Journal of Organometallic Chemistry, 233 (1982) C13—C16
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CROSS-COUPLING REACTIONS OF 1-ALKENYLBORANES WITH 3,4-EPOXY-1-BUTENE CATALYZED BY PALLADIUM OR NICKEL COMPLEXES

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(Received January 20th, 1982; in revised form March 4th, 1982)

Summary

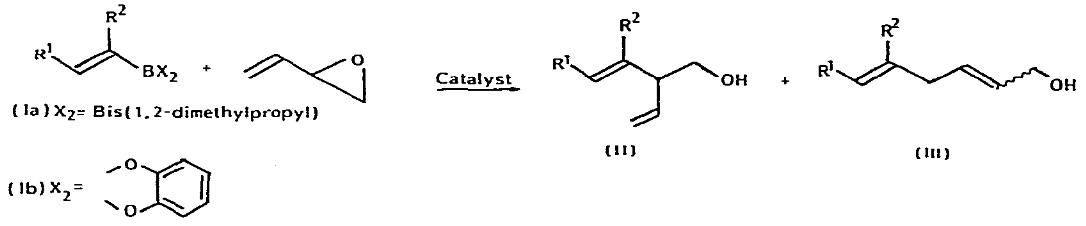
1-Alkenylboranes react with 3,4-epoxy-1-butene in the presence of palladium or nickel complexes to form the corresponding coupling products 2,5-alkadien-1-ol and 2-ethenyl-3-alken-1-ol, in high yields with in some cases high regioselectivity, and high turnover of the catalyst. The ratio of the two dienols can be reversed by changing the metal complex.

Cross-coupling reactions of organometallic compounds with organic halides catalyzed by transition metal complexes have been extensively studied to provide efficient methods for stereoselective synthesis of conjugated olefins [1,2]. We have previously reported that the reactions of alkenylboranes with a variety of organic halides such as alkenyl, alkynyl, aryl, allylic and benzylic halides in the presence of a catalytic amount of a palladium complex give the corresponding conjugated or homoconjugated olefins stereospecifically [2].

We now describe the reactions of alkenylboranes not only with organic halides but also with 3,4-epoxy-1-butene in the presence of a palladium or nickel catalyst to give two dienols (II and III) which arise from coupling at the C(2) or C(4) carbon atoms of 3,4-epoxy-1-butene (Scheme 1). The regioselectivity of this coupling reaction which involves a bifunctional substrate was found to be high in some cases and the ratio of II to III is reversed by changing the catalyst.

Typically, (*E*)-1-hexenylbis(1,2-dimethylpropyl)borane (Ia) [3] (1.1 mmol) and 3,4-epoxy-1-butene (1 mmol) in THF (3 ml) containing an appropriate

0022-328X/82/0000—0000/$02.75



SCHEME 1

metal complex (1—10 mmol%) were stirred for 15 h at room temperature under nitrogen and the unreacted borane was removed by oxidation with 3 *N* NaOH (1.3 ml) and 30% H_2O_2 (0.3 ml) for 1 h to afford a mixture of the two dienols II and III which were analyzed by GLC (15% Silicon OV-17 on Uniport B, 2 m).

Table 1 summarizes the results obtained with different amounts of various catalysts and indicates that the palladium complexes were found to be more effective than the nickel complexes.

TABLE 1

CROSS-COUPLING REACTIONS OF (*E*)-HEXENYLBIS(1,2-DIMETHYLPROPYL)BORANE (Ia) WITH 3,4-EPOXY-1-BUTENE IN THF

Catalyst	Mol of catalyst (%)	Yield of II and III (%)	Ratio of II/III
$Pd(PPh_3)_4$ [a]	5	27	62/38
$Pd(DBA)_2$ [b]	5	92	74/26
$Pd(OAc)_2$	5	52	33/67
$Pd(acac)_2$	5	58	34/66
$Pd(OAc)_2(PPh_3)$ [c]	5	12	34/66
$PdCl_2(PPh_3)_2$	5	17	41/59
$PdCl_2(PhCN)_2$	5	51	22/78
$Ni(acac)_2$ [d]	10	19	32/68
$Ni(acac)_2$ [d]	100	85	16/84
$NiBr_2(PPh_3)_2$	10	45	34/66
$Ni(PPh_3)_2$ [e]	10	85	63/37
$Ni(PPh_3)_4$ [f]	10	5	82/18

[a] Inorg. Synth., 13 (1972) 121. [b] T. Ukai, H. Kawazura, and Y. Ishii, J. Organometal. Chem., 65 (1974) 253. [c] H.A. Dieck, and R.F. Heck, J. Org. Chem., 40 (1975) 1083. [d] Solvent DMF. [e] Prepared from $NiBr_2(PPh_3)_2$ and BuLi at —78°C. A.A. Millard and M.W. Rathke, J. Am. Chem. Soc., 99 (1977) 4833. [f] Prepared from $Ni(acac)_2$, PPh_3 and Dibal. S. Baba and E. Negishi, J. Am. Chem. Soc., 98 (1976) 6729.

A noteworthy feature of this coupling reaction was its regioselectivity which appears to depend mainly on the nature of the catalyst used. Thus, dienol III was the predominant product when $PdCl_2(PhCN)_2$ or $Ni(acac)_2$ were used as the catalyst while dienyl II was the predominant product when a metal complex such as $Pd(DBA)_2$, $Pd(PPh_3)_4$, and $Ni(PPh_3)_n$ was used.

