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HOMOALLYLIC REARRANGEMENT OF CYCLOPROPYLCARBINYL BORATES

A STEREOSPECIFIC SYNTHESIS OF *TRANS*-4-ARYL-3-BUTENOLS[1]

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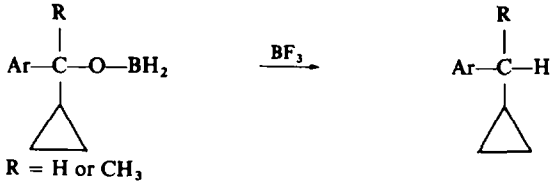
Abstract—Thermal decomposition of methyl aryl cyclopropylcarbinyl borates, followed by hydrolysis, gives rise to mixtures of 1-aryl-1-cyclopropylethylene, and of 4-aryl-3-pentenol. Similarly, aryl cyclopropylcarbinylborates yield *trans*-4-aryl-3-butenols, while dicyclopropyl carbinyl borate gives a mixture of *trans*- and *cis*-4-cyclopropyl-3-butenols.

INTRODUCTION

IT WAS recently shown[2] that in the presence of borontrifluoride carbon–oxygen bonds in some cyclopropylcarbinoxyboranes undergo O-alkyl fission to the corresponding carbonium ions, which are trapped by hydride, to yield the respective hydrocarbon.

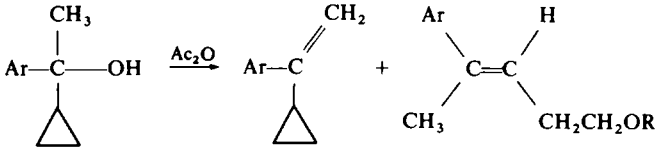


In an earlier paper[3] we demonstrated the influence of polar factors on the homoallylic rearrangement of arylcyclopropylmethyl carbinols (I). It was found that under the conditions employed, two concurrent reactions take place: elimination and rearrangement. It was also noted that electron-releasing substituents at the *para* position in the aromatic ring promote the rearrangement, at the expense of elimination, while the electron-withdrawing substituent chlorine favours elimination (1). Later,[4] it was shown that the elimination step is reversible, and addition of acetic acid in a 1·5 manner to the vinylcyclopropane system in II, gave the homoallylic acetates (IIIa), the stereochemistry of which has been established[4] (2).

Since it is known[5] that borates of tertiary alcohols decompose thermally to olefins when heated at 100–150°, a study of the thermal behaviour of cyclopropylcarbinyl borates was undertaken.

RESULTS

Preparation and thermal decomposition of borates from tertiary alcohols. Tri-(methyl aryl cyclopropylcarbinyl) borates were prepared by reacting the carbinol with equimolar amounts of borane (solution in tetrahydrofuran). The disproportiona-

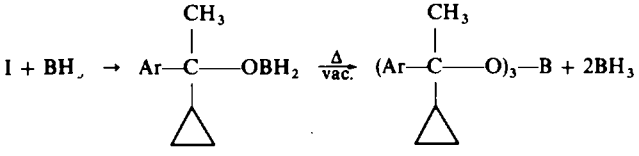


(1)

I II IIIa a: R = $COCH_3$ b: R = H

$$II + AcOH \rightarrow IIIa \quad (2)$$

tion of the alkoxyboranes was carried out by heating the reaction mixture in vacuum, and removing the diborane (Eq. 3).



(3)

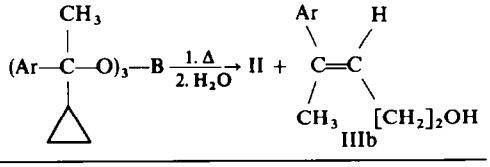
In separate experiments it was established that under these conditions no hydride remained in the reaction mixture, and that hydrogenolysis was negligible. Thermal decomposition experiments were carried out in a static nitrogen atmosphere. It was found that in boiling diglyme, the tertiary carbinylborates undergo facile reaction to yield, after hydrolysis, a mixture of 1-cyclopropyl-1-aryl ethylene (II), and 4-aryl-3-pentenol (IIIb).

The crude product mixtures were analysed by measuring relative peak intensities of the two components in the NMR spectrum.

