Tetrahedron. Vol. 28, pp. 5697 to 5702. Pergamon Press 1972. Printed in Great Britain

HYDROBORATION OF ALKYLIDENECYCLOPROPANES*

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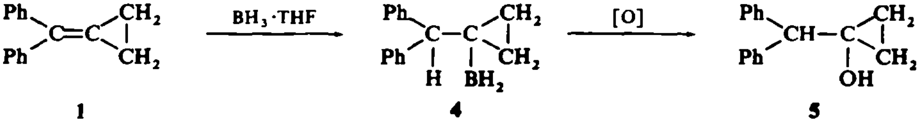
(*Received in Japan* 17 *July* 1972; *Received in the UK for publication* 10 *August* 1972)

Abstract—Hydroboration of diphenylmethylenecyclopropane (**1**) and α-methylbenzylidenecyclopropane (**2**) gives 1-diphenylmethyl-cyclopropanol (**5**) and 1-(α-methylbenzyl)cyclopropanol (**7**), respectively, by the attack of boron on cyclopropylidene carbon. With benzylidenecyclopropane (**3**), 1-phenyl-2-butanone (**16**), phenylcyclopropylcarbinol (**14**) and 1-phenyl-1,4-butanediol (**17**) is obtained. The diol is considered to be produced from intermediary cyclopropylborane (**11**) *via* homoallylic rearrangement and intramolecular hydroboration.

Hydroboration of olefinic compounds[1,2] proceeds so as to give a product resulting from attack of boron on the more electron-rich carbon of the original double bond. Reaction of methylene-cyclopropane with diborane was reported[3] to afford tris(3-butenyl)-borane *via* tris(cyclopropylmethyl)borane which was produced by the attack of boron on the least substituted terminal carbon atom. In order to obtain further information about the electronic effects of the cyclopropane ring on the directly fused double bond, hydroboration of alkylidenecyclopropanes investigated.

Diphenylmethylenecyclopropane[4] (**1**), α-methylbenzylidene-cyclopropane (**2**) and benzylidenecyclopropane[4] (**3**) were hydroborated with THF solutions of borane.

Reaction of **1** with BH_3 followed by oxidation with alkaline H_2O_2 gave 1-diphenylmethylcyclopropanol (**5**). The same sequence of reactions on **2** gave 1-(α-methylbenzyl)cyclopropanol (**7**) and 2-phenyl-3-pentanone (**8**). The formation of ketone **8** was accounted for by alkaline isomerization[5] of cyclopropanol **7**. For confirmation, the isolation of the intermediary boron compound **6** as stable compound **9** was attempted. Excess ethylene glycol[6] was added to the mixture of BH_3 and **2** so that the organoboron compound **6** was converted into ethylenedioxy compound **9**. Gas chromatography showed that the distillable product was homogeneous and NMR and MS[7] indicated the structure to be that of boron compound **9**. Additional evidence was obtained by the oxidation of organoboron compounds **6** or **9** with trimethylamine oxide[8] to give only cyclopropanol **7**.



