Bull. Chem. Soc. Jpn. Vol. 79, No. 3, 498–500 (2006)

Utilization of Industrially Available 2,3-Dichloro-1,3-butadiene for Direct Synthesis of 2,3-Diaryl-1,3-butadienes

Takakazu Yamamoto,*[1] **Takuma Yasuda,**[1]
Kazuaki Kobayashi,[1] **Isao Yamaguchi,**[1]
Take-aki Koizumi,[1] **Daisuke Ishii,**[1]
Masaru Nakagawa,[1] **Yoshihiro Mashiko,**[2]
and Norihiro Shimizu[3]

[1]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

[2]Organic Materials Research Center, Denki Kagaku Kogyo K. K., 2209 Omi, Itoigawa, Niigata 949-0393

[3]Electronic Materials Research Center, Denki Kagaku Kogyo K. K., 1135 Nakamura, Shibukawa, Gunma 377-8520

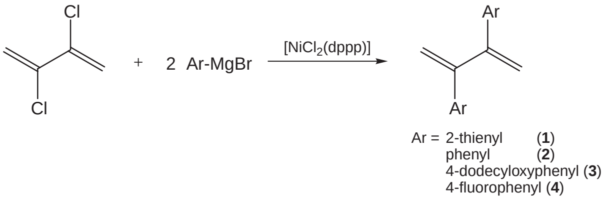
Received August 17, 2005; E-mail: tyamamot@res.titech.ac.jp

It is shown that industrially available 2,3-dichloro-1,3-butadiene is a useful starting material for the synthesis of 2,3-diaryl-1,3-butadienes. Ni(II)-catalyzed cross-coupling reaction of 2,3-dichloro-1,3-butadiene with ArMgBr (Ar = 2-thienyl, phenyl, 4-dodecyloxyphenyl, and 4-fluorophenyl) gives the corresponding 2,3-diaryl-1,3-butadienes in good yields.

1,3-Butadiene derivatives are useful materials for organic synthesis as monomers for poly(butadiene)s and as building blocks for natural product syntheses.[1] Especially, 2,3-diaryl-1,3-butadienes have a so-called cross-conjugated system, and much attention has been paid to their molecular structures and electronic properties.[2] There have been several reports on synthetic methods for 2,3-diaryl-1,3-butadienes. For example, dehydration of pinacol derivatives,[3] 1,4-debromination of 1,4-dibromo-2-olefins,[4] coupling of alkenyl halides catalyzed by Pd–C in the presence of LiCl,[5] Pd-catalyzed coupling of propynyl carbonates with organoborons and -tins,[6] Pd-catalyzed reaction of 2,3-bis(boryl)-1,3-butadiene with aryl halides,[7] Zr-mediated coupling of alkynes with vinyl bromide with skeletal rearrangement,[8] conversion of α,α'-diketo sulfides,[9] and Cu-catalyzed coupling reaction of 1,4-dimethoxy-2-butyne with aryl Grignard reagents[10] have been developed. However, these synthetic methods have problems such as low yields, necessity of multistep routes to synthesize the precursor, and complicated synthetic conditions. Incidentally, 2,3-dichloro-1,3-butadiene has been used industrially as a comonomer of chloroprene to produce chloroprene rubber.[11] Because nickel(II)-catalyzed coupling of vinyl halides with Grignard reagents[12,13] is useful to produce C–C coupling products, direct reaction of industrially produced 2,3-dichloro-1,3-butadiene with aryl Grignard reagents is considered to provide a new industrially profitable route to 2,3-diaryl-1,3-butadienes.

However, the usability of this route has not been examined. The high tendency of 2,3-dichloro-1,3-butadiene to be polymerized and synthetic chemists being unaware of this route seem to be the reasons. We now report that 2,3-dichloro-1,3-butadiene containing inhibitors of radical polymerization (e.g., 4-*t*-butylcatechol) can be handled normally as the starting material of 2,3-diaryl-1,3-butadienes.