The amount of styrene was estimated by measuring the intensity of the vinylic hydrogens at 5·2 and 4·8 ppm, relative to the aromatic peak area, whereas the amount of the rearranged homallylic alcohol was determined by its vinylic hydrogen absorption near 5·7 ppm and the allylic Me group at 2·0 ppm.

The results from the thermal decomposition experiments of the tertiary carbinyl borates are summarized in Table 1. From this Table it can be seen that the yield of

TABLE 1. PRODUCTS FROM THERMAL DECOMPOSITION OF TRI-(ARYLMETHYLCYCLOPROPYLCARBINYL) BORATES



IIIb

Aryl	yield of II (%)	yield of IIIb (%)
p-ClC_6H_4—	60	23
C_6H_5—	52	34
p-$CH_3OC_6H_4$—	33	44

the rearranged product (IIIb) increases with increase of the electron releasing ability of the substituent on the aromatic ring, in parallel to the rearrangement of I into IIIa.[3]

Preparation and thermal rearrangement of secondary cyclopropylcarbinylborates. In contrast to tertiary cyclopropylcarbinyl borates, which were prepared by reacting the carbinols with diborane, the secondary carbinylborates were prepared from the corresponding ketones. These were allowed to react with equimolar amounts of borane, and the resulting alkoxyboranes were disproportionated as described above. An exception to this is the case of *p*-anisyl cyclopropyl ketone, which is reduced by diborane to *p*-anisyl cyclopropylmethane.[2] However, this cyclopropyl-carbinylborate could be prepared by adding $\frac{1}{3}$ of a mole of borane to a mole of ketone. In spite of this precaution the yield from the anisyl derivative is low, because of hydrogenolysis.

The rearrangement of secondary cyclopropylcarbinyl borates was studied in some detail in the case of phenyl cyclopropylcarbinyl borate. By heating this borate in refluxing diglyme for 1 hr a 70–75% yield of *trans*-cinnamylcarbinol (IV) was obtained. The product did not contain any unrearranged phenyl cyclopropylcarbinol, but it was contaminated with other impurities, identified as ethers of cinnamyl carbinol with fragments of diglyme. Due to the presence of these impurities the utilization of diglyme as medium for the thermal decomposition was discontinued and other solvents were tried.

From Table 2 it can be seen that the polarity of the medium plays an important role in the rearrangement. In decalin no rearrangement is noted after 1 hr at 165°,

TABLE 2. INFLUENCE OF SOLVENT ON THE REARRANGEMENT OF PHENYL CYCLOPROPYLCARBINYL BORATE AT 165°

Solvent	time (hrs)	$C_6H_5CHOH—\triangleleft$ %	*trans* $C_6H_5—CH=CH—(CH_2)_2OH$ (IV)
Diglyme	1	0	75
Decalin	1	99	traces
O-$C_6H_4Cl_2$	1	50	50
O-$C_6H_4Cl_2$	4	traces	80

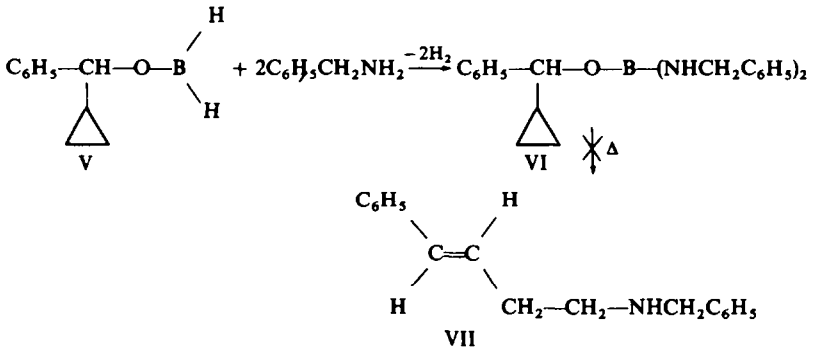
whereas in *o*-dichlorobenzene the half life time of the reaction is about 1 hr at the same temperature, and the reaction is complete after 4 hr. These conditions were adopted for the homoallylic rearrangements of the other secondary cyclopropylcarbinyl borates. The physical constants and analytical results of the products from these reactions are listed in Table 3.