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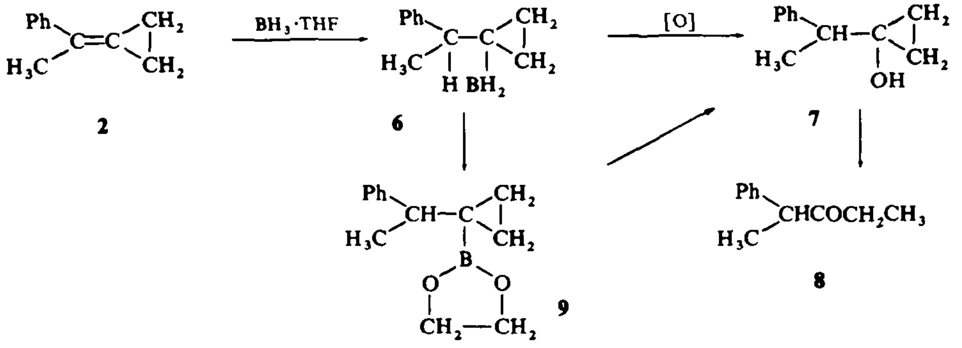
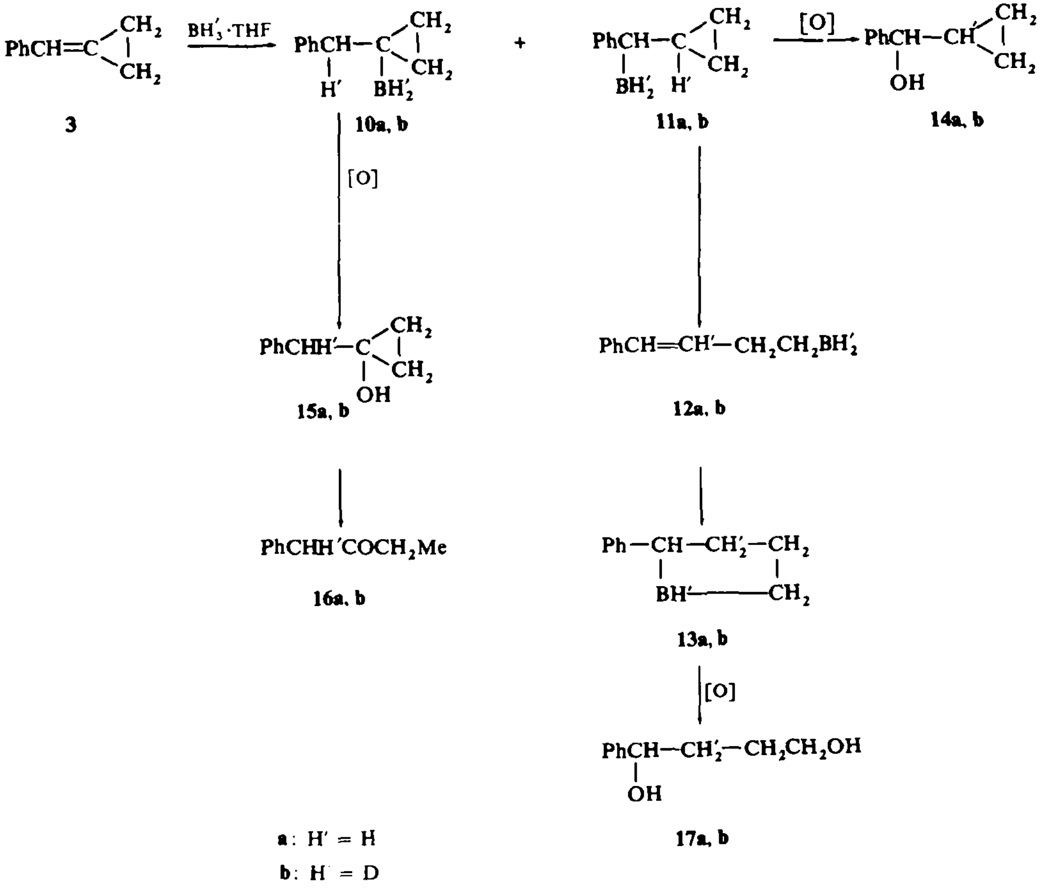
[*] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March 31–April 4, 1967, by K. Sisido, M. Tamura and K. Utimoto.



Hydroboration followed by oxidation of benzylidenecyclopropane (**3**) gave 1-phenyl-2-butanone (**16a**), phenylcyclopropylcarbinol (**14a**) and 1-phenyl-1,4-butanediol (**17a**). 1-Phenyl-2-butanone (**16a**) could be explained as an alkaline isomerization product of cyclopropanol **15a**.[5]

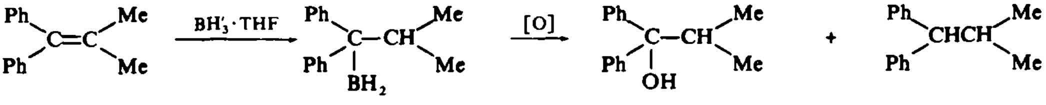


The production of 1-phenyl-1,4-butanediol (**17a**) was accounted for by homoallylic rearrangement[3] of intermediary cyclopropylmethylborane (**11a**) to **12a** and subsequent intramolecular hydroboration. This hydroboration process could be concluded to be intramolecular as compared with the orientation of boron in the case of the hydroboration of propenylbenzene (**26**).[9] If this process was intermolecular, the product would be a mixture of 1-phenyl-1,4-butanediol (**17a**) and 4-phenyl-1,3-butanediol because boron would attack both of the ethylene carbons. However, 4-phenyl-1,3-butanediol could not be identified. Since by the intramolecular process, 4-phenyl-1,3-butanediol could not be considered because of improbability of four-membered boretane ring formation, 1-phenyl-1,4-butanediol (**17a**) would account for the intramolecular hydroboration *via* borolane compound **13a**. The isolation of **13a** has not yet been accomplished.

