References and Notes

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(3) C. Furlani, A. Flamini, A. Sgamellotti, C. Bellitto, and O. Piovesana, *J. Chem. Soc., Dalton Trans.*, 2404 (1973).
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(6) The structure has been solved using 1483 observed diffraction intensities collected by counter methods. The refinement is in progress, the current R value being 0.06.
(7) J. R. Miller, *Adv. Inorg. Radiochem.*, **4**, 133 (1962).
(8) K. Krogman, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
(9) K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972).
(10) The structure has been solved using diffraction data collected by counter methods. Isotropic least-squares refinement gave $R = 0.08$, for 1213 independent reflections with $I \geqslant 3\sigma(I)$. Anisotropic refinement is in progress.

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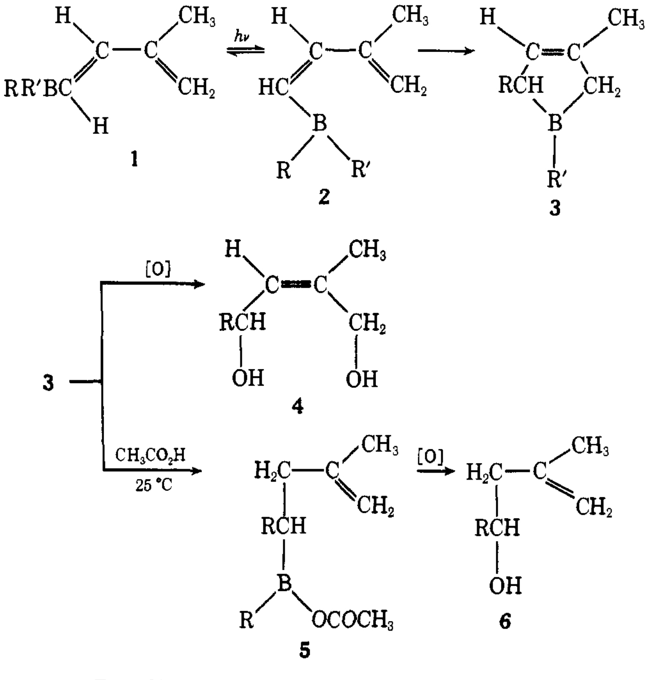
Boracyclopent-3-enes from Dialkyl-1,3-dienylboranes. A Convenient Stereoselective Route to Homoallylic Alcohols

Sir:

Ultraviolet irradiation of dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane (**1**, R = R′ = cyclohexyl) effects its cyclization to the boracyclopent-3-ene **3**.[1] This transformation has been rationalized as occurring via initial excited state trans–cis double-bond isomerization to *cis*-dienylborane **2**, which then undergoes cyclization with transfer of one cyclohexyl group from boron to the adjacent carbon.



R = alkyl, cycloalkyl: R′ = alkyl, cycloalkyl, or 1,1,2-trimethylpropyl

We now wish to report further studies of this photochemical reaction which have shown its great versatility with respect to the structural variations which can be accommodated in both the dialkyl- and dienylboryl moieties. Also, we have now discovered that nonphotochemically generated *cis*-1,3-dienylboranes undergo facile thermal cyclization to boracyclopent-3-enes, which represents a new process in organoborane chemistry. Finally, the boracyclopent-3-enes produced by either the photochemical or nonphotochemical routes from 1,3-dienylboranes may serve as precursors for stereoselective syntheses of homoallylic alcohols. Specifically, the described reactions of dienylboranes derived from isopropenylacetylene might prove to be useful in terpene synthesis for extending a carbon chain by one isoprene unit as indicated in the transformation **1** → **6**.