The structures of the homoallylic alcohols were derived from their NMR and IR spectra. The homoallylic alcohols from the aromatic series were of the *trans* structure, whereas 4-cyclopropyl-3-butenol resulting from the dicyclopropyl compound was a mixture of the *cis* and the *trans* isomers in a ratio of 1:3. The separation of the geometric isomers was achieved by preparative gas chromatography, using a carbowax 400-silver nitrate column.

The NMR and IR spectral data of 4-substituted 3-butenols are listed in Table 4.

Attempted rearrangements in the presence of an amine. To explore the possible utility of the thermal rearrangement of cyclopropylcarbinyl borates for the synthesis of other homoallylic derivatives we converted phenyl cyclopropyl carbinyloxyborane

(V) into phenyl cyclopropylcarbinyloxy-bis-benzylamino-borane (VI), according to the equation:



It was thought that VI may undergo thermal rearrangement into N-benzyl, cinnamylcarbinylamine (VII). In fact, we observed no reaction upon heating VI, in diglyme for 1 hr. After hydrolysis, only benzylamine and phenyl cyclopropylcarbinol could be found in the product mixture. From the above it is clear that the presence of two N atoms attached to the boron inhibit the rearrangement. Consequently, the following modification was attempted. Tri-(phenyl cyclopropylcarbinyl) borate was prepared and benzylamine was added to the solution of this compound. It was assumed that this would lead to the formation of the addition compound, VIII, in which only one nitrogen is coordinated to the boron.

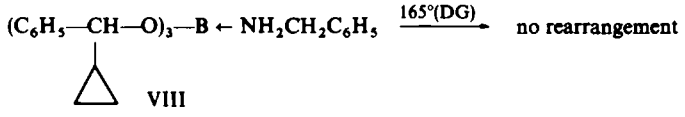
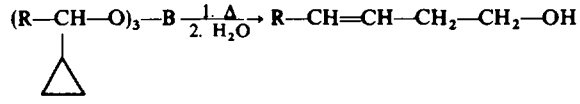


TABLE 3. PRODUCTS FROM THE THERMAL REARRANGEMENTS OF SEC-CYCLOPROPYLCARBINYL BORATES IN *o*-$C_6H_4Cl_2$ AT 170°

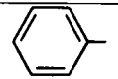
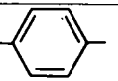
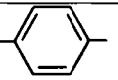
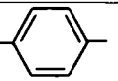


R	Yield %	b.p. °/mm	m.p.°	Analysis			
				Calc.		Found	
				C	H	C	H
C_6H_5—[a]	78	85–87/0·3	35	81·07	8·10	80·72	7·98
p-Cl—C_6H_4—[b]	59	110–113/0·2	—	65·70	6·03	65·50	6·10
p-CH_3O—C_6H_4—	43		75–77	74·30	7·87	74·03	7·98
p-CH_3—C_6H_4—	67	110–112/0·4	51–53	81·40	8·69	81·30	8·64
▷—[c]	77	52–54/0·3	—	71·00	9·47	70·85	9·55
CH_3—	no rearrangement was observed						

[a] Lit. b.p.: 102°/1·5 mm; m.p. 36°, R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.* **78**, 6079 (1956);
[b] Found: Cl, 19·35. Calc Cl, 19·45;
[c] mixture of *cis* and *trans* isomers in the ratio of 1:3.

TABLE 4. NMR AND IR SPECTRAL DATA OF 4-SUBSTITUTED-3-BUTENOLS

$$\underset{1}{R}\text{—}\underset{}{CH}\text{=}\underset{2}{CH}\text{—}\underset{3}{CH_2}\text{—}\underset{4}{CH_2}\text{—OH}$$

