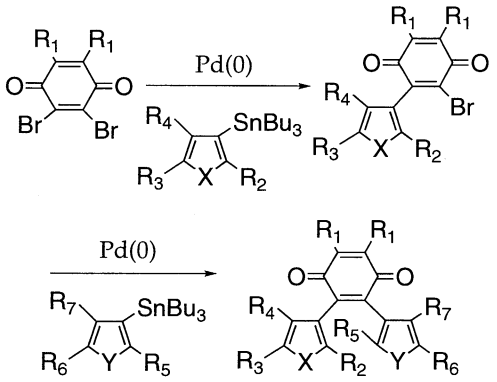
Synthesis of 2,3-Diarylquinone by Palladium Catalyzed Cross-Coupling of Dibromoquinones with Heteroarylstannanes

Seigo Yoshida, Hiroaki Kubo, Tetsuyuki Saika,*† and Shigeo Katsumura*
School of Science, Kwansei Gakuin University, Uegahara 1-1, Nishinomiya, Hyogo 662
†PRESTO, JRDC; Research Laboratories, DAISO Co., Ltd., Otakatsu 9, Amagasaki 660

(Received October 26, 1995)

The synthesis of various kinds of both symmetrical and asymmetrical diarylquinones has been realized by the palladium catalyzed cross-coupling of 2,3-dibromoquinones with tributylstannylheteroaromatics.

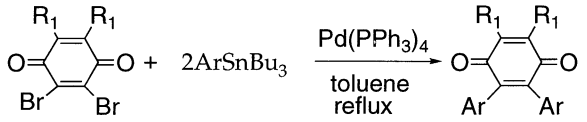
Diheteroarylquinones are very attractive not only for multimode chemical transducers, which integrates both photochromic and electrochromic groups,[1,2] but also for their biological activities caused by the electron transport property of quinone.[3] The synthesis of diheteroarylquinones, however, has not yet been established, although the syntheses of monoarylquinones by Pd(0)-Cu(I) catalyzed[4,5] or Pd(II) catalyzed[6] coupling have been reported. Now, our interest involves the synthesis and properties of the 2,3-diheteroarylsubstituted quinones, which are regarded as diarylethenes.[7] Herein, we disclose the synthesis of both symmetrical and asymmetrical diheteroarylquinones including the highly crowded ones by the Stille's type Pd(0) catalyzed coupling reaction.[8]



The requisite tributylstannylheteroaromatics were prepared by the bromination of the heteroaromatic compounds followed by the halogen-lithium exchange and then stannylation. For example, 5-methyl-4-tributylstannyl-2-trimethylsilylthiophene was synthesized by the regioselective lithiations[9] of 2,4-dibromo-5-methylthiophene followed by silylation or stannylation of the corresponding lithium anions, respectively (*n*-BuLi/ether/ TMSCl, 60% yield; *sec*-BuLi/ ether/ Bu_3SnCl, 87% yield). In the case of 2-cyano-1,5-dimethyl-4-tributylstannylpyrrole, bromination of the commercially available 2-cyano-1,5-dimethylpyrrole gave a 4-bromo compound in 71% yield along with the 3,4-dibromo compound (16% yield).[10] As the quinone part, we used 2,3-dibromonaphthoquinone and 2,3-dibromo-5,6-dimethylbenzoquinone, which was prepared from 2,3-dimethylphenol by oxidation with Fremy's salt[11] followed by bromination according to the slightly modified procedure in the literature.[12]

The palladium catalyzed cross-coupling of dibromoquinones with arylstannanes was realized by the Stille's procedure in good yields (Tables 1 and 2). In the case of the symmetrical diarylquinones, for example, treatment of one equivalent of the quinones and two equivalents of 3-tributylstannylthiophene in toluene with tetrakis(triphenylphosphine)palladium (2 mol%) followed by refluxing for 6 h afforded the dithiophenylquinones in 71-73% yield (Table 1, entry 1). In the case of 2,5-disubstituted 4-stannylthiophene or 4-stannylpyrrole, highly crowded diarylquinones, **2a**, **2b**,[13] **3a**, and **3b**[14] were obtained as a single stereoisomer in good yield (Table 1, entries 2 and 3). Benzothiophene and indole derivatives afforded the corresponding diarylquinones as a mixture of rotational isomers by NMR (Table 1, entries 4, 5,[15] and 6).[16] For

Table 1. Synthesis of symmetrical diarylquinone



A: R_1= , B: R_1= CH_3

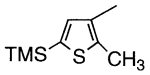
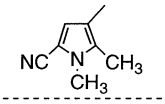
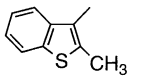
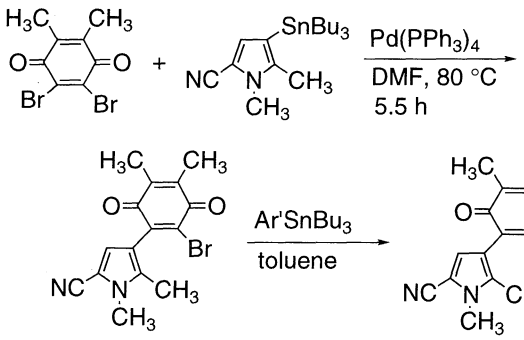
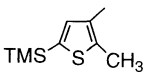
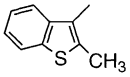
Entry	Ar	Time / h	A or B	Product(Yield %)
1.		6	A	**1a** (71)
		6	B	**1b** (73)
2.		73	A	**2a** (60)[13]
		40	B	**2b** (65)
3.		21	A	**3a** (67)
		18	B	**3b** (90)[14]
4.		39	A	**4a** (67)
		25	B	**4b** (65)
5.		44	A	**5a** (37)
6.		40	A	**6a** (71)
7.		24	A	**7a** (75)
		14	B	**7b** (72)