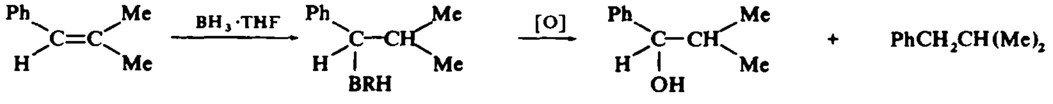
The same hydroboration was performed with borane-d_3. The deuterium positions of the respective compounds were determined by NMR and MS as described below. Analyses of the deuterium positions indicated that ketone **16a, b** was derived from cyclopropanol **15a, b** and that diol **17a, b** was obtained *via* homoallylic rearrangement of intermediary cyclopropylmethylborane **11a, b**.

The hydroboration of 1,1-dimethyl-2,2-diphenylethylene (**18**) and 1,1-dimethyl-2-phenylethylene (**19**) was compared with that of diphenylmethylenecyclopropane (**1**) and benzylidenecyclopropane (**3**) in order to elucidate the the effects of the cyclopropylidene group.

Alkaline H_2O_2 oxidation of the hydroboration product of **18** gave 1,1-dimethyl-2,2-diphenylethane (**22**) and 1,1-diphenyl-2-methylpropanol (**21**) in the ratio of 90:10. 1,1-Dimethyl-2,2-diphenylethane (**22**) was obtained by the alkaline hydrolysis[10,11] of organoboron compound (**20**). Trimethylamine oxide oxidation of the hydroboration product gave the same compounds in a ratio of 8:92. The formation of



18 **20** **21** **22**

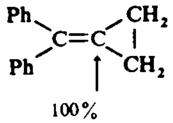


19 **23** **24** **25**

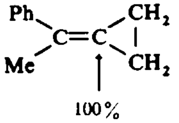
(R = H or 1-phenyl-2-methylpropyl)

1,1-diphenyl-2-propanol (**21**) and 1,1-dimethyl-2,2-diphenylethane (**22**) indicated that boron attacks the carbon atom having two Ph groups contrary to the case of diphenylmethylenecyclopropane **1**. Hydroboration and successive trimethylamine oxide oxidation of 1,1-dimethyl-2-phenylethylene (**19**) gave a mixture of 1,1-dimethyl-2-phenylethane (**25**) (1%), 1-phenyl-2-methylpropanol (**24**) (70%) and recovered **19** (15%) indicating that boron exclusively attacks the less substituted carbon. In the case of benzylidenecyclopropane, however, 76% attacks the less substituted carbon and 24% attacks the more substituted cyclopropylidene carbon.

The direction of attack of boron in the hydroboration of alkylidenecyclopropanes and related compounds are shown:



1



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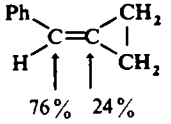

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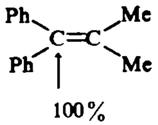
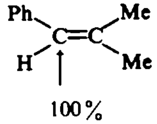
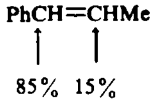


18



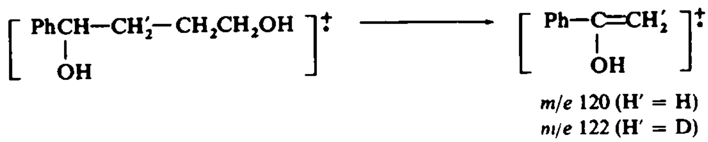
19



26[9]

These data indicate that the cyclopropylidene carbon has more electronegative character than the usual olefinic carbon because of high s-character of the exobonding orbital at the propylidene carbon.

The deuterium positions of **14b**, **16b** and **17b** were determined by NMR and mass spectra. In the mass spectra of **16a**, the ion at *m/e* 91 became *m/e* 92 by deuteration to **16b** showing that the deuteride attacked the benzyl group. For diol **17b**, the ion at 31 indicated the absence of deuterium at δ-position of the phenyl group and cation with *m/e* 107 showed the presence of hydroxybenzyl group. The movement of cation by deuteration from *m/e* 120 to *m/e* 122 could be explained as follows.



m/e 120 (H' = H)
m/e 122 (H' = D)

The NMR spectrum (Fig. 1) of the diol supported the position of the deuterium as β to the phenyl group.