R	NMR												IR
	1			2			3			4			
	No. of H	δ ppm	J c/s	No. of H	δ ppm	J c/s	No. of H	δ ppm	J c/s	No. of H	δ ppm	J c/s	CH=CH bending
	1	6·25[d]	16	1	6·11[tt]	16 6	2	2·32[q]	6	2	3·56[t]	6	965 cm^{-1} (CCl_4)
Cl 	1	6·28[d]	16	1	6·17[tt]	16 6	2	2·30[q]	6	2	3·67[t]	6	965 cm^{-1} (neat)
CH_3 	1	6·34[d]	15	1	6·12[tt]	15 6	2	2·30[q]	6	2	3·67[t]	6	958 cm^{-1} (KBr)
CH_3O 	1	6·38[d]	16	1	6·18[tt]	16 6·5	2	2·45[q]	6·5	2	3·53[t]	6·5	958–973 cm^{-1} (KBr)
 (*trans*)	1	5·04[td]	15·5 7·5	1	5·43[tt]	15·5 6·5	2	2·20[q]	6·5	2	3·56[t]	6·5	958 cm^{-1} (neat)
 (*cis*)	1	4·87[td]	10·2 9·5	1	5·28[tt]	10·2 7	2	2·43[q]	7	2	3·64[t]	7	730 cm^{-1} (neat)

d = doublet; t = triplet; q = quartet; td = two doublets; tt = two triplets

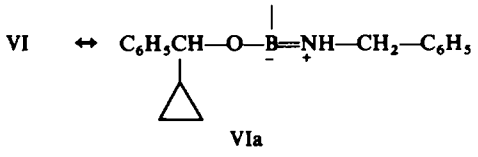
We observed that even in this case no thermal rearrangement takes place. In the reaction mixture we were able to establish only the presence of cyclopropyl-phenyl-carbinol and benzylamine.

Recently, we have shown that boron trifluoride catalyses the heterolytic O-alkyl bond fission in some alkoxyboranes, and in the presence of hydride the ions produced are trapped, and yield the corresponding hydrocarbons.[2] In order to examine the possible catalytic effect of borontrifluoride upon the homoallylic rearrangement, we added borontrifluoride to a solution of bis (phenyl cyclopropylcarbinyloxy) borane (XIB), which was produced from XIA under controlled conditions.

The addition of BF_3-etherate to the solution at 0° caused an exothermic reaction leading to a mixture comprised of benzyl cyclopropane (IX; 30%) and the following homoallylic derivatives: *trans*-cinnamylcarbinol (IV; 5%), *trans*-cinnamylcarbinyl methyl ether (Xa; 20%) and diethyleneglycol methyl *trans*-cinnamylcarbinyl ether (Xb; 40%).

DISCUSSION

Mechanism. The failure of the borate derivatives with N atoms coordinated to the boron, to undergo rearrangement, shows that the nitrogen exerts an inhibiting effect on the O-alkyl cleavage. A conceivable way to explain this, is to assume that the rearrangement proceeds by heterolytic fission to give the cyclopropyl carbinyl carbonium ion which yields allylcarbinyl derivatives. The coordination of nitrogen to the boron would be expected to inhibit such ionization by backdonating the unshared electrons of the nitrogen to the boron, rendering the borate moiety a poor leaving group, (VI ↔ VIa).



