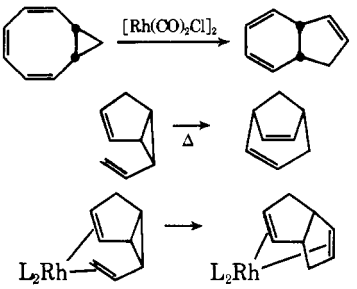
Rhodium(I) Catalysis of Vinylcyclopropane Epimerization and Ring Cleavage Rearrangements

Robert G. Salomon,* Mary F. Salomon, and Joseph L. C. Kachinski

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 2, 1976*

Abstract: Vinylcyclopropanes undergo a novel epimerization reaction in the presence of dicarbonyl rhodium(I) chloride dimer as catalyst. Studies with stereospecifically deuterium-labeled vinylcyclopropanes demonstrate that epimerization is coupled with trans-cis isomerization about the C–C π bond. Zero-order kinetics are observed for rhodium(I) catalyzed ring cleavage rearrangement of 1,1-dimethyl-2-vinylcyclopropane (**21**) and *anti*-7-vinylbicyclo[4.1.0]heptane (**32**). Though vinylcyclopropanes generally give 1,3- and 1,4-dienes by ring cleavage, **32** does not give any 1,3-dienes. These observations support a mechanism for ring cleavage involving initial coordination of the vinyl group with rhodium(I) and stereospecific *cis*-β-hydride elimination from a subsequent metallocyclic allylrhodium(III) alkyl intermediate. A key cyclic η^1-allylrhodium(III) alkyl species also readily accounts for the unique coupling of epimerization with isomerization.

The potential synthetic utility of metal promoted reactions of vinylcyclopropanes is exemplified by rhodium catalyzed rearrangements to give cyclopentenes (eq 1).[1] Transformation of vinylcylopropanes into cyclopentenes has attracted considerable recent interest in novel synthetic procedures.[2] However, these rearrangements require harsh conditions of high temperature. Catalysis could ameliorate the reaction conditions. Furthermore, rearrangements of vinylcyclopropanes may give completely different products in the presence or absence of transition metals. Thus, in the absence of transition metals, *endo*-7-vinylbicyclo[3.1.0]hex-2-ene gives bicyclo[3.2.1]-octa-2,6-diene by a [3.3] sigmatropic rearrangement (eq 2).[3] However, a stoichiometric rhodium(I) complex of the same vinylcyclopropane rearranges to the rhodium(I) complex of bicyclo[3.3.0]octa-2,6-diene,[4] the product of a net vinylcyclopropane to cyclopentene conversion (eq 3).



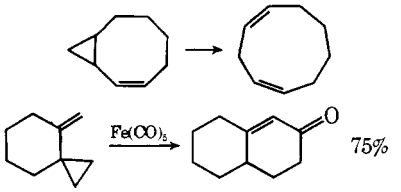
(1)

(2)

(3)

L_2 = hexafluoroacetylacetonate

In many cases, rhodium(I) catalyzes cleavage of vinylcyclopropanes to give dienes (vide infra) under milder conditions than required for similar thermal transformations (e.g., 1,5-homodienyl hydrogen shift: eq 4).[5] Nickel complexes and iron pentacarbonyl also catalyze ring cleavage isomerizations of vinylcyclopropanes to give dienes.[6] In some cases, iron pentacarbonyl transforms vinylcyclopropanes into cyclohexenones, in which the carbonyl group is derived from carbon monoxide (eq 5).[7]



(4)

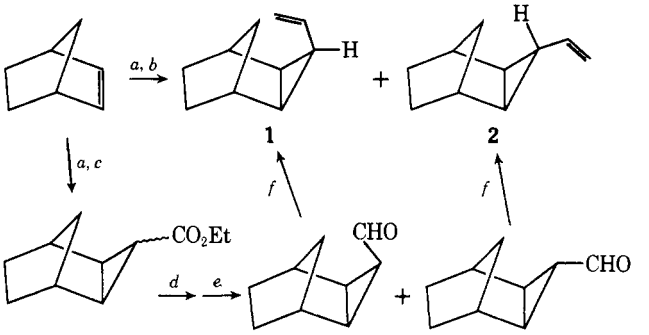
(5)

