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DIHYDROBORATION—CHROMIUM TRIOXIDE OXIDATION OF *gem*- AND *vic*-DIORGANOBORANES

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Summary

Representative cyclic and acyclic acetylenes were hydroborated using BH_3—THF, and the resulting mixture of 1,1- and 1,2-diorganoboranes was treated with chromium trioxide in pyridine. It appears that the 1,1-diorganoboranes are transformed to the corresponding alcohols and ketones, while the *threo*-1,2-diorganoboranes mainly give (*E*)-olefins via a *cis* stereospecific elimination.

Introduction

1,2- and 1,1-diorganoboranes are formed together on hydroborating acetylenes [1,2]. Dihydroboration of allene leads to the formation of 1,1-; 1,2- and a small amount of 1,3-diorganoborane [3]. The relative amounts of various diorganoboranes formed depend upon the structure of the parent acetylene or allene, and from a consideration of dihydroboration of an internal acetylene, it can be concluded that the 1,2-diorganoboranes (*vic*-borane) are the thermodynamically-controlled products and the 1,1-diorganoboranes (*gem*-borane) are the kinetically-controlled products. An alternative method of synthesizing 1,1- and 1,2-diorganoboranes has been proposed by Matteson [4]. These organoboranes very readily undergo base-catalysed hydrolysis to give monoorganoboranes. Subsequent oxidation with hydrogen peroxide yields alcohols and olefins as the major products along with small amounts of ketones and diols [3]. The mechanism for the formation of the various products has been established by Pasto [1]. A mixture of diorganoboranes from 1,2-cyclotridecadiene dihydroboration was treated with chromic acid and separately, with chromium

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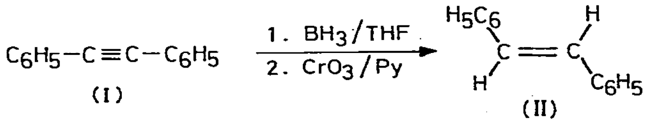
trioxide/pyridine with the objective of obtaining diketones [3], but surprisingly a mixture of (*E*)- and (*Z*)-cyclotridecene (85/15) was formed in 50% yield, along with cyclotridecanone in 3% yield. The mechanistic aspects of the reaction of chromium trioxide/pyridine with 1,2-diorganoboranes has been studied, and it has been postulated that the reaction proceeds via a cyclic transition state involving retention of configuration [5]. This prompted us to investigate the reaction of 1,1-diorganoboranes with the chromium trioxide/pyridine complex, and so some acetylenes were dihydroborated and the mixture of *gem*- and *vic*-diorganoboranes was treated with chromium trioxide/pyridine.

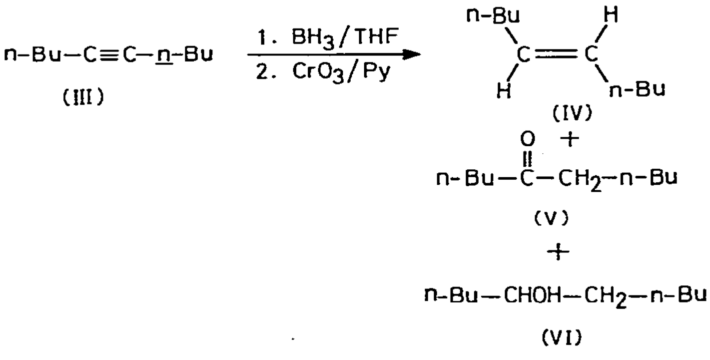
Results and discussion

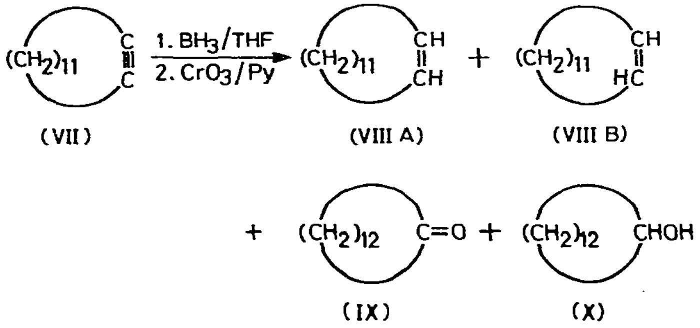
The dihydroboration reaction was carried out using a standard solution of borane/tetrahydrofuran (1/2 mol ratio of acetylene to borane) [6] under nitrogen and the resulting organoboranes were oxidized with chromium trioxide/pyridine in methylene chloride. The product mixture was analysed by GLC.

