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STEREOSPECIFIC PALLADIUM-PROMOTED VICINAL DIAMINATION OF OLEFINS

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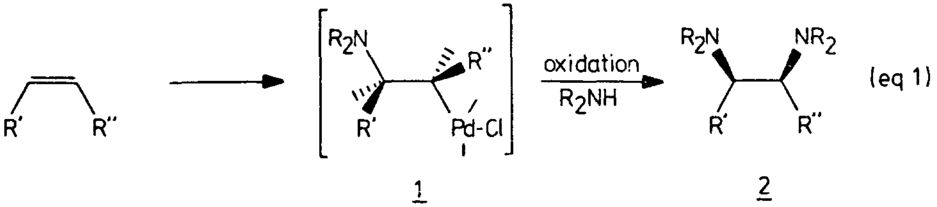
We have recently reported on the palladium-promoted oxyamination[1] and aziridination[2] of olefins. These transformations were obtained by aminopalladation[3] of the olefin followed by an oxidative cleavage of the palladium-carbon bond in the adduct. In the oxyamination study it was found[1] that vicinal diamines are formed as side-products from terminal olefins in the presence of excess amine. This observation led us to study the oxidation of β-aminoalkylpalladium compounds 1 in the presence of amine, using different oxidizing agents. We report here that olefins can be stereospecifically transformed into vicinal diamines 2 by an aminopalladation-oxidation sequence (eq 1), using oxidants such as bromine, *m*-chloroperbenzoic acid (MCPBA), and N-bromosuccinimide (NBS).



(eq 1)

Amination of the appropriate olefin at -40° gave the adduct 1. Treatment of 1 *in situ* with Br_2, MCPBA or NBS in the presence of amine produced the vicinal diamine. The following procedure was used in a small scale preparative experiment: $PdCl_2(C_6H_5CN)_2$ (3.84 g, 10 mmol) and 1-hexene (1.68 g, 20 mmol) were stirred in THF (30 ml) at 0°, under nitrogen, for 5 min. The solution was cooled to -40° and 30 ml of a 3 M dimethylamine solution in THF was added during 15 min under stirring. After the addition was complete, the reaction mixture was stirred for 45 min at -40°. MCPBA (10 mmol, 2.03 g (85% Aldrich)) was added and the temperature was maintained for an additional 15 min. The cooling bath was removed and the reaction mixture was allowed to reach room-temperature. After 3 hrs KBH_4 (0.6 g) was added, followed by slow addition of 10 ml of a 2 M NaOH solution. After stirring for 15 min the palladium black was filtered off and washed with ether. The organic phase was treated with charcoal and extracted with 4 M HCl (3 x 7 ml), the extract was washed with ether (2 x 5 ml) and made alkaline with NaOH pellets. The alkaline aqueous phase was extracted with ether (3 x 10 ml), the ether phase dried (K_2CO_3) and evaporated. Fractional distillation of the residue gave 0.95 g 1,2-bis(dimethylamino)hexane (56%), bp 95° (40 mm) (lit[4] bp 93-94° (35 mm)).

Table 1. Palladium-Promoted Diamination of Olefins

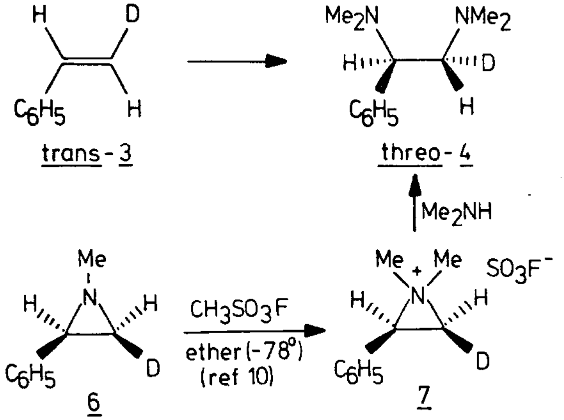
Olefin R'CH = CHR''	Oxidant	% Yield[a] of Vicinal Diamine[b] R'CH(NMe_2)CH(NMe_2)R''
Ethene	Br_2	60
1-Butene	Br_2	70
trans-2-Butene[g]	MCPBA[c]	45 (>95% *threo*)
1-Hexene	MCPBA	77 (56[d])
1-Decene	Br_2	70
1-Decene	$Pb(OAc)_4$	60[e]
1-Decene	MCPBA	81
1-Decene	NBS[f]	71
Styrene	Br_2	74
Styrene	MCPBA	87
trans-2-Octene[g]	MCPBA	35 (>97% *threo*)

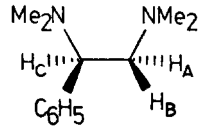
a. Yields were determined by glc and are based on the amount of palladium used. Unless otherwise noted, all reactions were run on a 1.6 mmol scale, as described in detail for a 10 mmol scale reaction of 1-hexene, using a two to fourfold excess of the olefin. b. All of the compounds were characterized by spectral methods and all new compounds gave correct elemental analyses. c. *m*-Chloroperbenzoic acid. d. Isolated yield after distillation from a 10 mmol scale experiment. e. In this case 10% of β-aminodecylacetate was formed together with the diamine. f. N-bromosuccinimide. g. These olefins gave about the same yield with Br_2 but in this case the stereoselectivity was lower.

