

Dihydroboration of cyclic allenes

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Abstract. The study on the dihydroboration of a large ring cyclic allene, 1,2-cyclotridecadiene and the smallest stable allene, 1,2-cyclononadiene is described. For example, a mixture of products containing isomeric cyclotridecene, bicyclo(10.1.0)-tridecane, cyclotridecanone, cyclotridecanol, isomeric cyclic 1,2-cyclotridecandiol and isomeric 1,3-cyclotridecandiol is obtained from dihydroboration-oxidation of 1,2-cyclotridecadiene. However, dihydroboration-hydrolysis-oxidation of 1,2-cyclotridecadiene affords mainly cyclotridecanol, whereas dihydroboration-oxidation with chromium trioxide-pyridine yields mainly a mixture of Z- and E-cyclotridecene. Reasonable mechanistic pathways have been suggested for the formation of products. The proposed unusual elimination reaction of 1,2-diorganoboranes with chromium trioxide has been substantiated using an authentic 1,2-diorganoborane from diphenyl acetylene. The reaction appears to be stereospecific with *threo*-diorganoborane furnishing predominantly E-alkene. The results with 1,2-cyclononadiene has also been rationalised on a similar basis.

Keywords: Cyclic allenes; dihydroboration; diorganoboranes; a novel elimination reaction.

1. Introduction

Although many investigations have been reported on the monohydroboration of allenes using diborane (Devaprabhakara and Gardner 1963), disiamylborane (Devaprabhakara *et al* 1968 and 1969), 4,4,6-trimethyl-1,3,2-dioxaborinane (Fish 1968) and 9-borabicyclo (3.3.1)-nonane (Chevolot *et al* 1974), surprisingly, a systematic dihydroboration study of allenes is still to be examined. Corsano (1963) has reported that propadiene, *n*-butylallene and phenylallene on dihydroboration with diborane followed by alkaline hydrogen peroxide oxidation of the intermediate organoboranes yield mainly 1,3-diols. We (Devaprabhakara and Mehrotra 1972) have recently communicated our initial interesting results on the dihydroboration study of 1,2-cyclotridecadiene (1A). The main object of the present study was to examine the effect of ring size on the diaddition of B-H to an allenic bond. Accordingly, we report herein our detailed examination on the dihydroboration of 1,2-cyclotridecadiene (1A) and 1,2-cyclononadiene (1B) with borane-tetrahydrofuran.

2. Results and discussion

The dihydroboration reaction was carried out using a standard solution of borane-tetrahydrofuran (1 : 1.3 mol ratio of allene: borane) in nitrogen atmosphere (Brown 1975). There obtained a white precipitate on allowing the reaction mixture to stir for sufficient time (12-14 hr). The resulting organoboranes were oxidised with alkaline hydrogen peroxide, and worked up in the usual manner. The mixture of products was carefully analysed by TLC and then subjected to column chromatographic separation. The identity of the products was established by comparison of GLC retention times and IR spectra with those of authentic samples or by elemental analysis and spectral data.

1,2-Cyclotridecadiene (1A) gave 5% of a mixture of hydrocarbons containing Z-cyclotridecene (Z-9A), E-cyclotridecene (E-9A) and bicyclo (10.1.0) tridecane (12A) in the ratio 1 : 7 : 2, 1.5% cyclotridecanone (7A), 27% cyclotridecanol (6A), 14% Z-1,2-cyclotridecandiol (Z-10A), 15% E-1,2-cyclotridecandiol (E-10A) and 3.5% of a mixture of isomeric diols which has been tentatively assigned as a mixture of Z- and E-1,3-cyclotridecandiol (13A). All the products except 13A were identified unambiguously using authentic samples (table 1).

1,2-Cyclononadiene (1B) under similar conditions provided 0.6% E-cyclononene (E-9B), 0.3% cyclononanone (7B), 31% cyclononanol (6B), 11% Z-1,2-cyclononandiol (Z-10B), 11% E-1,2-cyclononandiol (E-10B) and E-1,3-cyclononandiol (E-13B) (table 1).