In a study to determine both the scope of the photoinitiated cyclization reaction and the stereochemical fate of the migrating group, a 0.2 M solution of bis(*trans*-2-methylcyclohexyl)-3-methyl-*trans*-1,3-butadienylborane (**1**, R = R′ = *trans*-2-methylcyclohexyl)[2] in THF was irradiated with an unfiltered 450-W Hanovia lamp for 6 h. NMR examination of the photolysate revealed complete conversion to **3** as evidenced by the disappearance of the dienylborane's terminal methylene proton absorption at δ 5.3 and the simultaneous appearance of a new multiplet at δ 5.5.[3] Acetolysis of the photolysate led to a product whose ^{1}H NMR spectrum exhibited an absorption at δ 4.7, pointing to the presence of terminal vinyl protons as in **5**. Oxidation of the acetolysis reaction mixture with alkaline hydrogen peroxide afforded a 66% isolated yield of a mixture of diastereomeric homoallylic alcohols **6** (R = *trans*-2-methylcyclohexyl).[4,6] Consequently, migration of the 2-methylcyclohexyl moiety from boron to the adjacent carbon must have proceeded with complete retention of configuration.[7]

It should be noted that the synthesis of homoallylic alcohols by this procedure results in the use of only one of the two alkyl groups of the dialkylborane used in the hydroboration step. Fortunately, this problem can be circumvented by using thexylalkylboranes[8] as hydroborating agents. Thus, photolysis of thexyl(2-methyl-1-pentyl)- or thexylcyclopentyl(3-methyl-*trans*-1,3-butadienyl)borane (**1**, R = 2-methyl-1-pentyl or cyclopentyl; R′ = thexyl) resulted in the nearly exclusive migration of the primary and secondary alkyl groups, respectively. This was evidenced by the conversion of the photoproducts to 2,6-dimethylnon-1-en-4-ol and 3-methyl-1-cyclopentylbut-3-en-1-ol, respectively, upon sequential treatment with acetic acid and alkaline hydrogen peroxide.

To establish the scope of the photoinitiated cyclization reaction with respect to the dienyl moiety, 1-ethynylcyclohexene was hydroborated with disiamylborane (bis(1,2-dimethylpropyl)borane). Irradiation for 20 h of the dienylborane **7** (R = R′ = 1,2-dimethylpropyl) formed resulted in its conversion to the photoproduct **8**, whose NMR spectrum exhibited a multiplet at δ 5.4. Acetolysis of the photolysate followed by oxidation produced the corresponding alcohol **9** (R = 1,2-dimethylpropyl), indicating that protonation of the bis-allylic

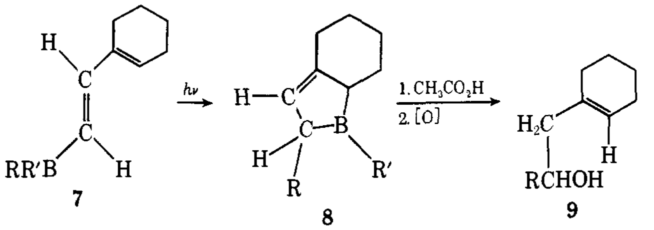
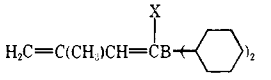
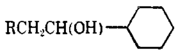
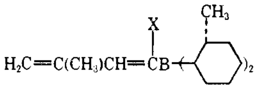
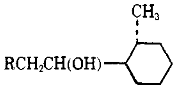
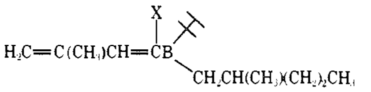
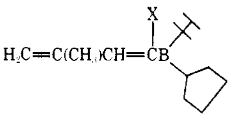
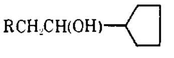
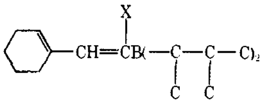
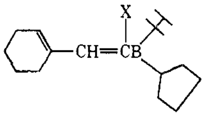
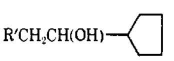
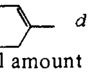


Table I. Yields of Alcohols Obtained from Acetolysis–Oxidation of Boracyclopent-3-enes

