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Palladium(II)-Catalyzed Acetoxylation and Chlorination of 2-Alkenyl *p*-Tolyl Sulfones

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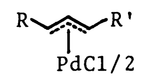
2-Alkenyl *p*-tolyl sulfones were converted into the corresponding 3-acetoxy(or chloro)-1-alkenyl *p*-tolyl sulfones *via* π-allylpalladium complexes which reacted regiospecifically with a nucleophile such as acetate anion or chloride anion in the presence of Cu(II).

π-Allylpalladium complexes (**1**) are usually prepared by various methods starting from alkadienes, alkenes, and 2-alkenyl acetates (or chlorides), and they have often been utilized in organic synthesis.[1] Formally, these complexes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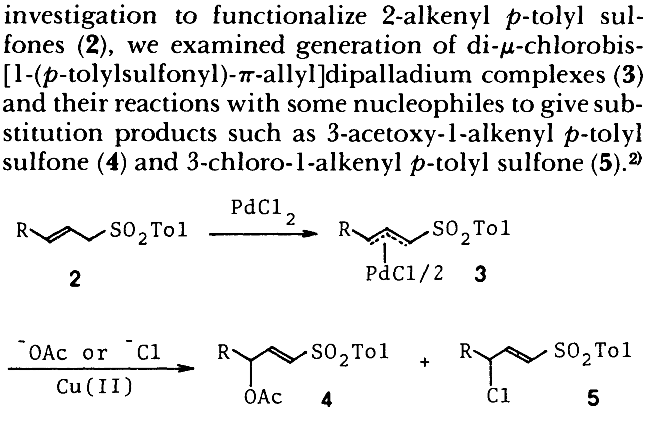
may be considered as allyl cation equivalents which react with various nucleophiles. In the course of our investigation to functionalize 2-alkenyl *p*-tolyl sulfones (**2**), we examined generation of di-μ-chlorobis-[1-(*p*-tolylsulfonyl)-π-allyl]dipalladium complexes (**3**) and their reactions with some nucleophiles to give substitution products such as 3-acetoxy-1-alkenyl *p*-tolyl sulfone (**4**) and 3-chloro-1-alkenyl *p*-tolyl sulfone (**5**).[2]



a: R = H b: R = CH_3 c: R = n-C_9H_{19} d: R = Ph

Scheme 1.

Recently, Trost and his coworkers reported on the reaction of 2-alkenyl phenyl sulfones with a Pd(O) complex, where the sulfonyl group behaves as a leaving group to form π-allylpalladium complexes.[3] This is in a sharp contrast with our findings that $PdCl_2$ reacts with **2** to give **3** without loosing the sulfonyl group. We have also found that **3** undergoes regiospecific displacement with acetate anion or chloride anion to give **4** or **5**, respectively.[4]

Results and Discussion

According to Trost's procedure for preparation of π-allylpalladium complexes from alkenes,[5] 2-propenyl *p*-tolyl sulfone (**2a**) was treated with $PdCl_2$ (1 mol equiv), $CuCl_2$ (6.1mol equiv), AcONa (13 equiv), and NaCl (13 equiv) in AcOH (60°/16h). Surprisingly, the expected π-allylpalladium complex (**3a**) was not formed, but 3-chloro-1-propenyl *p*-tolyl sulfone (**5a**) and 3-acetoxy-1-propenyl *p*-tolyl sulfone (**4a**) were obtained in 60 and 29% yields, respectively. When the amount of $CuCl_2$ was decreased to 3.4 mol equiv, the acetate **3a** became the predominant product (70% yield). Furthermore, it was found that only a catalytic amount of $PdCl_2$ was needed to transform **2a** into **4a** and/or **5a**. Thus, the reaction proceeded smoothly by the use of 0.10 or 0.03 mol equiv of $PdCl_2$ as shown in Table 1 (Runs 3—5). In these cases, a large excess of $CuCl_2$ appears to oxidize Pd(0) to regenerate Pd(II). Since prolonged reaction did not cause remarkable increase of **4a** (Runs 5 and 6 of Table 1), it was concluded that **4a** is not produced from **5a**. Similar results were also obtained in the reactions of other 2-alkenyl *p*-tolyl sulfones (**2b** and **2c**). In contrast, 3-phenyl-2-propenyl *p*-tolyl sulfone (**2d**) afforded 3-acetoxy-3-phenyl-1-propenyl *p*-tolyl sulfone (**4d**) even when a large excess (6.2—6.9 mol equiv) of $CuCl_2$ was employed (Run 17—19 in Table 1).

