 143.15 ppm.

Received: May 2, 2002 [Z19197]

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Reaction of "[$Mn^{II}(CH_2tBu)_2$]" with Bidentate Diimine Ligands: From Simple Base Adducts to C–C Activation of the Ligand**

Virginie Riollet, Christophe Copéret,* Jean-Marie Basset, Laurence Rousset, Denis Bouchu, Laurent Grosvalet, and Monique Perrin

Base adducts of dialkyl Mn^{II} complexes are typically monomeric tetrahedral high-spin systems;[1] our synthetic target is to extend these adducts to bidentate diimine ligands. Gambarotta and co-workers[2] recently reported an approach to Mn^{II} analogues of Brookhart–Gibson complexes[3] and compared their performance in olefin polymerization with those of Fe^{II} and Ni^{II} catalysts. In this approach, they showed that the reaction of [$MnCl_2L_2$] complexes with organolithium reagents gave the corresponding Mn^{I} and Mn^{0} alkyl complexes, that is, the lithium reagents alkylate and reduce the Mn^{II} dichloro complex. These results have led us to disclose our investigation on the reaction of a bisneopentyl Mn^{II} complex with bidentate Shiff base ligands that were designed to generate complexes with structure **1** (Scheme 1). The major difference in our approach is the reaction of diimine ligands

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[**] We are indebted to the CNRS and ESCPE Lyon for financial support. V.R. is grateful to the Région Rhône-Alpes for a predoctoral fellowship. We also thank Prof. R. A. Andersen (U. C. Berkeley), Prof. Dr. Koelher (TUM), Dr. R. Gauvin (LCOMS), and Dr. C. Boisson (LCPP) for helpful discussions.

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