In the present study, rhodium(I) catalysis of vinylcyclopropane rearrangements, including a novel epimerization reaction, is explored. The types and reactivities of transient organometallic species involved are characterized in order to provide a rational basis for development of new applications of homogeneous transition metal catalyzed rearrangements to organic synthesis.

Results

A. Syntheses of Rearrangement Substrates and Products. *syn*- and *anti*-3-Vinyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane. The *syn*- and *anti*-vinylcyclopropanes **1** and **2** were conveniently prepared in 25% yield as a 37:63 mixture by the reaction of vinyldiazomethane with norbornylene in the presence of cupric trifluoromethane sulfonate.[8] The structural assignments were confirmed by an independent multistep synthesis (Scheme I)

Scheme I

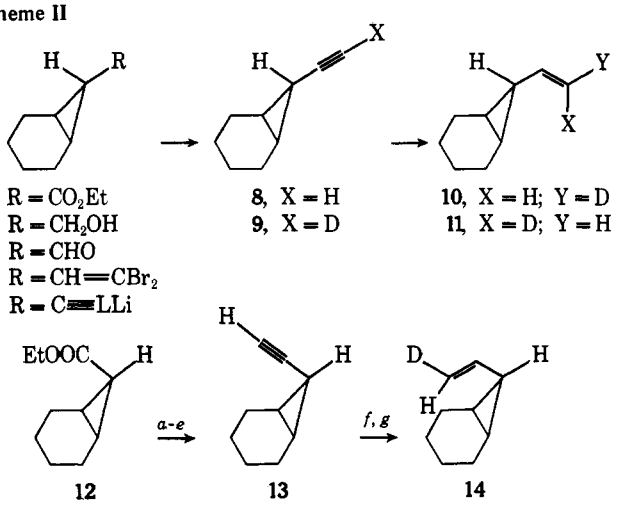


[a] $Cu(OTf)_2$. [b] $N_2CHCHCH_2$. [c] N_2CHCO_2Et. [d] $LiAlH_4$. [e] CrO_3–pyridine. [f] $Ph_3P{=}CH_2$.

commencing with the reaction of ethyl diazoacetate with norbornylene to give the syn and anti isomers of ethyl *exo*-tricyclo[3.2.1.0^{2,4}]octane-3-carboxylate, which have been described previously.[9] These were reduced with lithium aluminum hydride. Oxidation of the resulting diols with chromium trioxide in pyridine gave the corresponding aldehydes. The major aldehyde was identical with *exo*-tricyclo-[3.2.1.0^{2,4}]octane-*anti*-carboxyaldehyde, which has been described previously.[9] The minor aldehyde is, therefore, *exo*-tricyclo[3.2.1.0^{2,4}]octane-*syn*-carboxaldehyde. The aldehydes were converted to the corresponding vinylcyclopropanes via Wittig olefination.

Stereospecifically Deuterated 7-Vinylbicyclo[4.1.0]heptanes. *exo*-7-(*trans*-β-Deuteriovinyl)bicyclo[4.1.0]heptane (**10**) was prepared by hydroalumination–deuteriolysis[10] of *exo*-7-ethynylbicyclo[4.1.0]heptane (**8**) (Scheme II). The latter was obtained from *exo*-7-carboethoxynorcarane (**3**) by sequential reduction with lithium aluminum hydride to give **4** and oxi-