However, dihydroboration of 1A followed by hydrolysis with sodium hydroxide at 80° for 24 hr followed by oxidation with alkaline hydrogen peroxide at 0° afforded 7% of a mixture of Z-cyclotridecene (Z-9A) and E-cyclotridecene (E-9A) in the ratio 17 : 83 and 60% of cyclotridecanol (6A). On the other hand, dihydroboration-oxidation with chromium trioxide-pyridine yielded 50% of a mixture of Z-cyclotride-

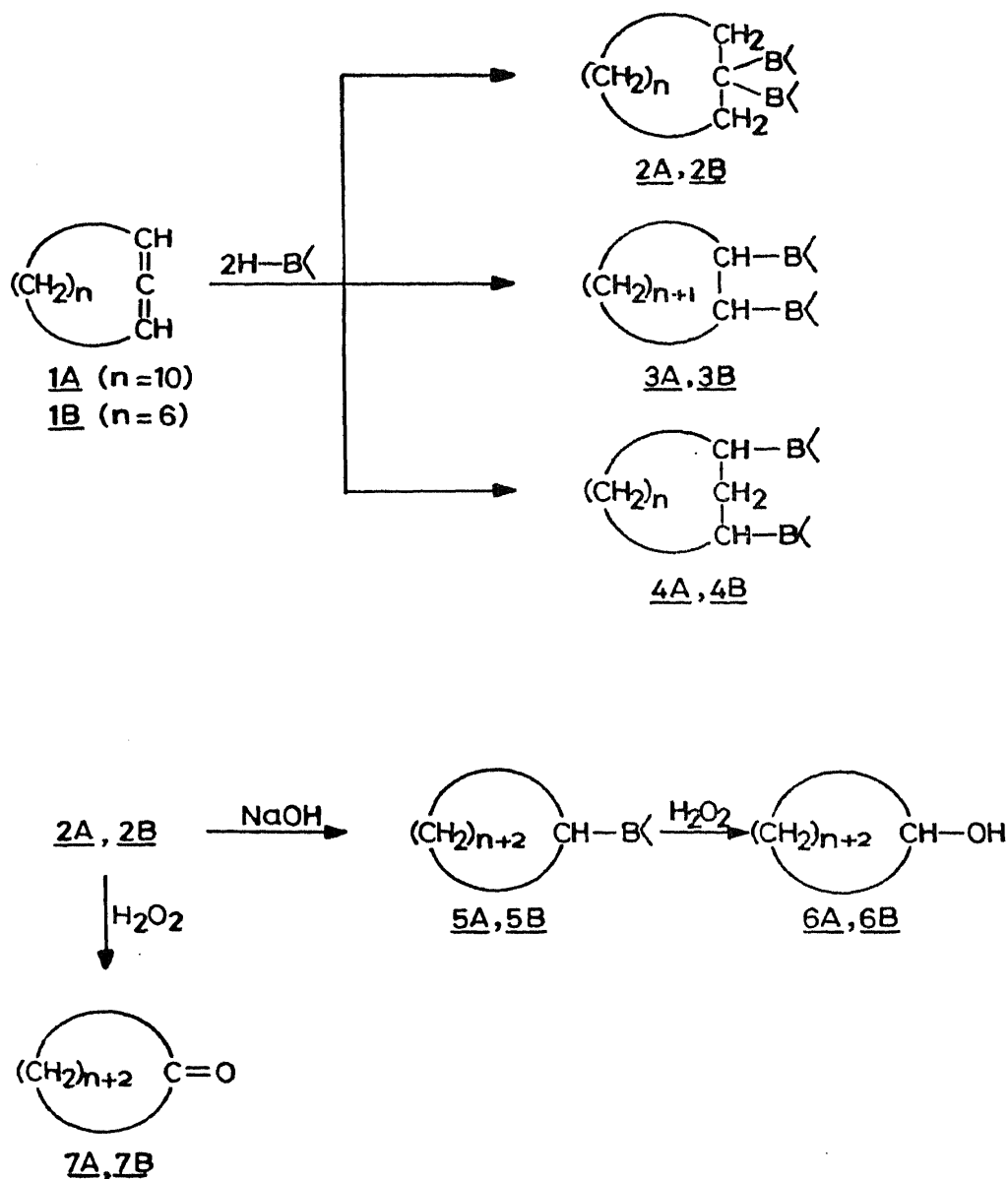
Table 1. Results of the dihydroboration of C-13 and C-9 allenes

