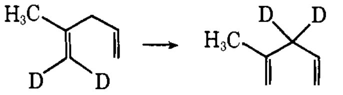
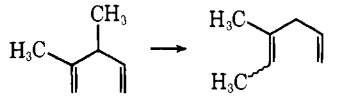
ucts from the rearrangements of 3-methyl- and 3,3-dimethyl-1,4-pentadiene by path a.

We have now labeled three carbons in the 1,4-pentadiene reactant with CH$_3$ or deuterium and have determined the fate of each label in the type II rearrangement product. 2-Methyl-1,4-pentadiene-*1*-d_2, 2.5% d_1, 97.2% d_2, 0.3% d_3 by mass spectrometry, was synthesized.[6] The position of the deuterium was unambiguously verified by the near absence of the C-1 proton resonance at τ 5.32. It was treated with the catalyst in chlorobenzene solution[8] for 120 min at 25°. The pmr spectrum of the recovered deuterio-2-methyl-1,4-pentadiene exhibited a multiplet resonance at τ 5.32 and a corresponding decrease in intensity of the doublet resonance of the C-3 allylic protons at 7.29. Very careful integration of the proton peak areas gave a C-1:C-2CH$_3$:C-3:C-4:C-5 proton ratio of 0.43:3.00:1.62:1.07:2.02 which may be compared to a ratio of 0.03:3.00:1.99:1.11:2.07 in the starting material. These values indicate that *ca.* 19% of the deuterium originally at C-1 now resided at C-3 and that little or no deuterium was present at other carbons. They imply that at least 38% of the molecules had fragmented *via* path b, Scheme I. Analysis by mass spectrometry demonstrated that the molecules were still predominantly d_2 (3.4% d_1, 94.3% d_2, 2.3% d_3). Therefore, little if any deuterium was lost by a MH addition–MD elimination sequence.[9] Similar analyses of the isomerization products indicated that they were *trans*-2-methyl-1,3-pentadiene (predominantly *1*-d_2) and 2,3-dimethyl-1,3-butadiene-*1*-d_2.



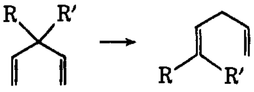
(2)

When 2,3-dimethyl-1,4-pentadiene was treated with the catalyst, it was converted to *only one* skeletally isomeric diene, 4-methyl-1,4-hexadiene (56% yield at 50% conversion). No 2-methyl-1,4-hexadiene or 2-methyl-1,5-hexadiene, the expected products from the Scheme I path a route, were detected.



(3)

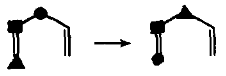
These experiments, along with the results from type II rearrangements of 3-methyl- and 3,3-dimethyl-1,4-pentadiene, eq 4, establish the nature of the skeletal



(4)

a, R = CH$_3$; R′ = H
b, R = R′ = CH$_3$

change in the type II rearrangement, eq 5. The results



(5)

are entirely consistent with path b of Scheme I and eliminate path a from consideration as a major route. Thus, the C–C σ bond-breaking steps in the type I and type II rearrangements appear to be mechanistically dissimilar. This conclusion is supported by our observation that the type I rearrangement can be accomplished by nickel species in the absence of an aluminum Lewis acid cocatalyst.[2b] The type II rearrangement has only been observed when the (R$_3$P)$_2$NiCl$_2$–R$_2$AlCl system is employed. Thus, the catalyst derived from ethylene bis(tri-*o*-tolyl phosphite)nickel and hydrogen chloride[2b] in toluene solution converted 3,3-dimethyl-1,4-pentadiene to only one isomeric product, 2,3-dimethyl-1,4-pentadiene. 2-Methyl-1,4-pentadiene-*1*-d_2, recovered after 5 hr treatment with these compounds, was unchanged, although 2,3-dimethyl-1,3-butadiene-*1*-d_2 and *trans*-2-methyl-1,3-pentadiene-*1*-d_2 were formed. 2,3-Dimethyl-1,4-pentadiene was not isomerized by the nickel(0) compound and hydrogen chloride. Experimental details and a complete discussion of these reactions will appear in our full paper which is in preparation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Received August 26, 1971

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[6] 2-Methyl-4-penten-1-ol-*1*-d_2 was prepared in 88% yield by treatment of the ethyl ester of 2-methyl-4-pentenoic acid[7] with lithium aluminum deuteride. The corresponding acetate was prepared in 81% yield from the alcohol. Pyrolysis of 2-methyl-4-pentyl-*1*-d_2 acetate at 600° afforded a 17% yield of 2-methyl-1,4-pentadiene-*1*-d_2 after distillation of the product mixture and isolation of the diene by preparative glpc.