Since the amounts of $CuCl_2$ were crucial to the ratio of **4a**:**5a**, we investigated the effect of $CuCl_2$ in more detail. As mentioned above, the acetate **4** was exclusively formed when about 6 mol equiv of $CuCl_2$ was used, whereas, when about 3 mol equiv of $CuCl_2$ was used, predominant formation of the chloride **5** was noted. Table 2 shows that the ratio of **4a**:**5a**, diminishes gradually with increase in the amount of $CuCl_2$ in the given reaction conditions. These phenomena might be attributable to a reversible reaction of $CuCl_2$ with AcONa. This may be supported by the fact that $CuCl_2$ reacted with 2 mol equiv of AcONa in AcOH to give the same mixture as that derived from $Cu(OAc)_2$ and NaCl in the molar ratio of 1:2.[6] This explanation is consistent with the observation that the absence of NaOAc increases the yield of **5a** though the reaction is somewhat slow (Runs 9 and 13 of Table 1).

*Preparation of Di-μ-chlorobis[1-(*p*-tolylsulfonyl)-π-allyl]dipalladium (3a) and Its Reaction with Nucleophiles.* As mentioned above, Trost's procedure[5] met with no success in obtaining **3a**. This may be because **3a** undergoes a smooth reaction with the coexisting AcONa in the presence of Cu(II) (*vide infra*). However, the reactions of **3b** and **3d** with nucleophiles appeared to be slow compared to that of **3a**. In fact, **3b** and **3d** were isolated by shortening the reaction time under similar conditions (see Experimental section). Later, it was found that the complex **3a** could also be obtained by treatment of **2a** with 1 mol equiv of $PdCl_2$ and 3 mol equiv of AcONa in AcOH at 60 °C for 24 h. The structures of these complexes (**3a**, **3b**, and **3d**) were deduced from their IR spectra and satisfactory elemental analyses. Although **3a** was partially soluble in DMSO, rapid decomposition occurred to give the corresponding 3-hydroxy-1-propenyl *p*-tolyl sulfone. This fact made it difficult to record its NMR spectrum.

TABLE 1. DIRECT CONVERSION OF **2** TO **4** AND **5**[a]

Run	R	$PdCl_2$ (mol equiv)[b]	$CuCl_2$ (mol equiv)[b]	Temp/°C (Time/h)	Yield/% **4**	Yield/% **5**
1	H	1.0	3.4	60(75)	70	—
2		1.0	6.1	60(16)	29	60
3		0.1	2.8	60(57)	72	—
4		0.1	6.1	60(20)	12	77
5		0.03	5.9	60(18)	5	76
6		0.03	5.9	60(96)	7	84
7	CH_3	1.0	2.7	60(39)→80(98)	75	—
8		1.0	6.1	80(13)	33	63
9		1.0[c]	5.4	80(49)	9	74
10		0.1	2.7	80(52)	80	—
11		0.1	6.1	80(36)	17	80
12		0.03	2.7	80(48)	79	—
13		0.03[c]	2.7	70—80(156)	14	68
14	n-C_9H_{19}	1.0	2.7	60(140)	80	—
15		0.03	3.0	80(60)	86	—
16		0.03	6.1	80(26)	2	26
17	Ph	1.0	6.2	60(96)→80(88)	60	—
18		0.1	6.9	80(144)	53	—
19		0.03	6.9	80(144)	41	—

[a] In the presence of $PdCl_2$, $CuCl_2$, AcONa (13 equiv), and NaCl (13 equiv) in AcOH. [b] mol equiv to **2**. [c] In the absence of AcONa.