Allene	Yield(%)			
	Hydrocarbon	Ketone	Alcohol	Diol
1,2-Cyclotridecadiene (<u>1A</u>)	Z-and E-Cyclo- tridecene (<u>9A</u>)	Cyclotridecanone (<u>7A</u>)	Cyclotridecanol (<u>6A</u>)	Z- and E-1,2-Cyclo- tridecandiol (<u>10A</u>) (29%)
	Bicyclo (10.1.0)- tridecane (<u>12A</u>) (5%)	(1.5%)	(27%)	Z- and E-1,3-Cyclo- tridecandiol (<u>13A</u>) (3%)
1,2-Cyclononadiene (<u>1B</u>)	E-Cyclononene (<u>9B</u>) (0.6%)	Cyclononanone (<u>7B</u>) (0.3%)	Cyclononanol (<u>6B</u>) (31%)	Z- and E-1,2-Cyclo- nonandiol (<u>10B</u>) (22%)
				E-1,3-Cyclononan- diol (<u>13B</u>) (0.8%)

cene (Z-9A) and E-cyclotridecene (E-9A) in the ratio 3 : 17 and 3 % of cyclotridecanone (7A).

In principle, two successive Z-additions of B-H bond to two orthogonal double bonds of 1 could give rise to 1, 1-, 1, 2-, and 1,3-diorganoboranes (2, 3 and 4) as shown in figures 1 and 2. There are three possible routes for the genesis of alcohol (6) *via* mono-organoboranes 5, 8 and 11. It has been established by Pasto (1964) that diorganoboranes of the type 2 and 3 undergo alkaline hydrolysis during the study of dihydroboration of diphenyl acetylene. The observed increase in the amount of cyclotridecanol (6A) formed when the time of hydrolysis was enhanced, is in agreement with Pasto's observation (1964). A very small amount of ketone (7) present in the reaction products is visualised *via* 2.

It has been shown that 1,2-cyclotridecadiene (1A) and 1,2-cyclononadiene (1B) undergo monohydroboration to provide mainly vinyl organoborane (Devaprabhakara *et al* 1968). Therefore, it is reasonable to assume that the Z-addition of B-H bond