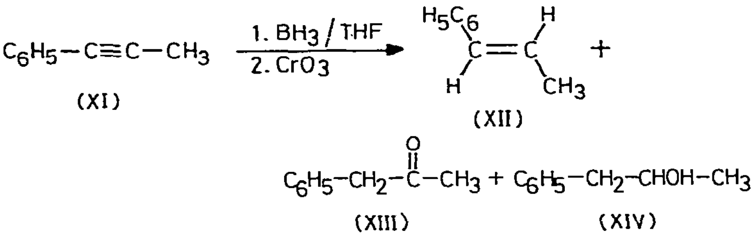
Diphenylacetylene (I) on dihydroboration followed by chromium trioxide oxidation yielded (*E*)-stilbene (II, 77%). 5-Decyne (III) on similar treatment and work up gave (*E*)-5-decene (IV, 54%) along with 5-decanone (V, 31%) and 5-decanol (VI, 15%). (*E*)- and (*Z*)-cyclotridecenes (VIIIA, 20%, VIIIB, 80%) were formed in 60%, when cyclotridecyne (VII) was dihydroborated and treated with chromium trioxide/pyridine. Further analysis of the crude mixture showed the presence of cyclotridecanone (IX, 25%) and cyclotridecanol (X, 15%). Alkyl-aryl-substituted acetylene (phenylpropyne, XI) also gave a mixture of (*E*)-1-phenylpropene (XII, 62%), 1-phenyl-2-propanone (XIII, 30%) and 1-phenyl-2-propanol (XIV, 8%).

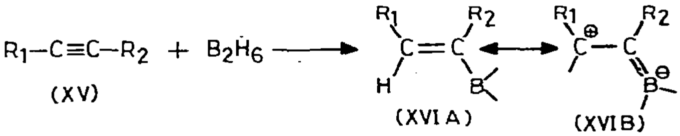
These products are formed via 1,1- and 1,2-diorganoboranes. The results of chromium trioxide/pyridine oxidation of acetylenes are listed in Table 1.

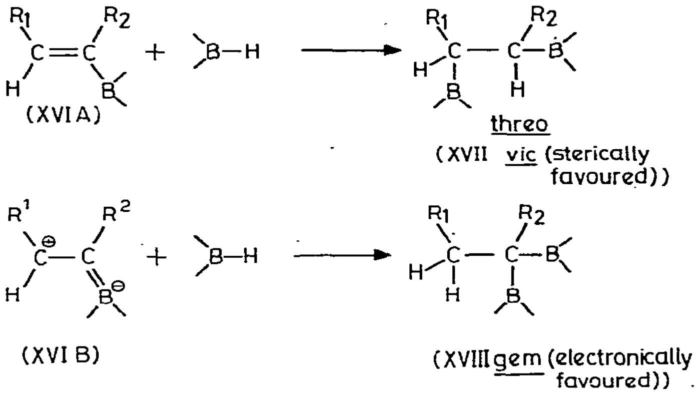












$R^1 = R^2 = C_6H_5$ (I)

$R^1 = R^2 = n-Bu$ (III)

R^1 $R^2 = (CH_2)$ (VII)

$R^1 = C_6H_5$; $R^2 = CH_3$ (XI)

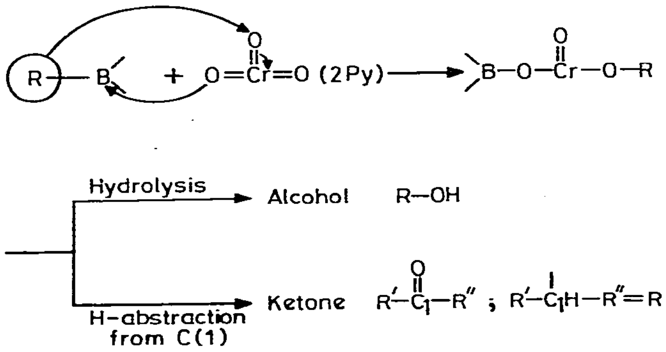
The cleavage of carbon—boron bonds with chromium trioxide normally gives ketones via the alcohols [3], but because of the participation of the other boron centre in the molecule the course of the reaction is changed and (*E*)-

