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Palladium-Catalyzed 1,2-Oxidation of Allenes

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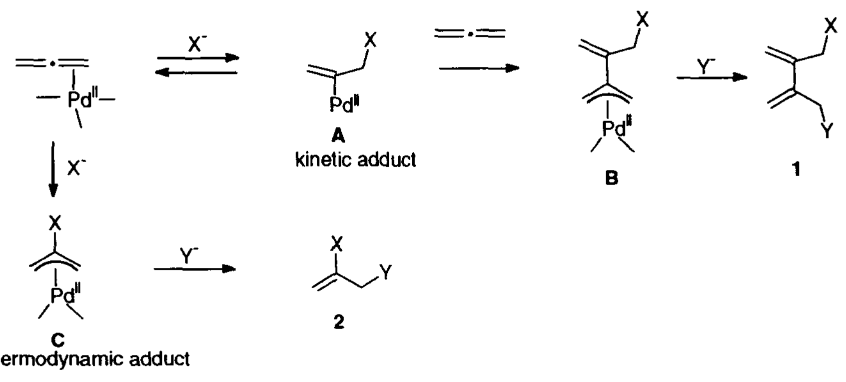
Abstract. Palladium-catalyzed oxidation of allenes with palladium acetate as the catalyst and *p*-benzoquinone as the oxidant in the presence of lithium bromide afforded 1,2-dibromides in a regioselective reaction. The reaction proceeds via a (π-allyl)palladium intermediate. Copyright © 1996 Elsevier Science Ltd

Palladium(II)-catalyzed oxidations of dienes are important organic transformations that have attracted considerable interest during recent years.[1-3] In particular palladium(II)-catalyzed oxidations of 1,3-dienes, which proceed via (π-allyl)palladium complexes, have found extensive use in regio- and stereoselective synthetic transformations.[3] In contrast to 1,3-dienes the corresponding 1,2-dienes (allenes) have found only limited use in palladium(II)-catalyzed oxidations.[4] On the other hand several recent studies have been devoted to palladium(0)-catalyzed reactions of allenes.[5-10] These reactions involve an insertion of the allene into a Pd-carbon or Pd-hydrogen bond.

Our goal was to develop selective oxidation reactions of allenes employing palladium catalysis. In analogy with the palladium-catalyzed 1,4-oxidation of 1,3-dienes we envisaged a 1,2-oxidation of allenes involving nucleophilic attack at carbon-2 of the allene with formation of π-allyl intermediate (Scheme 1 and Scheme 2).

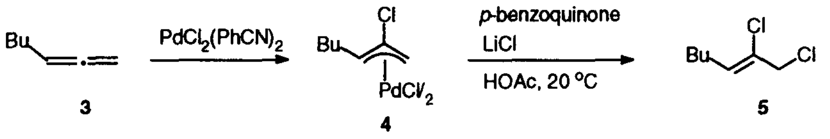
In one study the palladium-catalyzed oxidation of allenes with $CuCl_2$ as the oxidant was found to give dimerization product **1** (X = Y = Cl) in high selectivity (Scheme 1).[4] The problem seems to be that under these reaction conditions the kinetic adduct **A**, which is formed by halide attack at the terminal carbon, and which is in equilibrium with the allene complex, is trapped by insertion of excess allene into the palladium-vinyl bond to give a dimeric complex **B**. The latter complex is attacked by a second nucleophile to give **1**. It is known that

Scheme 1



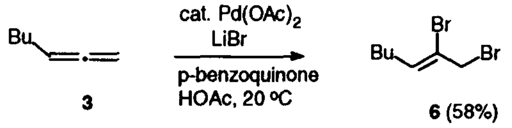
under certain conditions with stoichiometric amounts of palladium chloride, π-allyl complex **C** is formed.[11] We have now found conditions for preferential generation of the latter complex in a catalytic process, thus realizing the cycle in Scheme 2 in analogy with the 1,4-oxidation of 1,3-dienes.

We first studied the stoichiometric reaction for 1,2-oxidation of allenes. Reaction of 1,2-heptyne (**3**) with stoichiometric amounts of $PdCl_2(PhCN)_2$ afforded 2-chloro π-allyl complex **4** in 58% yield in analogy to the procedure described in ref. 11. The π-allyl complex **4** was treated with p-benzoquinone and LiCl in acetic acid,



(1)

which afforded the 1,2-disubstituted product **5** (eq. 1). Attempts to run this reaction under catalytic conditions failed and gave mainly dimer **1** (X = Y = Cl) in analogy with the results by Hegedus,[4] and only minor amounts of the desired 1,2-oxidation product **5** was formed. However, when the same reaction was run with LiBr in place of LiCl the monomeric dibromide **6** was obtained in 58% yield. The use of the phenyl substituted



(2)

allene **7** gave a more efficient reaction and now 1,2-dibromide **8** was isolated in 78% yield (Table 1, entry 2). The results from palladium-catalyzed 1,2-oxidation of a few other substituted allenes are given in Table 1. Thus, allenes **9**, **11**, **13** and **15** afforded the corresponding 1,2-bromides (**10**, **12**, **14**, **16**) in good isolated yields (entries 3-6).[12]

