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THE STEREOSELECTIVE ALLYLATION OF LITHIUM TRIALKYLALKYNYLBORATES BY ALLYL CARBONATE IN THE PRESENCE OF $Pd(PPh_3)_4$

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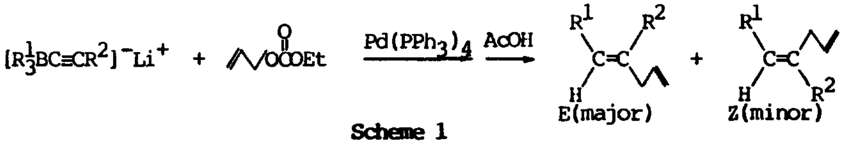
SUMMARY: The reaction of allylcarbonate with lithium trialkylalkynylborates catalysed by $Pd(PPh_3)_4$, affords 1,4-alkadienes in good yields and high stereoselectivity.

In recent years, much attention has been paid to the exploration of new reactions of lithium trialkylalkynylborate with various electrophiles, as these reactions can effectively form the new carbon-carbon bonds with high stereoselectivity. The electrophiles reported are iodine,[1] proton,[2] active alkylating reagents,[3] carbon dioxide,[4] metal chloride,[5] etc., but, ester group is inert to the organoborate. On the other hand, no report on the reaction of allyl carbonate with the organoborate has appeared in literature so far. In this paper we wish to report the results on the reaction of allyl carbonate with the organoborate.

Pelter found that the attack of allyl bromide as an electrophile on β-carbon of the alkynyl group in lithium trialkylalkynylborate was accompanied by the migration of an alkyl group from boron to α-carbon of the alkynyl group, after protonation, giving alkene with the ratio of about 60:40 of Z to E form.[3] Allyl carbonate cannot react with the organoborate directly. However, it was known that in the presence of $Pd(PPh_3)_4$, allyl carbonate can allylate various carbanions.[6] So we tried to use $Pd(PPh_3)_4$ as a catalyst for the reaction of allyl carbonate with the organoborate.

Fortunately, in the presence of $Pd(PPh_3)_4$,the allyl group of allyl carbonate can react with the organoborate, as other electrophiles do, to give the E-form alkenes predominantly in good yields, as shown in Scheme 1. The representative results of the reaction are shown in Table 1.



Scheme 1

The following procedure of the preparation of 5-allyl-5-dodecene is representative. A dry 50 ml-flask was charged under argon with 5 mmol of lithium trihexylhexynylborate[3] in THF(20ml). $Pd(PPh_3)_4$ 0.29g (0.25 mmol) and allyl carbonate 0.65g (5 mmol) in dry THF(10 ml) were added to the organoborate solution at -78°C. After stirring for 30 min, the reaction was continued for 24 h at 40°C. The reaction was quenched by the addition of acetic acid (4ml) at 25°C for 6 h. The acid and the solvent were removed as usual. The product 0.72g(70%) was isolated by silica gel column chromatography (petroleum ether as an eluant), and analysed by g.l.c. (capillary column OV-101 125m), revealing the ratio of E:Z was 87:13.

The structures of our products were determined by N.O.E. and g.l.c. techniques. The major product obtained by the reaction of lithium trihexyloctynylborate with allyl carbonate has the same retention time in g.l.c. as that of authentic E-7-allyl-7-tetradecene, which was prepared from 7-tetradecyne and allyl bromide by Suzuki's method.[7] In addition, the retention time

Table 1. Allylation of $[R^1_3BC\equiv CR^2]^-Li^+$ with allyl carbonate

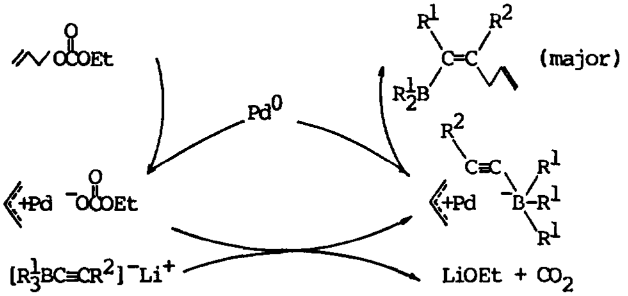
Run	R^1	R^2	isolated yield (E+Z)% of 1,4-dienes	E:Z
1	n-octyl	n-Bu	62	87:13
2	n-hexyl	n-Bu	70	87:13
3	n-hexyl	n-hexyl	63	84:16
4	n-octyl	n-pentyl	54	95:5
5	n-hexyl	n-pentyl	71	89:11
6	n-octyl	n-hexyl	60	87:13
7	n-octyl	$-CH_2OCH_3$	77	0:100
8	n-heptyl	$-CH_2OCH_3$	68	0:100

The IR,MS,^{1}HNMR and microanalyses of all products are in agreement with the assigned structures.

of the Pelter's major product obtained by the reaction of lithium trialkylalkynylborate with allyl bromide was in accord with that of our minor product, and the retention time of the Pelter's minor product with that of our major product. These facts suggest that the attacking group (allyl group) and the migrating one (alkyl group) are on the opposite side of the double bond in our major products.

Interestingly, in the case of lithium trioctyl-(3-methoxy-propyl)borate, a single geometrical isomer of alkene was obtained (Run 7 in Table 1). The structure of the alkene was determined by N.O.E. technique of ^{1}HNMR. A 9% increase of intensity was observed for the signal of vinylic proton (δ =5.39ppm) when the methylene proton (δ =2.80ppm) of allyl group was simultaneously irradiated. Such effect was hardly observed in the case of irradiating the methylene proton(δ= 3.91ppm) at $-CH_2-O-CH_3$. This fact indicates that the vinylic proton and allyl group are on the same side of the trisubstituted double bond,i.e.the attacking group(allyl group) and the migrating one (alkyl group) are on the opposite side. This is in agreement with that above-mentioned.

The reaction mechanism might be assumed as follows:



As allyl carbonates could be readily obtained from allyl alcohols, this reaction extends the use of organoborates and is applicable for the stereoselective preparation of 1,4-alkadienes, the structures of which are different from those obtained by Pelter's method.

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