TABLE 1

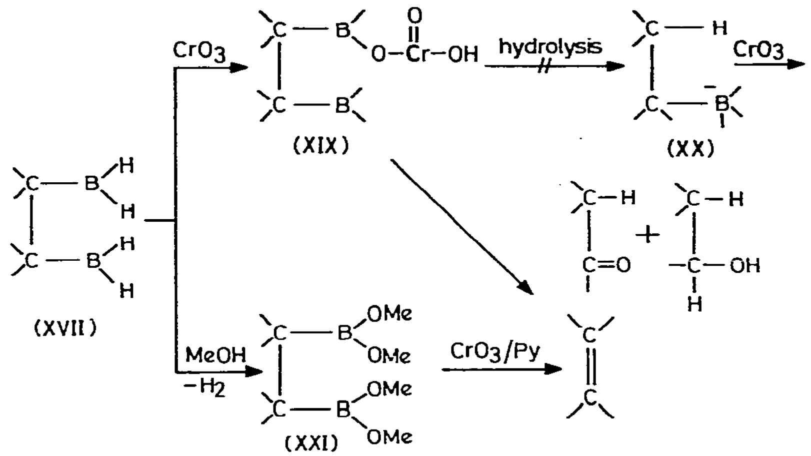
RESULTS OF DIHYDROBORATION FOLLOWED BY CHROMIUM TRIOXIDE/PYRIDINE OXIDATION OF ACETYLENES

Acetylene	Products (%)	Yield (%)	*gem* (%)	*vic* (%)
Diphenylacetylene (I)	(*E*)-Stilbene (II, 100)	77	0	100
5-Decyne (III)	(*E*)-5-Decene (IV, 54) 5-Decanone (V, 31) 5-Decanol (VI, 15)	70	46	54
Cyclotridecyne (VII)	(*E*)- and (*Z*)-cyclotridecene (VIII, 60) Cyclotridecanone (IX, 25) Cyclotridecanol (X, 15)	67	40	60
Phenylpropyne (XI)	(*E*)-1-phenylpropene (XII, 62) 1-phenyl-2-propanone (XIII, 30) 1-phenyl-2-propanol (XIV, 8)	80	38	62

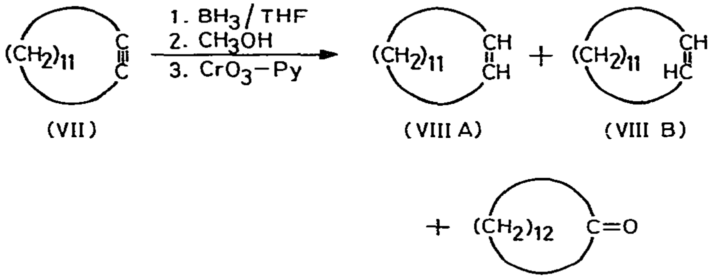
olefins are formed:



In reactions with organoboranes containing B—H bonds, chromium trioxide reacts faster with B—H bonds than with B—C bonds, and oxidation of B—H bonds could give rise to protons which would catalyse the hydrolysis. (The



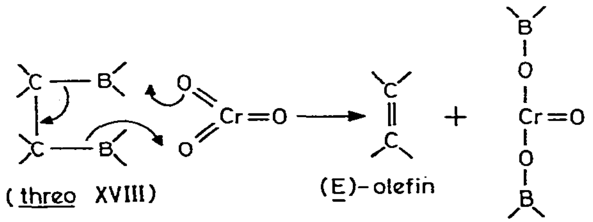
organoboranes formed under our conditions do contain residual hydride as evidenced by hydrogen evolution on addition of water). Thus a hydroborated mixture was treated with methanol and hydrogen evolution was observed. The excess of methanol was removed and the organoborane mixture, now containing B—OMe bonds in place of B—H bonds was oxidized. The products were olefins and ketones:



(VII) (VIII A) (VIII B) (IX)