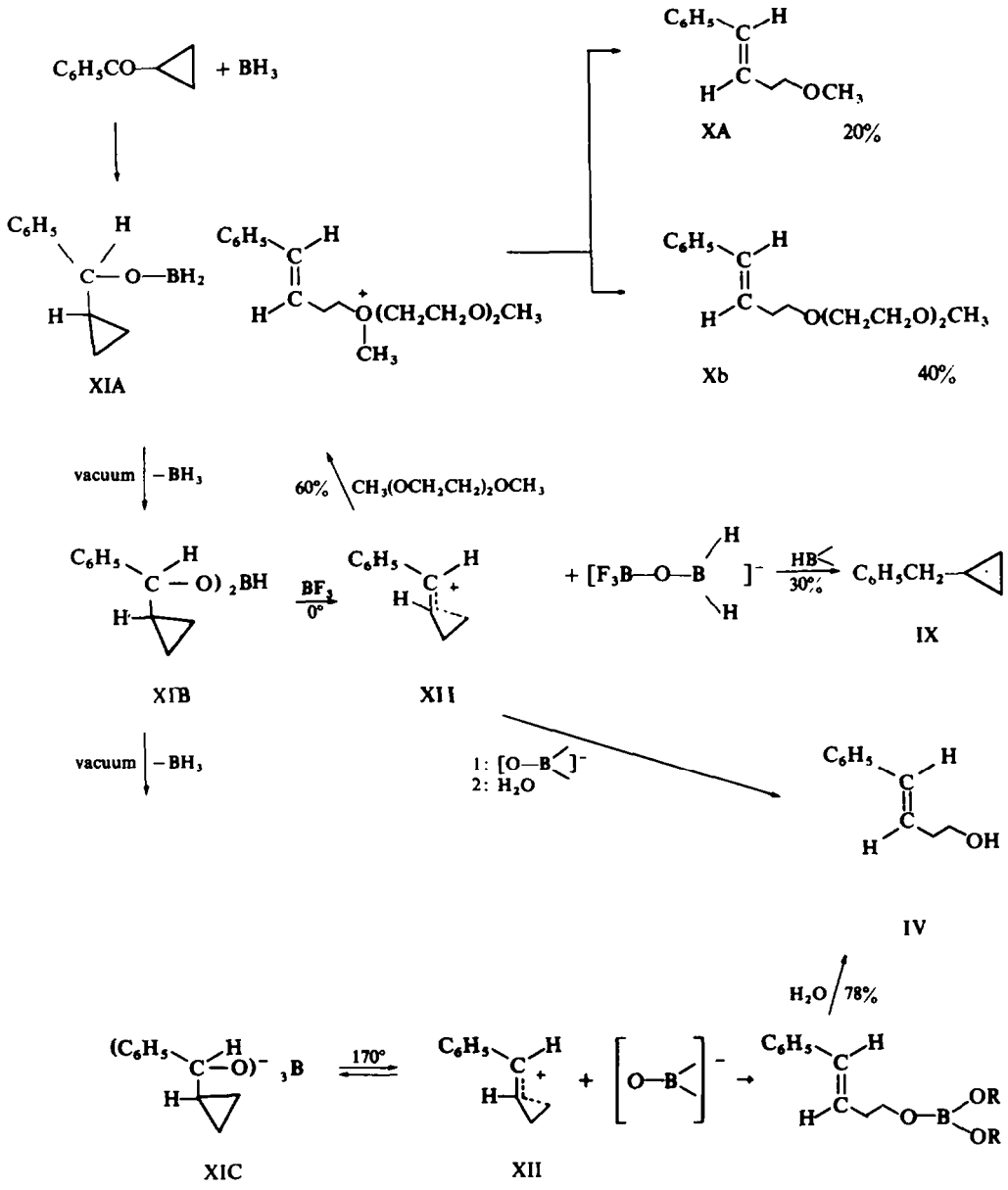
VIa

In contrast to the influence of the amine, boron trifluoride is expected to promote heterolysis by coordinating with the oxygen, thus conferring better leaving group properties to the borate moiety.[2]

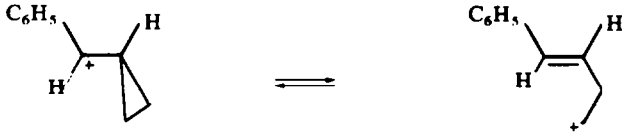
A plausible mechanism as outlined in Chart I is consistent with the results presented. The cyclopropylcarbinyloxyboranes XIB and XIC, which are prepared by disproportionation of XIA, may undergo ionization under the influence of heat or BF_3 to produce the delocalized carbonium ion XII.

In the thermal reaction of XIC the carbonium ion XII reacts with the borate anion to give the rearranged homoallylic borate which upon hydrolysis yields the alcohol IV. In the BF_3-catalyzed reaction, the carbonium ion XII from XIB is rapidly attacked by the hydride present to yield IX. The concurrent homoallylic rearrangement which proceeds at a slower rate, gives rise to the thermodynamically more stable products. It is reasonable to assume that BF_3 coordinates with the borate anion reducing thereby its nucleophilicity and consequently lowering the yield of IV. The carbonium ion attacks therefore the nucleophilic solvent to form the oxonium ion, which undergoes fragmentation to the cinnamylcarbinyl ethers (Xa and Xb).