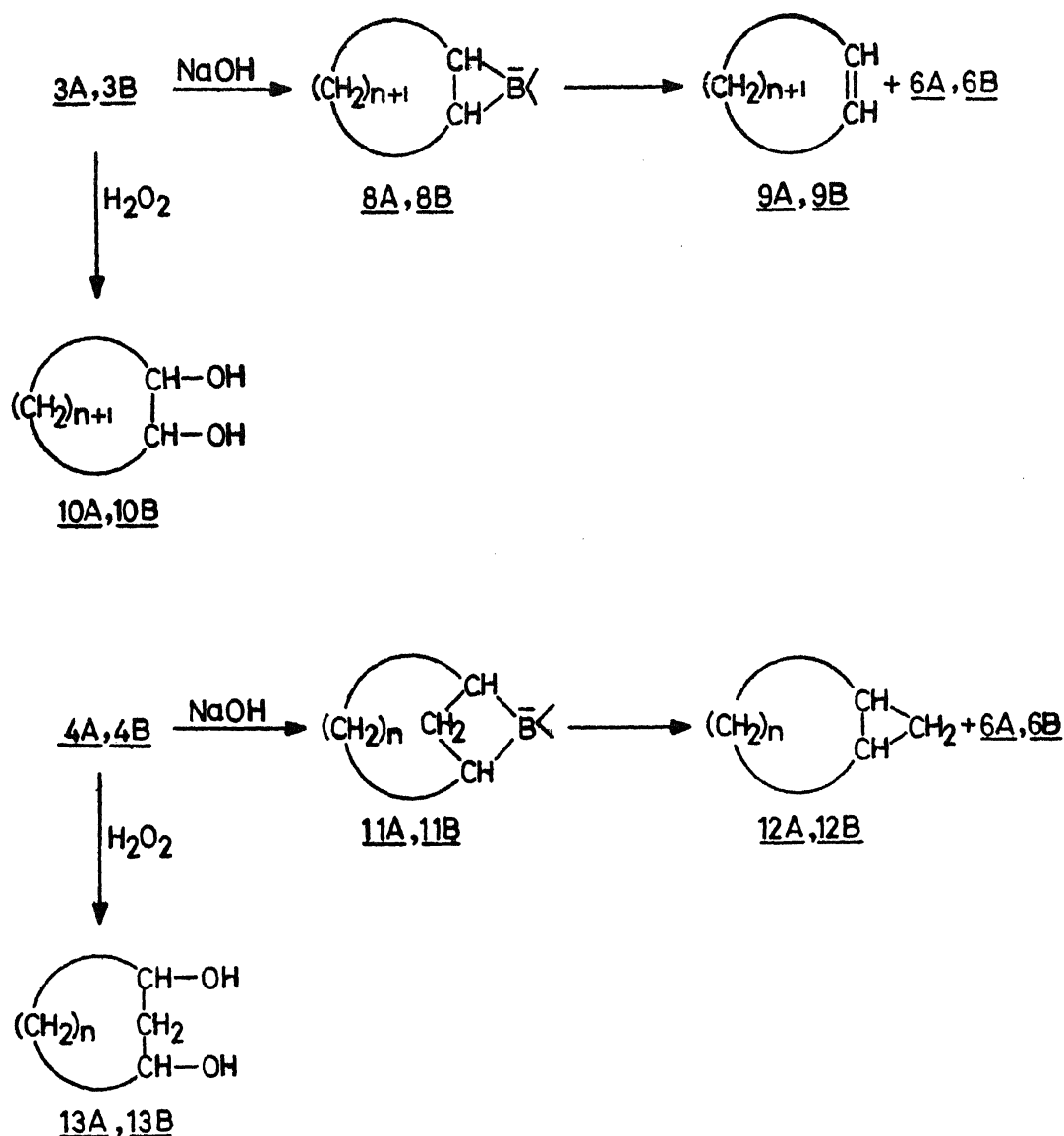


Figure 1. Possible mechanistic pathways for product formation.

should lead predominantly to the formation of 1,2-diorganoborane (3) with *threo* configuration. However, the formation of 1,2-diorganoborane (3) with *erythro* configuration from E-vinyl organoborane intermediate is also possible to some extent. The formation of E-cyclotridecene (E-9A) as the major product in the mixture of hydrocarbons from 1A or the formation of only E-cyclononene (E-9B) can be visualised *via* 8 by direct elimination in accordance with Pasto's mechanism (1964). The exclusive path for the formation of the anion 8 seems to be from 3 with retention in configuration. We suggest that the formation of the interesting bicyclic hydrocarbon 12A only in the case of 1A is possibly occurring *via* the bridged anion 11A. The formation of isomeric 1,2-diols (10) or 1,3-diols (13) is visualised *via* 3 and 4, respectively.

Brown and Garg (1961) have shown that organoboranes can be converted to the corresponding ketones by chromic acid oxidation. In view of this, an attempt was

made to find the relative amounts of 2, 3 and 4 formed in the dihydroboration of 1A. To our surprise chromium trioxide-pyridine oxidation of the intermediate organoboranes from dihydroboration of 1A gave mainly cyclotridecene (9A). The exclusive formation E-cyclotridecene (E-9A) from 14A (*threo*) can be explained via a two-step path or/and one-step path as shown in figure 2.

The substantiation of the proposed reaction pathway for the formation of E-9A from 14A (*threo*) has been established by preparation of *threo*-1,2-diorganoborane (17) from diphenyl acetylene (16) and its reaction with chromium trioxide-pyridine. This reaction produced E-stilbene (18) as the only isolable product in 70% yield

