

Preliminary communication

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## A novel tandem arylsulfonylation and cyclization of arylazoxy aryl sulfones with norbornene catalyzed by a palladium(0) complex

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### Abstract

The reaction of arylazoxy aryl sulfones with norbornene in the presence of tetrakis(triphenylphosphine)palladium(0) was found to give *cis,exo*-2,3-norbornane-fused 2,3-dihydrobenzo[b]thiophene 1,1-dioxides in good yield.

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Recently, much attention has been paid to palladium catalyzed reactions in organic syntheses [1]. Arylation of alkenes with aryl halides or aryl mercurious compounds catalyzed by a palladium complex is the well known Heck reaction [2]. We previously reported a novel arylation of olefins [3] or  $\alpha,\beta$ -unsaturated esters and nitriles [4] with arylazoxy aryl sulfones (**1**) catalyzed by a palladium(0) complex; a reaction mechanism via a diarylpalladium(II) species was proposed. In the course of our systematic studies on this reaction, we found a hitherto unknown tandem arylsulfonylation and cyclization of **1** with norbornene.

The reaction of phenylazoxy phenyl sulfone (**1a**) with norbornene proceeds smoothly in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in benzene to give *cis,exo*-2,3-norbornane-fused 2,3-dihydrobenzo[b]thiophene 1,1-dioxide (**2a**) and biphenyl (**3a**) in 65 and 43% yield, respectively. Similarly, the reactions of arylazoxy aryl sulfone (**1b–e**) with norbornene catalyzed by a palladium(0) complex were also carried out to give the corresponding *cis,exo*-norbornane-fused dihydrobenzothiophenes (**2**) and biaryls (**3**) in good yields. The results are summarized in Table 1.

The catalytic cycle of this novel reaction of **1** with norbornene is accounted for by Scheme 1. Oxidative addition of **1** to the palladium(0) catalyst forms adduct **4**, which selectively eliminates dinitrogen monoxide to give the aryl(arylsulfonyl)palladium(II) intermediate (**5**). *Syn*-addition of **5** to the carbon–carbon double bond of norbornene from the *exo*-side gives adduct **6**. Subsequently *ortho*-palladation occurs on the arylsulfonyl group to give the palladium(IV) complex **7**. The reductive elimination of **2** from **7** gives arylhydridopalladium(II) (**8**). The characteristic

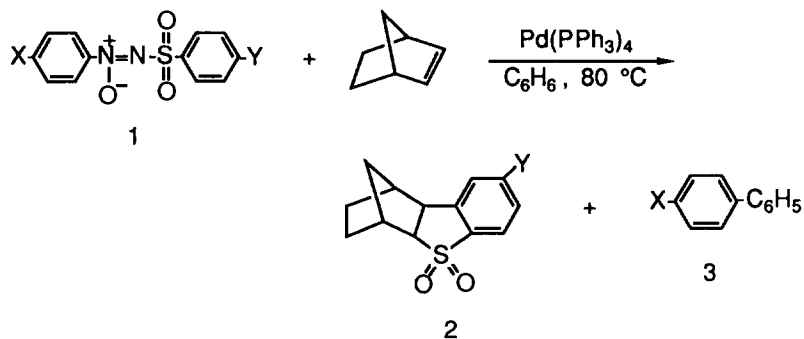
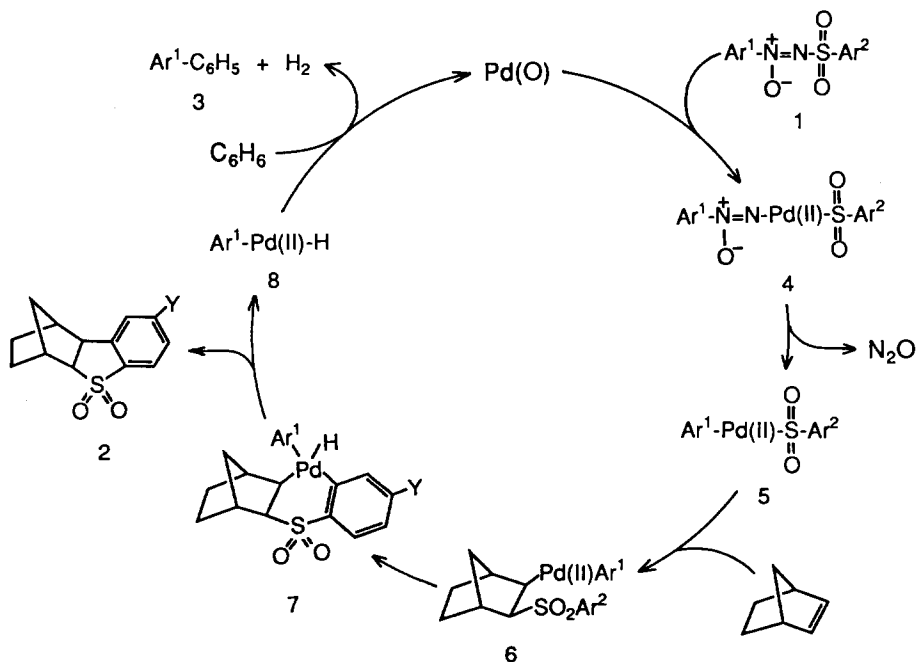


Table 1

Reactions of azoxysulfones **1** with norbornene catalyzed by a palladium(0) complex