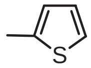
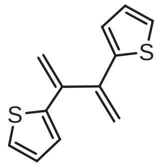
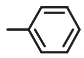
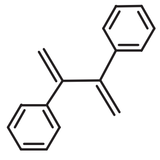
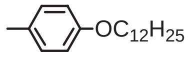
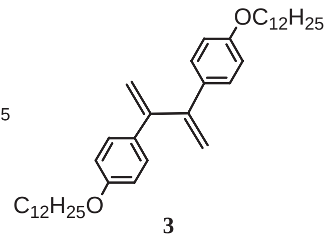
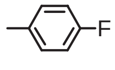
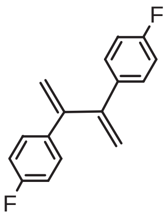
The coupling reactions of 2,3-dichloro-1,3-butadiene were carried out with ArMgBr, where Ar = 2-thienyl, phenyl, 4-dodecyloxyphenyl, or 4-fluorophenyl, by using [NiCl$_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) as the catalyst (Eq. 1). Details of the synthetic procedure are described in the Experimental section.



(1)

Table 1 shows the results of the coupling reactions. As shown in Table 1, the reaction gave the expected products in good yields. In this reaction, electron-withdrawing group-

Table 1. Synthesis of 2,3-Diaryl-1,3-butadienes

Entry	Ar	Product	Yield/%
1		 **1**	65
2		 **2**	52
3	 	 **3**	64
4	 	 **4**	56

Published on the web March 8, 2006; DOI 10.1246/bcsj.79.498

and electron-donating group-substituted aromatic rings can be introduced to the 2,3-position of 1,3-butadiene. **1**, **2**, and **4** have been prepared via different routes, whereas **3** is a new compound. The electronic spectrum of **3** in $CHCl_3$ showed one absorption band at $\lambda_{max} = 262$ nm ($\varepsilon = 17900$), which is shifted to a longer wavelength by 17 nm from that of **2** ($\lambda_{max} = 245$ nm in $CHCl_3$) due to the substitution of the long alkoxyl chain on the phenyl group. **3** exhibited photoluminescence at $\lambda_{max} = 363$ nm (λ_{max}(Ex) $= 260$ nm), though the intensity was very weak (quantum yield = 1.75%).

Long alkyl- and alkoxyl-group substituted aromatic compounds often display interesting chemical properties and reactivities,[14] and **3** is expected to be the building block for such materials. Compound **3** is the first example of 2,3-diaryl-1,3-butadienes having a long alkoxyl chain, and the convenient one-step synthesis of **3** will expand the scope of such kinds of compounds.

As described above, it has been shown that industrially available 2,3-dichloro-1,3-butadiene can be an important and key compound for the synthesis of 2,3-diaryl-1,3-butadienes.

Experimental

General and Materials. ^{1}H NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were recorded on a JASCO IR 810 spectrophotometer. UV–vis and photoluminescence spectra were measured with a Shimadzu UV-2550 UV–visible spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Thermal analysis was performed with a Shimadzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 differential scanning calorimeter and a Shimadzu TGA-50 thermogravimetric analyzer. An optical microscopy observation of the morphology of **3** was carried out using a BX-60 optical microscope (Olympus). 2,3-Dichloro-1,3-butadiene[15] produced industrially by Denki Kagaku Kogyo K. K. was obtained from a production line for chloroprene rubber, and 4-*t*-butylcatechol (TBC, 200 ppm by wt/wt) was added to 2,3-dichloro-1,3-butadiene. With TBC, 2,3-dichloro-1,3-butadiene was able to be kept for 7 days without apparent polymerization at low temperature (at about −30 °C). 4-Dodecyloxyphenyl bromide was prepared from 4-bromophenol and dodecyl bromide. $[NiCl_2(dppp)]$ was purchased from Aldrich and other reagents were purchased from Tokyo Kasei Kogyo Co., Ltd.

Preparation of 2,3-Di(2-thienyl)-1,3-butadiene (1). To a suspension of activated Mg (2.78 g, 115 mmol) in dry THF (20 cm^3) was added slowly a solution of 2-bromothiophene (17.2 g, 106 mmol) in dry THF (50 cm^3) under N_2 at 60 °C for 12 h. The resulting solution was transferred slowly to a 1:1 (v/v) solution of 2,3-dichloro-1,3-butadiene (40.0 mmol) in THF under N_2 at 0 °C. $[NiCl_2(dppp)]$ (0.51 g, 1.00 mmol) was added to the mixture and the mixture was stirred for 30 min at room temperature. After additional stirring at 50 °C for 24 h, the mixture was added to water, and the product was then extracted with hexane. The extract was washed with water and dried with Na_2SO_4. Evaporation of the solvent and purification by column chromatography (SiO_2, hexane) afforded **1** in 65% yield as a light yellow oil. The identification of the compound was performed according to the literature.[9]