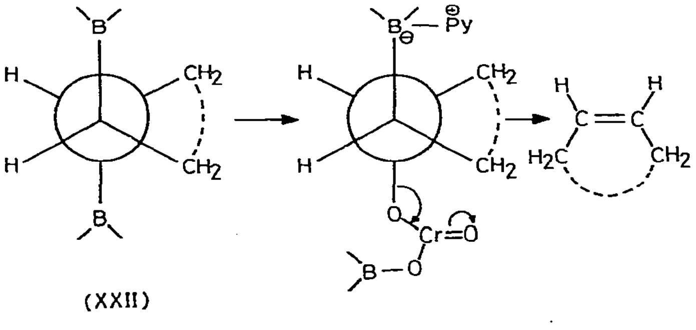
The 1,1-diorganoboranes will presumably give rise to the corresponding ketones and alcohols found. The fact, that alcohol is obtained from III, VII and XI indicates hydrolysis of *gem*-diorganoboranes to monoorganoboranes followed by oxidation, and it is known that *vic*-diorganoboranes do undergo hydrolysis [1]. The ketones (V, IX, XIII) and alcohols (VI, X, XIV) would be expected from the *vic*-diorganoboranes. In principle, hydrolysis of *vic*- and *gem*-diorganoboranes in presence of an excess of hydride is also a possibility.

That the amount of olefin formed is not changed by the methanol treatment of the organoborane mixture favours the view that (*E*)-olefins are formed from 1,2-diorganoboranes via a stereospecific *cis*-elimination [5] of two borons attached to *vicinal* carbon atoms:



(threo XVIII)

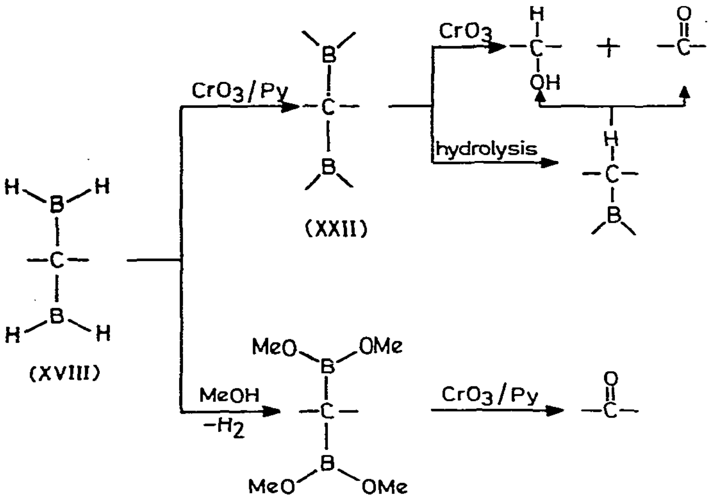
The small amount of (*Z*)-cyclotridecene formed is possibly produced via *trans*-elimination of 1,2-diboro compound.



(XXII)

The cyclic system can have conformation XXII which is well suited for *trans*-elimination, but such a possibility is ruled out for an acyclic system. In a control experiment, (*Z*)- and (*E*)-cyclotridecenes were treated with chromium trioxide/pyridine, and no change in the composition of the olefins was observed.

Carbenes are not formed from the 1,1-diboro compounds on treatment with chromium trioxide/pyridine, as evidenced by the fact that no 4-decene is obtained from hydroboration—oxidation of 5-decyne. Evidently, 1,1-diboro compounds give rise to ketones and alcohols.



Conclusion

It is concluded that the reaction of 1,2-diboro compounds with chromium trioxide/pyridine gives olefins, while 1,1-diboro compounds give ketones and alcohols. The amount of olefin isolated is a measure of the amount of isolated 1,2-diorganoborane formed in the hydroboration while the combined yield of ketone and alcohol is a measure of the amount of 1,1-diorganoborane so formed. The relative amounts of 1,1- and 1,2-diboro compounds obtained from various acetylenes can be interpreted in terms of the steric and electronic requirement of the parent acetylenes and intermediate monoorganoboranes.

Experimental

The boiling points are uncorrected. Elemental analyses were carried out by A.H. Siddiqui (Department of Chemistry, Indian Institute of Technology, Kanpur). IR spectra were recorded on a Perkin—Elmer 137 spectrometer as neat liquids between sodium chloride plates. GLC analyses were carried out with a Varian 90-P model instrument using carbowax 15M $10'\frac{1}{4}''$ and SE-30 $5'\frac{1}{4}''$ columns. THF was dried over lithium aluminium hydride, distilled, and kept under nitrogen. Borane [8], diphenylacetylene [9], 5-decyne [10], cyclotridecyne [11] and phenylpropyne [12] were prepared by established procedures. Their identities were confirmed by spectral and analytical data.

