Journal of Organometallic Chemistry, 51 (1973) 93–98

REACTIONS OF DISIAMYL(3-PHENYL-2-BUTENYL)BORANE WITH ALDEHYDES AND KETONES

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(Received August 26th, 1972)

SUMMARY

A substituted allyl organoborane, disiamyl(3-phenyl-2-butenyl)borane has been prepared *in situ* by the monohydroboration of 3-phenyl-1,2-butadiene with disiamylborane. It reacts readily with butyraldehyde, benzaldehyde, acrolein and acetone to give unsaturated alcohols, possibly via a six-membered transition state involving allylic rearrangement.

INTRODUCTION

Organoboranes are reactive intermediates in many new organic syntheses involving production of one or more carbon–carbon bonds. Carbon monoxide[1-3] and sodium cyanide[4-6] can bring about one-carbon homologation of the organoborane. Similarly, two-carbon homologation is achieved by using acetic acid derivatives in the presence of an appropriate base[7-12]. The facile alkylation of α,β-unsaturated carbonyl compounds raises the possibility of having a three-carbon homologation of the representative olefins via 1,4-addition[13-19]. However, saturated aldehydes, ketones, water, or alcohol do not cleave the carbon–boron bonds of trialkylboranes. A triallylborane is much more reactive than a trialkylborane and fast reactions of trialkylborane occur with aldehydes[20-22] quinones[23,24], water[20], alcohols[20,21], acetylenes[25,26], nitriles[27] and activated olefins[28,29]. We have shown previously that (substituted allyl)organoboranes undergo protonolysis with acetic acid with allylic rearrangement[30] and it seemed desirable to examine the reactions of DSPBB** with aldehydes and ketones. The present paper deals with the synthesis of DSPBB and its reactions with butyraldehyde (aliphatic aldehyde), benzaldehyde (aromatic aldehyde), acrolein (α,β-unsaturated aldehyde) and acetone (aliphatic ketone). It was thought that the reaction of DSPBB with acrolein would reveal not only the nature of addition but also the reactivity difference between alkyl and alkenyl groups.

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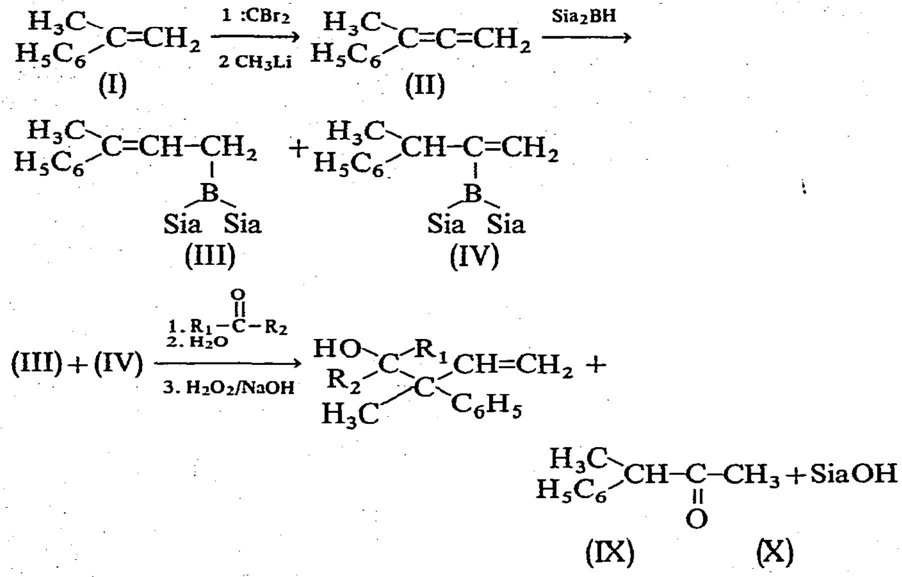
** DSPBB = disiamyl(3-phenyl-2-butenyl)borane.

