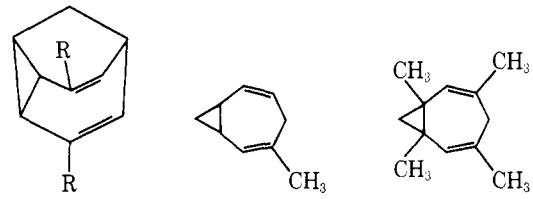
(decrease of the Hammett σ-constants) tends in the same direction. Nevertheless, the steric effect of substituents in 2,6-position destabilizes the homotropilidene-"boat" conformation which would result in the same substituent effect. Indeed force field calculations show that the energy of the "boat"-conformation of a **1a** (R = H) is about 4 ± 2 kcal/mol higher in energy than the "chair"-conformation, but this difference increases to about 8 ± 2 kcal/mol in **1c** (R = C_6H_5) and **1e** (R = CH_3).[14] The boat-like conformation of the transition state should cause a similar increase in energy comparing **1a, 1c,** and **1e.**

To prove this, we have prepared[15] the phenyl-substituted barbaralane **2b** starting from triasteranedione[16] and analyzed the rearrangement by means of ^1H NMR spectroscopy.[17]



2 3 4

Phenyl groups in the 2,6-position of **2** destabilize the transition state (Table I), but the effect is smaller compared to the couple **1a/1c.** This difference could be interpreted as the steric destabilization effect on the transition state of **1,** but generally the retarding effect of 2,6-substitution in **1** and **2** is quite different from the observation of Dewar et al. in substituted 1,5-hexadienes[2] and provides evidence that in (bridged) homotropilidenes the transition state is like D or E.

In this connection it is interesting to compare the barriers of **3** and **4** with **1a.** The steric destabilization should operate in **3** and **4** in the same manner like in **1e.** Consequently the net effect of zero in influencing the transition state should be a result of an electronic stabilization effect in the 1,3,5,7 position. This gives evidence that the character of the transition state is more allylic (D) than synchronous (E). Thus the investigation of (bridged) homotropilidenes opens the opportunity to study the substituent effect on the initial bond breaking type of the Cope rearrangement.

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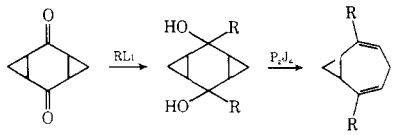

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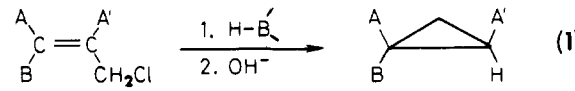
On the Stereochemistry of Conversion of Allylic Halides to Cyclopropanes via γ-Haloalkylboranes

Sir:

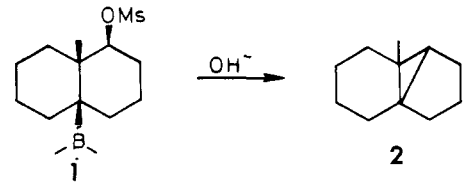
We wish to report that conversion of allylic halides to cyclopropanes by hydroboration followed by base-promoted cyclization[1-4] (1,3-elimination) of the intermediate γ-chloroborane is stereospecific. The relative locations of substituents in reactant and product are illustrated by eq 1.



(1)

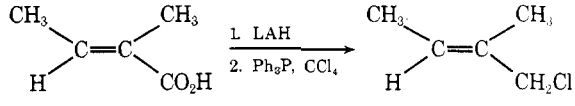
This two-step transformation was first reported by Hawthorne and Dupont[1] and has been the subject of several subsequent investigations.[1-4] A major improvement involves hydroboration with 9-borabicyclo[3.2.1]nonane (**9-BBN**).[3] This leads to increased regioselectivity in the desired direction and formation of a γ-chloroborane structurally predisposed to undergo base-promoted cyclization.[3,4]

In an earlier stereochemical investigation Marshall and Bundy[5] observed that the bicycloborane methane sulfonate (**1**) undergoes cyclization to give the tricyclic hydrocarbon (**2**) and noted that the 1,3-elimination involves inversion of both reaction centers. However, this is a biased system; cyclization with retention of configuration at either center leads to a highly strained product and is thus precluded from the outset.



i 2

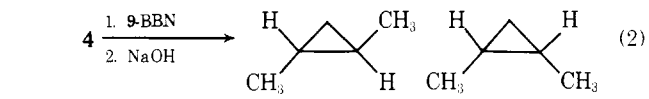
In this study we have converted the isomeric 1-chloro-2-methyl-2-butenes (**4**) to 1,2-dimethylcyclopropane. (*E*)-1-Chloro-2-methyl-2-butene (**4-*E***)[6] was derived from (*E*)-2-methyl-2-butanoic (tiglic) acid (**3-*E***) (Aldrich Chemical), or tiglaldehyde (Eastman Organic Chemicals) by reduction to (*E*)-2-methyl-2-buten-1-ol[6] with lithium aluminum hydride followed by conversion to **4-*E*** with triphenylphosphine and carbon tetrachloride.[7] Both configuration and location of the double bond were fully preserved, e.g., **3-*E*** (>99.9% *E* isomer)[8,9] gave **4-*E*** without detectable[9] intercontamination by either the geometric or allylic isomer.