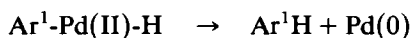
	X and Y in <b>1</b>		Products, Yield (%)			
	X	Y				
<b>1a</b>	H	H	<b>2a</b>	65	<b>3a</b>	43
<b>1b</b>	H	$\text{CH}_3$	<b>2b</b>	70	<b>3a</b>	45
<b>1c</b>	$\text{CH}_3$	H	<b>2a</b>	62	<b>3b</b>	40
<b>1d</b>	$\text{CH}_3$	$\text{CH}_3$	<b>2b</b>	80	<b>3b</b>	43
<b>1e</b>	Cl	Cl	<b>2c</b>	61	<b>3c</b>	45



Scheme 1

differences found in the palladium(0)-catalyzed reaction of **1** and norbornene compared with the reported reaction of **1** with acyclic and cyclic olefins [3] or unsaturated esters and nitriles [4] may be accounted for as follows: (a) norbornene is much more reactive than ordinary acyclic or cyclic olefins, and hence **5** adds to norbornene before it eliminates sulfur dioxide; (b) *ortho*-palladation on the arylsulfonyl group occurs in this case since there is no  $\beta$ -hydrogen at the *syn*-position to eliminate the arylpalladium(II) moiety in adduct **6**. *Syn*-addition and *syn*-elimination of an arylpalladium(II) moiety ( $\text{Ar}^1\text{Pd}$ ) containing  $\beta$ -hydrogen is reported by Kikukawa et al. in the case of ordinary olefins [5].

The sole biphenyl derivative formed was  $\text{Ar}^1\text{C}_6\text{H}_5$  (**3**) and no  $\text{Ar}^2\text{C}_6\text{H}_5$  was detected in the reaction mixtures. These findings suggest that the arylhydridopalladium(II) species (**8**), once formed, reacts with the solvent benzene to give biphenyl derivatives as shown in Scheme 1; however, no formation of hydrogen could be confirmed. The yield of biphenyl derivative **3** was lower than that of **2** in all the reactions. This may be accounted for by the reductive elimination occurring competitively from arylhydridopalladium(II) (**8**) to give arene and palladium(0):



Recently, Catellani and Chiusoli have reported an interesting reaction of bromobenzene with norbornene catalyzed by a palladium(0) complex in the presence of potassium butoxide to give double arylation and cyclization products, hexahydromethanotriphenylenes [6]. However, the present palladium(0)-catalyzed tandem arylsulfonylation/cyclization is a hitherto unknown reaction. Further studies on the scope and limitations of the novel reaction are in progress.

### General procedure

A solution containing arylazoxy aryl sulfone (**1**) (1.0 mmol), norbornene (1.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.01 mmol) in dry benzene (5 ml) was degassed by a freeze–thaw cycle, sealed in an ampoule, and kept at 80 °C for 24 h. The reaction mixture was subjected to short column chromatography on Florisil using benzene as eluent to remove the metal complex. The products were isolated from the reaction mixture by column chromatography on Florisil using hexane : ethyl acetate : chloroform (50 : 25 : 1) as the eluent and/or by gel-permeation chromatography, and their structures were determined by IR, NMR, and mass spectrometry. The structures of biphenyl, *p*-methylbiphenyl, and *p*-chlorobiphenyl were identified by comparison of their IR,  $^1\text{H}$  NMR, and mass spectral data with those of authentic samples.

*cis,exo*-2,3-Norbornane-fused 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**2a**): m.p. 137–138 °C; IR (neat) 1310 and 1145  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.10 (1H, d, *J* 11.0 Hz), 1.22 (1H, d, *J* 11.0 Hz), 1.26–1.78 (4H, m), 2.47 (1H, br s), 2.93 (1H, br s), 3.27 and 3.54 (2H, ABq, *J* 8.0 Hz), and 7.36–7.70 (4H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.4, 28.1, 33.6, 39.1, 43.0, 50.1, 66.1, 121.2, 126.7, 128.3, 128.8, 133.5, and 139.3; MS *m/z* 234 ( $M^+$ ), 216, 199, 167, 142, 137, and 129; HRMS found 234.0676;  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$  calc.: *M* 234.0714.

*cis,exo*-2,3-Norbornane-fused 5-methyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**2b**): m.p. 116–117 °C; IR (neat) 1320 and 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.12 (1H, d, *J* 11.1 Hz), 1.18 (1H, d, *J* 11.1 Hz), 1.27–1.73 (4H, m), 2.39 (3H, s), 2.46

(1H, br s), 2.92 (1H, br s), 3.23 and 3.47 (2H, ABq,  $J$  7.8 Hz), 7.16 (1H, s), and 7.21 and 7.54 (2H, ABq,  $J$  8.0 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.7, 27.4, 28.1, 33.6, 39.1, 43.0, 49.9, 66.5, 120.9, 126.9, 129.9, 138.5, 139.7, and 144.5; MS  $m/z$  248 ( $M^+$ ), 231, 213, 201, 181, 156, 151, and 143; HRMS found 248.0914;  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}$  calc.:  $M$  248.0871.

*cis,exo*-2,3-Norbornane-fused 5-chloro-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (**2c**): m.p. 131–132 °C; IR (neat) 1320 and 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.11 (1H, d,  $J$  11.0 Hz), 1.20 (1H, d,  $J$  11.0 Hz), 1.28–1.76 (4H, m), 2.48 (1H, br s), 2.94 (1H, br s) 3.28 and 3.50 (2H, ABq,  $J$  7.7 Hz), 7.35 and 7.60 (2H, ABq,  $J$  9.2 Hz), and 7.37 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.3, 28.1, 33.8, 39.2, 43.0, 49.7, 66.6, 122.5, 126.9, 129.5, 139.7, 140.0, and 141.4; MS  $m/z$  268 ( $M^+$ ), 234, 216, and 199; HRMS found 268.0356,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{SCl}$  calc.:  $M$  268.0324.

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