Novel Palladium-Catalyzed Diarylation and Dialkenylation Reactions of Norbornene Derivatives

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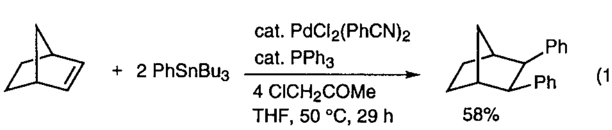
Abstract: Norbornene and its derivatives are diarylated or dialkenylated by aryl- or alkenyltributylstannanes, a palladium catalyst, and chloroacetone or chloroacetonitrile as a reoxidant.

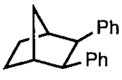
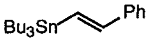
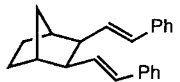
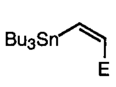
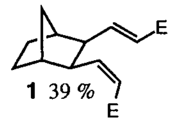
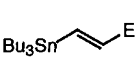
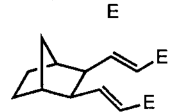
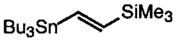
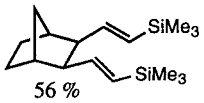
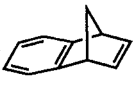
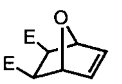
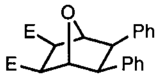
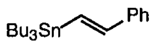
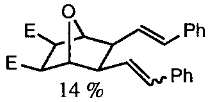
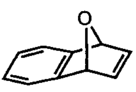
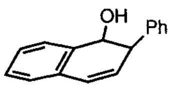
Transition metal catalyzed ternary coupling reaction, i.e., insertion of alkynes or alkenes into a cross–coupling reaction, is one of the recent interests.[1] Insertion of alkynes or alkenes into a homocoupling reaction is considered to be included in a similar category.[2,3] We recently reported a palladium-catalyzed stereoselective difunctionalization reaction of some internal alkynes by organotributylstannanes using copper(II) chloride as a reoxidant.[4] In this reaction, however, only limited internal alkynes (diphenylacetylene and acetylenedicarboxylate) and aryltributylstannanes were tolerable. Alkenyl- and alkynyltributylstannanes did not give the addition products at all, in this reaction. In 1993, Kikukawa *et al.* reported the oxidative homocoupling of organostannanes using chloroacetone or chloroacetophenone as a reoxidant.[5] We attempted to employ chloroacetone as a reoxidant for our difunctionalization reaction and found that norbornene and its derivatives could be difunctionalized by alkenylstannanes as well as arylstannanes. We report here our results.



(1)

To a tetrahydrofuran (THF) solution of dichlorobis(benzonitrile)palladium(II) (0.1 mmol) and triphenylphosphine (0.15 mmol) were added tributylphenylstannane (2.2 mmol), chloroacetone (4.0 mmol), and norbornene (1.0 mmol), successively. The resulting yellow solution was stirred at 50 °C for 29 h. The resulting brown mixture was diluted with hexane and washed with aqueous ammonium fluoride solution. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated to about 10 mL. The residual colorless solution was passed through a short silica gel column using hexane as the eluent. The elute was concentrated and the residual oil was subjected to silica gel column chromatography to provide *exo-cis*-2,3-diphenylbicyclo[2.2.1]heptane in 58% yield. The representative results are summarized in Table 1. *Exo-cis* products were the predominant or exclusive products in all cases. None of other isomers could be isolated. Chloroacetonitrile could be employed as a reoxidant as well as chloroacetone (run 2), whereas the following halides were not effective at all; bromoacetone, bromoacetonitrile, carbon tetrachloride, carbon tetrabromide, and chloroform. The alkenylations with (*E*)-alkenylstannanes were stereospecific, although not perfect, giving the 2,3-dialkenylbicyclo[2.2.1]heptanes mainly with retention of the geometries. The minor products if formed were the corresponding *E*,*Z*-isomers. On the other hand, the reaction of (*Z*)-tributylstannylacrylate was interesting. The main product was *exo-cis*-2-[(*Z*)-methoxycarbonylethenyl]-3-[(*E*)-methoxycarbonylethenyl]bicyclo-[2.2.1]heptane and *exo-cis*-(*Z*,*Z*)-2,3-bis(2-methoxycarbonylethenyl)-bicyclo[2.2.1]heptane was not detected at all (run 3). Isomerization alkenylstannanes was never observed in any case. In every case, the major byproduct was an 1,3-butadiene derivative formed *via* the direct homocoupling of the alkenylstannanes. To suppress its formation, the use of an excess of norbornene was inevitable (runs 2-5 and 8), while a stoichiometric amount of norbornene was enough in the diarylation (runs 1,6,7, and 9). The amount of chloroacetone could be reduced to 0.55 mol equiv to the stannane without lowering the yield (run 5).

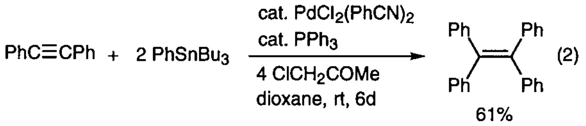
Table 1. Palladium(II) catalyzed dialkenylation and diarylation[a,b]

run	norbornene derivative	stannane	time	products yields/%
1[c]		$PhSnBu_3$	29 h	 58 %
2[d,e]			3 d	 76 %
3			41 h	 **1** 39 %
4[f]			22 h	 58 %
5			24 h	 56 %
6[c]		$PhSnBu_3$	51 h	 43 %
7[c]		$PhSnBu_3$	7 d	 trace
8			24 h	 14 %
9[c]		$PhSnBu_3$	35 h	 61 %

[a] Norbornene (1.4 mol equiv) and chloroacetone (1.8 mol equiv) were used at 50 °C in THF and the yields are based on the stannane, unless otherwise noted. [b] E : CO_2Me [c] Norbornene (1.0 mol equiv) was used. [d] Chloroacetonitrile was used in place of chloroacetone. [e] Equimolar amounts of norbornene and the stannane were used. [f] The stereoisomer **1** was also obtained in 11% yield

Diphenylation was examined with some norbornene derivatives. Benzonorbornene was diphenylated to afford the desired adduct in a moderate yield (run 6). On the other hand, the reaction of benzooxanorbornene resulted in monophenylation along with the ring cleavage to give 1,2-dihydro-2-phenyl-1-naphthol as a sole product (run 9).[6] Interestingly, the reaction of dimethyl *exo*-*cis*-7-oxabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate afforded the desired diarylated product and dialkenylated product, although the yields were not high, without giving the corresponding ring-opened side products, at all.

In our previous report, some internal alkynes were diarylated when copper(II) was a reoxidant, while norbornene derivatives could neither be diarylated nor dialkenylated.[4] On the other hand, with the present system, not only norbornenes but also diphenylacetylene could be diphenylated, although the yield was not as high as that in the copper case (eq 2).[7] Attempts to dialkenylate alkynes failed, however.



The present results suggest that choice of the reoxidant may alter the applicable pair of the substrates. Exploitation of other effective oxidants for further applicability and investigations of the reaction mechanism are now under way.

References and Notes

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7 The reaction at 50 °C for 3 d resulted in the formation of 20% yield of the desired product accompanied with a mixture of intractable byproducts.