CHART I


C6H5CO + BH3
XIA
XA 20%
Xb 40%
vacuum −BH3
60% CH3(OCH2CH2)2OCH3
BF3 0°
XIB
XII
+ [F3B—O—B]−
HB 30%
C6H5CH2
IX
vacuum −BH3
1: [O—B]−
2: H2O
IV
H2O 78%
170°
XIC
XII
OR
OR

Alternatively the present results can be explained by assuming the formation of the rapidly equilibrating ions XIIA and XIV.



XIIA XIV

Since XIIA is expected to be more stable than XIV, due to stabilization by the aromatic and cyclopropanic rings, the rapid reaction with hydride would be expected to yield benzyl cyclopropane, while reaction with less powerful nucleophiles such as borate anion and diglyme would yield the thermodynamically more stable homoallylic products.

Stereochemistry. From the evidence presented here it is clear that while the thermal decomposition of secondary aryl cyclopropylcarbinylborates leads exclusively to a single isomer, that of *trans*-4-aryl-3-butenols, the reaction of dicyclopropylcarbinylborate gives rise to a mixture of the *cis* and the *trans* isomers. The results accumulated so far[6] indicate that the preferred conformation in cyclopropylcarbinyl carbonium ions for maximum overlap between the bond orbitals of the cyclopropane and the vacant p-orbital of the carbonium ion can be attained when the cyclopropane ring "bisects" the carbonium ion plane.

In the case of aryl cyclopropylcarbonium ions two limiting conformations can be envisioned: (XIIA and XIIB).

XIIA XIIB

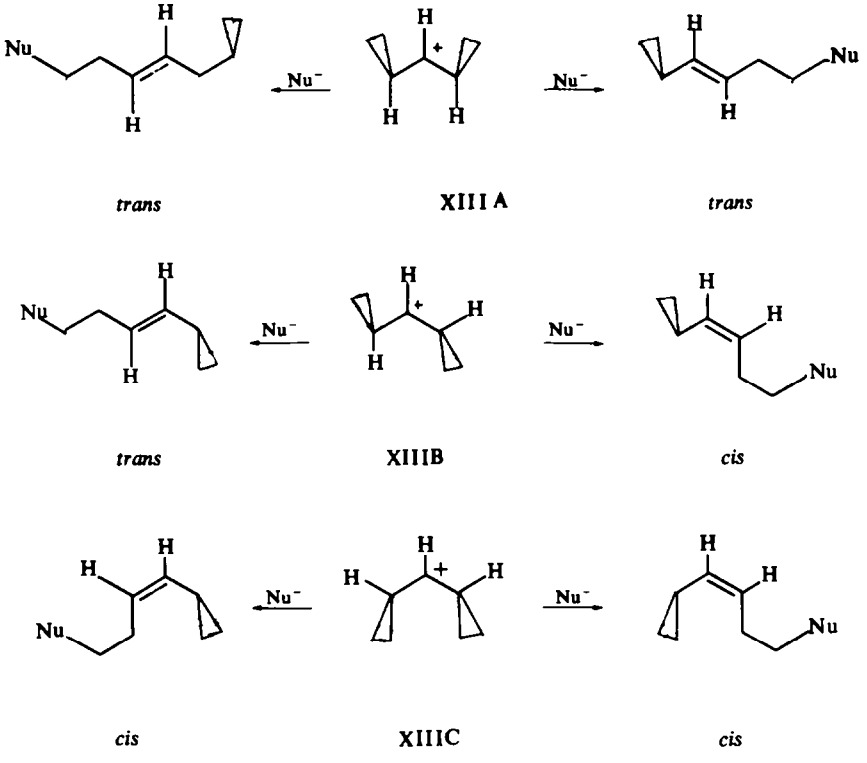
Structure XIIB represents the high energy conformer due to nonbonded interactions between the *ortho* hydrogens of the aromatic ring and the methylene hydrogens of the cyclopropane, whereas the lower state conformer is XIIA. The cyclopropane ring opening in this conformer should lead to *trans*-4-aryl-3-butanol, the isomer which is actually obtained, whereas conformer XIIB should yield the *cis*-4-aryl-3-butenol, which was not observed.