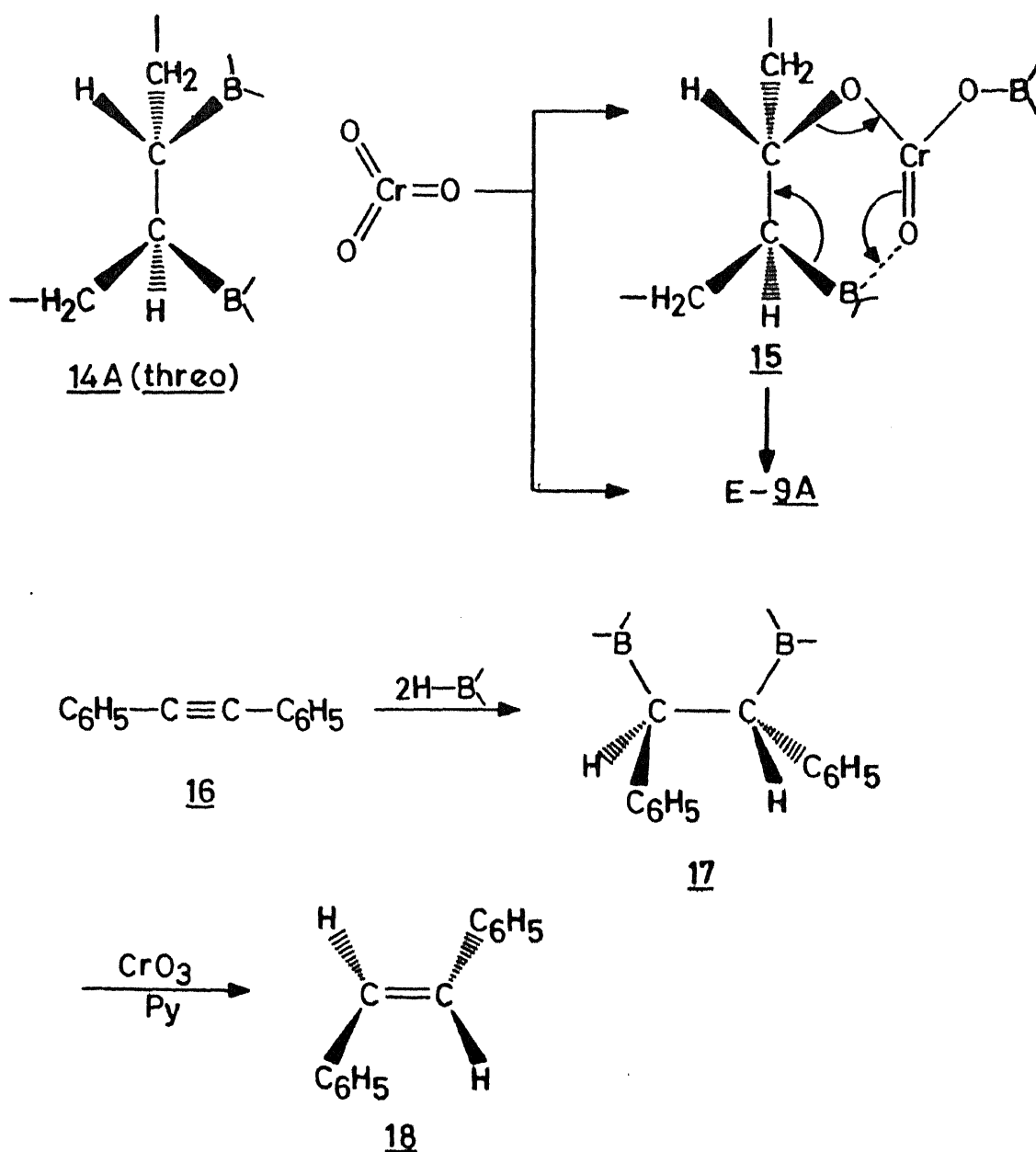


Figure 2. Possible mechanistic pathway for the unusual elimination reaction of 1,2-organoborane with chromium trioxide-pyridine.

(figure 2). The identity of 18 was established by mixed mp and comparison of IR with that of an authentic sample. Thus, our results demonstrate that deboration of 1,2-diorganoborane (17) occurs exclusively by *cis*-elimination (Devaprabhakara *et al* 1975).

In the proposed concerted mechanism (one-step) for this new elimination reaction (figure 2), a seven-membered transition state having 8 electrons is involved. Alternatively, the first-step of a two-step process could involve the breakage of the Cr-O d-p π -bond to form B-O bond, and the take-up of the d-p π -electrons by the chromium atom which results in 15. The stereochemistry of the reaction can be explained as the electron deficient boron is capable of complexing with oxygen of the chromium trioxide in 15. The intermediate 15 can undergo cleavage of the bonds as shown in the figure 2 to produce E-9A.

3. Conclusions

Our results show the similarities and differences of the dihydroboration-oxidation reactions of C-9 and C-13 allenes. The observed differences between C-9 and C-13 systems like the higher total yield of the reaction products in the case of C-13, non-formation of bicyclic hydrocarbon from C-9, and non-formation of Z-cyclononene (Z-9B) and Z-1,3-cyclononandiol (Z-13B) may be attributed to the difference in size of the two rings. Furthermore, the present study has also lead to the discovery of a new and a novel elimination reaction of 1,2-diorganoborane (2) with chromium trioxide-pyridine whose stereochemistry has been demonstrated to be *cis*.