The results in Table 1 show that terminal olefins are diaminated in good yields. Yields from internal olefins are lower, mainly due to the lower reaction rate[5] of these olefins in the aminopalladation step. *m*-Chloroperbenzoic acid (MCPBA) appears to be the most efficient oxidizing agent. Oxidants other than those shown in Table 1 were tried without success. Thus oxidation of the dimethylaminopalladation adduct from 1-decene with *tert*-butylhydroperoxide gave only 12%, and potassium persulfate only traces of the diamin. Chromium trioxide, potassium bichromate or cerium(IV) sulfate gave no detectable amount of vicinal diamine.

When bromine was used as the oxidant it was expected that some diamine would form from vicinal dibromide, the latter being expected from attack by bromine on the unreacted olefin. However, control experiments[6] showed that no diamine was formed from 1,2-dibromodecane under the reaction conditions.

The diamination process is stereospecific. *cis*- and *trans*-β-Deuteriostyrene (3)[7,8] were diaminated[9] and gave in each case a different diastereoisomer, as shown by NMR-analysis. For the configurational assignement of these diastereoisomers, and hence stereochemical assignment of terminal protons in the undeuterated diamine 5, *threo*-4 was prepared by an independant method from the aziridine 6[2], *via* the aziridinium salt 7. The diamine *threo*-4 obtained in this way was identical to the diamination product from *trans*-3, thus showing that the diamination process is an over-all *cis*-process (>90% *cis*-addition).





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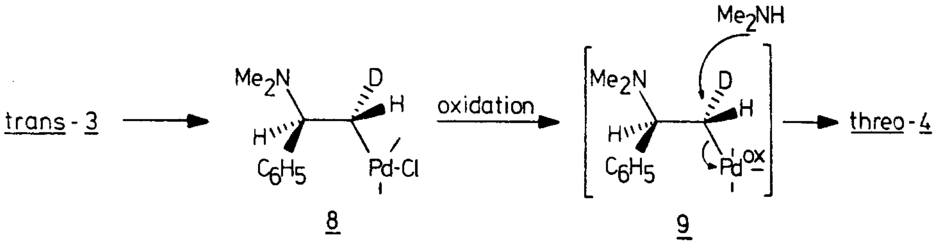
NMR-data for 5 (CCl_4, TMS)
H_A = 2.49, H_B = 2.68,
H_C = 3.31 ppm
J_{AB} = 12.7, J_{AC} = 7.3,
J_{BC} = 6.0 Hz

A probable mechanism for the diamination reaction is outlined in Scheme 1. In the first step the olefin undergoes a *trans*-aminopalladation[11] to give the σ-complex 8. This step is followed by an oxidation-induced nucleophilic displacement of palladium by amine. On oxidation, 8 is probably transformed into an oxidized intermediate 9, which may be a palladium(IV) complex.

Scheme 1



Organopalladium(IV) compounds have been suggested previously[2,12] in the bromine-promoted nucleophilic displacement of palladium, and an organopalladium(IV) complex has recently been reported[13] to form on oxidative addition of chlorine to the corresponding palladium(II) complex. Inversion of configuration at carbon in the oxidative cleavage of palladium-carbon bonds appears to be a general phenomenon when the replacing nucleophile is free in solution[1,2,12,14]. This inversion mechanism is also found in the oxidative cleavage of iron-[15] and cobalt-carbon[16] bonds.

Vicinal diamination of olefins is of potential synthetic interest. Although the diamination procedure presented here has limitations, our results should nevertheless be useful since vicinal diamines are not easily prepared from olefins by other methods[17].

The results in this paper do not only show that vicinal diamines can be prepared from olefins in a "one-pot" procedure but also show that a number of different oxidants promote the nucleophilic displacement of palladium.

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6. To a solution of $PdCl_2(C_6H_5CN)_2$ (0.78 mmol) in THF (5 ml) at -40° was added 3 ml of a 2.5 M solution of dimethylamine in THF, followed by 1,2-dibromodecane (0.78 mmol). Following the usual workup procedure no 1,2-bis(dimethylamino)decane could be detected.
7. *trans*-β-Deuteriostyrene was prepared by hydroalumination[8a] of phenylacetylene followed by D_2O quenching and *cis*-β-deuteriostyrene by hydroalumination of β-deuteriophenylacetylene followed by H_2O quenching. Unfortunately, the formation of $C_6H_5C{\equiv}CAlR_2$ during the reaction resulted in some unchanged phenylacetylene at the end of the reaction. Unchanged phenylacetylene was removed by treatment with $CuCl$-NH_3.
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17. Except for indirect routes *via* aziridines or *via* vicinal dibromides (which give vicinal diamines on high temperature aminolysis), vicinal diamines have to our knowledge been prepared from olefins in only two other instances. Compound 5 has been reported to form in 30% yield, when styrene was reacted with dimethylaminoradicals in the presence of $ZnCl_2$ (C.J. Michejda and D.H. Campbell, *J. Amer. Chem. Soc.*, 96, 929 (1974)). It has recently been reported that bis- and tris(*tert*-butylimido) osmium(VIII) compounds transform an olefin into the corresponding 1,2-bis(*tert*-butylamino)alkane. (A.O. Chong, K. Oshima and K.B. Sharpless, *J. Amer. Chem. Soc.*, 99, 3420 (1977)).