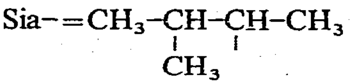
RESULTS AND DISCUSSION

Disiamylborane was prepared by the hydroboration of 2-methyl-2-butene in a nitrogen atmosphere[33]. A solution of 3-phenyl-1,2-butadiene (II) in dry tetrahydrofuran was added to the disiamylborane within 5 min and was allowed to attain room temperature to give disiamyl(3-phenyl-2-butenyl)borane (III) as the major product, along with a small amount of vinylorganoborane (IV). The resulting mixture was treated with the appropriate aldehyde or ketone, stirred for the required time and oxidized with alkaline hydrogen peroxide.

DSPBB (III) underwent a remarkably ready reaction with aldehydes to give β,γ-unsaturated secondary alcohols (V)–(VII). With ketone the reaction was found to be somewhat sluggish, and it led to the formation of the β,γ-unsaturated tertiary alcohol (VIII) in about 60% yield. The reaction can be schematically represented as follows:



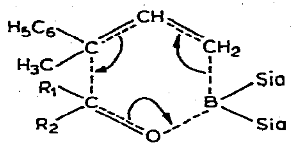
(V), $R_1 = CH_3{-}CH_2{-}CH_2{-}$; $R_2 = H$
(VI), $R_1 = C_6H_5{-}$; $R_2 = H$ (1)
(VII), $R_1 = CH_2{=}CH{-}$; $R_2 = H$
(VIII), $R_1 = R_2 = CH_3{-}$



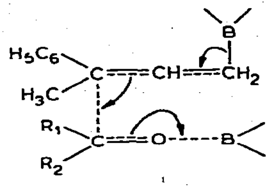
$Sia{-} = CH_3{-}\underset{CH_3}{CH}{-}CH{-}CH_3$

The reaction of DSPBB with butyraldehyde followed by hydrolysis and oxidation gave 3-methyl-3-phenyl-1-hepten-4-ol (V) in addition to the expected siamyl alcohol (X) and a small amount of 3-phenyl-2-butanone (IX). The ketone is presumably produced by the oxidation of the vinylorganoborane (IV) obtained by the attack of boron at the central carbon of the allenic linkage. 1,2-Diphenyl-2-methyl-3-buten-1-ol (VI) was obtained in 65% yield from DSPBB and benzaldehyde. Acrolein with DSPBB gave 4-phenyl-4-methyl-1,5-hexadiene-3-ol (VII). A tertiary alcohol, 2,3-dimethyl-3-phenyl-4-penten-2-ol (VIII) was obtained from DSPBB and acetone, along with 3-phenyl-2-butanone and siamyl alcohol.

The results of the reactions of DSPBB with aldehydes and ketones clearly indicate that the reaction involves the migration of 3-phenyl-2-butenyl group with rearrangement in preference to the siamyl group. In the light of these observations the formation of olefinic alcohols can be visualized as involving a six-membered cyclic transition state rather than a non-cyclic S_E2' process[35] or a radical addition mechanism. This proposal is further substantiated by the following facts: (*i*), no 1,4-addition product is formed with acrolein; (*ii*), no reaction takes place with ethyl acetate or ethyl acrylate even in the presence of the added nucleophile like sodium acetate; (*iii*), formation of only rearrangement product in every case; (*iv*), the difference in reactivity between aldehydes and ketones.



Six-membered transition state



S_E2' Process

The reactions of DSPBB with aldehydes and ketones provide convenient syntheses of β,γ-unsaturated alcohols. Preliminary dehydration experiments with β,γ-unsaturated alcohols indicated that it is possible to use these unsaturated alcohols in the synthesis of substituted 1,4-dienes.

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 on a Varian A-60 spectrometer in deuterated chloroform with TMS as the internal standard. Gas liquid chromatographic (GLC) analyses were done with Aerograph Model 90-P instrument using 3 ft by 1/4 inch silicone rubber column. Column chromatography was carried out on basic alumina (E. Merck). Microanalyses were carried out by Mr. A. H. Siddiqui, Microanalyst, Department of Chemistry, Indian Institute of Technology, Kanpur-16, India.