Table 2. Synthesis of asymmetrical diarylquinone



Entry	Ar'	Time / h	Temp / °C	Yield / %
1.		91	100	**8** (88)[17]
2.		44	100	**9** (92)
3.		66	120	**10** (46)
4.		19	100	**11** (87)

the synthesis of asymmetrical diarylquinones, we chose 2-cyano-1,5-dimethyl-4-stannylpyrrole as one part of the aryl group because of its good reactivity. Treatment of 2,3-dibromo-5,6-dimethylbenzoquinone and equimolar 2-cyano-1,5-dimethyl-4-stannylpyrrole with the same palladium catalyst in DMF at 80 °C for 5.5 h afforded the monoarylquinone in 68% yield along with 12% of the diarylquinone. After isolation, the monoaryl-quinone was treated with various heteroaromaticstannanes in toluene at 100 or 120 °C for 19-91 h to afford the desired asymmetrical diarylquinones (Table 2).[17]

The synthesis of diarylquinones was thus realized by the palladium catalyzed cross-coupling reaction of dibromoquinones with heteroaromaticstannanes. The present method was applicable for the highly crowded diarylquinone synthesis, and would be the general method for the synthesis of 2,3-diarylquinones.

References and Notes

1 T. Saika, M. Irie, and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, **1994**, 2123.

2 To invent multimode chemical transducers, several quinone derivatives with photochromic groups have been synthesized; T. Saika, T. Iyoda, K. Honda, and T. Shimidzu, *J. Chem. Soc., Parkin Trans. 2*, **1993**, 1181 and references cited therein.

3 The Chemistry of Functional Groups. The Chemistry of the Quinoid Compounds; ed. by S. Patai and Z. Rappoport, Jone Wiley & Sones, New York (1988), Vol 2.

4 L. S. Liebeskind and S. W. Riesinger, *J. Org. Chem.*, **58**, 408 (1993).

5 N. Tamayo, A. M. Echavarren, and M. C. Paredes, *J. Org. Chem.*, **56**, 6488 (1991).

6 T. Itahara, *J. Org. Chem.*, **50**, 5546 (1985).

7 M. Irie, *J. Syn. Org. Chem. Jpn.*, **49**, 373 (1991) and references cited therein.

8 D. R. Mckean, G. Parrinello, A. F. Renaldo, and J. K. Stille, *J. Org. Chem.*, **52**, 422 (1987).

9 S. Katsumura, K. Ichikawa, and H. Mori, *Chem. Lett.*, **1993**, 1525.

10 3,4-Dibromo-2-cyano-1,5-dimethylpyrrole was converted into 4-bromo compound by the regioselective lithiation at the 3-position followed by protonation. The structure of 4-bromo compound was confirmed by NOE experiments; 3-bromo compound showed the NOE between 4-H and 5-CH_3, while 4-bromo compound showed no NOE.

11 H-J. Teuber and W. Rau, *Chem. Ber.*, **86**, 1036 (1953).

12 L. I. Smith and F. L. Austin, *J. Am. Chem. Soc.*, **64**, 528 (1942).

13 **2b:** mp 97-98.5 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.21(18 H, s), 2.11(6 H, s), 6.63(2 H, s), 7.78(2 H, m), 8.18(2 H, m); ^{13}C NMR(100 MHz, $CDCl_3$) δ -0.20, 14.53, 126.59, 131.83, 132.25, 133.69, 136.07, 136.42, 142.72, 144.73, 184.07; UV(MeOH) λ_{max} 325 nm(ε 5800), 433(2300); MS *m/z* 372(M^+).

14 **3b**: mp 213.5-214.5 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 1.82(6 H, s), 2.10(6 H, s), 3.59(6 H, s), 6.52(2 H, s); ^{13}C NMR(100 MHz, $CDCl_3$) δ 11.85, 12.61, 32.65, 103.74, 113.60, 114.75, 120.83, 134.57, 137.35, 140.92, 186.25; UV(MeOH) λ_{max} 308 nm(ε 4900), 474(1700); MS *m/z* 372(M^+).

15 The relatively lower yield of the diindolylquinone resulted from the instability of 1-*t*-butyldimethylsilyl-3-stannylindol.

16 K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311(1990).

17 **8**: mp 148.5-150 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 1.67(3 H, s), 2.04(3 H, s), 2.11(6 H, s), 3.52(3 H, s), 6.53(1 H, s), 6.65(1 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.20, 11.50, 12.68, 14.70, 32.55, 103.71, 113.73, 114.75, 121.19,131.82, 135.06, 136.25, 136.50, 137.84, 139.09, 140.79, 141.11, 143.80, 186.22, 186.72; MS *m/z* 422(M^+).