A likely mechanism for the palladium-catalyzed 1,2-oxidation is given in Scheme 2. This mechanism is reminiscent of that of the corresponding 1,4-oxidation of conjugated dienes and involves a (π-allyl)palladium

Scheme 2

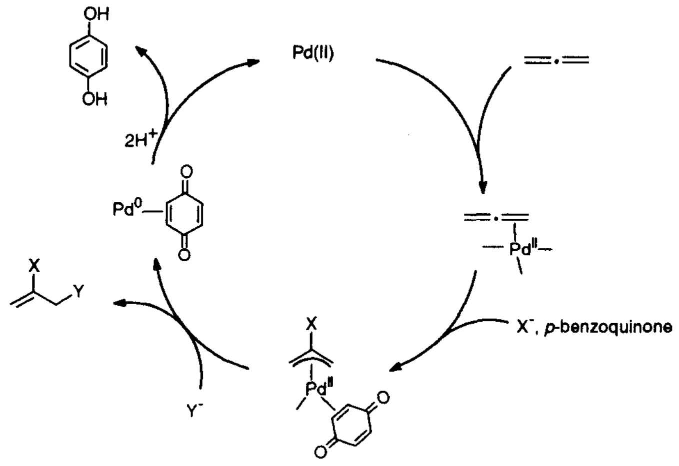
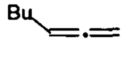
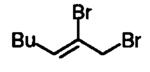
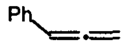
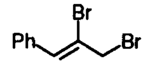
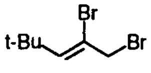
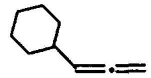
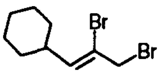
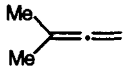
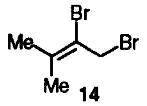
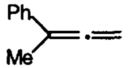
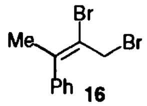


Table 1. Palladium-Catalyzed 1,2-Bromination of 1,2-Allenes[a]

Entry	Allene	Product	*E/Z*	% yield[b]
1	 **3**	 **6**	17/83	58 (84[c])
2	 **7**	 **8**	27/73	78
3	 **9**	 **10**	70/30	54
4	 **11**	 **12**	52/48	69
5	 **13**	 **14**	-	77
6	 **15**	 **16**	92/8	63

a. The reaction was performed at room temperature in acetic acid with 5 mol% of Pd(OAc)$_2$ employing 2.5 equiv. of LiBr and 2.5 equiv. of p-benzoquinone towards the substrate. The concentration of the substrate allene was 0.24 M. The reaction time was 5h except for entry 4 where it was 48h. b. Isolated yield after work-up. Pure samples of *E* and *Z* isomers were obtained by flash chromatography. c. This figure refers to the GC yield.

intermediate as well as Pd-quinone complexes. In both reactions coordination of the diene (1,2- or 1,3-diene) and subsequent nucleophilic attack produces a (π-allyl)palladium intermediate. Coordination of benzoquinone to the metal in the π-allyl complex induces attack by a second nucleophile and gives the product and a Pd(0)-quinone complex. The latter complex undergoes an internal redox reaction to give Pd(II) and hydroquinone.[13]

In a competitive experiments with a mixture of LiBr and LiCl in the palladium-catalyzed 1,2-oxidation of 3-methyl-1,2-butadiene (**13**) a mixture of 1,2-dibromide and 1-chloro-2-bromo product was obtained. Thus, the halide in the 2-position is always bromide.

It is interesting to note that bromination of terminal allenes with Br$_2$ gives the 2,3-dibromide.[14] The present method produces the 1,2-dibromide in high selectivity and under very mild oxidative conditions which should tolerate a variety of different functionality.

The products obtained from the palladium-catalyzed 1,2-bromination of allenes should be useful for further transformations. For example, 1,2-bromoalkenes are useful as masked α-bromoketone equivalents.[15] Furthermore, the allylic halide can be substituted by nucleophiles either very mildly via Pd(0) catalysis or thermally via an S$_N$2 reaction. The vinyl bromide thus obtained can undergo a number of transformations such as metal-catalyzed carbonylation,[16] palladium-catalyzed coupling reactions,[17] or coupling with a cuprate.[18]

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12. Selected NMR data: **1,2-Dibromo-3-methyl-2-butene (14)** ^{1}H NMR ($CDCl_3$) δ 4.37 (s, 2H, CH_2Br), 1.92 (s, 3H, CH_3), 1.86(s, 3H, CH_3); ^{13}C NMR ($CDCl_3$,) δ 138.6, 115.7, 36.3, 25.8, 20.5; **(*E*)-1,2-Dibromo-3-phenyl-2-butene (16)** ^{1}H NMR ($CDCl_3$) δ 7.42-7.25 (m, 5H, aromatic), 4.21 (q, J = 0.7 Hz, 2H, CH_2Br), 2.23 (t, J = 0.7 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$,) δ 142.8, 140.4, 128.7 (two C), 127.9, 126.9 (two C), 120.1, 37.9, 26.5.
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