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Stereoselective Synthesis of Multisubstituted Butadienes through Directed Mizoroki–Heck Reaction and Homocoupling Reaction of Vinyl(2-pyridyl)silane

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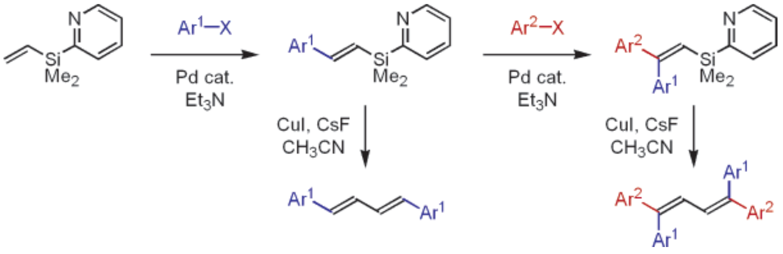
ABSTRACT



We have developed the homocoupling reaction of alkenyl(2-pyridyl)silanes mediated by CuI and CsF, in which the strong directing effect of the 2-pyridyl group was observed. The homocoupling reaction was successfully integrated with the Mizoroki–Heck reaction of vinyl(2-pyridyl)silane with aryl halides, enabling a rapid and stereoselective synthesis of multisubstituted butadienes. From a relatively small compound library, it was possible to detect a number of fluorescent butadienes with a wide range of fluorescence color variations (blue to reddish-orange).

As exemplified by 1,1,4,4-tetraphenyl-1,3-butadiene, which is known as a useful blue-emitting material in organic electroluminescent devices,[1] an extended π-system based on a multisubstituted butadiene structure should be an interesting target as a functional material. However, the paucity of general methods for the stereoselective synthesis of multisubstituted butadienes hampers the rapid construction and property-evaluation of such extended π-systems.[2] We herein report a rapid and stereoselective synthesis of multisubstituted butadienes through Pd- and Cu-mediated sequential assembly of π-systems onto the C═C core of vinyl(2-pyridyl)silane.

Recently, we reported that the otherwise difficult Mizoroki−Heck reaction of vinylsilanes was efficiently promoted by appending a catalyst-directing 2-pyridyl group on silicon (Scheme 1).[3] Because of the strong directing effect of the 2-pyridyl group, a hard-to-achieve double Mizoroki−Heck reaction is also feasible (Scheme 1).[4] We also found that the thus-obtained alkenyl(2-pyridyl)silanes (**2** and **3**) undergo efficient Hiyama-type silicon-based cross-coupling reactions with aryl halides, producing di- and triarylethenes

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[1] Selected examples: (a) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281. (b) Kim, J.-H.; Noh, S.; Kim, K.; Lim, S.-T.; Shin, D.-M. *Synth. Met.* **2001**, *117*, 227.

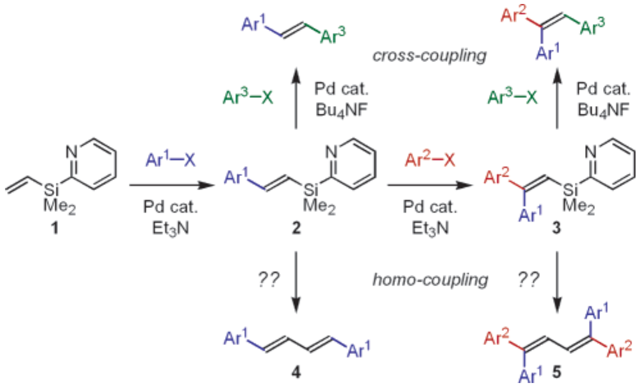
[2] For previous synthesis of tetraphenylbutadiene, see: (a) Wittig, G.; von Lupin, F. *Chem. Ber.* **1928**, *61*, 1627. (b) Simes, B. E.; Rickborn, R.; Flournoy, J. M.; Berlman, I. B. *J. Org. Chem.* **1988**, *53*, 4613. (c) Feit, B.-A.; Buzhansky, L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1777.

[3] Itami, K.; Mitsudo, K.; Kamei, T.; Koike, T.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 12013.

[4] Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 11577.