4. Experimental

Boiling points (bp) are uncorrected. Melting points (mp) were taken in open capillaries using Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer model 137B or 521 spectrophotometer as liquid films between sodium chloride plates or using potassium bromide discs. Gas-liquid chromatography (GLC) analyses were made with Aerograph model 90-P instrument using 5 ft or 10 ft by $\frac{1}{8}$ inch 15% silicone rubber SE-30 or 10% carbowax column (% by weight on 60/80 mesh chromosorb P). Silica gel (NCL) or basic alumina (BDH) was used for thin layer chromatography (TLC). Column chromatography was done on basic alumina, column being prepared from its slurry in petroleum ether (60-80°). Microanalyses were done at the Microanalytical Laboratory of the Department of Chemistry, Indian Institute of Technology, Kanpur.

4.1. Starting materials

Z-Cyclooctene (Columbia), cyclododecene (Columbia), bromoform (E-Merck), potassium (Fischer), lithium (E Merck), methyl iodide (E-Merck), 30% hydrogen peroxide (BDH), and sodium borohydride (Metal Hydrides Inc.) were used. Diglyme (Ansul Co). was kept over calcium hydride (Metal Hydride Inc.) for 24 hr, decanted and distilled over slight excess of lithium aluminium hydride (Metal Hydride Inc.) under reduced pressure (bp 63-64° at 15 mm). Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of dry ether (E-Merck) so as to ensure an excess of this component and distilled under reduced pressure (bp 46-47° at 10 mm) over calcium hydride. Tetrahydrofuran was refluxed over sodium, decanted and

distilled over lithium aluminium hydride. *t*-Butyl alcohol (BDH) was refluxed over metallic sodium for about 5 hr and the fraction boiling at 79–80° was collected. Chromium trioxide (BDH) was stored in a vacuum desiccator over phosphorus pentoxide (BDH) prior to use. Analytical grade pyridine (BDH) was used without further purification.

1,2-Cyclononadiene and 1,2-cyclotridecadiene were prepared according to the procedure of Moore and Ward (1962). Their properties corresponded well with those reported (Moore and Ward 1962 and Nozaki *et al* 1966). Diphenyl acetylene was synthesised as described by Smith and Falkof (1955) and characterised by mixed mp using an authentic sample. A solution of borane in tetrahydrofuran was made according to Brown's (1975) procedure and its molarity was estimated before use.

4.2. Dihydroboration-alkaline hydrogen peroxide oxidation of 1,2-cyclotridecadiene

1,2-Cyclotridecadiene (3.56 g, 0.02 mol) in dry tetrahydrofuran (40 ml) was taken in a 250 ml three-necked flask equipped with a water condenser, pressure equilibrating dropping funnel, a low temperature thermometer and an inlet-outlet for dry nitrogen gas. The flask was immersed in ice-salt bath and borane in tetrahydrofuran (34 ml, 0.8 M) was added through the dropping funnel over a period of 45 min at 0–5°. The reaction mixture was allowed to stir for 1 hr at 0–10° and for 20 hr at room temperature. The reaction mixture was then carefully hydrolysed using water (5 ml) which gave 0.034 mol of unreacted hydride. Sodium hydroxide (1.2 g, 0.03 mol) dissolved in water (6 ml) was added to the mixture and allowed to stir for 15 min. During alkaline hydrolysis 80 ml of hydrogen was evolved. The mixture was subsequently oxidised using 30% hydrogen peroxide (20 ml), extracted with ether, washed with water and dried over anhydrous magnesium sulphate. Crude product (2.7 g) obtained after removal of the solvent showed 6 spots on a silica gel coated plate with chloroform-benzene (1 : 3). The material was chromatographed on a column prepared from a slurry of 160 g of basic alumina in petroleum ether (60–80°). Elution of the column with petroleum ether (60–80°) afforded 180 mg (5%) of a liquid product. GLC analysis of the liquid product on a 10 ft 10% carbowax column indicated it to be a mixture of *Z*-cyclotridecene, *E*-cyclotridecene and bicyclo(10.1.0) tridecane in the ratio 1 : 7 : 2. These three components were separated by GLC and identified by comparison of GLC retention times and IR with those of authentic samples.

Further elution of the column with petroleum ether (60–80°) yielded 60 mg (1.5%) of cyclotridecanone whose identity was established using an authentic sample. A solid (1.0 g, 27%) was obtained on eluting the column with petroleum ether-benzene (1 : 1) mixture, and this solid material was identified as cyclotridecanol using an authentic sample.