TABLE 2. EFFECT OF THE AMOUNT OF $CuCl_2$ IN THE REACTION OF **2a**[a]

$CuCl_2$ (mol equiv)	Time h	Yield/% **4a**	Yield/% **5a**	Ratio **4a**:**5a**
6.1	20	12	77	13:87
5.5	40	8(11)[b]	54(75)[b]	13:87
5.0	90	20(60)[b]	8(24)[b]	71:29
4.0	83	78(82)[b]	—	100:0
2.8	57	72	—	100:0

[a] Using $PdCl_2$ (0.1 mol equiv), AcONa (13 equiv), and NaCl (13 equiv) in AcOH at 60 °C. [b] The yield based on the unrecovered **2a**.

TABLE 3. REACTION OF **3a**[a]

Run	Additive (mol equiv) $CuCl_2$	NaCl	$Cu(OAc)_2$	AcONa	Yield/% **4a**	**5a**	**3a**
1	2.0	—	—	—	14	43	23
2	—	3.0	—	—	2	—	91
3	2.0	3.0	—	—	9	80	—
4	—	—	2.0	—	3	2	—[b]
5	—	—	—	3.0[c]	18	—	74
6	—	—	2.0	3.0	74	—	—
7	—	3.0	2.0	—	35	29	—

[a] Stirring in AcOH at 60 °C for 48 h. [b] An unidentified complex mixture which might be composed of **3a** and $Cu(OAc)_2$ was formed. [c] Treatment of **3a** with 3.0 mol equiv of AcONa in AcOH at 80 °C for 48 h afforded **4a** in 88% yield.

With regard to the reactions of **3a** with acetate anion, it was observed that combined use of AcONa and $Cu(OAc)_2$ was effective to give **4a** (Table 3). Thus, **4a** was obtained in 74% yield on heating a mixture of **3a**, AcONa, and $Cu(OAc)_2$ in AcOH at 60 °C for 48 h. However, treatment of **3a** with either $Cu(OAc)_2$ or AcONa at 60 °C produced only **4a** in low yields. Analogously, stirring of **3a** with NaCl alone in AcOH did not give **5a**, and merely slow reaction of **3a** was noted when it was allowed to react with $CuCl_2$ in AcOH. However, when both $CuCl_2$ and NaCl were added to a solution of **3a** in AcOH, the reaction proceeded smoothly to afford **5a** in 80% yield together with a small amount (9%) of **4a**. In the reaction of **3a** with $Cu(OAc)_2$ and NaCl, both **4a** and **5a** were formed in 29 and 35% yields, respectively. These results indicate that a smooth conversion of **3a** to either **4a** or **5a** can be accomplished in the presence of both Cu(II) and a nucleophile (acetate anion or chloride anion, respectively). This may be interpreted in terms of the following mechanism: Cu(II) contacts the Pd(II)Cl part in **3a** to assist its departure and concurrently the nucleophile attacks the allylic carbon. At the present time, we cannot preclude the possibility that the attack of the nucleophile and the oxidation of Pd(II) of **3a** with Cu(II) occur simultaneously to give directly Pd(0) and the substitution product (**4a** or **5a**). Here it should be noted that the attack of the nucleophiles on **3a** took place at the carbon γ to the sulfonyl group to give **4** and **5**. Since the sulfonyl group is well known as a strong electron-withdrawing group,[7] the γ carbon in the allylic system of **3a** can be considered to be more positive than the α carbon. Therefore, the γ carbon appears to be the favorable site for the approach of a nucleophile.[8]