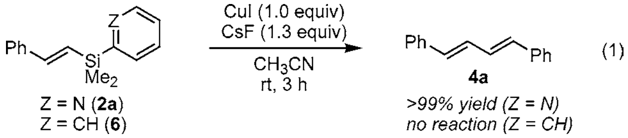
10.1021/ol048620i CCC: $27.50

Scheme 1



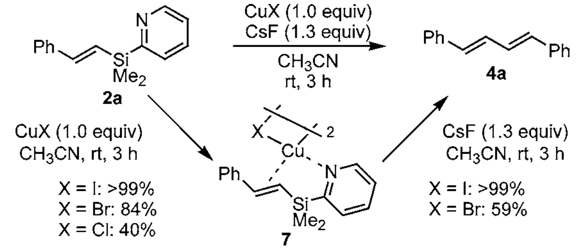
in a regio- and stereoselective manner (Scheme 1).[2,5] We envisaged that if we could develop a procedure for the homocoupling reaction of alkenyl(2-pyridyl)silanes (**2** and **3**), a new synthetic avenue toward multisubstituted butadienes (**4** and **5**) would be established (Scheme 1). In addition, such a transformation should also be useful as a detagging protocol for the 2-pyridylsilyl group in the phase tag strategy using this group.[6]

Although there are a number of reports on the homocoupling reaction of organosilanes,[7] the applications to alkenyl(2-pyridyl)silanes resulted in disappointing outcomes in many cases, presumably because activating groups such as fluoride are necessary for these methods. During further investigations, we found that the use of CuI in combination with CsF resulted in efficient homocoupling of (*E*)-styryl-(2-pyridyl)silane (**2a**) in CH_3CN to afford (*E*,*E*)-1,4-diphenyl-1,3-butadiene (**4a**) quantitatively (eq 1).[8] Interestingly, the corresponding phenyl analogue **6** remained unaffected under otherwise identical conditions. Therefore, a promoting effect of the 2-pyridyl group in homocoupling was obvious at this point.



(1)

Scheme 2



Subsequently we found that the stoichiometric reactions of **2a** with CuX produced Cu complexes **7** (as halogen-bridged dimers) in moderate to high yields (Scheme 2). Although satisfactory X-ray crystal structure analysis was not possible with these complexes, we succeeded in the X-ray crystal structure analysis of the *p*-tolyl analogue **8**, which unambiguously ascertained the vinyl-N chelation to copper (Figure 1). Moreover, we found that the further treatment of **7** with CsF did afford **4a** in reasonable yield (Scheme 2; see also eq 1 and ref 8).

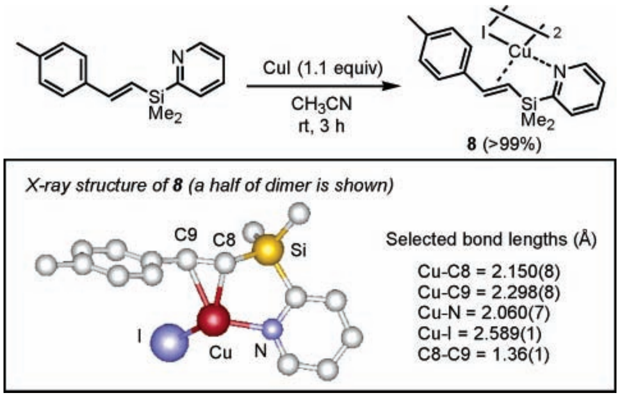


Figure 1. Synthesis and X-ray structure of **8**.

Currently, we assume that the homocoupling occurs through Si-to-Cu transmetalation to generate alkenylcopper species, followed by their homocoupling. The suitably positioned pyridyl group should help the C=C bond to coordinate to copper through precoordination and/or vinyl-N chelation, thereby allowing subsequent transmetalation very efficiently. As expected from the results in eq 1 and Scheme 2, the treatment of CuX with **6** did not produce such a Cu complex at all, which clearly supports the directing effect of the 2-pyridyl group in the formation of key Cu-olefin complexes.

With an efficient procedure established, we next embarked on the homocoupling of various alkenyl(2-pyridyl)silanes (**2** and **3**), which can be prepared stereoselectively by the Mizoroki–Heck reaction of vinyl(2-pyridyl)silane (**1**) with

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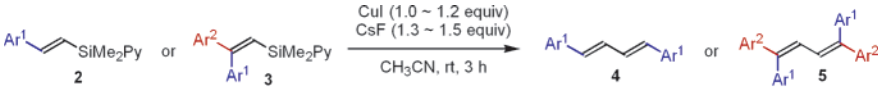
(5) Itami, K.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 5600.

