Pergamon

Tetrahedron Letters 39 (1998) 691–694

TETRAHEDRON
LETTERS

Palladium Catalyzed Hydrosulfination of Allenes with Tosylhydrazine Leading to Allylsulfones

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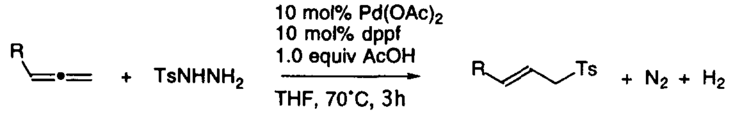
Received 30 September 1997; revised 11 November 1997; accepted 14 November 1997

Abstract: The palladium catalyzed reaction of allenes **1** with tosylhydrazine in the presence of 1 equiv AcOH and 10 mol% dppf gave the corresponding allylsufones **2** in moderate to good yields.

Recently, the attention has been greatly focused on the transition metal catalyzed direct addition of pronucleophiles to an unactivated double bond.[1-4] These addition reactions using transition metal catalysts make it possible to synthesize the targeting compounds directly in short steps, and therefore are very useful from a standpoint of atom economy. We previously reported that activated methylene and methyne compounds (pronucleophiles) add to the double bond of allenes in the presence of palladium catalysts to give the corresponding addition products in good to high yields (hydrocarbonation reaction).[1a-1f] We have continued to investigate the direct addition reaction of not only carbon-pronucleophiles but also heteroatom-pronucleophiles to the double bond of allenes by using palladium catalysts. As a result, we have succeeded in adding nitrogen-pronucleophiles to allenes (hydroamination reaction).[1g] Now, we report that the reaction of allenes **1** with tosylhydrazine in the presence of catalytic amounts of palladium gives the corresponding allylsulfones **2** (eq 1). This is a new type of hydrosulfination reaction[5] catalyzed by palladium complexes in which the tosyl group of tosylhydrazine adds to the double bond of allenes and nitrogen is released from tosylhydrazine.



1 2 (1)

The results are summarized in Table 1. Initially, phenylallene **1a** (1 equiv) was treated with tosylhydrazine (1.2 equiv) in the presence of 5.0 mol% $Pd_2(dba)_3 \cdot CHCl_3$, 10 mol% dppf, and 1 equiv AcOH (acidic condition) in THF at 70°C for 3h, and the corresponding allylsulfone **2a** was obtained in 55% yield (entry 1). The use of 10 mol% $Pd(OAc)_2$, instead of 5.0 mol% $Pd_2(dba)_3 \cdot CHCl_3$, also gave **2a** in 56% yield (entry 2). We tested other palladium catalysts and other phosphine ligands, but the above combination gave the best result with the respect to both chemical yield and reaction time. In addition, the use of 2 equivalents of **1a** increased chemical yield up to 84% yield (entry 3). The reaction using $Pd(OAc)_2$ as a catalyst proceeded

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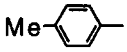
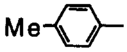
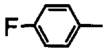
PII: S0040-4039(97)10637-2

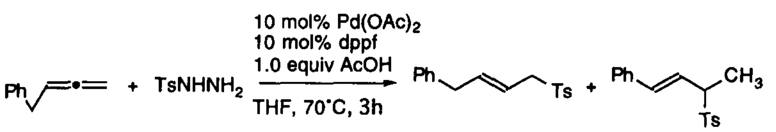
without the addition of AcOH, though it took 6h to complete the reaction (entry 4). The reaction under the neutral conditions gave **2b** in 50% yield (entry 4), and almost the same yield was obtained in the reaction under the acidic conditions (entry 5). To investigate the influence of the electronic effect of the phenyl substituent on chemical yield, *para*-substituted arylallenes **1b** and **1c** were treated with tosylhydrazine. The corresponding allylsulfones **2b** and **2c** were obtained in 55% and 52% yield, respectively (entries 5, 6), suggesting that the electronic effect does not play an important role to chemical yield. Alkyl substituted allenes **1d** and **1e** also reacted with tosylhydrazine to give **2d** and **2e** in 44% and 50% yield, respectively (entries 7, 8).

