ORGANIC LETTERS

2005
Vol. 7, No. 22
4859−4861

Preparation and Reaction of 2-Aryl-3-silyl-1,3-butadiene

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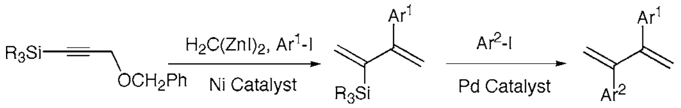
Received July 2, 2005

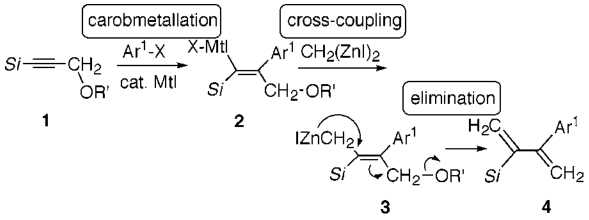
ABSTRACT



A conjugated π-electron compound, 2-aryl-3-silyl-1,3-butadiene, was easily prepared from 1-benzyloxy-3-silyl-2-propyne, bis(iodozincio)methane, and an aryl halide in the presence of nickel catalyst. A subsequent cross-coupling reaction of the product with another aryl halide gave an unsymmetrical 2,3-diaryl-1,3-butadiene efficiently.

Conjugated π-electron compounds such as aryl-substituted polyenes attract a lot of attention from material scientists.[1] The most common and effective strategy to construct the aryl-substituted polyene skeleton has been stepwise assembling of alkene and arene units by means of cross-coupling reaction.[2] One drawback of the methodology is that some undesirable π-bond isomerization, including polymerization, may occur under the cross-coupling reaction conditions. To prevent such isomerization, reseachers have tuned and modifed the organometallic compound that is one of the cross-coupling partners. For example, Denmark reported recently an efficient coupling of unsymmetrical 1,4-bissilyl-1,3-butadiene with an aryl halide to construct 1-silyl-4-aryl-1,3-butadiene. The compound can be transformed into an unsymmetrical 1,4-diaryl-1,3-butadiene or the conjugated polyenes through further cross-coupling reaction.[3] Hiyama showed an efficient preparation of 2,3-bisboryl-1,3-butadiene, which is a potent precursor for 2,3-diaryl-1,3-butadiene or dendralene.[4,5] In these methods, bissilylated or -borated 1,3-butadiene is the key intermediate, on which selective cross-coupling in the right sequence was performed. Several examples that are based on carbometalation have also been reported.[2b,6] In these methods, an intermediate that is formed by transition metal catalyzed carbometalation between alkyne and aryl halide undergoes an additional cross-coupling reaction or Heck reaction. We have reported a series of synthetic studies of bis(iodozincio)methane.[7] This *gem*-dizinc reagent is prepared from diiodomethane, zinc, and a catalytic amount of lead(II) chloride as reported previously.[8] If an intermediate **2** via a carbometalation of aryl halide to propargyl derivative **1** (Scheme 1) undergoes a cross-coupling reaction with bis(iodozincio)methane, the obtained

Scheme 1



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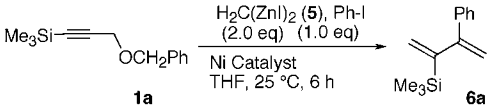
10.1021/ol051557s CCC: $30.25 © 2005 American Chemical Society
Published on Web 09/24/2005

allylzinc derivative **3** will be transformed into a 1,3-butadiene derivative **4** via elimination of zinc alkoxide. Accoding to this method, 2-aryl-3-silyl-1,3-butadiene, which is a convenient precursor for unsymmetrical 2,3-diaryl-1,3-butadiene, can be prepared in one step. Treatment of 3-trimethylsilyl-1-bezyloxy-2-propyne (**1a**) with bis(iodozincio)methane and iodobenzene in the presence of some palladium catalyst that was prepared from $Pd_2dba_3\cdot CHCl_3$ and PAr_3 (Ar = phenyl, *p*-tolyl, 2-furyl, 3,5-bis(trifluoromethyl)phenyl) resulted in quantitative recovery of alkyne **1a**.[9] As shown in Scheme 2, however, use of Ni(II) catalyst gave the desired 2-aryl-3-silyl-1,3-butadiene **6a**. Optimization of the yield of **6a** by tuning the nickel(II) catalyst was examined, as shown in Scheme 2. The catalyst prepared from 2 mol % of $Ni(cod)_2$ and 3 mol % of $P(2\text{-furyl})_3$ improved the yield of **6a** to 99%.