General procedure for dihydroboration of acetylenes

A 250 ml three-necked round-bottom flask fitted with a pressure-equalizing dropping funnel and an inlet and outlet for nitrogen was cooled in an ice/salt mixture bath. The appropriate acetylene (10 mmol) dissolved in dry THF (15 ml) was placed in the flask. BH_3/THF (2 *M*, 10 ml, 20 mmol) was added during 0.5 h, and the dropping funnel was rinsed with THF (5 ml) to ensure quantitative borane addition. The mixture was stirred for 4 h at 0° C and then for 12 h at room temperature.

General procedure for chromium trioxide/pyridine oxidation of the dihydroboration product from acetylenes

A solution of the chromium trioxide/pyridine complex was obtained by adding chromium trioxide (5 g, 50 mmol) to a magnetically stirred solution of pyridine (8.7 g, 110 mmol) in 200 ml of methylene dichloride. The solution was added during 0.5 h to the organoborane mixtures obtained from the acetylenes and the mixture was stirred for 6 h. Ether (300 ml) was added and the mixture was stirred for 10 min, then filtered. The filtrate was washed with diluted NaOH (10%), diluted HCl (5%), water, $NaHCO_3$, again with water till neutral, and dried over magnesium sulphate. The solvent was removed by distillation to give the products.

Dihydroboration—oxidation of diphenylacetylene

Diphenyl acetylene (1.80 g, 10 mmol) was treated with borane in THF (2 *M*, 10 ml, 20 mmol). To the product mixture was added a solution of chromium trioxide/pyridine obtained from chromium trioxide (5.0 g, 50 mmol) and pyridine (11.8 g, 150 mmol) in methylene dichloride (200 ml). The usual work up followed by recrystallization from ethanol gave (*E*)-stilbene (1.32 g, 77%), m.p. and mixed m.p. 125° C.

Dihydroboration—oxidation of 5-decyne

5-Decyne (1.50 g, 10 mmol) was hydroborated in the usual way and oxidised with chromium trioxide (5.0 g, 50 mmol)/pyridine (11.8 g, 150 mmol). The usual work-up yielded a fraction (1.05 g, 70%) of b.p. 60—80° C/5 mmHg. GLC analysis of the distillate on the Carbowax column showed the presence of (*E*)-5-decene, 5-decanone and 5-decanol in the ratio 54/31/15. Pure compounds were obtained by preparative GLC and characterized by comparison of their IR spectra with those of authentic samples.

Dihydroboration—oxidation of cyclotridecyne

Following the general procedure, cyclotridecyne (1.78 g, 10 mmol) was hydroborated and oxidized. The usual work-up gave a mixture of products (1.20 g, 67%), b.p. 82—106° C/2 mmHg. The distilled material showed four peaks on the SE-30 column. Pure compounds were isolated by preparative GLC and identified as (*Z*)- and (*E*)-cyclotridecenes (20/80), cyclotridecanone, and cyclotridecanol in the ratio 60/25/15.

Dihydroboration—oxidation of phenylpropyne

Phenylpropyne (2.32 g, 20 mmol) was dihydroborated and then oxidised with chromium trioxide (10 g, 100 mmol) and pyridine (23.6 g, 300 mmol). The products (1.84 g, 80%) of b.p. 51—60° C/35 mmHg and 60—86° C/2 mmHg were analysed by GLC on the Carbowax column. This revealed the presence of (*E*)-1-phenylpropene, 1-phenyl-2-propanone and 1-phenyl-2-propanol in the ratio 62/30/8.

Dihydroboration/methanol treatment oxidation of cyclotridecyne

Cyclotridecyne (1.78 g, 10 mmol) was hydroborated. Methanol was added to destroy the residual hydride. THF and methanol were removed under vacuum at room temperature under nitrogen. The organoborane obtained was oxidised with chromium trioxide (5 g, 50 mmol)/pyridine (11.8 g, 150 mmol), and the usual work-up yielded a product (1.20 g, 67%) of b.p. 70° C/0.25 mmHg. GLC analysis showed it to consist of (*Z*)- and (*E*)-cyclotridecenes and cyclotridecanone in the ratio 11/44/45.

Acknowledgement

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