[7] G. I. Fray and N. Polgar, *J. Chem. Soc.*, 2036 (1956).

[8] Diene isomerization experiments were conducted in toluene or chlorobenzene solution at room temperature in a manner described previously.[4] All diene products described in the text were collected *via* preparative glpc and were identified by their pmr spectra.

[9] Further evidence shows that metal hydride addition to a methyl-substituted vinyl group in the 1,4-diene is not favored. (1) We have never detected the formation of a type I skeletal rearrangement product or a double bond migration product derived from initial addition of metal hydride to a methyl-substituted double bond. (2) Geometric isomerization of *trans*- and *cis*-1,4-hexadiene does not occur. (3) Deuteriums at positions 4 and 5 in *cis*-1,4-hexadiene are not exchanged with the catalyst hydrogen pool.[10] (4) Treatment of *trans*-1,4-hexadiene and 2-methyl-1,4-pentadiene with the catalyst at 50–85° has afforded hydrogenation products *trans*-2-hexene and 2-methyl-1-pentene, but hydrogenation of the more highly substituted double bond does not occur.

[10] P. A. Pinke, Ph.D. Thesis, University of North Dakota, 1970.

[11] (a) NSF Predoctoral Fellow, 1967–1970; (b) NDEA Predoctoral Fellow, 1965–1968; (c) PRF Predoctoral Fellow, 1969–1970.

A Novel Method for the Stereoselective Introduction of Olefinic Side Chains onto Cyclic Systems *via* the Hydroboration–Iodination of Alkynes[1]

Sir:

Recently we reported that addition of 6 *N* sodium hydroxide and iodine to the vinylborane derived from cis hydroboration of 1-hexyne with dicyclohexylborane results in a transfer of one cyclohexyl group from boron to the adjacent carbon followed by deboronoiodination to give the isomerically pure cis olefin.[2] It was suggested that migration of the cyclohexyl group proceeds

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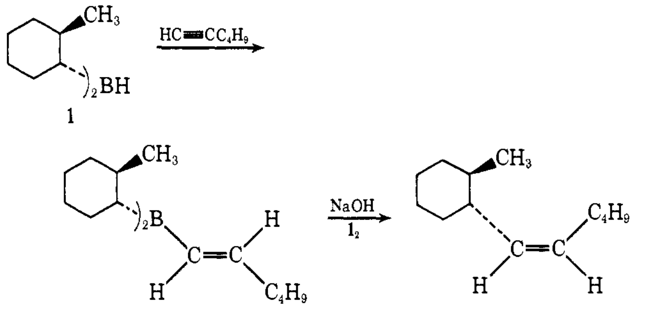
[1] This research was supported by the National Science Foundation through Grant No. GP-9398.

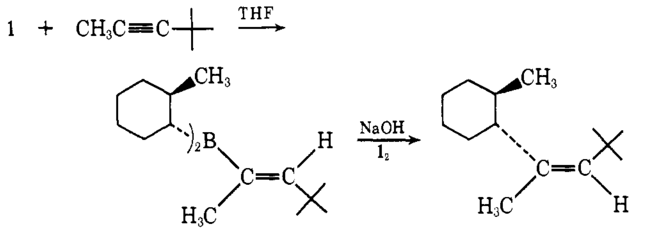
[2] G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 3652 (1967).

with inversion at the migration terminus, and that deboronoiodination occurs in a trans manner.[2]

