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CARBON–BORON BOND CLEAVAGE IN ALLYL ORGANOBORANES

INDU MEHROTRA AND D. DEVAPRABHAKARA
Department of Chemistry, Indian Institute of Technology, Kanpur-16 (India)

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SUMMARY

Allylic rearrangement has been shown to occur during protonolysis of allyl organoboranes obtained from monohydroboration of monosubstituted and 1,1-disubstituted acyclic allenes with disiamylborane*.

INTRODUCTION

Brown and Zweifel[1] have shown that the hydroboration of 1-hexene and styrene with disiamylborane followed by alkaline hydrogen peroxide oxidation gives 98–99% primary alcohols. The authors concluded that this indicated not only the steric equivalence of phenyl and n-alkyl groups but also the absence of electrical effect by the phenyl substituent. Our results on the monohydroboration–oxidation of monosubstituted and 1,1-disubstituted allenes also suggest that when disiamylborane is used as the hydroborating agent the attack of boron primarily is at the methylene carbon atom of the allenic linkage, yielding allyl organoboranes[2]. The observed selectivity could be dictated solely by the steric requirement of the allene in the transition state for hydroboration proposed by Brown[3]. In the present paper, we describe the allylic rearrangements observed during the protonolysis of allylic organoboranes obtained from monohydroboration of 1,2-octadiene, 3-ethyl-1,2-pentadiene, phenylpropadiene and 3-phenyl-1,2-butadiene.

RESULTS AND DISCUSSION

The acyclic allenes were synthesized by Moore and Ward's procedure[4], and their properties agreed with those in the literature[5–8]. Disiamylborane was prepared by the hydroboration of 2-methyl-2-butene in an atmosphere of dry nitrogen[9]. A solution of the appropriate allene in diglyme [bis(2-methoxyethyl)ether] was added to the disiamylborane solution during 5 min and the mixture was allowed to attain room temperature (approx. 3 h). The resulting organoboranes were treated with glacial acetic acid at room temperature for 24 h and worked up in the usual manner[10]. The identity of the products was established by comparison of gas liquid chromatographic (GLC) retention times and infrared spectra (IR) with those of authentic

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* Siamyl = 1,2-dimethylpropyl.

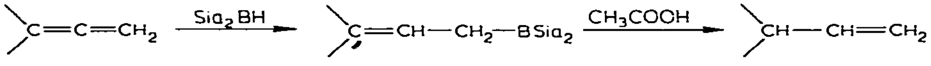
TABLE 1

RESULTS OF THE MONOHYDROBORATION—PROTONOLYSIS OF SOME ACYCLIC ALLENES

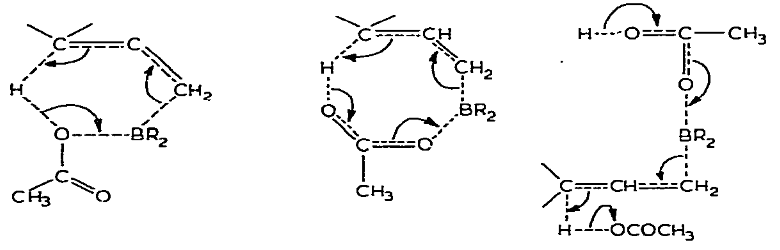
Allene	Product composition (%)	Yield (%)
1,2-Octadiene	1-Octene (82) *cis*-2-Octene (8) *trans*-2-Octene (10)	38
3-Ethyl-1,2-pentadiene	3-Ethyl-1-pentene (98) 3-Ethyl-2-pentene (2)	20
Phenylpropadiene	Allylbenzene (91) *cis*-Propenylbenzene (9)	25
3-Phenyl-1,2-butadiene	3-Phenyl-1-butene (100)	27

samples. Wherever necessary, nuclear magnetic resonance (NMR) spectra were also used in the characterization of the products.

The results are summarized in Table 1. A general scheme for the monohydroboration–protonolysis of acyclic allenes studied may be represented as follows:



Our results indicated that the protonolysis of the initially formed allyl organoboranes proceeds with rearrangement, and we confirmed this by a deuterolysis experiment. The NMR spectrum of the olefinic product obtained from monohydroboration of 3-phenyl-1,2-butadiene followed by treatment with *O*-deuterioacetic acid showed that deuterium had been incorporated in the benzylic position [CH_3–CD–(C_6H_5)–CH=CH_2]. The formation of the terminal olefin can best be visualized through a six-membered cyclic transition state[11] involving hydroxyl oxygen of the carboxylic acid. An eight-membered cyclic transition state[11] which involves carbonyl oxygen or the non-cyclic S_E2' process similar to the one proposed for allylic Grignard reagent[12] cannot be ruled out at present but is less likely.



R= Sia [–CH(CH_3)–CH(CH_3)$_2$]

Undoubtedly the small amounts of internal olefins formed arise from protonolysis of vinyl organoboranes and/or allyl organoboranes without rearrangement. Our attempt to increase the yield of the product in the case of phenylpropadiene by carrying out the protonolysis at 80° for 2 h resulted in the formation of n-propylbenzene (8%), allylbenzene (8%), *cis*-propenylbenzene (74%) and *trans*-propenylbenzene (10%). We attribute this to the isomerization of the initially formed allyl organoborane to the vinyl organoborane before protonolysis, since we find that no isomerization of allylbenzene to propenylbenzene occurs under similar conditions. The low yield may be due to the competitive protonolysis of the trialkylborane to yield either unsaturated or saturated hydrocarbon, since the protonolysis of the trialkylborane with acetic acid is known to proceed readily only for the first group[13].