*Requisite Additives for the $PdCl_2$-Catalyzed Conversion of **2** to **4** or **5**.* For the $PdCl_2$-catalyzed conversion of **2** to **4** or **5**, three steps must be taken into consideration: (i) transformation of **2** into the intermediary π-allylpalladium complex **3**; (ii) the reaction of **3** with a nucleophile to give Pd(0) and the substitution product (**4** or **5**); and (iii) oxidation of Pd(0) to regenerate Pd(II). The final step can be achieved by oxidation with the coexisting Cu(II). As described previously, Cu(II) and a nucleophile appear to be neccessary to the second step. Of course, it may be also possible that the second and final steps take place simultaneously. Hitherto, Trost and his coworkers reported that three additives, $CuCl_2$, AcONa, and NaCl, were required for efficient production of π-allylpalladium complexes from acyclic and cyclic olefins and $PdCl_2$.[5] This may not be the present case because treatment of **2a** with $PdCl_2$ and AcONa gave **3a** (*vide supra*) and $PdCl_2$ (0.03 mol equiv) could catalyze the transformation of **2a** to **5a** in the presence of $CuCl_2$ (2 mol equiv) and NaCl (3 mol equiv) in AcOH (60 °C/48 h: 80% yield).

For the transformation of **2a** into **4a** using 1 mol equiv of $PdCl_2$, combined use of AcONa (2 mol equiv) and $Cu(OAc)_2$ (3 mol equiv) promoted the reaction to give **4a** in 88% yield (60 °C/ 48 h). However, the use of a catalytic amount of $PdCl_2$ did not result in complete transformation even in the presence of large amounts of $Cu(OAc)_2$ (4 mol equiv) and AcONa (6 mol equiv). To our surprise, however, Pd(II)-catalysis was successful if NaCl (3 mol equiv)was added. When **2a** was stirred with $PdCl_2$ (0.03 mol equiv), NaCl (3 mol equiv), $Cu(OAc)_2$ (2 mol equiv), and AcONa (6 mol equiv) in AcOH 60 °C for 48 h, **4a** was obtained in 92% yield. In the $PdCl_2$-catalyzed conversion of **2a** to **5a** in the copresence of $CuCl_2$ and NaCl, NaCl not only supplies chloride anion but also is essential to the initiation of the reaction. Such a role of NaCl is intriguing, but we so far find no satisfactory interpretation. A possible explanation is that NaCl transforms $PdCl_2$ and $Pd(OAc)_2$, which is produced by oxidation of Pd(0) with $Cu(OAc)_2$, to the soluble palladates formulated as $Na_2[PdCl_n(OAc)_{4-n}]$.[9] Scheme 3 summarizes this proposed mechanism for the conversion of **2** to **4** and/or **5**.

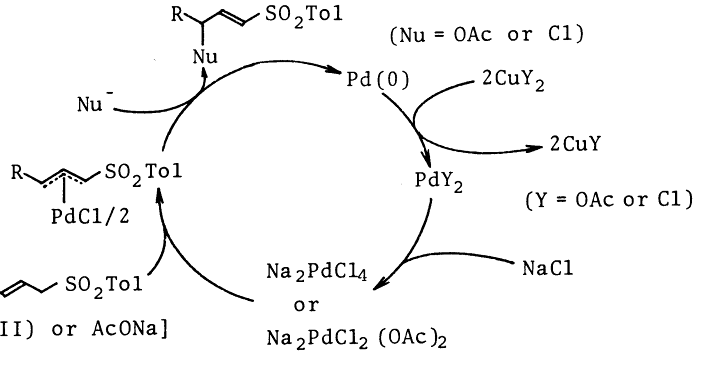
Thus, the $PdCl_2$-catalyzed transformation of **2a** into **4a** or **5a** can be achieved by performing the reaction using $Cu(OAc)_2$–AcONa–NaCl or $CuCl_2$–NaCl, respectively. The reaction was also applied to other 2-alkenyl *p*-tolyl sulfones. The results were summarized in Table 4, showing that the present reaction conditions are general for syntheses of **4** or **5**.

Experimental

Melting points were determined on a hot-stage microscope apparatus (Yanagimoto) and are uncorrected. ^1H NMR spectra were obtained on a Hitachi R-600 spectrometer. Infrared spectra were determined with a JASCO A-200 spectrometer.