Preparation of 2,3-Diphenyl-1,3-butadiene (2). Preparation was carried out analogously by using activated Mg (2.78 g, 115 mmol), bromobenzene (15.7 g, 100 mmol), and a 1:1 (v/v) solution of 2,3-dichloro-1,3-butadiene (40.0 mmol) in THF. **2** was obtained in 52% yield as a white solid after purification. Identification of the compound was performed by comparing its ^{1}H NMR data with those of commercially available **2**. Use of a smaller amount of the Grignard reagent (PhMgBr/2,3-dichloro-1,3-butadiene = 1:1) gave **2** in 23% yield, and the intermediate 2-phenyl-3-chloro-1,3-butadiene was not detected in the ^{1}H NMR spectrum of the reaction product. This indicated that the intermediate species had high reactivity toward PhMgBr.

Preparation of 2,3-Bis(4-dodecyloxyphenyl)-1,3-butadiene (3). Preparation was carried out analogously by using activated Mg (2.78 g, 115 mmol), 1-bromo-4-dodecyloxybenzene (36.0 g, 106 mmol), and a 1:1 (v/v) solution of 2,3-dichloro-1,3-butadiene (40.0 mmol) in THF. **3** was obtained in 64% yield as a pale yellow solid after purification. Found: C, 83.38; H, 10.66; O, 5.79%. Calcd for $C_{40}H_{62}O_2$: C, 83.56; H, 10.87; O, 5.57%. ^{1}H NMR ($CDCl_3$) δ 7.30 (d, 4H, $J = 8.8$ Hz), 6.77 (d, 4H, $J = 8.8$ Hz), 5.45 (d, 2H, $J = 1.6$ Hz), 5.21 (d, 2H, $J = 1.6$ Hz), 3.90 (t, 4H, $J = 6.4$ Hz), 1.74 (m, 4H), 1.42 (m, 4H), 1.38–1.29 (m, 32H), 0.87 (t, 6H, $J = 6.8$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 158.6, 149.4, 132.4, 128.4, 114.1, 67.9, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3, 26.1, 22.8, 14.2; IR (KBr disk, cm^{-1}) 2953, 2920, 2851, 1607, 1511, 1469, 1293, 1249, 1177, 1031, 902, 832, 720, 506.

Preparation of 2,3-Bis(4-fluorophenyl)-1,3-butadiene (4). Preparation was carried out analogously by using activated Mg (0.70 g, 28.8 mmol), 1-bromo-4-fluorobenzene (3.0 mL, 27.3 mmol), and a 1:1 (v/v) solution of 2,3-dichloro-1,3-butadiene (10.4 mmol) in THF. **4** was obtained in 56% yield as a colorless solid after purification. **4** had been previously prepared by other method.[10,16] ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 4H), 6.94 (m, 4H), 5.48 (d, 2H, $J = 1.2$ Hz), 5.29 (d, 2H, $J = 1.2$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 162.3 (J(C–F) $= 247$ Hz), 148.6, 135.9 (J(C–F) $= 2.7$ Hz), 128.5 (J(C–F) $= 8.0$ Hz), 115.1 (J(C–F) $= 21$ Hz); IR (KBr disk, cm^{-1}) 3051, 1601, 1506, 1227, 1161, 1106, 1013, 905, 842, 751, 541, 502, 492.

References

1 For recent reviews, see: a) R. V. Kaberdin, V. I. Potkin, V. A. Zapol'skii, *Russ. Chem. Rev.* **1999**, *68*, 765. b) A. Zapf, M. Beller, *Top. Catal.* **2002**, *19*, 101. c) A. A. Vasil'ev, E. P. Serebryakov, *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 1341.