To determine the full scope of this reaction involving cyclic systems, we have now investigated whether the migrating group in the iodination of appropriate vinyldialkylboranes migrates with retention or inversion of configuration.[3] We selected as a model compound for this study the vinylborane derived from the monohydroboration of 1-hexyne with bis(*trans*-2-methylcyclohexyl)borane (**1**).[4] Treatment of the vinylborane successively with 6 *N* sodium hydroxide and a solution of iodine in tetrahydrofuran yielded 85% *trans*-1-methyl-2-(*cis*-1-hexenyl)cyclohexane.[5] Thus, migration of the 2-methylcyclohexyl moiety occurred with *retention of configuration.*



Similarly, iodination of vinyldicycloalkylboranes obtained from the hydroboration of disubstituted alkynes provides a tool for preparing cyclic systems containing 1,2-disubstituted vinyl side chains. In this connection it should be noted that dialkylboranes exhibit a high regiospecificity for the less substituted carbon of unsymmetrically disubstituted acetylenes.[6] Thus, hydroboration of methyl-*tert*-butylacetylene with **1** followed by treatment of the intermediate vinylborane with NaOH–I$_2$ gave exclusively *trans*-1-methyl-2-(*trans*-4,4-dimethyl-2-pentenyl)cyclohexane.[7]

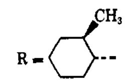
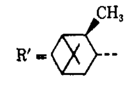
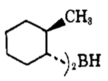
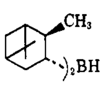


This novel stereospecific reaction involving cycloalkane systems may be applied to any substituted cyclic olefin, provided that its hydroboration can be stopped at the dialkylborane stage. For example, hydroboration of α-pinene with borane in a 2:1 ratio produces diisopinocampheylborane,[8] which subsequently reacts readily with acetylene. Treatment of the resultant vinyldialkylborane with NaOH–I$_2$ afforded isopinocampheylethylene.[9] Similarly, iodination of the vinylboranes obtained from hydroboration of 1-hexyne and 3-hexyne with diisopinocampheylborane resulted in stereoselective introduction of mono- and disubstituted vinyl groups, respectively, onto the isopinocampheyl ring.

Finally, having accomplished the stereospecific introduction of cis olefinic groups onto cycloalkane rings, we then directed our efforts to the stereospecific introduction of the corresponding trans olefinic groups. We had previously established that α-halovinylboranes, synthesized from 1-halo-1-alkynes and dialkylboranes, undergo anionotropic rearrangement when treated with sodium methoxide.[10] The rearrangement occurs with inversion of configuration at the migration terminus by backside attack of the alkyl group at the carbon bearing the halogen substituent. Protonolysis of the intermediate vinylborane with acetic acid proceeds with retention of configuration to afford trans olefins.[10] Provided that the alkyl group migrates with retention of configuration, this reaction sequence should lead to a simple stereospecific introduction of the desired trans olefinic groups.

Hydroboration of 1-bromo-1-hexyne with **1** followed by successive treatment of the resultant α-halovinylborane with sodium methoxide and acetic acid pro-

Table I. Yields of Olefins Derived from the Hydroboration–Iodination Reaction of Alkynes with Dicycloalkylboranes

Hydroborating agent	Alkyne	Olefin products[a]  ; 	Isolated yields, %
	$HC\equiv CC_4H_9$	$\begin{smallmatrix}R\\H\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}C_4H_9\\H\end{smallmatrix}$	70
	$CH_3C\equiv C{+}$	$\begin{smallmatrix}R\\CH_3\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}C_4H_9\text{-}t\\H\end{smallmatrix}$	68[b]
	$BrC\equiv CC_4H_9$	$\begin{smallmatrix}R\\H\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}H\\C_4H_9\end{smallmatrix}$	64[b,c]
	$HC\equiv CH$	$R'CH=CH_2$	65[d]
	$HC\equiv CC_4H_9$	$\begin{smallmatrix}R'\\H\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}C_4H_9\\H\end{smallmatrix}$	71[d]
	$C_2H_5C\equiv CC_2H_5$	$\begin{smallmatrix}R'\\C_2H_5\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}C_2H_5\\H\end{smallmatrix}$	71[d]
	$BrC\equiv CC_4H_9$	$\begin{smallmatrix}R'\\H\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}H\\C_4H_9\end{smallmatrix}$	69[d,e]

[a] The spectral and microanalytical data for all new compounds reported are consistent with the structures proposed. [b] For structural assignment see ref 7 and 5. [c] After completion of the hydroboration the tetrahydrofuran was removed under reduced pressure and the remaining vinylborane was diluted with acetic acid, then refluxed at 120° for 12 hr. [d] For structural assignment see ref 9. [e] The protonolysis was carried out in tetrahydrofuran at 65° for 6 hr.