The regioselectivity appears to depend also upon the nature of the alkenylborane. Table 2 summarizes the results obtained with six 1-alkenylboranes (Ia) and three *B*-(1-alkenyl)-1,3,2-benzodioxaboroles (Ib) by four different procedures (A—D). A comparison of the results obtained by procedure A with those obtained by procedure D indicates that alkenylboranes (Ib) unexpectedly

TABLE 2

RESULTS OF REACTIONS OF 1-ALKENYLBORANES (Ia) AND *B*-(1-ALKENYL)-1,3,2-BENZODIOXABOROLES (Ib)

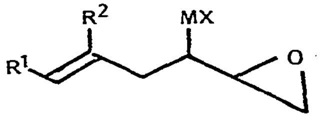
Alkenylborane		Yield (%) ^{a} of II and III, (Ratio of II/III)			
R^1	R^2	A	B	C	D
Bu^n	H	92	51	85	70
		(74/26)	(22/78)	(16/84 ^{b})	(24/76)
Hex^n	H	75	46	81	66
		(69/31)	(23/77)	(19/81 ^{c})	(25/75)
Hex^n	Me_3Si	trace	trace	73	—
				(0/100 ^{d})	
Me	Me	68	68	82	65
		(70/30)	(18/82)	(18/82 ^{e})	(36/64)
2-Propenyl	H	52	40	60	—
		(47/53)	(28/72)	(22/78 ^{f})	
Ph	H	87	69	83	—
		(62/38)	(30/70)	(40/60 ^{g})	

[a] Based on 3,4-epoxy-1-butene used and determined by GLC. Procedures: A: Conducted in THF at room temperature for 15 h using 5 mol% of $Pd(DBA)_2$ and 10% excess of Ia. Procedure B: Conducted in THF at room temperature for 15 h using 5 mol% of $PdCl_2(PhCN)_2$ and 10% excess of Ia. Procedure C: Conducted in DMF at room temperature for 15 h using an equimolar amount of $Ni(acac)_2$ and 10% excess of Ia. Procedure D: Conducted in a sealed tube at 80° C for 4 h using 1 mol% of $Pd(DBA)_2$ and 10% excess of Ib in THF. [b] *E,E/Z,E* = 96/4. [c] *E,E/Z,E* = 94/6. [d] *E,Z/Z,Z* = 57/43. [e] *E,E/Z,E* = 95/5. [f] *E,E/Z,E* = 95/5. [g] *E,E/Z,E* = 96/4.

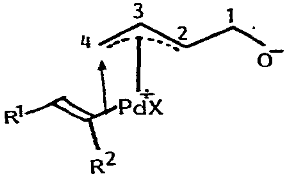
reacted with reverse regioselectivity while all alkenylboranes (Ia) gave the dienols with similar regioselectivity as found for (*E*)-1-hexenylbis(1,2-dimethylpropyl)borane.

It has been confirmed by ^{1}H NMR spectroscopy with the aid of a paramagnetic shift reagent, $Eu(dpm)_3$, that the configuration of the starting alkenylboranes is retained in both dienol II and III in all cases and that the stereochemistry of the resulting double bond in dienol III is predominantly *E* (94/6 *E/Z*) with the exception of dienol III prepared from 1-trimethylsilyl-1-octenylborane.

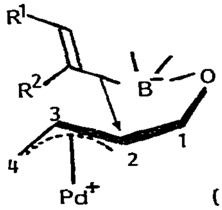
Further experiments are necessary in order to define the mechanism which can explain the competitive formation of the two dienols as well as the reverse regioselectivities observed for the two groups of catalysts. The following rationalization, however, seems to explain the results obtained in the present experiments: Dual mechanisms may competitively be operating here; dienol III may mainly be formed by catalysis of metal complexes in oxidation state II, either through opening of an oxiran ring in an intermediate A formed by addition of RCH=CHMX, which was generated from transmetallation between MX_2 and alkenylborane, to 3,4-epoxy-1-butene or through reductive elimination of π-allylpalladium(IV) [4] or -nickel(IV) complexes B, [5], formed by addition of alkenylmetal(II) complexes, generated from transmetallation between metal(II) complexes and alkenylboranes to 3,4-epoxy-1-butene. The alkenyl group would preferentially be linked with the sterically less-hindered C(4) atom when complexes B collapse. On the other hand, dienol II may predominantly be formed by catalysis of palladium(0) complexes via an intermediate such as C formed by a coordination reaction of alkenylboranes to oxygen of a zwitterionic π-allyl complex [6,7]. The alkenyl group in C could then attack the more hindered C(2) atom of the π-allyl unit to give dienol II preferentially. Similar regioselectivity through a five-membered cyclic transition state has recently been found in a palladium-catalysed coupling reaction [8]. However, it is not certain why the regioselectivity observed with Ia is opposite to that of Ib when the catalyst used is identical.



(A)



(B)



(C)

This new method of C—C bond formation should be of synthetic value in transforming acetylenes into dienols with four more carbon atoms without using a base [9,10].

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10 Subsequent to the completion of this work, two papers dealing with the preparation of allyl alcohols by 1,4-addition of nucleophiles to substituted 3,4-epoxy-1-butenes and vinyl epoxides catalyzed by a palladium complex have been reported. J. Tsuji, J. Kataoka, and Y. Kobayashi, Tetrahedron Lett., 22 (1981) 2575; B.M. Trost and G.A. Molander, J. Amer. Chem. Soc., 103 (1981) 5969.