JOC*Note*

Palladium−Triethylborane-Triggered Direct and Regioselective Conversion of Allylic Alcohols to Allyl Phenyl Sulfones†

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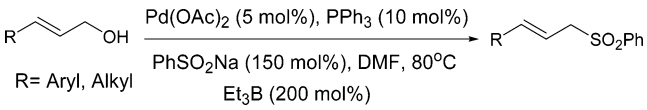
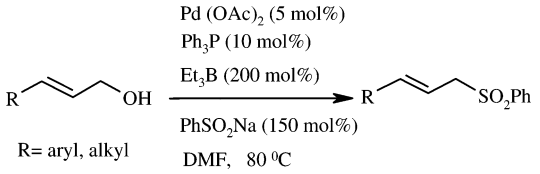
Received March 21, 2005



A combination of $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and Et_3B (200 mol %) promotes the formation of allyl phenyl sulfones from the allylic alcohols directly with excellent yields under mild conditions. The activation of an alcohol group is not necessary which is achieved in situ. The conjugated dienols also were equally effective for the said transformation.

The presence of a phenyl sulfonyl group in a scaffold provides access to multiple diversity.[1] This diversity-driven functionality naturally attracts wide application. The phenyl sulfone group has the ability to stabilize an adjacent carbanion and allows new bond formation reactions. Its utility is enhanced in an "allylic" environment. The allyl sulfone can now become an electrophile[2] and also become an equivalent to a 1,3- or 1,1-dipole, as perfectly exemplified by Trost et al.[3] The phenyl sulfone group was also utilized as a precursor for the radical/radical ion source by using SmI_2[4] and other appropriate reagents.[5] The allyl phenyl sulfones are also an excellent source for regio- and diastereoselective diene synthesis via a Julia olefination procedure.[6] The phenyl sulfonyl group is usually introduced by S_N2 displacement of an alcohol via a halide or mesylate.[7] Alternatives to this are oxidations of existing phenyl sulfides, rearrangement of allylsulfinates, displacement of nitro groups, and so forth.[8] Surprisingly, there is no direct one-step conversion of allyl alcohol to allyl phenyl sulfone,[9] which is highly desirable keeping in mind some of the disadvantages involved in the halogenation, mesylation, nitration, and other activation protocols of allyl alcohols. Tamaru et al. have achieved one-step activation and addition of allyl alcohol moieties onto active methylene groups and indoles under a similar set of conditions.[10]

SCHEME 1



In this note, we report the general and direct conversion of allyl alcohol to allyl phenyl sulfone using $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), Et_3B (200 mol %), and sodium phenylsulfinate (150 mol %) in hot DMF (80 °C) (Scheme 1). Attempts to trigger this reaction with few easily accessible Lewis acids such as $BF_3{\cdot}OEt_2$, $AlCl_3$, and $ZnCl_2$ did not result in the formation of desired product.

We first explored the reaction of cinnamyl alcohol (Table 1, entry 1) with sodium phenylsulfinate under the influence of Et_3B, $Pd(OAc)_2$, and PPh_3 to observe a smooth conversion to the corresponding phenyl sulfone **1a** in a yield of over 80%. To justify the addition of Et_3B, an experiment was carried out in the absence of Et_3B to isolate only 15% of the sulfone product **1a** (Table 2).

A few other experiments were also attempted by changing either the solvent or concentration of catalyst, but it was observed that the optimum amounts of Et_3B (200 mol %), $Pd(OAc)_2$ (5 mol %), and PPh_3 (10 mol %) were essential. In the second instance, the citronellol derivative (Table 1, entry 8) was treated under identical conditions to obtain the corresponding sulfone **8a** in excellent yield without any traces of the allylic rearrangement product. A few other cinnamyl alcohol analogues (entries 2−6) were also ideal precursors for the transformation. To expand the horizon of this new method further, the allyl derivatives of the furanose

† IICT Communication No. 040606.