The distribution of the *cis-trans* isomers in the product from dicyclopropylcarbinylborate clearly suggests that the presumed carbonium ion intermediate populates more than one of the following conformations XIIIA–XIIIC.

Recently, Pittman and Olah[6b] have considered the NMR spectrum of dicyclopropylcarbinyl cation in SO_2—FSO_3H—SbF_5 at $-60°$, and interpreted the results in terms of two possible conformations XIIIA and XIIIC. This was inferred from the splitting pattern of the hydrogen on the central carbon, which appears as a sharp triplet, showing that both α-hydrogens are magnetically equivalent. On energy

grounds conformation XIIIA is favored relative to XIIIC as the former has less steric interactions between the hydrogens of cyclopropyl groups.

If the carbonium ion intermediate in the thermal rearrangement of dicyclopropyl carbinylborate exists only as XIIIA, the reaction should give the *trans* isomer as the sole product. In fact the reaction yielded a mixture of 25% *cis* and 75% *trans*-4-cyclopropyl-3-butenol, indicating that conformers XIIIB and/or XIIIC take part in the reaction. Since the interaction between the ring hydrogens in XIIIC should be more pronounced than in XIIIB the abundance of the former conformer is likely to be very small, if any.



The observed *cis*/*trans* distribution in products can be best explained by assuming that conformers XIIIA and XIIIB are equally populated. The notable population of XIIIB (not observed at low temperature[6b]) by the intermediate in our reaction, can conceivably be attributed to our relatively high reaction temperature.*

EXPERIMENTAL

All m.ps and b.ps are uncorrected. NMR spectra were measured on a Varian A-56-60 instrument. Chemical shifts are given in ppm downfield from TMS which was used as an internal standard.

* The observed mixture of *trans*- and *cis*-4-cyclopropyl-3-butenols cannot arise from equilibration of the two geometric isomers, as it has been shown that under thermodynamic conditions only the *trans*-product is obtained.[7]

Preparation and thermal decomposition of tri-(methyl cyclopropyl aryl carbinyl) borates

The tertiary carbinol (25 mmoles) was dissolved in 10 ml dry diglyme in a 100 ml hydroboration flask equipped with a condenser attached to a gasmeter. A 2·5M soln of borane in THF (10 ml) was introduced by a hypodermic syringe at 0°. The ice-water bath was removed and the H_2 evolution measured. When the theoretical amount of gas had been liberated, the condenser was attached to vacuum and the reaction mixture immersed in an oil bath, the temp of which was raised slowly to 70° and kept at this temp for 15 min. The vacuum was disconnected, the apparatus filled with nitrogen and the mixture heated under reflux for 1 hr. After cooling, water was added and the mixture extracted with pentane from which the diglyme was removed by water extraction. After drying, the pentane was removed and the residue analyzed by measuring relative peak intensities of the two components in the NMR spectrum.

General procedure for the preparation and thermal decomposition of tri-(arylcyclopropylcarbinyl) borates and tri-(dicyclopropylcarbinyl) borate

Ketone (25 mmoles) was placed in a 100 ml hydroboration flask equipped with a condenser attached to a gasmeter and 10 ml of 2·5M soln of borane in THF was introduced by a hypodermic syringe at 0°. After 2 hr at room temp 10 ml of the selected solvent was injected and the top of the condenser was connected to the vacuum, while the reaction flask was stirred and heated in an oil bath to 60° for 30 min. The vacuum was disconnected, the apparatus was filled with nitrogen and the reaction mixture heated in an oil bath at 170° for 1 to 4 hr. The solvent was removed by vacuum distillation (oil pump 0·5–1 mm). Water and NaOH were added and the organic material was extracted with ether. After drying over Na_2SO_4 and removal of the ether the residue was purified by vacuum distillation. Gas chromatographic analyses were performed on a 6 ft diethyleneglycol succinate column in an F and M 720 programmed temp gas chromatograph.