Materials

Diglyme (Ansul Co.) was kept over calcium hydride for 24 h, decanted and distilled over slight excess of lithium aluminium hydride under reduced pressure (b.p. 63–64°/15 mmHg). Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of dry ether so as to ensure an excess of this component and distilled under reduced pressure from calcium hydride (b.p. 46–47°/10 mmHg). Tetrahydrofuran (BDH) was refluxed over sodium, decanted and distilled from lithium aluminium hydride. Sodium borohydride (Metal Hydride Inc.) was used as supplied. Butyraldehyde (BDH), benzaldehyde (BDH), acrolein (Fluka AG) and acetone (BDH) were distilled before use. 2-Methyl-2-butene (Aldrich Co.) was used for the preparation of disiamylborane. 3-Phenyl-1,2-butadiene (II) was prepared by the two-step sequence[31] starting from α-methylstyrene (BDH) (I), and its properties agreed with those in the literature[32].

Preparation of disiamyl(3-phenyl-2-butenyl)borane (III) in situ

2-Methyl-2-butene (1.4 g, 0.02 mol) in 15 ml dry tetrahydrofuran was placed in a 100 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer and an inlet and an outlet for nitrogen. The flask was immersed in ice bath, and 7 ml of a 1.6 *M* solution of borane (0.1 mole) in tetrahydrofuran[33] was added, the temperature being maintained at 0–5°. The mixture was allowed to stand at 0° for 1 h, and 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol) was then added during 5 min. The mixture was left for 3 h to attain room temperature, and then stirred for 1 h more at room temperature, to give mainly DSPBB in tetrahydrofuran[34].

Reaction of DSPBB with butyraldehyde

The organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol), 2-methyl-2-butene (1.4 g, 0.02 mol) and 7 ml of 1.6 *M* borane solution in tetrahydrofuran were treated with butyraldehyde (0.72 g, 0.01 mol). The mixture was allowed to stir for 1 h, treated with water, and then oxidized with alkaline hydrogen peroxide. The usual work-up of the reaction provided 3.0 g of a liquid product. GLC analysis of the liquid product on a 3 ft silicone rubber column showed three components. Two minor components were identified as 3-phenyl-2-butanone (IX) and 3-methyl-2-butanol (X), by comparison of GLC retention times and IR spectra using authentic samples. The major component and 3-phenyl-2-butanone were separated from the mixture by column chromatography on basic alumina. Elution with petroleum ether gave 0.12 g (8%) of 3-phenyl-2-butanone[36]. Further elution of the column with benzene gave 1.2 g (60%) of a liquid, b.p. 100–110° (bath temperature) at 1 mmHg. The IR spectrum of this liquid showed bands at 3500, 1040 (–OH); 989, 920 (–CH=CH$_2$); and 1600 cm^{-1} (aromatic ring). The NMR spectrum had signals at δ 7.4 (m, 5H) aromatic protons, 6.25 (dd, J_{cis} 8.0 and J_{trans} 11.0 Hz, 1 H) olefinic methine protons, 5.0–5.4 (m, 2 H) terminal methylene protons, 3.9 (m, 1 H) methine proton, and 1.0–1.4 ppm (m, 11 H) methyl, methylene and hydroxy protons. Thus, the compound was identified as 3-methyl-3-phenyl-1-hepten-4-ol (V). (Found: C, 84.20; H, 9.50. $C_{14}H_{20}O$ calcd.: C, 84.35; H, 9.80.)

