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Reactions of Arylazoxy Aryl Sulfones with α,β-Unsaturated Esters and Nitriles in the Presence of a Palladium(0) Catalyst[1)]

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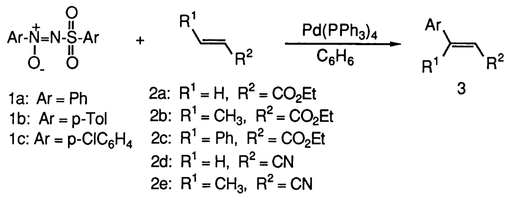
Synopsis. The reactions of arylazoxy aryl sulfones (**1**) with α,β-unsaturated esters and nitriles in the presence of a palladium(0) catalyst were found to give aryl-substituted esters and nitriles in good yield.

Recently, much attention has been paid to the palladium catalyzed substitution reaction of vinylic hydrogen by aryl and vinyl halides.[2)] Kikukawa et al. have first demonstrated that arenediazonium salts react with olefins in the presence of a palladium(0) catalyst to give arylated olefins in high yield.[3)] We previously reported that the reactions of arylazo aryl sulfones[4)] or arylazoxy aryl sulfones[5)] (**1**) with cyclic and acyclic olefins catalyzed by tetrakis(triphenylphosphine)palladium(0) in benzene gave aryl-substituted olefins in high yield. We found that the reactions of **1** with α,β-unsaturated esters and nitriles catalyzed by a palladium(0) complex gave aryl-substituted compounds, and the results will be described herein.

Results and Discussion

The reaction of phenylazoxy phenyl sulfone (**1a**) (1.0 mmol) with ethyl acrylate (**2a**) (5.0 mmol) proceeds smoothly in the presence of catalytic tetrakis(triphenylphosphine)palladium(0) in benzene in a degassed sealed tube at 80 °C for 24 h to give ethyl (*E*)-3-phenylpropenoate (**3a**) (0.89 mmol) and ethyl 3,3-diphenylpropenoate (**3b**) (0.33 mmol). The latter product may be produced by the arylation of **3a** once formed. When the palladium(0) catalyzed reaction of **1a** with ethyl acrylate was carried out in the presence of tri-butylphosphine (0.10 mmol), **3a** was formed (1.20 mmol) as the sole product. Similarly, the reactions of arylazoxy aryl sulfones (**1**) with α,β-unsaturated esters and nitriles catalyzed by a palladium(0) complex afforded aryl-substituted compounds (**3**) in good yield. However, the arylation of α,β-unsaturated ketones by **1** under similar conditions did not occur. The reason is not clear at the present time. The arylation occurred selectively at β-position of the α,β-unsaturated ester or nitrile, and no aryl-substituted compound at the α-position was detected. The results are summarized in Table 1.

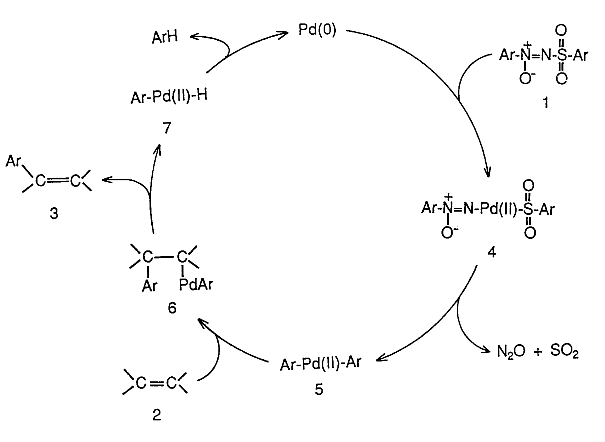


In the cases of Entries 2—4, 6 and 9, an aryl-substituted product was formed 1.20—1.57 mol/mol arylazoxy aryl sulfone. These results suggest that both of the aryl groups of **1** are participating for the arylation. A plausible catalytic cycle for this reaction is shown in Scheme 1. Oxidative addition of **1** to a palladium(0) catalyst gives arylazoxy(arylsulfonyl)palladium(II) species (**4**) which split off dinitrogen monoxide and sulfur dioxide to give the diarylpalladium (II) intermediate (**5**). Subsequent addition of **5** to the