Gas chromatographic separation of cis- *and* trans-*4-cyclopropyl-3-butenols.* The two stereoisomers were separated in an Aerograph A-90-P gas chromatograph on a 2 m ¼" column of 10% Carbowax 400 + 20% $AgNO_3$ on Diatoport P 60/80 mesh. Column temp: 100°; inj. port temp: 210°; detector temp: 190°; Helium flow rate 120 ml/min. The composition of the mixture and the purity of the fractions separated were checked on the same column at the same conditions, except the Helium flow rate which was 50 ml/min.

Attempted thermal rearrangements in the presence of benzylamine

(a) Cyclopropyl phenyl ketone (25 mmoles) was dissolved in 10 ml diglyme and 10 ml of 2·5M borane soln in THF was introduced by a hypodermic syringe. After stirring for 1 hr at room temp, 5·35 g benzylamine (50·0 mmoles) was injected to the reaction flask. The reaction mixture was refluxed until the H_2 evolution stopped (500 ml H_2). The apparatus was attached to vacuum and heated to remove THF. After disconnecting the vacuum, the reaction mixture was heated in nitrogen atmosphere for 1 hr at 170°. After work up the product mixture was analysed by VPC and found to contain benzylamine and phenylcyclopropyl carbinole.

(b) Cyclopropyl phenyl ketone (25 mmoles) was dissolved in 10 ml diglyme and 10 ml of 2·5M borane soln in THF was introduced by a hypodermic syringe. After 2 hr at room temp, the apparatus was connected to vacuum and heated to 60° for 30 min. After disconnecting the vacuum 5·35 g benzylamine was added and the mixture was heated to 170° for 1 hr. After further treatment as in the preceeding experiment, only phenyl cyclopropyl carbinol and benzylamine were obtained.

Borontrifluoride catalysed homoallylic rearrangement of phenylcyclopropyl carbinyl borate in the presence of hydride

A 2·5M soln of borane in tetrahydrofurane (COMe) was added at 0° to a soln of 25 mmoles of phenyl cyclopropyl ketone in 10 ml diglyme. After 2 hr at room temp, the soln was heated *in vacuo* to 40° with stirring for 20 min. The vacuum was disconnected and under nitrogen the soln was cooled to 0° and 0·93 ml BF_3 etherate (7·5 mmoles) was injected. An exothermic reaction occurred and a white ppt appeared. After stirring for 20 hr at room temp, 10 ml of 3N NaOH and 20 ml water was added, and the reaction mixture extracted with ether. Most of the diglyme was removed by extraction of the ether soln with cold water, and the ether was removed after drying over Na_2SO_4. The residue was analysed by VPC using a 6 ft ¼ in diethyleneglycol succinate on diatoport W (60–80 mesh) column with temp programming. Initial temp: 120°, final temp: 210° programme rate: 4°/min. Detector temp: 280°. The residue was found to consist of four components:

Peak No. 1, (30%) was identified as benzyl cyclopropane (IX) by comparison with an authentic sample. Peak No. 2 (20%) was isolated by preparative VPC and was identified as *trans*-4-phenyl-3-butenyl methyl

ether (Xa). (Found: C, 81·28; H, 8·87. Calc for $C_{11}H_{14}O$: C, 81·50; H, 8·65%); NMR spectrum: δ 7·22, 5H; δ 6·3, doublet, J = 15 c/s, 1H; δ 6·20, two triplets, J_d = 15 c/s, $J_{tr.}$ = 6 c/s, 1H; δ 3·42, triplet, J = 6 c/s, 2H; δ 3·28 singlet, 3H; δ 2·42, quartet, J = 6·5 c/s, 2H. Peak No. 3 (5%) was identified as *trans*-4-phenyl-3-butenol (IV). Peak No. 4 (40%) was isolated by preparative VPC, and was identified as diethylene-glycol monomethyl, mono-*trans*-cinnamylcarbinylether (Xb). (Found: C, 71·71; H, 8·86. Calc. for $C_{15}H_{22}O_3$: C, 71·97; H, 8·86%); NMR spectrum: δ 7·43, 5H; δ 6·32 doublet, J = 15 c/s, 1H; δ 6·27, two triplets, J_d = 15 c/s, J_{tr} = 6 c/s, 1H; δ 3·55, broad peak, 10H; δ 3·29, singlet, 3H; δ 2·44, quartet, J = 6·5 c/s, 2H.

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