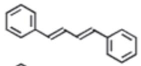
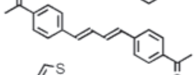
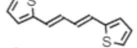
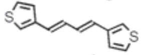
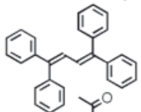
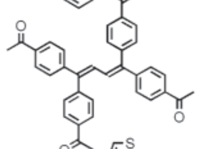
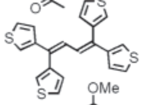
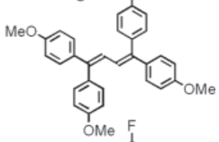
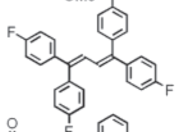
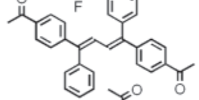
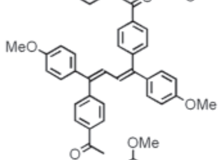
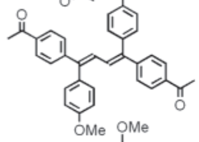
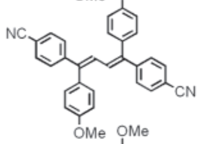
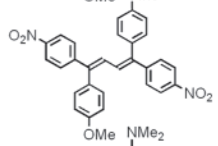
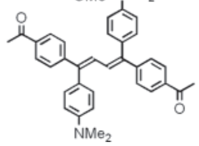
(6) Reviews: (a) Yoshida, J.; Itami, K. *Chem. Rev.* **2002**, *102*, 3693. (b) Yoshida, J.; Itami, K. *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 1086.

(7) Pd-mediated methods: (a) Weber, W. P.; Felix, R. A.; Willard, A. K.; Koenig, K. E. *Tetrahedron Lett.* **1971**, 4701. (b) Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542. (c) Yamaguchi, S.; Ohno, S.; Tamao, K. *Synlett* **1997**, 1199. (d) Yoshida, H.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Chem. Commun.* **2003**, 1510. Cu-mediated methods: (e) Yoshida, J.; Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 1141. (f) Kang, S.-K.; Kim, T.-H.; Pyun, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 797. (g) Nishihara, Y.; Ikegashira, K.; Toriyama, F.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 985. Ag-mediated methods: (h) Mueller, R.; Dressler, M.; Dathe, C. *J. Prakt. Chem.* **1970**, *312*, 150. (i) Tamao, K.; Matsumoto, H.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 1137.

(8) Other Cu and Ag complexes (with CsF co-promoter) also mediated the homocoupling of **2a**: CuCl (59%), CuBr (59%), $[Cu(CH_3CN)_4]PF_6$ (87%), $AgBF_4$ (65%).

Table 1. CuI/CsF-Mediated Homocoupling Reaction of Alkenyl(2-pyridyl)silanes



entry	silane	Ar^1	Ar^2	product (yield)	
1	**2a**	C_6H_5	-		**4a** (>99%)
2	**2b**	C_6H_4Ac-4	-		**4b** (47%)
3	**2c**	2-thienyl	-		**4c** (70%)
4	**2d**	3-thienyl	-		**4d** (46%)
5	**3aa**	C_6H_5	C_6H_5		**5aa** (58%)
6	**3bb**	C_6H_4Ac-4	C_6H_4Ac-4		**5bb** (62%)
7	**3dd**	3-thienyl	3-thienyl		**5dd** (38%)
8	**3ee**	C_6H_4OMe-4	C_6H_4OMe-4		**5ee** (63%)
9	**3ff**	C_6H_4F-4	C_6H_4F-4		**5ff** (51%)
10	**3ab**	C_6H_5	C_6H_4Ac-4		**5ab** (61%)
11	**3be**	C_6H_4Ac-4	C_6H_4OMe-4		**5be** (56%)
12	**3eb**	C_6H_4OMe-4	C_6H_4Ac-4		**5eb** (50%)
13	**3eg**	C_6H_4OMe-4	C_6H_4CN-4		**5eg** (63%)
14	**3eh**	C_6H_4OMe-4	$C_6H_4NO_2$-4		**5eh** (24%)
15	**3ib**	$C_6H_4NMe_2$-4	C_6H_4Ac-4		**5ib** (48%)

aryl halides (Scheme 1).[9,10] The results are summarized in Table 1. Both **2** and **3** underwent homocoupling under the influence of CuI/CsF to give structurally and electronically diverse multisubstituted butadienes (**4** and **5**) in moderate to high yields. In all cases examined, virtually complete retention of stereochemistry during the homocoupling was observed. Therefore, a set of stereoisomers such as **5be** and **5eb** can be prepared at will by simply changing the addition order of aryl halides in the double Mizoroki−Heck reaction step (Scheme 1).