Table 1. Reaction of Azoxysulfones with Olefins Catalyzed by a Pd(0) Complex at 80 °C[a)]

Entry	Arylazoxy aryl sulfone	Olefin	Reaction time/h	Product				Yield[b)]
					Ar	R^1	R^2	
1	**1a**	**2a**	24	**3a**	Ph	H	CO_2Et	0.89[c)]
2	**1a**[d)]	**2a**	24	**3a**	Ph	H	CO_2Et	1.20
3	**1a**	**2c**	24	**3b**	Ph	Ph	CO_2Et	1.57
4	**1a**	**2c**	48	**3b**	Ph	Ph	CO_2Et	1.52
5	**1b**	**2a**	24	**3c**	*p*-Tol	H	CO_2Et	0.93
6	**1b**	**2a**	48	**3c**	*p*-Tol	H	CO_2Et	1.38
7	**1c**	**2a**	24	**3d**	*p*-ClC_6H_4	H	CO_2Et	0.76
8	**1a**	**2d**	24	**3e**	Ph	H	CN	0.54
9	**1a**	**2e**[e)]	24	**3f**	Ph	CH_3	CN	1.46
10	**1b**	**2d**	24	**3g**	*p*-Tol	H	CN	0.61
11	**1b**	**2e**	24	**3h**	*p*-Tol	CH_3	CN	0.60
12	**1c**	**2d**	24	**3i**	*p*-ClC_6H_4	H	CN	0.84
13	**1c**	**2e**	48	**3j**	*p*-ClC_6H_4	CH_3	CN	0.91

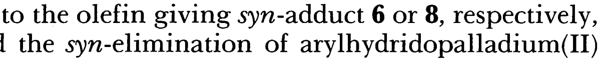
a) All reactions were performed with 1.0 mmol of arylazoxy aryl sulfone (**1**), 5.0 mmol of olefin, and 0.01 mmol of tetrakis(triphenylphosphine)palladium(0) in benzene (5.0 cm^3) in a degassed sealed tube at 80 °C. b) Yield (mol/mol of arylazoxy aryl sulfone) was determined by GC. c) Ethyl 3,3-diphenylpropenoate (**3b**) was formed (0.33 mmol) together with **3a**. d) *n*-Bu_3P (0.1 mmol) was added. e) Crotononitrile (10.0 mmol) was added.



Scheme 1.

olefin gives the adduct (**6**) from which elimination of an arylpalladium moiety and β-hydrogen gives the aryl-substituted olefins (**3**) and the arylhydridopalladium(II) (**7**). The palladium(0) catalyst is regenerated by reductive elimination of an arene from **7**.

The intermediate **7** will be able to add to a further molecule of olefin to give the adduct (**8**). By the subsequent elimination of dihydridopalladium(II) (**9**) from **8**, an aryl-substituted olefin (**3**) will also be formed as shown in Scheme 2. The palladium(0) catalyst is regenerated by the reductive elimination of hydrogen from **9**, although the formation of hydrogen was not confirmed by MS. The reductive elimination process of an arene from **7** giving palladium(0) shown in Scheme 1 and the addition process of **7** to **2** giving the adduct **8** shown in Scheme 2 are considered to be occurring competitively. Therefore, **3** has a possibility to form 1.0—2.0 mmol from 1.0 mmol of arylazoxy aryl sulfone used.

