Tetrahedron Letters Vol. 22, pp 127 - 130
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0040-4039/81/0108-0127$02.00/0

A STEREOSPECIFIC SYNTHESIS OF CONJUGATED (E,Z)- AND (Z,Z)-ALKADIENES BY A PALLADIUM-CATALYZED CROSS-COUPLING REACTION OF 1-ALKENYLBORANES WITH 1-ALKENYL BROMIDES

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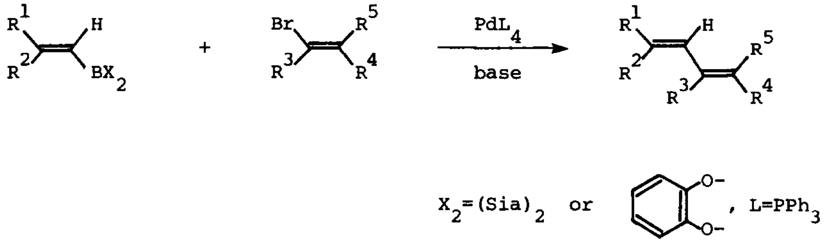
Summary: The reactions of (Z)-1-alkenyldisiamylboranes with (Z)- or (E)-1-alkenyl bromides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium and sodium ethoxide gave the corresponding conjugated (Z,Z)- or (Z,E)-alkadiene with high stereospecificity. The reactions of (E)-1-alkenyl-1,3,2-benzodioxaboroles with (Z)- or (E)-1-alkenyl bromides similarly gave the corresponding coupled products while retaining the configurations of the starting alkenylboranes and the alkenyl bromides.

The (E)- and (Z)-forms of 1-alkenylboranes are easily prepared *via* hydroboration of appropriate alkynes or haloalkynes. This availability of both geometrical forms of 1-alkenylboranes is a great advantage over other related alkenylmetallics as a reagent for the coupling reaction; once stereospecificity in the C-C bond formation by the reaction of these stereo-defined alkenylboranes with organic halides is established, the reaction permits the synthesis of alkadienes while preserving their geometry in an exactly predicted manner.

We have previously reported that the reactions of (E)-1-alkenylboranes with a variety of organic halides, i.e., 1-alkenyl,1) 1-alkynyl,1) aryl,2) allylic,3) and benzylic halides,3) in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$ as well as a base yielded the corresponding cross-coupled products in high yields. The alkenes or the dienes obtained by the reactions of (E)-1-alkenylboranes with organic halides or with (E)-alkenyl halides were alkenes having (E)-configuration or dienes having (E,E)-configurations in all the cases, suggesting that the reaction takes place while retaining the original configurations of both the starting alkenylboranes and the halides.

We now wish to report that the reaction of (Z)-1-alkenylboranes4) with (Z)-1-alkenyl bromides or with 1-haloalkyne also takes place readily under conditions similar to the case of the (E)-isomer and gives almost exclusively the cross-coupled products while retaining the original

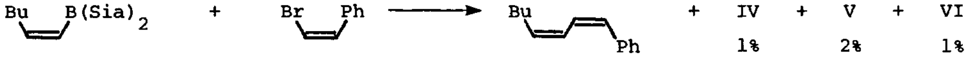


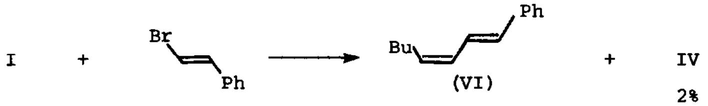
(1)

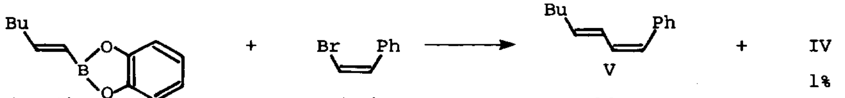
configurations of the alkenylboranes and the alkenyl bromides [Eq. (1), e.g., R^1=H, R^2=butyl, R^3=R^4=H, R^5=Ph].