Reaction of DSPBB with benzaldehyde

Benzaldehyde (1.06 g, 0.01 mol) was added to the organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol), 2-methyl-2-butene (1.4 g, 0.02 mol) and 7 ml of 1.6 *M* borane solution in dry tetrahydrofuran. The mixture was stirred for 1 h and oxidized with alkaline hydrogen peroxide. The usual work-up afforded 3.7 g of viscous oil, which gave 0.14 g (10%) of 3-phenyl-2-butanone and 1.5 g (65%) 1,2-diphenyl-2-methyl-3-buten-1-ol (VI), b.p. 100°/0.01 mmHg. The IR spectrum showed absorptions at 3500, 1030 (–OH); 3030, 1600, 720 (aromatic ring), 915 and 1000 cm^{-1} (–CH=CH$_2$). The NMR spectrum showed signals at δ 7.3–7.5 (m, 10 H) aromatic protons, 6.46 (dd, J_{cis} 8.0 and J_{trans} 11.0 Hz, 1 H) olefinic methine proton, 5.2(m, 3 H) terminal methylene and benzylic protons, 1.96 (s, 1 H) hydroxyl proton and 1.4 ppm (s, 3 H) methyl protons. (Found: C, 85.40; H, 7.50. $C_{17}N_{18}O$ calcd.: C, 85.71; H, 7.56%.)

Reaction of DSPBB with acrolein

To the organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol) was added freshly distilled acrolein (0.56 g, 0.01 mol). After the usual work-up, removal of the solvent afforded 3.2 g of crude product. The column chromatographic separation gave 0.14 g (10%) of 3-phenyl-2-butanone and 1.1 g (60%) of 4-phenyl-4-methyl-1,5-hexadien-3-ol (VII), b.p. 90–95° (bath temperature)/1 mmHg. The IR spectrum showed bands at 3500, 1040 (–OH); 3050, 1700, 1600 (aromatic ring), 990 and 920 cm^{-1} $(-CH=CH_2)$. The NMR spectrum showed signals at δ 7.3 (m, 6 H) aromatic and hydroxyl protons, 6.2 (dd, J_{trans} 11.0 and J_{cis} 8.0 Hz, 1 H) methine olefinic proton attached to benzylic carbon, 5.70 (dd, J_{trans} 10.0 and J_{cis} 5.0 Hz, 1 H) olefinic methine proton adjacent to the hydroxy bearing carbon, 5.25 (m, 4 H) terminal methylene protons, 4.4 (bd, 1 H) allylic methine proton and 1.4 ppm (s, 3 H) methyl protons. (Found: C, 82.96; H, 8.40. $C_{13}H_{16}O$ calcd.: C, 82.97; H, 8.50%.)

Reaction of DSPBB with acetone

Acetone (0.58 g, 0.01 mol) was added at room temperature to the organoboranes obtained from 3-phenyl-1,2-butadiene (1.3 g, 0.01 mol). The mixture was refluxed for 12 h at 70° with stirring and then cooled to 0°. The usual oxidation and work-up of the reaction mixture gave 3 g of a liquid, which on column chromatographic separation gave 0.14 g (10%) of 3-phenyl-2-butanone and 1.0 g (60%) of 2,3-dimethyl-3-phenyl-4-hepten-2-ol (VIII), b.p. 90–95° (bath temperature)/1 mmHg. The IR spectrum showed bands at 3500, 1030 (–OH); 3030, 1600, 720 (phenyl ring); 1000 and 915 cm^{-1} $(-CH=CH_2)$. The NMR spectrum showed signals at δ 7.3 (s, 5 H) aromatic protons, 6.55 (dd, J_{cis} 8.0 and J_{trans} 11.0 Hz, 1 H) olefinic methine protons, 5.35–4.9 (m, 2 H) terminal methylene protons, 1.6 (s, 4 H) methyl and hydroxyl protons, 1.18 (s, 3 H) methyl protons and 1.10 ppm (s, 3 H) methyl protons. (Found: C, 82.19; H, 9.50. $C_{13}H_{18}O$ calcd.: C, 82.10; H, 9.40%)

ACKNOWLEDGEMENT

The authors wish to thank Dr. Nitya Nand, Central Drug Research Institute, Lucknow, India for the nuclear magnetic resonance spectra.

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