3-E 4-E

(*Z*)-1-Chloro-2-methyl-2-butene (**4**-*Z*) was obtained in a similar way from (*Z*)-2-methyl-2-butanoic (angelic) acid (**3**-*Z*).[10] In this case **3**-*Z* (99.5% *Z* isomer) gave **4**-*Z* consisting of 98.8 ± 0.4% *Z* isomer.[6,9] Configurations of angelic (**3**-*E*) and tiglic (**3**-*Z*) acids have been unequivocally established by x-ray analysis.[11] Thus the method of synthesis establishes configurations of the allylic chlorides. This assignment is confirmed by the NMR spectra. The vinyl proton shift is δ 5.43 for **4**-*Z* and δ 5.59 for **4**-*E* ($DCCl_3$). These values, and the shift differences, are in good agreement with values obtained by a model-compound method for calculating shifts of olefinic protons.[12]

The isomeric 1-chloro-2-methyl-2-butenes (**4**) were converted to dimethylcyclopropane by a method developed by Brown and Rhodes[3] which involves hydroboration with **9**-BBN. The pertinent data are summarized under eq 2.[9] Data for **4**-*E* and **4**-*Z* are averages for four and three independent experiments. The isomeric dimethylcyclopropanes were



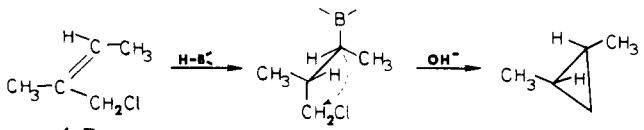
(2)

>99.9% **4**-**E** ⟶ 0.3 ± 0.1% 99.7 ± 0.1%

98.7 ± 0.1% **4**-**Z** ⟶ 96.3 ± 0.2% 3.7 ± 0.2%

identified by comparison of properties with authentic samples.[13]

Syn hydroboration[4] of **4**-*Z* leads to the erythro γ-chloroborane (**5**). Similarly **4**-*E* gives the threo diastereomer. Presumably cyclization involves coordination of the base with the boron atom to form an ate complex which undergoes 1,3-elimination.[3,4] The present results show that this proceeds with inversion of configuration of the carbon–boron center.



4-**Z** **5**

This stereochemical result is in contrast to that generally observed with organoboranes. Most nonradical reactions are stereospecific and proceed with retention of configuration of the carbon atom bonded to boron.[4] However, these cases differ mechanistically from the 1,3-elimination and involve migration of an alkyl group from boron to an adjacent electron deficient atom.[4] The base-promoted halogenation of organoboranes is presumably mechanistically related to the 1,3-elimination (electrophilic attack at a carbon atom bonded to boron in an ate complex)[4] and also proceeds with predominating inversion.[14]

The present data show that the cyclopropane synthesis (eq 1) is highly stereoselective. However, there is some loss of configuration in one of the steps. The greater loss with **4**-*Z* than with **4**-*E* suggests this occurs before the cyclization step because the conformation for concerted 1,3-elimination appears more favorable for the erythro chloroborane (**5**) than for the threo diastereomer. The slight loss could result from isomerization of the allylic chloride prior to reaction,[15] or a less than 100% syn addition.

The high stereoselectivity of this two-step transformation suggests that asymmetric hydroboration[16] followed by cyclization may be a useful method for preparing optically active disubstituted cyclopropanes.

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New Synthetic Reagents. 2-Methoxy-3-phenylthiobuta-1,3-diene. A Novel Annelating Agent

Sir:

We wish to report the preparation of a versatile new diene, 2-methoxy-3-phenylthiobutadiene (**1**), which serves as an annelating agent to introduce a masked β-ketosulfide moiety as an integral part of the annelation. Such a structural feature has been shown to be versatile in elaborating organic structures.[1]

Moreover, the regiochemistry of the annelation indicates that the phenylthio, rather than the methoxy group, is controlling in the thermal process, whereas the methoxy group plays a greater controlling role in the catalyzed reaction—an unusual dichotomy.[2] *The ease of desulfurization of organic compounds suggests the application of this directive effect of sulfur as an approach for obtention of a regiochemistry that complements that obtained with the usual dienes* such as 2-methoxybutadiene.[2,3]

2-Phenylthiocyclobutanone,[4] prepared from 2-bromocyclobutanone[5] (PhSNa, DMF, 0°, 1 h), is O-methylated (KH, THF–DMF, $(CH_3O)_2SO_2$, −78° → 0°) to give 1-methoxy-2-phenylthiocyclobutene (**2**)[4] in 46% yield (from bromocyclobutanone). No purification of the intermediates starting from cyclobutanone is necessary. The cyclobutene **2** is purified on Baker alumina eluting first with hexane and then 1–2% ether in hexane. Pyrolysis, by dropping a hexane solution of **2** through a 40 cm hot tube packed with glass helices (150 ml free volume, flow rate ~500 ml/min, 340°) that has been pretreated with *O,N*-bistrimethylsilylacetamide, gives the desired diene **1**[4,6] in nearly quantitative yields. The sensitivity of the diene towards polymerization makes it desirable to place a trace amount of 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer in the cold traps, and to store the diene over this stabilizer. We normally utilize the diene within a week of its preparation.

Reaction of diene **1** with dienophiles, either neat or in toluene solution at reflux, produces the desired adducts (see Table I).[7] The question of the regiospecificity was directly answered in the cases of entries 4, 5, and 7 and it is assumed that the same