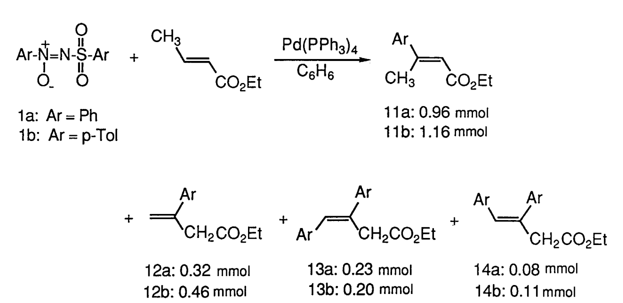


Scheme 2.

The (E)-isomers of aryl-substituted compounds were formed stereoselectively as shown in Table 1. These results are accounted for by the *syn*-addition of diarylpalladium(II) (**5**) or arylhydridopalladium(II) (**7**) to the olefin giving *syn*-adduct **6** or **8**, respectively, and the *syn*-elimination of arylhydridopalladium(II) (**7**) or dihydridopalladium(II) (**9**) giving an (E)-isomer. Similar *syn*-addition and *syn*-elimination process of arylpalladium species have been reported by Heck[6] and Kikukawa et al.[3]

When the phenylation of ethyl crotonate with **1a** was carried out under similar conditions, aryl-substituted compounds **11a** was formed together with unexpected products **12a**, **13a**, and **14a**. Similar results were obtained in the reaction of **1b** with ethyl crotonate in the presence of the palladium(0) catalyst.

The product **12** may be formed by the reaction of **1** with ethyl 3-butenoate which is considered to be formed by the palladium(0) catalyzed isomerization of ethyl crotonate since palladium catalyzed isomerization of olefins is known.[7] The products **13** and **14** may be formed by the secondary arylation of **12** once formed. However, crotononitrile did not afford such unexpected compounds as shown in Table 1. The difference between these two olefins is not clear at present.



Experimental

Measurement. IR spectra were determined on a Hitachi 260-10 spectrometer with samples as either neat liquids or KBr discs. ^{1}H NMR spectra were measured on a JEOL JNM-PMX 60SI (60 MHz) and a Varian Gemini-200 (200 MHz) spectrometers. ^{13}C NMR spectra were measured on a JEOL JNM Fx90Q FT NMR (90 MHz) spectrometer. ^{1}H and ^{13}C NMR signals were referenced to Me_4Si as an internal standard. Mass spectra were measured on a JEOL JMS DX-300 spectrometer by the electron impact (EI) ionizing technique at 70 eV. Gas chromatography was performed using a Hitachi 263-30 gas chromatograph with SE-30 (10%) 1 m stainless column. Gel permeation chromatography was performed using a JAL LC-08 liquid chromatograph with JAIGEL-1H ($20\phi \times 600$ mm$\times 2$) using chloroform as eluant.

Materials. All solvents were distilled and stored under nitrogen. Phenylazoxy phenyl sulfone (**1a**), mp 119—121 °C (123 °C)[8], p-tolylazoxy p-tolyl sulfone (**1b**), mp 102—104 °C (106 °C),[8] and p-chlorophenylazoxy p-chlorophenyl sulfone (**1c**), mp 174.5—175.0 °C were prepared by the published procedures.[8] Tetrakis(triphenylphosphine)palladium(0) was prepared by the methods described in the literature.[9] α,β-Unsaturated esters and nitriles of Tokyo Kasei Chemicals were purified by distillation prior to use.

General Procedures for the Reaction of Arylazoxy Aryl Sulfones (1) with α,β-Unsaturated Esters or Nitriles. A solution containing **1** (1.0 mmol), α,β-unsaturated ester or nitrile (5.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.01 mmol) in dry benzene (5.0 cm^3) was degassed by a freeze-thaw cycle, sealed in an ampoule and heated at 80 °C for 24 or 48 h. The reaction mixture was subjected to short column chromatography on Florisil using benzene as eluant to remove the metal complex. The yields of the products were determined by GC using undecane as the internal standard. The products were isolated from the reaction mixture by the use of gel permeation chromatography and/or column chromatography over silica gel (Wakogel C-60) and identified by IR, NMR, and mass spectra. The structures of ethyl (E)-3-phenylpropenoate (**3a**),[10] ethyl 3,3-diphenylpropenoate (**3b**),[11] ethyl (E)-3-(p-tolyl)propenoate (**3c**),[12] ethyl (E)-3-phenyl-2-butenoate (**11a**),[18] and ethyl (E)-3-(p-tolyl)butenoate (**11b**)[13] were identified by comparison of their IR, ^{1}H NMR, and mass spectral data with those of authentic samples. The structures of the following products were determined by their IR, NMR, and mass spectra.

