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THE PALLADIUM-CATALYZED CROSS-COUPLING REACTION OF 1-ALKENYLBORANES WITH ALLYLIC OR BENZYLIC BROMIDES. CONVENIENT SYNTHESES OF 1,4-ALKADIENES AND ALLYLBENZENES FROM ALKYNES VIA HYDROBORATION

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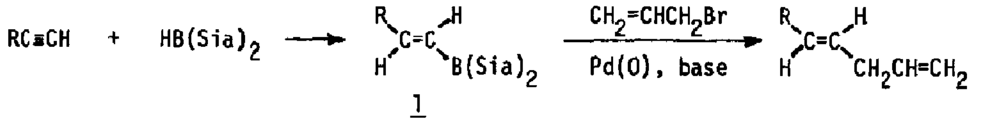
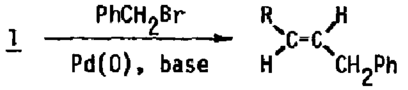
Summary: The reactions of allylic or benzylic bromides with 1-alkenyldisiamylboranes readily available from 1-alkynes in the presence of sodium hydroxide and catalytic amounts of tetrakis-(triphenylphosphine)palladium to give corresponding 1,4-alkadienes or allylbenzenes in good yields.

1-Alkenylboranes, readily obtainable from alkynes via hydroboration, have been recently shown to be a versatile synthetic intermediate.[1] Previously, we have discovered that 1-alkenylboranes readily react with alkyl halides such as alkenyl halides,[2] alkynyl halides,[2] and aryl halides[3] in the presence of catalytic amounts of palladium catalyst to give the cross-coupling products. In an attempt to develop the reaction of such alkenylboranes, we examined the possibility of palladium catalyzed cross-coupling reactions with allylic and benzylic bromides. The reactions provide new stereoselective procedures for the syntheses of 1,4-alkadienes (eq. 1) and allylbenzenes (eq. 2).



(1)

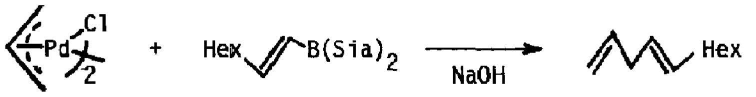


(2)

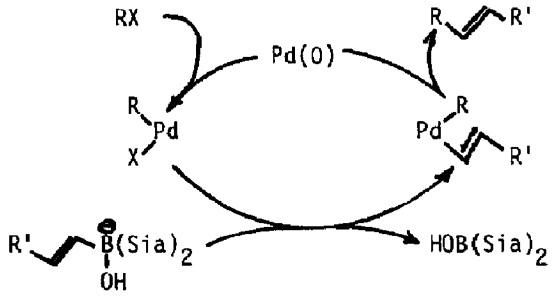
When we initially attempted the reaction of 1-alkenyldisiamylboranes[1] in benzene with allylic or benzylic bromides in the presence of palladium complexes such as tetrakis(triphenylphosphine)-palladium, unsatisfactory results were obtained. However, an addition of bases to such a reaction mixture was found to cause the reaction to proceed smoothly. The reaction is catalytic with respect to the palladium complex employed. Among various kinds of bases we examined, aqueous sodium hydroxide was satisfactory for the reaction reported here. Lewis bases such as trialkylamines did not accelerate the desired cross-coupling reaction. Under such conditions, the reaction took place readily without producing significant amounts of any other by-products.[5]

The following procedure for the preparation of 1-phenyl-2-heptene is representative. A dry 25 ml-flask was charged under nitrogen atmosphere with 0.173 g (0.15 mmol) of $Pd(PPh_3)_4$[6] and 5 ml of dry benzene. To this solution was added benzyl bromide (1.03 g, 6 mmol) at room temperature. After stirring for 10 min, (E)-1-butenyldisiamylborane[7] in benzene (10 ml of 0.5 M solution) and aqueous 2M-NaOH (5 ml) were added. The reaction mixture was refluxed for 2 h under stirring, followed by oxidation with 3M-NaOH (1.5 ml) and 30%-H_2O_2 (1.5 ml) for 1 h at room temperature to remove the residual organoborane. The product was extracted with benzene, and the extract thus obtained was analyzed by GLC, revealing the formation of 1-phenyl-2-heptene (4.95 mmol, 9 An analytically pure sample was obtained by preparative GLC (20%-Silicone SE-30 on Uniport B, after distillation. The GLC examination of the product indicated the presence of a sharp sin peak (>99%), presumably E-isomer, the stereochemistry of which was established by IR (965 cm^{-1}) and direct comparison with the authentic sample of Z-isomer.[8]