2 For recent articles, see: a) S. Fielder, D. D. Rowan, M. S. Sherburn, *Angew. Chem., Int. Ed.* **2000**, *39*, 4331. b) M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **2000**, *6*, 1955. c) J. Ichikawa, M. Fujiwara, S. Miyazaki, M. Ikemoto, T. Okauchi, T. Minami, *Org. Lett.* **2001**, *3*, 2345. d) D. A. Shultz, R. M. Fico, Jr., S. H. Bodner, R. K. Kumar, K. E. Vostrikova, J. W. Kampf, P. D. Boyle, *J. Am. Chem. Soc.* **2003**, *125*, 11761. e) M. Klokkenburg, M. Lutz, A. L. Spek, J. H. van der Maas, C. A. van Walree, *Chem. Eur. J.* **2003**, *9*, 3544.

3 a) K. Sisido, H. Nozaki, T. Iwako, *J. Am. Chem. Soc.* **1949**, *71*, 2037. b) P. J. Baldry, *J. Chem. Soc., Perkin Trans.* **1975**, 1913. c) Y. Ogata, A. Kawasaki, M. Haba, T. Tsujino, *J. Org. Chem.* **1977**, *42*, 2423. d) A. Kawamoto, H. Uda, N. Harada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3279. e) T. Iwashita, M. Suzuki, T. Kusumi, H. Kakisawa, *Chem. Lett.* **1980**, 383. f) R. A. Wagner, U. H. Brinker, *Synthesis* **2001**, 376.

4 L. Engman, S. E. Byström, *J. Org. Chem.* **1985**, *50*, 3170.

5 P.-H. Lee, D. Seomoon, K. Lee, *Org. Lett.* **2005**, *7*, 343.

6 J. Böhmer, R. Grigg, *Tetrahedron* **1999**, *55*, 13463.

7 M. Shimizu, T. Kurahashi, T. Hiyama, *Synlett* **2001**, 1006.

8 T. Takahashi, Z. Xi, R. Fischer, S. Huo, C. Xi, K. Nakajima, *J. Am. Chem. Soc.* **1997**, *119*, 4561.

9 J. Nakayama, H. Machida, R. Saito, *Chem. Lett.* **1985**, 1173.

10 Y. Ishiono, I. Nishiguchi, F. Takihira, T. Hirashita, *Tetrahedron Lett.* **1980**, *21*, 1527.

11 P. R. Johnson, *Rubber Chem. Technol.* **1976**, *49*, 650.

12 a) K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374. b) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S.-i. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

13 For recent reviews, see: a) V. A. Pavlov, *Usp. Khim.* **2001**, *70*, 1175. b) A. Yamamoto, *J. Organomet. Chem.* **2002**, *635*, 5. c) K. Tamao, *J. Organomet. Chem.* **2002**, *653*, 23. d) T. Hayashi, *J. Organomet. Chem.* **2002**, *653*, 41. e) M. R. Netherton, G. C. Fu, *Adv. Synth. Catal.* **2004**, *346*, 1525.

14 For recent articles, see: a) E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer, P. Bäuerle, *Angew. Chem., Int. Ed.* **2000**, *39*, 2680. b) K. Naka, T. Uemura, Y. Chujo, *Macromolecules* **2002**, *35*, 3539. c) T. Yamamoto, Y. Muramatsu, B.-L. Lee, H. Kokubo, S. Sasaki, M. Hasegawa, T. Yagi, K. Kubota, *Chem. Mater.* **2003**, *15*, 4384. d) J. E. Gano, D. J. Osborn, III, N. Kodali, P. Sekher, M. Liu, E. D. Luzik, Jr., *J. Org. Chem.* **2003**, *68*, 3710. e) Z. Wu, S. Wu, Y. Liang, *Spectrochim. Acta, Part A* **2003**, *59*, 1631. f) M. Surin, E. Hennebicq, C. Ego, D. Marsitzky, A. C. Grimsdale, K. Müllen, J.-L. Brédas, R. Lazzaroni, P. Leclére, *Chem. Mater.* **2004**, *16*, 994. g) J. E. Klare, G. S. Tulevski, K. Sugo, A. de Picciotto, K. A. White, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 6030.

15 2,3-Dichloro-1,3-butadiene is also handled in DuPont Performance Elastomers K.K. and Bayer Ltd.

16 I. Wurster, L. Mans, G. Kallinowski, W. Vogt, *Makromol. Chem., Rapid Commun.* **1984**, *5*, 579.