Elution of the column with petroleum ether-benzene (1 : 3) mixture gave *E*-1,2-cyclotridecandiol (620 mg, 15%) whereas elution with ether yielded *Z*-1,2-cyclotridecandiol (600 mg, 14%). Authenticity of the isomeric diols was established by comparison of IR spectra and mixed mp with authentic samples. Column was ultimately drained with methanol to get a viscous oil (150 mg, 3%) which could not be crystallised at all. IR spectrum showed the presence of only alcoholic group. TLC showed two spots. On the basis of these facts and elemental analysis, this product has been tentatively assigned as a mixture of isomeric 1,3-cyclotridecandiol.

Anal. for $C_{13}H_{26}O_2$ Calcd: C, 72.89; H, 12.15%.
Found: C, 72.85; H, 12.00%.

4.3. Dihydroboration-hydrolysis-oxidation with alkaline hydrogen peroxide of 1,2-cyclotridecadiene

1,2-Cyclotridecadiene (890 mg, 5 mmol) was hydroborated with borane in tetrahydrofuran (9 ml, 0.8 M). The mixture of organoboranes was allowed to stir with sodium hydroxide solution (20 ml, 0.02 mol) at 80° for 24 hr. The reaction mixture was then cooled to 0° and oxidised using 30% hydrogen peroxide (20 ml). The usual work-up procedure gave a mixture of Z-and E-cyclotridecene (70 mg, 7%) in 17 : 83 ratio and cyclotridecanol (560 mg, 60%).

4.4. Dihydroboration-oxidation with chromium trioxide-pyridine of 1,2-cyclotridecadiene

A solution of pyridine complex of chromium trioxide was obtained by adding chromium trioxide (1.0 g, 0.01 mol) to a magnetically stirred solution of pyridine (1.58 g, 0.02 mol) in methylene dichloride (25 ml) and the reaction mixture was allowed to stir for 15 min. The solution was added to the organoboranes prepared from 1,2-cyclotridecadiene (890 mg, 5 mmol) in dry tetrahydrofuran (10 ml) and borane in tetrahydrofuran (9 ml, 0.8 M) and stirred for 2 hr. The usual isolation procedure gave a mixture of Z-and E-cyclotridecene (450 mg, 50%) in 15 : 85 ratio and cyclotridecanone (65 mg, 3%).

4.5. Dihydroboration-oxidation of 1,2-cyclononadiene

Following the general procedure described for the dihydroboration of 1,2-cyclotridecadiene, 1,2-cyclononadiene (1.84 g, 0.015 mol) was hydroborated using borane in tetrahydrofuran (26 ml, 0.8 M). The usual work-up afforded a crude product (1.22 g) which on column chromatographic separation provided E-cyclononene (12 mg, 0.6%), cyclononanone (6 mg, 0.3%), cyclononanol (670 mg, 31%), Z-1, 2-cyclononandiol (250 mg, 11%), E-1, 2-cyclononandiol (250 mg, 11%) and E-1, 3-cyclononandiol (20 mg, 1.5%). All the products were identified by the usual procedure using authentic samples.

4.6. Preparation and reaction of threo-1,2-diorganoborane from diphenyl acetylene with chromium trioxide-pyridine

Diphenyl acetylene (1.8 g, 0.01 mol) was taken in dry tetrahydrofuran (15 ml) in a 500 ml three-necked flask. To it was added borane in tetrahydrofuran (15 ml, 1.86 M) at 0°. The reaction mixture was stirred for 4 hr at 0° and then for 12 hr at room temperature under the atmosphere of dry nitrogen gas. The residual hydride was destroyed by addition of water (5 ml).

A solution of pyridine complex of chromium trioxide was obtained by adding chromium trioxide (3.0 g, 0.03 mol) to a magnetically stirred solution of pyridine (6.3 g, 0.08 mol) in methylene dichloride (50 ml). The solution was added to the organoborane prepared from diphenyl acetylene (1.8 g, 0.01 mol) in 30 min. The reaction mixture

was stirred for 2 hr and extracted with ether. The combined ether extract was washed until neutral, and dried over anhydrous magnesium sulphate. The ether was removed to get E-stilbene (1.2 g, 70%). The TLC of the crude product gave a single spot. Recrystallisation from absolute ethanol gave pure E-stilbene whose identity was established using an authentic sample by mixed mp and comparison of IR.

Acknowledgements

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