Table 1. Pd Catalyzed Hydrosulfination Reaction of Allenes[a]

Entry	Allene R	 1	Product 2	Yield, %
1	Ph	**1a**	**2a**	55[b]
2	Ph	**1a**	**2a**	56
3	Ph	**1a**	**2a**	84[c]
4		**1b**	**2b**	50[d]
5		**1b**	**2b**	55
6		**1c**	**2c**	52
7	Hept	**1d**	**2d**	44
8	*t*-Bu	**1e**	**2e**	50

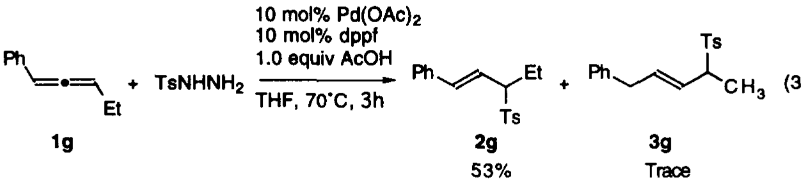
[a] Unless otherwise indicated, the reaction of **1** (1 equiv) with tosylhydrazine (1.2 equiv) was carried out under $Pd(OAc)_2$ (10 mol%) / dppf (10 mol%) / AcOH (1 equiv) catalyst condition in THF at 70°C for 3h. [b] $Pd_2(dba)_3CHCl_3$ (5 mol%) was used. [c] Two equivalents of **1a** was used. [d] No AcOH was added and the reaction time was 6h.

Interestingly, the reaction of benzylallene **1f** with tosylhydrazine gave an isomerized allylsulfone **3f** in 47% yield as a major product along with a trace amount of expected allylsulfone **2f** (eq 2). On the other hand, the reaction of disubstituted allene **1g** with tosylhydrazine gave the expected allylsulfone **2g** in 53% yield as a major product along with a trace amount of isomerized allylsulfone **3g** (eq 3). Although it is not clear why heptylallene **1d** did not give an isomerized product, the formation of isomerized products **3f** and **3g** suggests intervention of π-allypalladium intermediate.



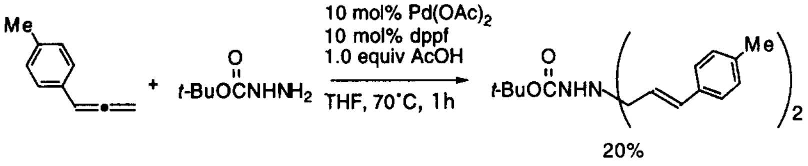
(2)

1f **2f** Trace **3f** 47%



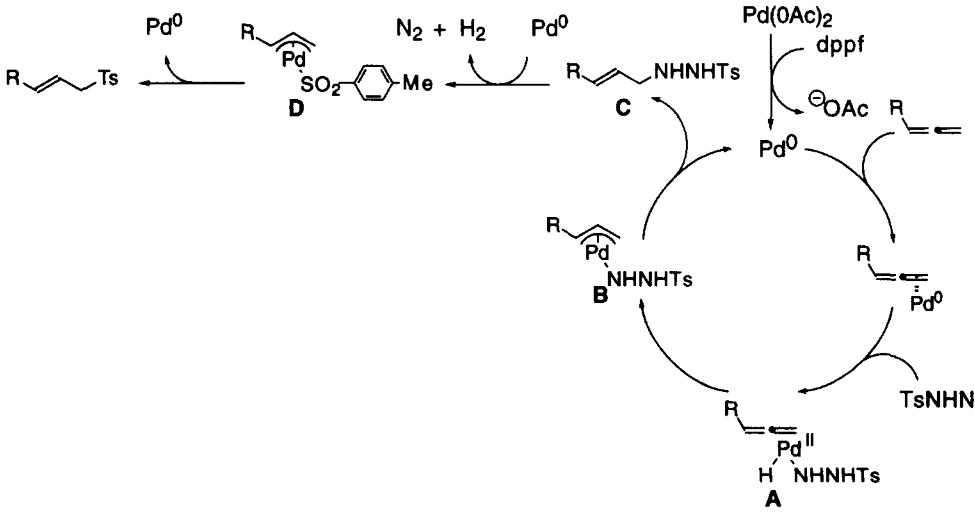
(3)