Representative results of the present reaction are summarized in Table 1. This new cross coupling reaction is applicable to representative 1-alkenyldisiamylboranes and allylic or benz bromides. However, allylic acetates, such as 3-acetoxycyclohexene and allylacetate were not applicable. In the reaction with 1-bromo-2-butene the carbon-carbon bond formation occured two positions, the ratio of straight to branched chain dienes was 72:28, in accordance with th mechanism involving π-allylpalladium intermediate.[9] It was found that di-μ-chlorobis(η-allyl) palladium[10] obtained from allyl chloride and sodium palladate in the presence of carbon monoxi reacts with an equimolar amount of (E)-1-octenyldisiamylborane in the presence of aqueous NaOH give the 1,4-undecadiene in a 36% yield within 30 min at 0 °C (eq. 3). Consequently, the π-allylpalladium formed via the oxidative addition of allyl bromides to Pd(PPh$_3$)$_4$ seems to be intermediate in this reaction. Thus, the most plausible catalytic cycle for the reaction is lined in Scheme 1 as proposed in other related palladium catalyzed reactions.[11]



(3)

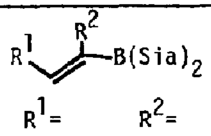


RX = allylic or benzylic bromide.

Scheme 1

Although there have been other published procedures which provide similar conversion by means of hydrometalation such as hydroalumination,[12] hydroboration,[13] and hydrosilylation,[14] the scope of many of these reactions is limited by the nature of the metalhydrides involved or procedure employed.

Table 1. Palladium-Catalyzed Cross-Coupling Reaction of 1-Alkenyldisiamylboranes with Allylic or Benzylic Bromides a)

 R^1=	R^2=	Allylic or benzylic bromide c)	Product	Yield b) (%)
Butyl	H	CH_2=$CHCH_2Br$	1,4-Nonadiene	87
Butyl	H	CH_3CH=$CHCH_2Br$	2,5-Decadiene	53
			3-Methyl-1,4-nonadiene	21
Butyl	H	3-Bromocyclohexene	1-(3-Cyclohexenyl)-1-hexene	42
Butyl	H	$PhCH$=$CHCH_2Br$	1-Phenyl-1,4-nonadiene	53
Butyl	H	$PhCH_2Br$	1-Phenyl-2-heptene	99
Hexyl	H	$PhCH_2Br$	1-Phenyl-2-nonene	75
Ethyl	Ethyl	$PhCH_2Br$	2-Ethyl-1-phenyl-2-pentene	86
Phenyl	H	$PhCH_2Br$	1,3-Diphenylpropene	97
Butyl	H	p-$BrPhCH_2Br$	1-(4-Bromophenyl)-2-heptene	48
Butyl	H	m-$MePhCH_2Br$	1-(4-Methylphenyl)-2-heptene	99
Butyl	H	p-MeO_2CPhCH_2Br	1-(4-Carbomethoxyphenyl)-2-heptene	75

a) The reactions of alkenylboranes with allylic or benzylic halides were carried out in benzene at reflux temperature for 2 h by using 3 mole % of $Pd(PPh_3)_4$ as a catalyst and two equivalents of aqueous 2M-NaOH as a base.

b) Based on the alkenylborane employed and determined by GLC.

c) The ratio of allylic bromide/alkenylborane = 2, and benzylic bromide/alkenylborane = 1.2 for all the cases.

References and Notes

1) C. F. Lane and G. W. Kabalka, Tetrahedron, 32, 981 (1976).
2) N. Miyaura, K. Yamada, and A. Suzuki, Tetrahedron Lett., 3437 (1979).
3) N. Miyaura and A. Suzuki, J. Chem. Soc. Chem. Comm., 866 (1979).
4) The corresponding 2-(1-alkenyl)-1,3,2-benzodioxaboroles[2,3] were found to be not suitable for these reactions, because undesirable side reactions, allylation and benzylation of catechol occur competitively.
5) In the reaction with 1-bromoethylbenzene, we obtained the homocoupling product, 2,3-diphenylbutane as the main product.

6) D. R. Coulson, Inorg. Synth., 13, 121 (1972).
7) After the hydroboration of alkynes with disiamylborane, THF was evaporated at 15 mmHg for 2 h, and then the residue was dissolved in dry benzene. On the hydroboration of alkynes, see H. C. Brown, "Organic Synthesis *via* Boranes," John Wiley & Sons, New York, 1975.
8) An authentic sample of the Z-isomer of 1-phenyl-2-heptyne was prepared by the hydroboratio protonolysis[7] of 1-phenyl-2-heptyne, and its retention time on GLC (capillary column, apiezon grease, 45 m) was longer than that of the E-isomer.
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