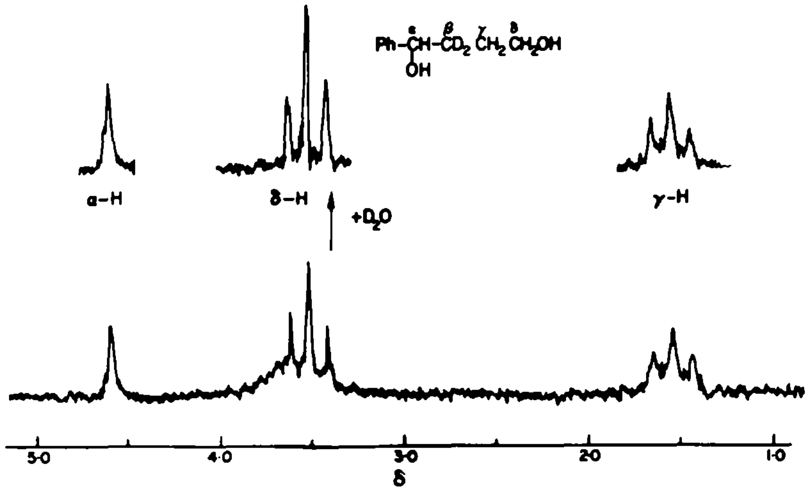


FIG. 1. NMR spectrum of 1-phenyl-1,4-butanediol-2,2-d_2 (**17b**).

EXPERIMENTAL

GC was carried out on Shimadzu GC-2C and GC-4APT, with 3 m × 3 mm stainless steel column packed with 30% PEG-6000 and 30% HVSG on Chromosorb W (80–100 mesh). IR spectra were recorded as liquid films on Shimadzu IR-27. NMR spectra were measured at 60 MHz with Varian Associate A-60 and Japan Electron Optics C-60-H machines. Mass spectra were obtained on Hitachi RMU-6 and RMS-4 spectrometers. UV spectra were recorded on an Hitachi EPS-2 spectrometer. Elemental analyses were carried out by Mrs. K. Huzimoto of this laboratory using Yanagimoto sutomatic analyzer CHN Corder MT-1.

Hydroboration of diphenylmethylenecyclopropane (1). To a solution of 1·20 g (5·8 mmol) of **1** in 20 ml of THF was added under N_2 16·7 ml of THF solution of borane containing 11 mmol of BH_3. The mixture was stirred for 5 h at room temp and to this was added 5 ml of 3N NaOH aq and 1·9 ml of 30% H_2O_2. After refluxing for 2 h, the product was ether extracted. GLC showed 1-diphenylmethylcyclopropanol (**5**) as the only volatile product. Distillation gave 1·10 g (84%) of **5**, b.p. 154° 4 mm, m.p. 78·0–80·0°; IR (Nujol) 3270 (w), 2950 (s), 1600 (w), 1464 (s), 1378 (s), 1275 (m), 1205 (m), 1185 (m), 1165 (m), 1020 (m), 945 (m), 925 (m), 780 (m), 760 (m) cm^{-1}; NMR ($CDCl_3$) (δ ppm) 0·68–0·87 (m, 4H), 2·07 (broad, 1H, disappears on addn. of D_2O), 3·84 (s, 1H), and aromatic hydrogens. (Found: C, 85·91; H, 7·30. Calc. for $C_{16}H_{16}O$: C, 85·68; H, 7·19%).

Hydroboration of α-methylbenzylidenecyclopropane (2). To an ice-cooled solution of 0·80 g (5·6 mmol) of **2** in 20 ml of THF was added 11 ml of THF solution of diborane containing 24 mmol BH_3 under N_2. After stirring for 3 h NaOH aq (6 g NaOH in 20 ml of H_2O) and 15 ml of 30% H_2O_2 were added and the mixture stirred for 2 h under reflux. Distillation of the extracted gave 0·79 g (87%) (73–79° 3 mm), of a mixture, which, according to GLC, consisted of 82% 1-(α-methylbenzyl)cyclopropanol (**7**) and 18% 2-phenyl-3-pentanone (**8**). Separation was carried out by GLC. The semicarbazone of **8** had m.p. 134–135° (lit[12] 135·4–136·4°).

When the same reaction was carried out with 0·31 g (7·8 mmol) of NaOH 99% pure (GLC) **7** was obtained in an 88% yield.