Ethyl (E)-3-(p-chlorophenyl)propenoate (3d): IR (neat)

2910, 1710, and 1610 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, *J*=6.0 Hz), 4.18 (2H, q, *J*=6.0 Hz), 6.27 and 7.49 (2H, ABq, *J*=15.0 Hz), and 7.07—7.41 (4H, m); MS *m/z* 210 (M$^+$) and 182.

(*E*)-3-Phenyl-2-propenenitrile (3e): IR (neat) 3100, 2210, 1600, 1330, and 1210 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=5.91 and 7.48 (2H, ABq, *J*=15.0 Hz), and 7.45 (5H, s); MS *m/z* 129 (M$^+$), 115, 104, and 78.

(*E*)-3-Phenyl-2-butenenitrile (3f): IR (neat) 2250 and 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.44 (3H, s), 5.57 (1H, s), and 7.38 (5H, s); MS *m/z* 143 (M$^+$), 128, 115, 104, and 78.

(*E*)-3-(*p*-Tolyl)-2-propenenitrile (3g): IR (neat) 2200, 1600, and 1510 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.36 (3H, s), 5.77 and 7.59 (2H, ABq, *J*=16.8 Hz), and 7.18 and 7.25 (4H, ABq, *J*=4.2 Hz); MS *m/z* 143 (M$^+$), 129, and 115.

(*E*)-3-(*p*-Tolyl)-2-butenenitrile (3h): IR (neat) 2240 and 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.32 (3H, s), 2.37 (3H, d, *J*=1.1 Hz), 5.51 (1H, q, *J*=1.1 Hz), and 7.16 and 7.27 (4H, ABq, *J*=9.6 Hz); MS *m/z* 157 (M$^+$), 147, 129, 115, and 91; HRMS Found: 157.0930, Calcd for $C_{11}H_{11}N$: M, 157.0891.

(*E*)-3-(*p*-Chlorophenyl)-2-propenenitrile (3i): IR (neat) 2200, 1620, 1590, and 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.85 and 7.33 (2H, ABq, *J*=16.8 Hz), and 7.34 (4H, s); MS *m/z* 163 (M$^+$), 136, and 128.

(*E*)-3-(*p*-Chlorophenyl)-2-butenenitrile (3j): IR (neat) 3020, 2210, and 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.42 (3H, d, *J*=1.1 Hz), 5.55 (1H, q, *J*=1.1 Hz), and 7.37 (4H, s); MS, *m/z* 177 (M$^+$), 162, 142, and 101; HRMS Found: 177.0370, Calcd for $C_{10}H_8NCl$: M, 177.0346.

Ethyl (*E*)-3-phenyl-2-butenoate (11a)[10]**:** IR (neat) 1700, 1620, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, *J*=7.1 Hz), 2.57 (3H, d, *J*=1.2 Hz), 4.20 (2H, q, *J*=7.1 Hz), 6.12 (1H, q, *J*=1.2 Hz), and 7.32—7.46 (5H, m); MS, *m/z* 190 (M$^+$), 161, 145, 117, and 91.

Ethyl (*E*)-3-(*p*-tolyl)-2-butenoate (11b)[13]**:** IR (neat) 1710, 1620, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, *J*=7.1 Hz), 2.35 (3H, s), 2.56 (3H, d, *J*=1.2 Hz), 4.20 (2H, q, *J*=7.1 Hz), 6.13 (1H, q, *J*=1.2 Hz), and 7.16 and 7.37 (4H, ABq, *J*=8.2 Hz); MS, *m/z* 204 (M$^+$), 184, and 159.