Treatment of **2a** *with* $PdCl_2$*,* $CuCl_2$*, AcONa, and NaCl in AcOH.* *(a) The Use* ca. *3 mol equiv of* $CuCl_2$: After a suspension containing $PdCl_2$ (468 mg: 2.64 mmol), NaCl (1.91 g: 32.7 mmol), AcONa (1.77 g: 21.6 mmol), and $CuCl_2$ (1.18 g: 8.78 mmol) in AcOH (15 ml)–Ac_2O (1.0 ml) was stirred at 90—98 °C for 2 h, the suspension was cooled to 60 °C. To this, a solution of **2a** (504 mg: 2.62 mmol) in AcOH (10 ml) was added and the resulting mixture was further stirred at 58—64 °C for 75 h. Then, water (20 ml) was added and the mixture was extracted with four 35 ml-portions of benzene. The extracts were combined and washed successively with water, saturated aqueous $NaHCO_3$, brine, and water. After being dried over anhydrous $MgSO_4$, the extract was evaporated and separated by column chromatography on silica gel using benzene–dichloromethane (1 : 1) as an eluent to afford **4a** (454 mg: 70% yield): mp 23—24 °C; IR (neat) 1745, 1384, 1318, 1303, 1280, 1230, 1148, 1095, 1038, 816, 663 cm^{-1}: ^1H NMR ($CDCl_3$) δ=2.06 (3H, s), 2.43 (3H, s), 4.78 (2H, dd, J=0.9 and 3.5 Hz), 6.61 (1H, td, J=0.9 and 15 Hz), 7.02 (1H, td, J=3.5 and 15 Hz), 7.32 (2H, d, J=9 Hz), and 7.79 (2H, d, J=9 Hz). Calcd for $C_{12}H_{14}O_4S+1/20\ C_6H_6$: C, 57.22; H, 5.58%. Found: 57.31; H, 5.58%.

This compound was hydrolyzed to give 3-hydroxy-1-propenyl *p*-tolyl sulfone. A solution containing **3a** (171 mg: 0.67 mmol) and conc. hydrochloric acid (0.5 ml) in methanol (20 ml) was stirred at room temperature for 48 h. After addition of water (20 ml), the mixture was extracted with



Scheme 2.

Table 4. $PdCl_2$-Catalyzed preparation of **4** or **5**

R	2→4[a]		2→5[b]	
	Conditions Temp/°C (Time/h)	Yield/%	Conditions Temp/°C (Time/h)	Yield/%
H	80(49)	92	80(30)	89
CH_3	100(30)	90	80(20)→100(56)	68
n-C_9H_{19}	100(65)	73	100(84)	57

a) Using $PdCl_2$ (3 mol%), $Cu(OAc)_2$ (2.0 mol equiv), AcONa (6.0 equiv), and NaCl (3.0 equiv) in AcOH.
b) Using $PdCl_2$ (5 mol%), $CuCl_2$ (3.0 mol equiv), and NaCl (3.0 equiv), in AcOH.

four 30 ml-portions of dichloromethane. The extracts were combined, washed with water, and evaporated under reduced pressure to give colorless crystals (131 mg: 92% yield) which were purified by recrystallization from carbon tetrachloride-dichloromethane to afford colorless needles (100 mg): mp 122—123 °C; IR (KBr) 3605, 1295, 1286, 1274, 1137, 1079, 942, 811, 665, 536, 523 cm^{-1}: ^{1}H NMR (CDCl$_3$) δ=2.43 (3H, s),4.34 (2H, m), 6.60 (1H, diffused d, *J*=15 Hz), 7.03 (1H, td, *J*=3 and 15 Hz), 7.33 (2H, d, *J*=8 Hz), 7.77 (2H, d, *J*=8 Hz). Calcd for $C_{10}H_{12}O_3S$: C, 56.59; H, 5.70%. Found: C, 56.61; H, 5.66%.