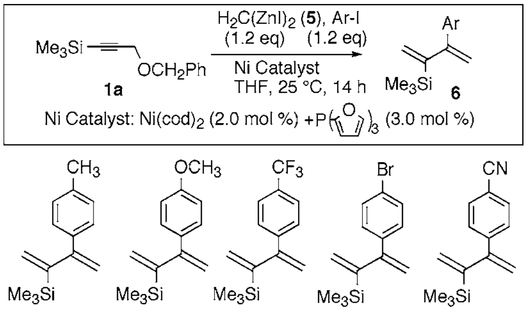
Scheme 2



Ni Catalyst	6a
$NiCl_2(dppe)$ (10 mol %)	39%
$NiCl_2(P(p\text{-}OMeC_6H_4)_3)_2$ (10 mol %)	16%
$Ni(cod)_2$ (10 mol %), $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ (20 mol %)	72%
$Ni(cod)_2$ (10 mol %), $P(2\text{-furyl})_3$ (20 mol %)	84%
$Ni(cod)_2$ (2 mol %), $P(2\text{-furyl})_3$ (3 mol %)	99%

Using the nickel catalyst, we examined the reaction of **1a** with bis(iodozincio)methane (**5**) and various aryl iodides, as shown in Scheme 3. It is notable that the reaction of 4-bromo-1-iodobenzene gave the 4-bromophenyl substituted butadiene **6e** in excellent yield. The product may be a substrate for another cross-coupling reaction as aryl bromide.

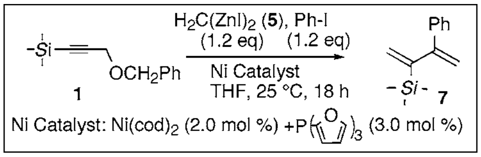
Scheme 3



6b 100% **6c** 96% **6d** 83% **6e** 96% **6f** 32%

The trimethylsilyl group is not an attractive group as an organometallic reagent for the Hiyama coupling reaction. The various organosilyl compounds, instead of the trimethylsilyl group, have often been used in attempts to form a hypercoordinated silyl group, which is the key intermediate for the cross-coupling.[10] Trost demonstrated that the benzyldimethylsilyl group benefits the cross-coupling reaction, as it is easily transformed into the fluorodimethylsilyl group, which is the important hypercoordinated silyl group precursor.[11] We had also reported that the (2,6-dimethoxyphenyl)-dimethylsilyl group can be transformed into the fluorodimethylsilyl group with BF_3−acetic acid complex.[12] As shown in Scheme 4, the propyne derivatives with these silyl groups (**1b**−**d**) were examined for the reaction. In each case, the 2-phenyl-3-silyl-1,3-butadiene **7b**−**c** was obtained in good yield.[13]

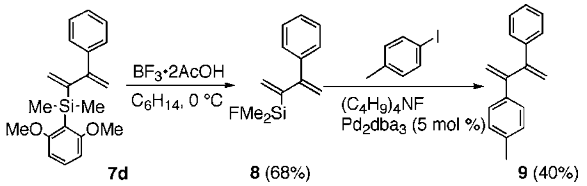
Scheme 4



Si:	yield of **7**
$PhMe_2Si$ (**1b**)	76% (**7b**)
$(PhCH_2)Me_2Si$ (**1c**)	97% (**7c**)
$(2,6\text{-}(MeO)_2C_6H_3)Me_2Si$ (**1d**)	92% (**7d**)

As shown in Scheme 5, 2,3-diaryl-1,3-butadiene was prepared using **7d**. A transformation of **7d** into fluorosilane derivative **8**,[12] followed by cross-coupling reaction with 4-iodotoluene, gave the 2,3-diaryl-1,3-butadiene **9**.