Ethyl 3-phenyl-3-butenoate (12a): IR (neat) 3010 and 1730 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, t, *J*=7.1 Hz), 3.49 (2H, d, *J*=1.1 Hz), 4.08 (2H, q, *J*=7.1 Hz), 5.21 (1H, t, *J*=1.1 Hz), 5.52 (1H, s), and 7.24—7.44 (5H, m); MS *m/z* 190 (M$^+$), 161, 145, 117, and 91.

Ethyl 3-(*p*-tolyl)-3-butenoate (12b): IR (neat) 1720 and 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.18 (3H, t, *J*=7.1 Hz), 2.33 (3H, s), 3.49 (2H, d, *J*=1.1 Hz), 4.11 (2H, q, *J*=7.1 Hz), 5.18 (1H, t, *J*=1.1 Hz), 5.51 (1H, s), and 7.14 and 7.32 (4H, ABq, *J*=8.3 Hz); MS *m/z* 294 (M$^+$), 249, 221, 206, and 129.

Ethyl (*E*)-3,4-diphenyl-3-butenoate (13a): IR (neat) 3010 and 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, t, *J*=7.1 Hz), 3.71 (2H, s), 4.10 (2H, q, *J*=7.1 Hz), 7.03 (1H, s), and 7.24-7.53 (10H, m); MS *m/z* 266 (M$^+$), 193, 178, 115, and 91.

Ethyl **(*E*)-3,4-di(*p*-tolyl)-3-butenoate (13b):** IR (neat) 1730, 1600, 1320, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.16 (3H, t, *J*=7.1 Hz), 2.35 (6H, s), 3.68 (2H, s), 4.09 (2H, q, *J*=7.1 Hz), 6.96 (1H, s), 7.14 and 7.18 (4H, ABq, *J*=2.1 Hz), and 7.27 and 7.38 (4H, ABq, *J*=8.5 Hz); MS *m/z* 294 (M$^+$), 249, and 221; HRMS Found: *m/z* 294.1581, Calcd for $C_{20}H_{22}O_2$ M, 294.1619.

Ethyl (*Z*)-3,4-diphenyl-3-butenoate (14a): IR (neat) 2950, 1740, 1440, 1320, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, t, *J*=7.1 Hz), 3.47 (2H, s), 4.06 (2H, q, *J*=7.1 Hz), 6.56 (1H, s), 6.95—7.38 (10H, m); MS *m/z* 266 (M$^+$), 237, 193, 178, and 165; HRMS Found: 266.1298, Calcd for $C_{18}H_{16}O_2$: M, 266.1307.

Ethyl (*Z*)-3,4-di(*p*-tolyl)-3-butenoate (14b): IR (neat) 1710 and 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.14 (3H, t, *J*=7.1 Hz), 2.22 (3H, s), 2.31 (3H, s), 3.43 (2H, s), 4.06 (2H, q, *J*=7.1 Hz), 6.50 (1H, s), 6.86 and 6.90 (4H, ABq, *J*=8.0 Hz), and 7.08 (4H, s); MS *m/z* 294 (M$^+$), 249, 221, 206, and 129.

The products **12a**, **13a**, and **14a** were ozonized in dichloromethane at −78 °C and then treated with dimethyl sulfide. Ethyl benzoylacetate was obtained in each reactions. IR (neat) 1745 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, *J*=7.2 Hz), 3.94 (2H, s), 4.18 (2H, q, *J*=7.2 Hz), and 7.20—7.97 (5H, m); MS *m/z* 192 (M$^+$), 164, 146, 120, 105, and 77. The formation of benzaldehyde was also observed by GC-MS in the ozonolysis of **13a** and **14a**. These results support the structures of compounds **12a**, **13a**, and **14a**.

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