In the analogous manners, **4b** and **4c** were obtained. **4b**: An oil; IR (neat) 1742, 1373, 1317, 1303, 1235, 1145, 1082, 661, 568, 548, 539 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.36 (3H, d, *J*=6 Hz), 2.03 (3H, s), 2.41 (3H, s), 5.25—5.72 (1H, m), 6.43 (1H, dd, *J*=1.6 and 16 Hz), 6.90 (1H, dd, *J*=4 and 16 Hz), 7.31 (2H, d, *J*=8 Hz), and 7.73 (2H, d, *J*=8 Hz). Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01%. Found: C, 58.08; H, 6.15%. **4c**: An oil; IR (neat) 3030, 2860, 1748, 1375, 1320, 1301, 1235, 1150, 1087, 665 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.25—1.82 (19H, m), 2.01 (3H, s), 2.44 (3H, s), 5.13—5.56 (1H, diffused s), 6.37 (1H, d, *J*=15 Hz), 6.83 (1H, dd, *J*=4 and 15 Hz), 7.31 (2H, d, *J*=8 Hz), and 7.74 (2H, d, *J*=8 Hz). Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01%. Found: C, 58.08; H, 6.15%.

(b) The Use of ca. *6 mol equiv of* $CuCl_2$: After a suspension containing PdCl$_2$ (370 mg: 2.09 mmol), CuCl$_2$ (1.70 g: 12.7 mmol), AcONa (22.2 g: 27.1 mmol), and NaCl (1.55 g: 26.5 mmol), in AcOH (23.0 ml)–Ac$_2$O (1.0 ml) was stirred at 90—95 °C for 2 h, **2a** (410 mg: 2.09 mmol), was added along with AcOH (4.0 ml), and the resulting mixture was stirred at 60 °C for 16 h. After addition of water (50 ml) and extraction with four 70-ml portions of benzene–dichloromethane (3:1), the extracts were combined and washed with water, saturated aqueous NaHCO$_3$, and brine. Then, after the extract was dried over anhydrous MgSO$_4$, the solution was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel using benzene–hexane and benzene–AcOEt as eluents to give **4a** (156 mg: 29% yield) and **5a** (291 mg: 60% yield). An analytical sample of **5a** was obtained by recrystallization from benzene–hexane: mp 58—59 °C; IR (KBr) 3046, 2921, 1302, 1276, 1141, 861, 709, 587, 530, 501 cm^{-1}: ^{1}H NMR (CDCl$_3$) δ=2.44 (3H, s), 4.19 (2H, dd, *J*=1.1 and 5.0 Hz), 6.66 (1H, dd, *J*=1.1 and 14.8 Hz), 6.97 (1H, dt, *J*=5.0 and 14.8 Hz), 7.32 (2H, d, *J*=8.0 Hz), and 7.77 (2H, d, *J*=8.0 Hz). Calcd for $C_{10}H_{11}O_2ClS$: C, 52.06; H, 4.81%. Found: C, 51.97; H, 4.80%.

Similarly, the following compounds were obtained. **5b**: Mp 37—38 °C (from hexane); IR (KBr) 1315, 1303, 1281, 1145, 1088, 963, 840, 808, 671, 578, 543 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.62 (3H, d, *J*=6.8 Hz), 2.44 (3H, s), 4.63 (1H, diffused quintet, *J*=6 Hz), 6.61 (1H, dd, *J*=14.8 and 0.6 Hz), 6.92 (1H, dd, *J*=14.8 and 5.6 Hz), 7.37 (2H, d, *J*=8.3 Hz), and 7.77 (2H, d, *J*=8.3 Hz). Calcd for $C_{11}H_{13}O_2ClS$: C, 53.99; H, 5.26%. Found: C, 54.02; H, 5.35%.

5c: Mp 30—31 °C; IR (neat) 2925, 2851, 1315, 1302, 1285, 1143, 1186, 811, 653, 588 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.67—1.90 (19H, m), 2.44 (3H, s), 4.44 (1H, dt, *J*=6.4 and 5.7 Hz), 6.55 (1H, d, *J*=14.7 Hz), 7.22 (2H, d, *J*=8.1 Hz), and 7.74 (2H, d, *J*=8.1 Hz). Calcd for $C_{19}H_{29}O_2ClS$: C, 63.93; H, 8.19%. Found: C, 63.95; H, 8.11%.