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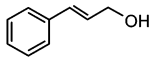
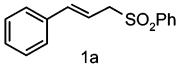
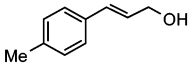
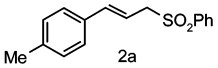
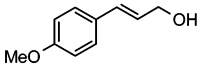
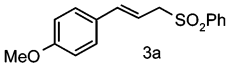
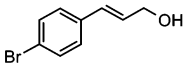
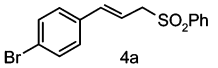
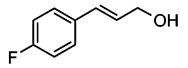
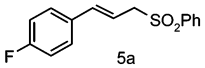
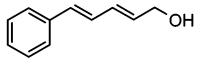
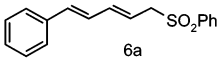
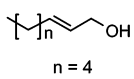
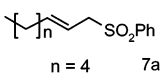
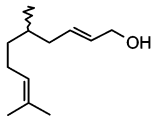
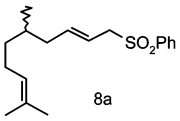
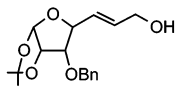
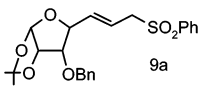
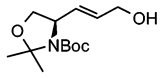
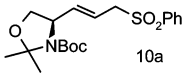
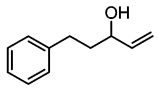
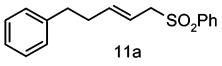
10.1021/jo0505728 CCC: $30.25
Published on Web 07/01/2005

TABLE 1. Palladium−Triethylborane-Triggered Direct and Regioselective Conversion of Allylic Alcohols to Allyl Phenyl Sulfones

Entry	Substrate	Product	Time (h)	Yield[a] (%)
1		 1a	12	94
2		 2a	12	91
3		 3a	12	91
4		 4a	12	81
5		 5a	12	78
6		 6a	12	90
7	 n = 4	 n = 4 7a	16	79
8		 8a	16	89
9		 9a	16	80
10		 10a	16	81
11		 11a	14	92

[a] Yields calculated after column chromatography. Products were characterized by ^{1}H NMR and mass spectrometry.

derivative in entry 9 and amino acid (Garner aldehyde) in entry 10 were treated under the present protocol. Entry 11 describes the displacement reaction on a secondary alcohol that yielded the olefin-migrated product **11a** in 92% yield exclusively. The products thus obtained would be useful precursors for chiral natural and unnatural products synthesis. Mechanistically, we believe Et_3B coordinates with oxygen and Pd(0), forming a π-allylpalladium species that in turn undergoes an S_N2 displacement with the sodium phenylsulfinate (Scheme 2).[11] Further applications of this method are of present interest in our research group.

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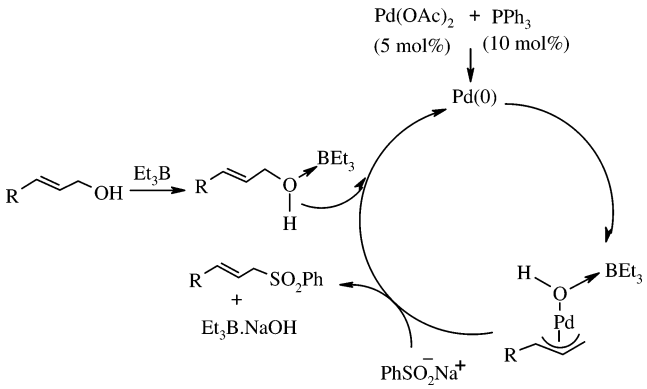
TABLE 2. Palladium−Triethylborane Optimization on Sulfonylation of 3-Phenyl-2-propenol to {[(2*E*)-5-Phenylpent-2-enyl]sulfonyl}benzene

entry	$Pd(OAc)_2$ (mol %)	PPh_3 (mol %)	Et_3B (mol %)	solvent	temp (0 °C)	yield (%)
1	5	10	–	DMF	80	15
2	5	10	50	DMF	80	30
3	5	10	200	THF	65	30
4	5	10	200	CH_3CN	80	30

SCHEME 2. Reaction Mechanism for Allylic Sulfonation of Allylic Alcohols Promoted by $Pd(OAc)_2$-PPh_3/Et_3B



Experimental Section

Typical Experimental Procedure. Into a nitrogen-purged flask containing $Pd(OAc)_2$ (8 mg, 0.03 mmol) and PPh_3 (19 mg, 0.07 mmol) were added successfully DMF (5 mL), cinnamyl alcohol (100 mg, 0.7 mmol), Et_3B (1.49 mL, 1.49 mmol, 1 M solution in THF), and sodium phenylsulfinate (183 mg, 0.7 mmol). The reaction mixture was stirred at 80 °C (see Table 1), during which the reaction was monitored by means of TLC. After dilution with diethyl ether (2 × 30 mL), the mixture was washed with water, the organic layer was dried over Na_2SO_4 and concentrated in vacuo, and the residue is purified by column chromatography over silica gel to provide sulfone (180 mg, 94% yield).

Acknowledgment. V.J., B.S., and C.N. thank CSIR, New Delhi, for financial support. We also thank the reviewers for useful suggestions.

Supporting Information Available: Detailed experimental procedures and compound characterization data (^{1}H NMR, ^{13}C NMR, and HRMS). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0505728