There are several noticeable points on this hydrosulfination reaction. Firstly, the tosyl group adds regioselectively to the γ-position of allenes. The product arose from the addition at the more hindered α-position was not obtained at all. Secondly, only *trans*-allylsulfones were obtained without the formation of isomeric *cis*-allylsulfones. Thirdly, $Pd(OAc)_2$ catalyzed reactions proceed not only under the acidic conditions but also under the neutral conditions. The addition of AcOH accelerated the reaction. On the other hand, the reaction using $Pd_2(dba)_3 \cdot CHCl_3$ as a catalyst proceeds smoothly only under the acidic conditions. Finally, the reaction of *p*-methylphenylallene with *t*-butyl carbazate under the same conditions as above gave the corresponding allylhydrazine (eq 4). This is a normal hydroamination reaction as observed previously.[1g]



(4)

A proposed mechanism for this hydrosulfination reaction is shown in Scheme 1, although it is speculative. Pd(II) would be reduced in a reaction mixture to Pd(0) species, and the double bond of allene would coordinate to Pd(0). Oxidative insertion of Pd(0) into the N-H bond of tosylhydrazine would produce Pd(II) intermediate **A**. Hydropalladation to the coordinating allene would afford π-allylpalladium intermediate **B**. Reductive elimination would lead to the formation of allylhydrazine intermediate **C**[6] and Pd(0) catalytic species. Subsequently, intermediate **C** would be converted to π-allylpalladium intermediate **D** with releasing N_2 and H_2.



Scheme 1. Hydrosulfination Reaction Mechanism

Reductive elimination would give Pd(0) species and the allysulfones as the final product. The role of acetic acid would probably be the acceleration of the formation of π-allylpalladium intermediate **B**.[7] The reason why isomerized products **3f** and **3g** were obtained in the reaction of **1f** and **1g** with tosylhydrazine could be explained by the formation of 1,3-diene derivatives from π-allylpalladium intermediate **B** and **D**; 1,3-diene derivatives could be produced by β-hydrogen elimination of the π-allylpalladium intermediates. Hydrosulfination reaction of these 1,3-diene derivatives would afford isomerized products **3f** and **3g**.

Although further investigation is needed to clarify the mechanism for the unprecedented hydrosulfination reaction, we are now in a position to synthesize various allysulfones directly from allenes and tosylhydrazine.

The hydrosulfination reaction of phenyallene **1a** with tosylhydrazine is representative. Acetic acid (29 μl, 0.50 mmol) and **1a** (68 μl, 0.50 mmol) were added to a solution of $Pd(OAc)_2$ (11.3 mg, 0.050 mmol) and dppf (27.8 mg, 0.050 mmol) in THF (0.40 ml), then a THF (0.60 ml) solution of tosylhydrazine (111.8 mg, 0.60 mmol) was added under Ar atmosphere. The reaction mixture was stirred for 3h at 70°C. After the completion of reaction, the reaction mixture was filtered through a florisil short column using *n*-hexane/ethyl acetate (1/1) as an eluent. The solvent was evaporated and the product was purified by a silica gel column chromatography using *n*-hexane/ethyl acetate (10/1 - 4/1) as an eluent. 1-(*p*-Methylbenzenesulfonyl)-3-phenyl-2-propene **2a** was obtained in 56% yield (76.6 mg, 0.28 mmol).

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5. For a review, see: Dzhemilev, U. M.; Kunakova, R. V. *J. Organomet. Chem.* **1993**, *455*, 1-27 and references cited therein.
6. The reaction of intermediate C (R = Ph) under the same reaction condition as in eq 1 gave **2a** in 57% yield. Further, the reaction of intermediate C with *t*-butylallene **1e** gave **2a** and **2e** in 26% and 51% yield, respectively.
7. See: ref. 1g.