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(3) For a summary regarding the stereochemistry of various rearrangement reactions involving trialkylboranes, see H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **91**, 2150 (1969).

(4) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(5) The isolation of *trans*-2-methylcyclohexylcarbinol from ozonolysis of the olefin followed by reduction with LiAlH$_4$ establishes the trans configuration at the 2-methylcyclohexyl moiety. The stereochemical relationship of the olefinic hydrogens is based on ir and nmr data.

(6) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Amer. Chem. Soc.*, **93**, 3395 (1971).

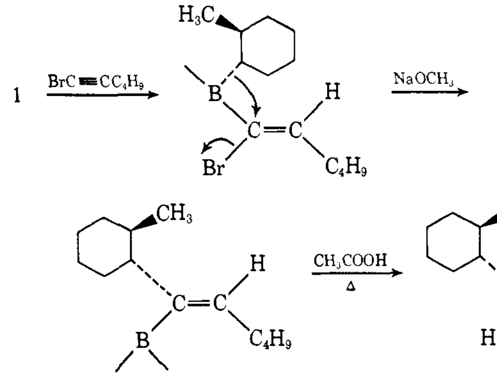
(7) The structural assignment is based on the stereochemical result observed in the analogous reaction using 1-hexyne.

(8) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

(9) The structural assignment is based on the stereochemical result observed in the analogous reaction using bis(*trans*-2-methylcyclohexyl)borane.

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

duced *trans*-1-methyl-2-(*trans*-1-hexenyl)cyclohexane,[5] again pointing to retention of configuration in the migrating 2-methylcyclohexyl group.[5,11] Similar results were obtained *via* the corresponding reaction with diisopinocampheylborane. A summary of the yields observed in each of these reactions is given in Table I.



Thus, procedures have now been developed for the stereoselective introduction of simple vinyl groups, cis and trans 2-substituted vinyl groups, and 1,2-disubstituted vinyl groups onto cycloalkane rings. These procedures should be exceedingly useful in stereospecific syntheses of compounds for natural product studies. We are currently exploring the synthetic potentialities of the hydroboration–iodination reaction with alkynes containing various functional groups.

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[11] The experimental conditions for the synthesis of this olefin are analogous to those reported in ref 10.

[12] National Defense Education Act Fellow (Title IV) at the University of California, Davis, for 1970–1971.

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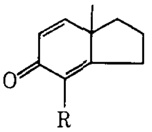
Received July 10, 1971

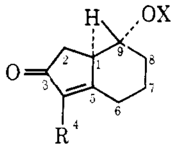
Photochemical Rearrangements of 6/5-Fused Cross-Conjugated Cyclohexadienones. Application to the Total Synthesis of *dl*-Oplopanone[1]

Sir:

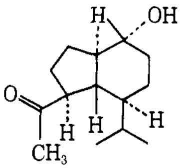
Earlier we reported that the methyl-substituted 6/5-fused cross-conjugated cyclohexadienone Ia undergoes photochemical rearrangement in aqueous acetic acid to produce the 5/6-fused hydroxy IIa (X = H) in high yield.[2] We have now found that the corresponding methoxydienone Ib[3] undergoes a similar rearrangement on irradiation in glacial acetic acid for 4 hr using a 450-W Hanovia lamp fitted with a Pyrex sleeve to give an 85% yield of the acetoxy ketone IIb (X = Ac), mp 54.5–55°. The stereochemistry of IIb (X = Ac) was assigned on the basis of the similarity of its nmr spectrum to that of IIa (X = H) and to the related 5/7-fused hydroxy and acetoxy ketones prepared by irradiation of the corresponding 4-methyl[5a,b] and 4-methoxy[5c] 6/6-fused systems, respectively. The nmr spectrum (CCl_4) of IIb (X = Ac) showed a singlet at δ 1.28 for the C-9 methyl group, a singlet at δ 1.97 for the acetate methyl group, and a singlet at δ 3.90 for the methoxy group. An apparent triplet (J = 4 Hz) at δ 3.08 and an apparent doublet (J = 4 Hz) at δ 2.27 were assigned to the C-1 proton and to the C-2 methylene protons, respectively. The ir spectrum (film) of IIb (X = Ac) showed absorptions at 1732 (acetate C=O), 1710 (C=O), 1650 cm^{-1} (C=C).