Dienylborane	X	Reaction conditions[a,b]	Homoallylic alcohol product[c]	Yield, %[d]
	H	$h\nu$, 6 h		69
	I	A, 1 h at 25 °C		77[e]
	I	B, 1 h at 25 °C		64[e]
	H	$h\nu$, 6 h		66
	I	B, 1 h at 25 °C		64
	H	$h\nu$, 6 h	$RCH_2CH(OH)CH_2CH(CH_3)(CH_2)_2CH_3$	68
	H	$h\nu$, 6 h		70
	I	A, 1 h at 25 °C		77
	H	$h\nu$, 20 h	$R'CH_2CH(OH)CH(CH_3)CH(CH_3)_2$	62
	I	A, 2 h at 50 °C		74[f]
	H	$h\nu$, 36 h		<10
	I	A, 6 h at 50 °C		73

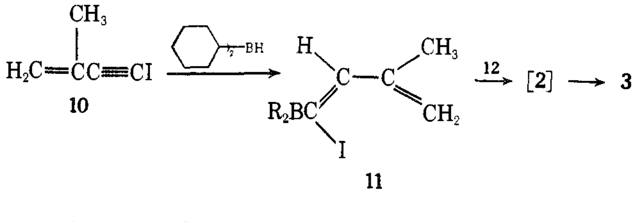
[a] The photolyses were carried out at ambient temperature. [b] A, potassium tri-*sec*-butylborohydride; B, lithium triethylborohydride. [c] R = $CH_2{=}CH(CH_3)-$, R' =  [d] The spectral and analytical data are consistent with the proposed structures. [e] Yield by GLC analysis. [f] The alcohol contained a small amount of an unknown compound.

borane **8** proceeded in a highly regiospecific manner.[4] Unfortunately, however, the corresponding photoreactions of thexylalkyl(vinylcyclohexenyl)boranes were extremely slow and resulted in appreciable polymerization.

A summary of the homoallylic alcohol syntheses effected via various dialkyl-*trans*-1,3-dienylboranes is shown in Table I

One unanswered question concerning the mechanism of the photochemical cyclization of dialkyldienylboranes is the stage at which radiationless decay occurs. It is clear that the trans–cis isomerization of the boron-substituted trans double bond (**1** ⇄ **2**) occurs in the excited state. However, subsequent cyclization of the resultant *cis*-dienylborane (**2**) and migration of an alkyl group from boron to the adjacent carbon producing the boracyclopent-3-ene (**3**) could either be further transformations of the reactive dienylborane excited state or transformations of a ground state resulting from radiationless decay of the excited *cis*-dienylborane. To investigate this possibility, a nonphotochemical preparation of dicyclohexyl-3-methyl-*cis*-1,3-butadienylborane (**2**, R = R' = cyclohexyl) was attempted.

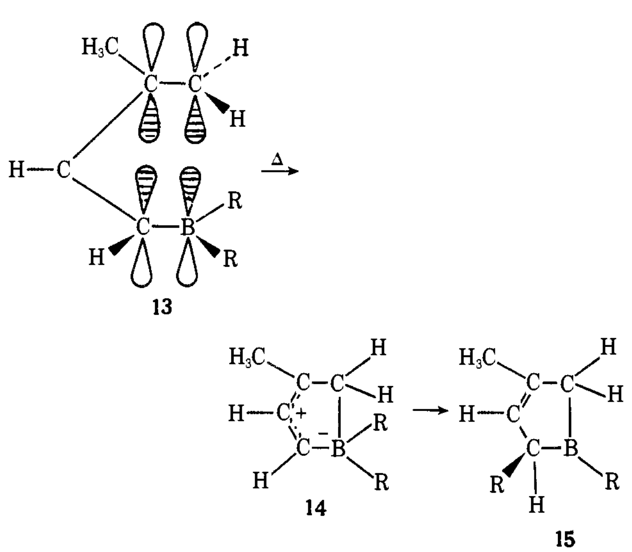
Recently, it was reported that addition of potassium tri-*sec*-butyl- or lithium triethylborohydride to α-halovinylboranes produced the corresponding *cis*-alkenylboranes in high yields.[9] Thus, dicyclohexyl(1-iodo-3-methyl-(*Z*)-1,3-butadienyl) borane (**11**), derived via monohydroboration of **10**,[10] was treated at −25 °C with a solution of potassium tri-*sec*-butylborohydride (**12**) in tetrahydrofuran. The NMR spectrum of the mixture in the vinyl proton region showed a multiplet at δ 5.5 and was identical with that of the mixture obtained from photolysis of **1** (R = R' = cyclohexyl). Oxidation of the organoborane with alkaline hydrogen peroxide yielded 54% 1-cyclohexyl-3-methylbut-3-ene-1,4-diol (**4**), whereas acetolysis-oxidation produced the alcohol **6** in 77% yield.[11] These results indicate that the *cis*-dienylborane **2** formed undergoes spontaneous cyclization to **3**. It is important to note here that the corresponding *trans*-1,3-dienylborane **1** is stable at room temperature for prolonged periods of time.