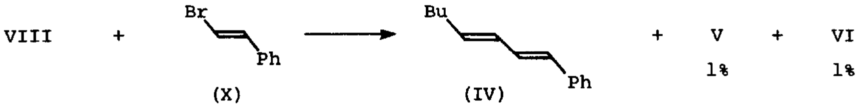
(Z)-1-Hexenyldisiamylborane (I) and (Z)-β-styryl bromide[5] in benzene containing two equivalents of 2 mol dm^{-3} sodium ethoxide in ethanol and 1-3 mole % of $Pd(PPh_3)_4$ were heated under reflux for 2 h. The product, separated by preparative GLC, was (1Z,3Z)-1-phenyl-1,3-octadiene (III), a thermodynamically most unstable diene amongst the four possible isomers, in a 37% yield. Three other isomeric dienes, (1E,3E)- (IV), (1Z,2E)- (V), and (1E,3Z)-dienes (VI) were also obtained but only in very low yields (1, 2 and 1%) [Eq. (2)]. Similarly, the reactions of (Z)-1-hexenyldisiamylborane (I) with (E)-β-styryl bromide (VII) gave (1E,3Z)-diene almost exclusively [Eq. (3)].

The reactions of (E)-1-hexenyl-1,3,2-benzodioxaborol (VIII) with (Z)-β-styryl bromide or with the isomeric (E)-olefin under the similar conditions gave (1E,3Z)-1-phenyl-1,3-octadiene or its (1E,3E)-isomer as the almost exclusive products in 86 and 91% yields [Eqs. (4) and (5)], while accompanied by their isomeric dienes as the minor products.[6]


(I) (II) (III) 37% + IV 1% + V 2% + VI 1% (2)

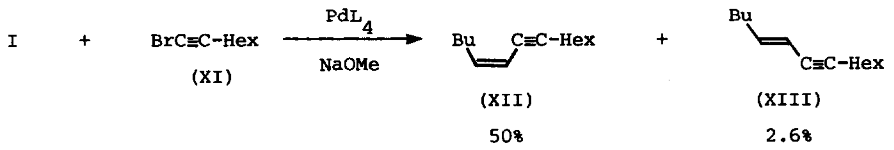

I + (VII) → (VI) 49% + IV 2% (3)


(VIII) + (IX) → V 86% + IV 1% (4)


VIII + (X) → (IV) 91% + V 1% + VI 1% (5)

The reaction of (Z)-1-hexenyldisiamylborane (I) with 1-bromooctyne (XI) was also found to yield (5Z)-5-tetradecen-7-yne (XII) in a 50% yield, accompanied by a 2.6% yield of (5E)-isomer

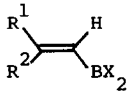
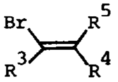
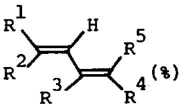
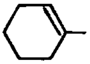
(XIII) [Eq. (6)]. The (Z)-configuration of (XII) was confirmed by the magnitude of the coupling constant of the olefinic protons in the NMR spectrum (J = 11 Hz) and by the absence of a band at 955 cm^{-1} in the IR spectrum.



(6)

The results including those from the reactions of several more (E)- and (Z)-alkenylboranes with a variety of (E)- and (Z)-alkenyl bromides are summarized in the Table. The results clearly show that this palladium-catalyzed alkenyl-alkenyl cross-coupling reaction is highly stereospecific and gives the products while retaining the original configurations of both the starting alkenylboranes and the halides.

Table. Results of Palladium-catalyzed Cross-coupling Reaction of 1-Alkenylboranes with 1-Alkenyl Bromides[a]

Expt. No.							$Pd(PPh_3)_4$ mol %	Yield[b] of  (%)	Isomeric purity (%)
	R^1	R^2	X_2[c]	R^3	R^4	R^5			
1	Bu	H	BDOB	H	H	Ph	1	86	98
2	H	Bu	Sia	H	Ph	H	3	49	99
3	H	Bu	Sia	H	H	Ph	3	42	89
4	Bu	H	BDOB	H	H	Hex	1	88	99
5	H	Bu	Sia	H	H	Hex	3	49	98
6	Ph	H	BDOB	H	H	Ph	3	89	98
7		H	BDOB	H	H	Ph	3	87	98
8	H	Bu	Sia	Ph	H	H	3	55[d]	99

[a] The reaction was carried out in benzene containing two equivalents of 2 mol cm^{-3} sodium ethoxide in ethanol at 80 °C for 2 h under nitrogen, using 10% excess of 1-alkenyl-1,3,2-benzodioxaboroles or 30% excess of 1-alkenyldisiamylboranes.

[b] Based on GLC analysis. The isolated products were adequately characterized by IR, ^1H NMR, the mass spectra and the elemental analyses.