Under the similar conditions, 3-phenyl-2-propenyl *p*-tolyl sulfone (**2d**) gave **4d**: mp 108—109 °C; IR (KBr) 3080, 2925, 1739, 1314, 1301, 1236, 1139, 673, 536 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.02 (3H, s), 2.41 (3H, s), 6.18 (1H, dd, *J*=1.5 and 4.5 Hz), 6.25 (1H, dd, *J*=1.5 and 15 Hz), 6.99 (1H, dd, *J*=4.5 and 15 Hz), 7.16—7.61 (7H, broad), and 7.68 (2H, d, *J*=8 Hz). UV (EtOH) 207 (ε 11700), 239 (12000), and 277 (562) nm. Calcd for $C_{18}H_{18}O_4S$: C, 65.44; H, 5.49%. Found: C, 65.42; H, 5.43%. No **5d** was obtained in this reaction.

Acid hydrolysis of **4d** was also performed by the procedure similar to that of **3a**. 3-Hydroxy-3-phenyl-1-propenyl *p*-tolyl sulfone: mp 134—135 °C; IR (KBr) 3590, 1314, 1307, 1276, 1137, 1078, 975, 813, 756, 704, 691, and 543 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ= 2.43 (3H, s), 2.70 (1H, d, *J*=6 Hz, OH), 5.15—5.49 (1H, m), 6.66 (1H, d, *J*=16 Hz), 7.18 (1H, dd, *J*=3.5 and 16 Hz), 7.15—7.46 (7H, m), 7.70 (2H, d, *J*=8 Hz). Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%. Found: C, 66.79; H, 5.64%.

Isolation of the π-Allylpalladium Complex (3a). A suspension involving **2a** (1.96 g: 10.0 mmol), PdCl$_2$ (1.77 g: 10.0 mmol), and AcONa (1.65 g: 20 mmol) in AcOH (100 ml)–Ac$_2$O (5 ml) was stirred at 60 °C for 24 h. The deposited solid was collected by filtration and transfered into a beaker. Then, the solid was triturated with benzene (10 ml) and the benzene was discarded by decantation. After this procedure was repeated five times, the solid was washed with five 10 ml-portions of water and dried over sulfuric acid under reduced pressure. An analytical sample was obtained as follows. **3a** was dissolved in DMSO–AcOH (3:2) under ice-cooling and then excess of AcOH was added to deposit **3a**. The solid (**3a**) was filtered and washed with water and dichloromethane: mp 152—164 °C (decomp); IR (KBr) 1310, 1299, 1140, 1092, 820, 802, 788, 656, 573, and 552 cm^{-1}. Calcd for $C_{10}H_{11}O_2ClPdS$: C, 35.63; H, 3.29%. Found: C, 35.23; H, 3.29%.

Isolation of the π-Allylpalladium Complexes (3b and 3d). After a suspension containing PdCl$_2$ (460 mg: 2.59 mmol), NaCl (1.94 g: 23.6 mmol), AcONa (2.77 g: 33.8 mmol), and CuCl$_2$ (943 mg: 7.01 mmol) in AcOH (14 ml)–Ac$_2$O (3 ml) was stirred at 95—105 °C for 2 h, a solution of **2b** (553 mg: 2.63 mmol) in AcOH (5 ml) was added and the resulting mixture was stirred at 60—65 °C for 76 h. After addition of benzene (20 ml), the mixture was extracted with four 20-ml portions of benzene. The yellow solid floating in the benzene layer was collected by filtration, washed with benzene, and dried in a desiccator to give **3b** (621 mg) as a greenish yellow solid. An analytical sample was obtained by dissolution in DMSO–AcOH (3: 1) followed by reprecipitation by addition of water: mp: 168—170 °C; IR (KBr) 3060, 1595, 1308, 1301, 1150, 1079, 820, 806, 799, 654, 566 cm^{-1}. Calcd for $C_{11}H_{13}O_2ClPdS+0.9H_2O$: C, 35.96; H, 4.06%. Found: C, 35.82; H, 3.70%.