Cyclization of sterically more hindered *cis*-dienylboranes, however, proceeds much more slowly. Thus, the α-halodienylborane obtained from the hydroboration of 1-iodo-2-cyclohexenylacetylene with disiamylborane afforded, after addition of an equimolar amount of **12**, the corresponding *cis*-dienylborane which cyclized very slowly at room temperature. Complete conversion to the boracyclopent-3-ene **8** was achieved, however, by heating the dienylborane at 50 °C for 2 h. Acetolysis and oxidation of the organoborane yielded 74% alcohol **9** (R = 1,2-dimethylpropyl). A summary of the homoallylic alcohols produced via thermal cyclization of *cis*-dienylboranes is also shown in Table I.

Two characteristic features of the thermal cyclization of *cis*-dienylboranes having counterparts in the photoinitiated cyclizations of *trans*-dienylboranes are retention of configuration of the migrating group and nearly exclusive migration of a primary or secondary alkyl group attached to boron in competition with the thexyl group. Thus, the results obtained in this latter study strongly suggest that, in the photolysis of *trans*-dienylboranes, both cyclization and alkyl group migration are thermal reactions following initial photochemical trans–cis double-bond isomerization of the diene and radiationless decay.

Finally, the thermal cyclization of a *cis*-dienylborane may be regarded as an electrocyclic reaction of the pentadienyl cation type bond system. Orbital symmetry conservation would allow a conrotatory ring closure of the five π-orbital, four electron array **13** (shown as the pentadienyl cation HOMO) to the zwitterionic intermediate **14**. Suprafacial shift of an alkyl group on boron with retention, also a ground-state allowed process, would complete the sequence to **15**. This 1,2-alkyl shift



13

14

15

with retention is the boron analogue of the well-known Wagner-Meerwein rearrangement.

Acknowledgment. We thank Professors K. G. Hancock and R. Huisgen for helpful discussions, and we gratefully acknowledge support of the work by the National Science Foundation (CH76-03738).

References and Notes

(1) G. M. Clark, K. G. Hancock, and G. Zweifel, *J. Am. Chem. Soc.*, **93**, 1308 (1971).

(2) The dienylborane was obtained via monohydroboration of isopropenylacetylene with bis(*trans*-2-methylcyclohexyl)borane:. G. Zweifel, G. M. Clark, and N. L. Polston, *J. Am. Chem. Soc.*, **93**, 3395 (1971).

(3) The NMR data do not permit an unequivocal structural assignment for the boracyclopent-3-ene intermediate **3**. It should be noted that the multiplet observed in the NMR spectrum of the photolysis mixture is a characteristic feature of 1,3-dialkylcyclopentenes: J. D. White and D. N. Gupta, *J. Am. Chem. Soc.*, **90**, 6171 (1968).

(4) The allylic rearrangement observed on acetolysis of **3** is characteristic of allylic boranes,[5] and the fact that double-bond protonation and C–B bond cleavage proceeded in only one of the two possible directions is to be expected.

(5) B. M. Mikhailov, *Organomet. Chem. Rev. A*, **8**, 1 (1972).

(6) The alcohol **5** was hydrogenated, oxidized to the ketone, and then subjected to the Baeyer-Villiger degradation. Reduction of the resultant ester afforded exclusively *trans*-2-methylcyclohexanol and 3-methyl-1-butanol, thus establishing the configuration of the 2-methylcyclohexyl moiety.

(7) Since we have not established that *cis*-2-methylcyclohexyl migrates with retention, it is conceivable that the migration with retention observed for *trans*-2-methylcyclohexyl merely reflects stereoselective formation of the more stable product.