Scheme 5



7d **8** (68%) **9** (40%)

This sequential carbometalation and cross-coupling method can be also applied to diiodoarene. The method will give an arene with two silylbutadienyl groups. Diiodo arenes **10a**−**c** were treated with **1a** and bis(iodozincio)methane (**5**) in the presence of nickel catalyst to give the highly conjugated π-electron compounds **11a**−**c** in good yields (Scheme 6).

We propose in Scheme 1 that a mechanism of these transformations may be initiated by carbonickelation of arylnickel iodide, which is formed by oxidative insertion of low-valent nickel to aryl iodide. Two other routes are possible for the formation of 2-aryl-3-silyl-1,3-butadiene. One con-

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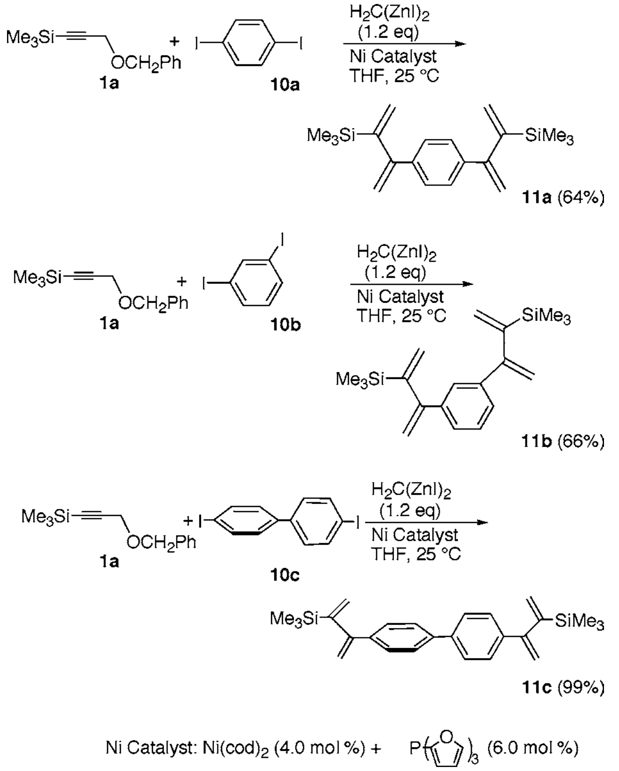
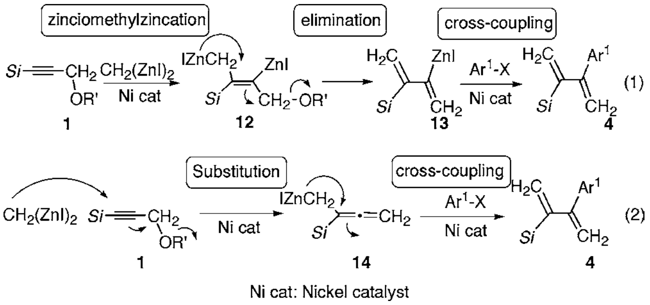
Scheme 6



Scheme 7



tains an iodozinciomethylzincation as the first step (eq 1 in Scheme 7), and the other is formation of allenylzinc **14** as an intermediate by nickel-catalyzed S_N2' reaction (eq 2 in Scheme 7). In some cases, nickel-catalyzed carbozincation is a reasonable route, as reported previously.[14−16] A route similar to that in eq 2 was shown in our previous report about the reaction between propargylic bromide and bis(iodozincio)methane (**5**) in the presence of palladium catalyst, which affords butadienyl zinc species in situ.[9] In the present case, however, treatment of **1a** with bis(iodozincio)methane (**5**) in the presence of nickel catalyst prepared from $Ni(cod)_2$ and $(2\text{-furyl})_3P$ resulted in the quantitative recovery of **1a**. For these reasons, we prefer Scheme 1. Even in this case, the carbometalation of arylnickel iodide to propargylic ether **1** occurs under equilibrium and transmetalation of the alkenyl nickel species **2** with bis(iodozincio)methane should be the crucial reaction for these transformations.[17]

Acknowledgment. This work was supported financially by the Japanese Ministry of Education, Science, Sports, and Culture. Financial support from Chugai Pharmaceutical Co., Ltd. and Takahashi Industrial and Economical Research Foundation are also acknowledged.

Supporting Information Available: Experimental details and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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