7: IR (liquid film) 3320 (s), 3090 (s), 3000 (s), 2960 (s), 1600 (m), 1450 (s), 1260 (s), 1215 (s), 1030 (m), 1010 (s), 955 (s), 930 (s), 778 (s), 760 (s), 700 (s) cm^{-1}; NMR ($CDCl_3$) (δ ppm) 0·5–0·76 (m, 4H), 1·34 (d, 3H), 1·68 (broad, s, 1H), 2·42 (quart, 1H), 7·2 (arom. H, 5H). (Found. C, 81·35; H, 8·59. Calc. for $C_{11}H_{14}O$: C, 81·44; H, 8·70%).

Ethylenedioxyborane 9. To an ice-cooled THF solution of 0·52 g (3·6 mmol) of **2** was added 3·3 ml of THF solution of boranecontaining 7·2 mmol of BH_3 and stirred for 2 h at room temp. Then 1 ml of ethylene glycol was added dropwise and the mixture stirred for 2 h at room temp. The reaction was added to water and ether extracted. Distillation of the extract gave 0·47 g (61 %) of **9**, b.p. 116° 3 mm; IR (liquid film) 3060 (m), 2970 (s), 1495 (s), 1480 (m), 1440 (s), 1410 (s), 1395 (s), 1232 (s), 1160 (s), 1140 (s), 1028 (s), 1015 (s), 915 (s), 770 (s), 700 (s), 680 (s) cm^{-1}; NMR ($CDCl_3$) (δ ppm) 0·42 (m, 2H), 0·75 (m, 2H), 1·41 (m, 3H), 2·20 (q, 1H), 4·02 (s, 4H), 7·2 (arom. H, 5H). *m/e* (rel. %) 217 (2), 216 (M^+) (8), 215 (4), 201 (13), 188 (19), 129 (16), 117 (32), 107 (10), 105 (100), 91 (19), 79 (19), 77 (21), 51 (12). (Found: C, 72·01; H, 8·06. Calc. for $C_{13}H_{17}O_2B$: C, 72·26; H, 7·93 %).

Oxidation of 9 *with alkaline hydrogen peroxide.* To a THF solution of 1·10 g (5 mmol) of **9** were added 5 ml NaOH aq containing 0·4 g NaOH and 1·2 g of 30% H_2O_2. The mixture was stirred for 3 h under reflux and ether extracted. Distillation of the extract gave 0·60 g (74 %) of cyclopropanol **7** (99 % purity).

Oxidation of 9 *with trimethylamine oxide.* To a solution of 0·42 g (2 mmol) of **9** in a small amount of THF was added 0·75 g of trimethylamine oxide and the mixture stirred for 3 h under reflux to give a quantitative yield of **7**.

Hydroboration-oxidation of benzylidenecyclopropane (3). A THF solution of 2·00 g (15·4 mmol) of **3** was treated as above with 72 mmol of borane. Distillation gave three fractions in a ratio of 24 :45 :31 which separated by GC and were identified (by comparison with the authentic samples) as 1-phenyl-2-butanone (**16a**),[13] phenylcyclopropylcarbinol (**14a**)[14] and 1-phenyl-1,4-butanediol (**17a**).[15]

Hydroboration of benzylidenecyclopropane (3) *with borane-*d_3. Borane-d_3 was generated by the dropwise addition of a solution of 0·580 g (13·8 mmol) of $NaBD_4$ in 20 ml of diglyme into a stirred diglyme solution of 3·8 g (27 mmol) of $BF_3 \cdot Et_2O$ 1·2 g of **3** as above, gave deuterized products **14b**, **16b**, and **17b** in essentially the same ratio.

Hydroboration-oxidation of 1,1-*dimethyl-*2,2-*diphenylethylene* (**18**). As above, 2·20 g of **18** gave 2·40 g of a mixture of 1,1-dimethyl-2,2-diphenylethane (**22**)[16] and 1,1-diphenyl-2-methylpropanol (**21**)[17] in a ratio of 90 :10.

Oxidation with trimethylamine oxide instead of alkaline H_2O_2 gave **22** and **21** in a ratio of 8 :92.

Hydroboration-oxidation of 1,1-*dimethyl-*2-*phenylethylene* (**19**). A THF solution of 0·66 g of **19** was treated with 1·8 mmol of borane at room temp for 1 h. Trimethylamine oxide (2·0 g) was added to the mixture and refluxed for 4 h. The cooled mixture was poured into water and ether extracted, dried and concentrated. Separation on silica afforded **24** (70 %), **25** (1 %), and **19** (15 %).

Acknowledgements—The authors are indebted to Mr H. Kusakabe for mass spectrometry and to Mrs K. Huzimoto for the elemental analyses.

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