EXPERIMENTAL

Boiling points are uncorrected. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer as thin films between sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform on a Varian A-60 spectrometer. Gas liquid chromatographic (GLC) analyses were made with Aerograph Model 90-P instrument using 5 ft or 10 ft or 15 ft by $\frac{1}{4}$ inch columns. The following liquid phases were employed (percentage by weight on 60/80 mesh chromosorb W): 15% SE-30 silicone rubber, 15% carbowax 20M, 15% carbowax 20M/silver nitrate, 15% propylene glycol/silver nitrate and 15% ucon.

Materials

Diglyme (Ansul Co.) was kept over calcium hydride for 24 h, decanted, and distilled from slightly excess of lithium aluminium hydride under reduced pressure. Boron trifluoride diethyl etherate (Eastman) was treated with a small quantity of dry diethyl ether (to ensure an excess of this component) and distilled under reduced pressure from calcium hydride. Sodium borohydride from Metal Hydrides Inc. (98%) was used without purification. 2-Methyl-2-butene (Aldrich Co.) was used for the preparation of disiamylborane.

The acyclic allenes, 1,2-octadiene, 3-ethyl-1,2-pentadiene, phenylpropadiene and 3-phenyl-1,2-butadiene were prepared by two-step sequence starting from the appropriate olefin[4]. Their properties corresponded well with those reported[5–8].

Monohydroboration–protonolysis of 1,2-*octadiene*

Pulverized sodium borohydride (1.06 g, 0.028 mole), 2-methyl-2-butene (4.9 g, 0.07 mole) and dry diglyme (28 ml) were placed in a 250 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer and an inlet and an outlet for dry nitrogen gas. Boron trifluoride diethyl etherate (6.2 g, 0.04 mole, 10% excess) in diglyme (10 ml) at −5 to 0° was added during 30 min, a positive pressure of nitrogen being maintained. The mixture was allowed to stand at 0° for 1 h, then 1,2-octadiene (3.85 g, 0.035 mole) was added during 5 min. The mixture was left for ~3 h to attain room temperature. Glacial acetic acid (10 ml) was added, and the mixture was stirred at room temperature for 24 h. It was then poured into ice-cold water, and organic products were extracted with pentane, and the extract was washed with water until neutral and dried over anhydrous magnesium sulphate. After removal of the solvent, distillation of the residue gave 1.5 g (~38%) of mixed olefins boiling at 121–122° at 754 mm. GLC analysis on a 15 ft propylene glycol/silver nitrate column showed the presence of 82% 1-octene, 8% *cis*-2-octene and 10% *trans*-2-octene. The identity of the individual product(s) was established by comparison of GLC retention times and IR spectra with those of the authentic samples.

Monohydroboration–protonolysis of 3-ethyl-1,2-pentadiene

The procedure described for monohydroboration–protonolysis of 1,2-octadiene was followed. From 3-ethyl-1,2-pentadiene (2.4 g, 0.025 mole), sodium borohydride (0.76 g, 0.02 mole), 2-methyl-2-butene (3.5 g 0.05 mole) and boron trifluoride etherate (3.9 g, 0.027 mole), there was obtained 0.48 g (~20%) of a mixture of olefins, b.p. 104–108° (bath temperature) at 754 mm. GLC analysis of the mixture on a 10 ft carbowax/silver nitrate column showed 98% 3-ethyl-1-pentene and 2% 3-ethyl-2-pentene. Only 3-ethyl-1-pentene was separated by GLC, and was identified by comparison of IR and NMR spectra with that of an authentic sample. The minor product was identified only by comparison of GLC retention times with those of an authentic sample.

Monohydroboration–protonolysis of phenylpropadiene

The organoboranes obtained from phenylpropadiene (2.3 g, 0.02 mole), sodium borohydride (0.57 g, 0.015 mole), 2-methyl-2-butene (2.8 g, 0.04 mole) and boron trifluoride etherate (3.10 g, 0.02 mole) after treatment with glacial acetic acid (10 ml) at room temperature for 24 h gave 0.6 g (~25%) of a mixture of olefins, b.p. 75–80° (bath temperature) at 40 mm. The mixture contained 91% allylbenzene and 9% *cis*-propenylbenzene as analysed by GLC on a 10 ft carbowax column. The products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples.

Protonolysis at 80° for 2 h gave a 28% yield of a mixture of olefins, in which were present n-propylbenzene (8%), allylbenzene (8%), *cis*-propenylbenzene (74%) and *trans*-propenylbenzene (10%).

Monohydroboration–protonolysis of 3-phenyl-1,2-butadiene

Following the procedure described for 1,2-octadiene, from 3-phenyl-1,2-butadiene (2.6 g, 0.02 mole), sodium borohydride (0.57 g, 0.015 mole), 2-methyl-2-butene (2.8 g, 0.04 mole) and boron trifluoride etherate (3.12 g, 0.022 mole, 10% excess), there was obtained 0.71 g (~27%) of 3-phenyl-1-butene, b.p. 66–70° at 13 mm. GLC analysis showed it to be a single component, and its IR and NMR spectra were identical with those of an authentic sample. The IR spectrum had two bands at 990 and 920 cm^{-1} characteristic of a monosubstituted olefin. The NMR spectrum showed a sharp singlet at δ 7.12 (5 protons), multiplet at 6.28–5.68 (1 proton), 5.20–4.80 (2 protons), and 3.40 (1 proton), and a doublet at 1.30 (3 protons, $J = 8.5$ Hz).

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