I



II



III

a, R = CH_3
b, R = OCH_3

The similarity of the skeleton and stereochemistry of IIb (X = Ac) to that of the sesquiterpene oplopanone III, isolated from *Oplopanax japonicus* by Minato and coworkers,[6] made a synthetic route to the natural product involving the photochemical rearrangement of the dienone IVa appear attractive. Condensation of 1,4-dimethoxy-2-butanone[4] with 2-methyl-5-isopropylcyclopentanone[7] using potassium ethoxide in ether at 10° followed by cyclization of the diketone intermediate with ethanolic potassium hydroxide gave the methoxy enone V (~20%): bp 89–90° (0.04 mm); nmr (CCl_4) δ 0.83 and 0.95 (d of d, J = 7 Hz, 6 H, C-6 $(CH_3)_2CH$–), 1.19 (s, 3 H, C-9 CH_3), 3.61 ppm (s, 3 H, OCH_3); ir (film) 1675 (C=O), 1631 cm^{-1} (C=C). The assignment of the β configuration of the isopropyl side chain in V was based upon subsequent conversions and the fact that examination of models suggests that $A^{1,3}$ strain[8] involving the C-4 methoxy group and the C-6 isopropyl group appears to be greater when the isopropyl side chain is in the α configuration.

Oxidation of V with freshly prepared selenium dioxide in *tert*-butyl alcohol gave a 5:1 mixture (apparently the equilibrium mixture)[9] of compounds IVa and IVb in 65% yield. The isomers were separated by chromatography on silica gel. The major isomer (IVa) showed bp 94–97° (0.07 mm); nmr (CCl_4) δ 0.92 and 0.97 (d of d, J = 7 Hz, 6 H, C-6 $(CH_3)_2CH$), 1.21 (s, 3 H, C-1 CH_3), 3.79 (s, 3 H, OCH_3), 5.99 and 6.88 ppm (AB

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[1] This investigation was supported by Public Health Service Research Grants No. GM 15044 from the National Institute of General Medicine and No. CA 12193 from the National Cancer Institute.

[2] D. Caine, W. J. Powers, III, and J. T. Gupton, Abstracts of Papers, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 23–27, 1970, No. ORGN 97.

[3] (a) The dienone Ib was prepared by condensation of 1,4-dimethoxy-2-butanone (ref 4) with 2-methylcyclopentanone using potassium ethoxide in ether, followed by oxidation of the resulting 6/5-fused enone with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in *p*-dioxane. This compound showed bp 74–77° (0.03 mm); nmr (CCl_4) δ 1.22 (s, 3 H, C-9 CH_3), 3.68 (s, 3 H, C-4 OCH_3), 6.01 and 6.99 ppm (AB quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1649 (C=O), 1608 cm^{-1} (C=C). (b) Correct elemental analysis and exact mass data have been obtained for all new compounds herein.

[4] E. Wenkert and D. A. Berges, *J. Amer. Chem. Soc.*, **89**, 2507 (1967).

[5] (a) D. Caine and J. B. Dawson, *J. Org. Chem.*, **29**, 3108 (1964); (b) P. J. Kropp, *ibid.*, **29**, 3110 (1964); (c) Caine and P. F. Ingwalson, unpublished work.

[6] K. Takeda, H. Minato, and M. Ishikawa, *Tetrahedron, Suppl.*, No. 7, 219 (1965).

[7] This compound was prepared by a modification of the method of K. Sisido, S. Kurozumi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966).

[8] F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

[9] The composition of the mixture was unchanged when it was treated under a variety of equilibrating conditions, and pure IVa was converted into the same 5:1 mixture on being allowed to stand on a silica gel column for several days.