(8) E. Negishi and H. C. Brown, *Synthesis*, 77 (1974).

(9) E. Negishi, R. M. Williams, G. Lew, and T. Yoshida, *J. Organomet. Chem.*, **92**, C4 (1975).

(10) G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.*, **89**, 5086 (1967).

(11) Alternatively, lithium triethylborohydride may be used to effect cyclization. However, in this case the yields of homoallylic alcohols obtained are slightly lower.

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Synthesis, Structure, and Synthetic Utility of Thallium(I) Tricyanovinylcyclopentadienide

Sir:

Owing to its highly electrophilic nature, tetracyanoethylene (TCNE) has been shown to undergo a wide range of reactions, including insertion, substitution, and addition, as well as the formation of charge-transfer complexes, with a variety of organometallic complexes.[1] Recent work in this laboratory has demonstrated that the reaction of TCNE with cyclopentadienylthallium (TlCp) results in the formation of thallium(I) tricyanovinylcyclopentadienide (I) and that I has found use as a general reagent for the synthesis of tricyanovinyl-substituted metallocenes.

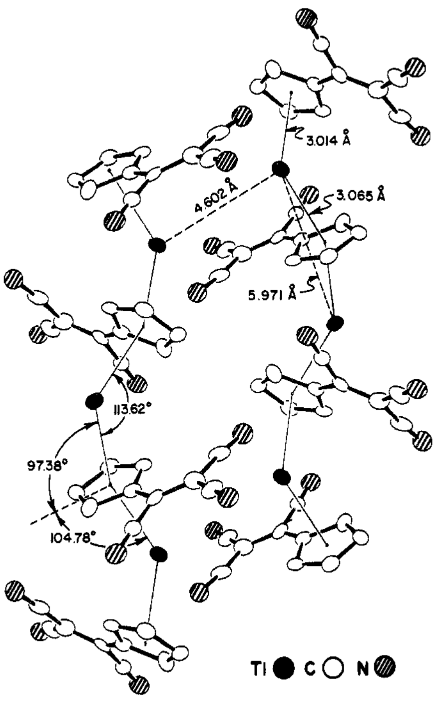

Figure 1. The crystal structure of thallium(I) tricyanovinylcyclopentadienide.

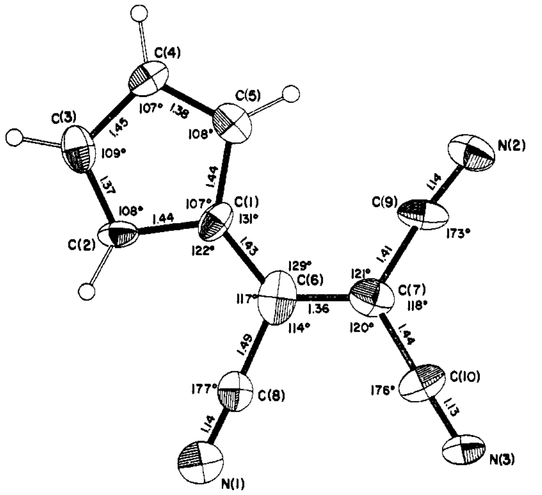

Figure 2. The structure of the tricyanovinylcyclopentadienide anion and bonded distances and angles. All distances are ±0.02 Å and angles are ±1°.

Reaction of an equimolar acetonitrile solution of TlCp and TCNE at room temperature for 1 h results in the formation of a 90% yield of I, according to eq 1.

$$\mathrm{TlC_5H_5 + TCNE \rightarrow Tl^+[C_5H_4C(CN)C(CN)_2]^- + HCN} \qquad (1)$$

The reaction mixture turns initially bright blue, but gradually turns a dark red color characteristic of I. This suggests that the reaction may involve the initial formation of a π complex, followed by nucleophilic attack of TlCp at the TCNE double bond and finally elimination of HCN to form the corresponding carbanion. Similar mechanisms have been proposed for the tricyanovinylation of aromatic compounds[2] and more recently for the reactions of Grignard reagents with TCNE.[3]

The NMR spectra and other physical data for all new cy-