Interestingly, most of the multisubstituted butadienes (**4** and **5**) prepared were found to be fluorescent. The photophysical properties of these compounds are listed in Table 2. As expected, the absorption maxima as well as emission maxima were found to depend heavily on the nature of the terminal aryl groups (Ar^1 and Ar^2). For example, the λ_{abs} and λ_{em} values increase as the phenyl group is replaced by the *p*-acetylphenyl group (**4a** → **4b**; **5aa** → **5ab** → **5bb**), presumably reflecting effective extension of π-conjugation with terminal carbonyl groups. More interestingly, when Ar^1 and Ar^2 groups are in a donor/acceptor (push/pull) relationship, a significant bathochromic shift of absorption and fluorescence is observed (**5be**, **5eb**, **5eg**, **5eh**, and **5ib**). Such a donor/acceptor substitution can bring about the reddish-orange emission (**5ib**) from otherwise blue-fluorescent material **5aa**.

Table 2. Photophysical Properties of Multisubstituted Butadienes[a]

4 or **5**	Ar^1	Ar^2	UV−vis λ_{abs} (nm)	fluorescence λ_{em} (nm)
4a	C_6H_5		333	381
4b	C_6H_4Ac-4		368	425
4c	2-thienyl		363	430
4d	3-thienyl		322	394
5aa	C_6H_5	C_6H_5	348	449
5bb	C_6H_4Ac-4	C_6H_4Ac-4	381	480
5dd	3-thienyl	3-thienyl	353	435
5ee	C_6H_4OMe-4	C_6H_4OMe-4	365	448
5ff	C_6H_4F-4	C_6H_4F-4	345	435
5ab	C_6H_5	C_6H_4Ac-4	376	472
5be	C_6H_4Ac-4	C_6H_4OMe-4	389	499
5eb	C_6H_4OMe-4	C_6H_4Ac-4	391	500
5eg	C_6H_4OMe-4	C_6H_4CN-4	383	490
5eh	C_6H_4OMe-4	$C_6H_4NO_2$-4	417	593
5ib	$C_6H_4NMe_2$-4	C_6H_4Ac-4	322	578

[a] UV−vis absorption and fluorescence spectra were measured in $CHCl_3$.

The emissive behaviors of representative compounds upon irradiation of light (365 nm) in $CHCl_3$ are shown in Figure 2. As apparent from the picture, fluorescence color variations over a wide range of wavelengths (blue to reddish-orange) were realized. Since the parent tetraphenylbutadiene (**5aa**) has been used as a material in organic electroluminescent devices, these multisubstituted butadienes might be also useful for such purpose.

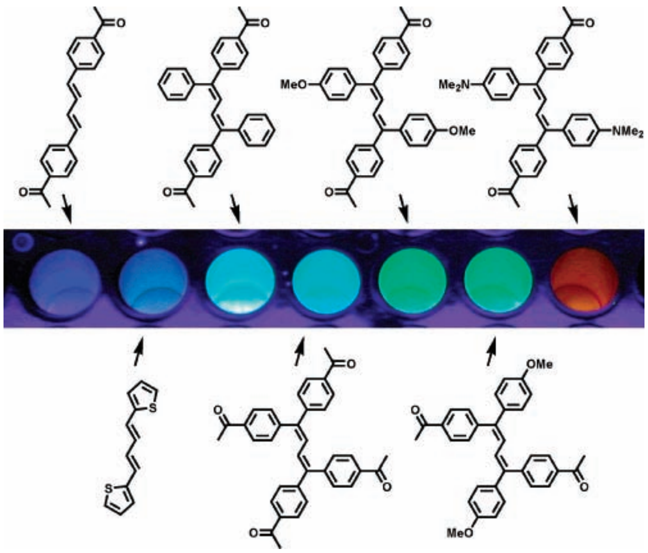


Figure 2. Emissive behaviors of representative compounds.

In summary, we have developed the homocoupling reaction of alkenyl(2-pyridyl)silanes mediated by CuI and CsF, in which the strong directing effect of the 2-pyridyl group was observed. The homocoupling reaction was successfully integrated with the Mizoroki−Heck reaction of vinyl(2-pyridyl)silane with aryl halides, enabling a rapid and stereoselective synthesis of multisubstituted butadienes. The discovery of a number of fluorescent materials with a wide range of color variations speaks well for the potential of the current synthetic strategy in the development of functional organic materials. Investigations along this line are currently ongoing in our laboratory.

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

Supporting Information Available: Experimental procedures and characterization data for all new compounds, including data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See Supporting Information for the preparation of **2** and **3**.

(10) Dimethyl(2-pyridyl)vinylsilane (**1**) is now commercially available from Tokyo Kasei Kogyo Co., Ltd (TCI). Catalog Number: D2935.