[c] Sia; 3-methyl-2-butyl, BDOB; 1,3,2-benzodioxaboryl

[d] This diene is thermally unstable and isomerizes to 2-phenyl-2,4-octadiene in a 88% yield at 200 °C for 1 h. Care must be exercized in GLC analysis or in distillation to keep the temperature as low as possible.

The following procedure for the preparation of (5Z,7Z)-5,7-tetradecadiene is typical. A dry 50 ml-flask equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser is flushed with nitrogen. In the flask is placed a mixture of $Pd(PPh_3)_4$[7)] (0.162 g, 0.15 mmol) in 10 ml of benzene, (Z)-1-hexenyldisiamylborane[8,9)] (6.5 ml of 1 mol dm^{-3} solution in benzene, 6.5 mmol), sodium ethoxide in ethanol (5 ml of 2 mol dm^{-3} solution, 10 mmol) and (Z)-10-octenyl bromide[10)] (0.955 g, 5 mmol) under nitrogen. After reflux for 2 h, the unreacted organoborane is removed by oxidation by adding of 3 mol dm^{-3} aqueous sodium hydroxide (2.0 ml) and 30% hydrogen peroxide (2.0 ml) to the solution successively and stirring for 2 h at room temperature. After the usual work-up the product is extracted with hexane.

Analysis of the extracts by GLC indicated the formation of 2.45 mmol (49%) of (5Z,7Z)-tetradecadiene. An analytically pure sample was obtained by preparative GLC (SE-30, 15% on Uniport B, 2m). n_D^{20}=1.4657, ^1H NMR (CCl_4, TMS); δ, 0.91 (m, 6H), 1.1-1.5 (m, 12H), 1.9-2.3 (m, 4H), 5.39 (dt, *J* = 7 and 10 Hz, 2H), and 6.21 (d, *J* = 10 Hz, 1H) ppm. IR (neat) 3010, 3040, 1600 cm^{-1}.

In summary, the above results established that the cross-coupling of alkenylboranes with organic halides proceeds with high stereospecificity and provides an excellent method for the preparation of conjugated alkadienes while preserving their predicted geometry. It should be emphasized, however, that the synthesis of (Z,Z)- or (Z,E)-alkadienes can hardly be achieved by the coupling reactions with other organometallics.

Acknowledgement: We are grateful to the Ministry of Education of Japan for a Grant-in-Aid for Scientific Research.

REFERENCES AND NOTES

(1) N. Miyaura, K. Yamada, and A. Suzuki, Tetrahedron Lett., 3437 (1979).

(2) N. Miyaura and A. Suzuki, J. Chem. Soc., Chem. Commun., 867 (1979).

(3) N. Miyaura, T. Yano, and A. Suzuki, Tetrahedron Lett., 2865 (1980).

(4) (Z)-Alkenylboranes are generally stable and can be stored at -20 °C for several weeks. However, in some cases, *ca* a half of (Z)-hexenylborane was found to be isomerized to the (E)-isomer at room temperature 5 days after its preparation. In our previous paper we reported[1)] that the reaction of (Z)-hexenylborane with (E)-hexenyl bromide gave a 1:1 mixture of (E,E)- and (E,Z)-dienes. This result was later found to be due to the isomerization of the starting (Z)-hexenylborane to the (E)-isomer. It is advisable therefore to use the reagent immediately after its preparation.

(5) S. J. Cristol and W. P. Norris, J. Amer. Chem. Soc., **75**, 2645 (1953).

(6) A mixture of four isomers of 1-phenyl-1,3-octadiene has been prepared by a modified Wittig reaction. B. Bogdanović and S. Konstantinović, Synthesis, 481 (1972).

(7) D. R. Coulson, Inor. Synth., **13**, 121 (1972).

(8) J. B. Campbell and C. A. Molander, J. Organometal. Chem., **156**, 71 (1978); (Z)-1-Hexenyldisiamylboarne thus obtained was dissolved in benzene after evaporation of solvent under high vacuum (10^{-2} mmHg for 2 h).

(9) For the preparation of (E)-1-alkenyl-1,3,2-benzodioxaboroles, see H. C. Brown "Organic Synthesis via Boranes" John Wiley & Sons, New York, 1975. The alkenylbenzodioxaboroles should be purified by distillation before use.

(10) H. C. Brown, T. Hamaoka, and N. Ravindran, J. Amer. Chem. Soc., **95**, 6456 (1973).

(Received in Japan 3 October 1980)