The benzene layer was washed with water and saturated aqueous NaHCO$_3$, dried over anhydrous MgSO$_4$, evaporated, and chromatographed on silica gel [elution with benzene- dichloromethane (1:2)] to give **4b** (142 mg: 20% yield).

In the similar manner, **3d** was obtained: mp 193—194 °C (decomp). Calcd for $C_{16}H_{15}O_2ClPdS+0.7H_2O$: C, 45.13; H, 3.88%. Found: C, 45.08; H, 3.69%.

Reaction of **3a** *with* $CuCl_2$ *and NaCl. A Typical Procedure*: A suspension containing **3a** (506 mg: 1.50 mmol), CuCl$_2$ (404 mg: 3.00 mmol), and NaCl (263 mg: 4.50 mmol) in AcOH (19.5 ml)–Ac$_2$O (0.7 ml) was stirred at 60 °C for 48 h. After addition of water (40 ml), the mixture was extracted with four 50-ml portions of benzene–dichloromethane (3:1) and the organic layer was washed successively with water, saturated aqueous NaHCO$_3$, brine, and water. The organic layer was dried over anhydrous MgSO$_4$, the solvents were removed, and the resultant residue was subjected to column chromatography on silica gel using hexane–benzene (4:1) and benzene–ethyl acetate (4:1) as eluents to afford **5a** (272 mg), a mixture (6.7 mg) of **5a** and **4a** (9:1), and **4a** (35 mg). The yields of **5a** and **4a** were calculated to be 80 and 9%, respectively.

In the similar manners, **3a** was subjected to the reaction in the presence of various additives. The results were summarized in Table 3.

$PdCl_2$-Catalyzed Conversion of **2a** *to* **4a**. *A Typical Procedure*: A suspension involving **2a** (393 mg: 2.0 mmol), PdCl$_2$ (10.6 mg: 0.06 mmol), Cu(OAc)$_2$ (726 mg: 4.0 mmol), AcONa (985 mg: 12.0 mmol), and NaCl (351 mg: 6.0 mmol), in AcOH (26 ml)–Ac$_2$O (1 ml) was stirred at 60 °C for 48 h.

After addition of water (40 ml), the resulting mixture was extracted with four 60-ml portions of benzene–dichloromethane (4:1) and then the extract was washed successively with water, saturated aqueous $NaHCO_3$, brine, and water. The extract was dried over anhydrous $MgSO_4$, the solvents were removed, and the resultant residue was subjected to column chromatography on silica gel using hexane–benzene (9:11) and benzene- ethyl acetate (3:2) as eluents to give **4a** (476 mg: 92% yield).

Analogously, **2b** and **2c** were converted to **4b** (90% yield) and **4c** (73% yield), respectively, under the conditions described in Table 4.

*$PdCl_2$-Catalyzed Conversion of **2a** to **5a**. A Typical Procedure*: A suspension involving **2a** (1.00 g: 5.1 mmol), $PdCl_2$ (27.1 g: 0.153 mmol), $CuCl_2$ (2.06 g: 15.3 mmol), and NaCl (894 mg: 15.3 mmol) in AcOH (26 ml)–Ac_2O (1 ml) was stirred at 80 °C for 30 h. After water (100 ml) was added, the resulting mixture was extracted with four 60-ml portions of benzene–dichloromethane (4:1). Then the organic layers was combined and washed successively with water, saturated aqueous $NaHCO_3$, brine, and water. This layer was dried over anhydrous $MgSO_4$, the solvents were removed, and the resultant residue was subjected to column chromatography on silica gel using hexane–benzene (9:11) and benzene–ethyl acetate (3:2) as eluents to give **5a** (1.09 g: 89% yield).

Similarly, **2b** and **2c** were converted **5b** (68% yield) and **5c** (57% yield), respectively, under the conditions described in Table 4.

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