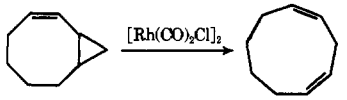
Scheme II



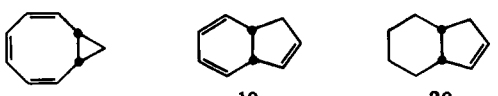
[a] $LiAlH_4$. [b] CrO_3–pyridine. [c] $PH_3P{=}CBr_2$. [d] *n*-BuLi. [e] H_2O. [f] *i*-Bu_2AlH. [g] D_2O.

dation with chromium trioxide in pyridine to give **5**, Wittig olefination with dibromomethylene triphenylphosphorane, reaction of the resulting vinyl dibromide **6** with *n*-butyllithium, and protonation with water of the lithium acetylide **7** to give **8**.[11] Deuteration of **7** with deuterium oxide gave the corresponding deuterated acetylene (**9**), which gave *exo*-7-(*cis*-β-deuteriovinyl)bicyclo[4.1.0]heptane (**11**) upon hydroalumination protolysis. *endo*-7-(*trans*-β-Deuteriovinyl)bicyclo[4.1.0]heptane (**14**) was prepared analogously via *endo*-7-ethynylbicyclo[4.1.0]heptane (**13**) from 7-carboethoxynorcarane (**12**).

B. Rhodium Catalyzed Rearrangements. Bicyclo[6.1.0]non-2-ene (15). For comparison with the rhodium(I) catalyzed rearrangement of bicyclo[6.1.0]nona-2,4,6-triene reported previously,[1] the monoolefin **15** was heated in refluxing benzene in the presence of dicarbonylrhodium(I) chloride dimer (**16**). *cis,cis*-1,4-Cyclononadiene (**17**) was obtained (68%) as the sole

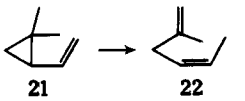


volatile product. The same rearrangement proceeded much more slowly with tris(triphenylphosphine)chlororhodium(I) as catalyst. No reaction occurred under similar conditions with silver fluoroborate, iron nonacarbonyl, tetrakis(triphenyl phosphite)nickel(0), chromium hexacarbonyl, cupric hexafluoroacetylacetonate, mercuric trifluoroacetate, bis(benzonitrile)dichloropalladium(II), norbornadienerhodium(I) chloride dimer, or rhodium(III) trichloride. It is especially noteworthy that unlike **18**, which gives **19** exclusively, **15** does not give any of the corresponding cyclopentene **20**. The same

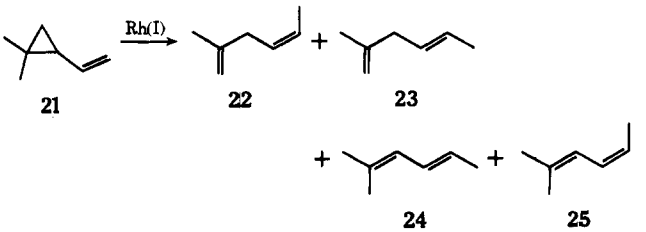


products, i.e., **17** from **15** and **19** from **18**, are obtained from the uncatalyzed thermal rearrangements of these vinylcyclopropyl derivatives.[5] The **15** to **17** rearrangement is formally a 1,5-homodienyl hydrogen shift.[5f]

1,1-Dimethyl-2-vinylcyclopropane (21). If the ring cleavage rearrangement of **15** involved rhodium catalysis of an orbital symmetry allowed 1,5-homodienyl hydrogen shift, then 1,1-dimethyl-2-vinylcyclopropane (**21**) should yield *cis*-2-methyl-1,4-hexadiene (**22**) in a similar catalyzed reaction. In

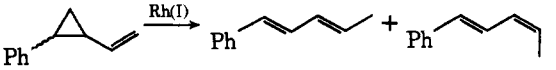


fact, in the presence of dicarbonylrhodium(I) chloride dimer (10 mol %), **21** gives not only **22** (29%), but also *trans*-2-methyl-1,4-hexadiene (**23**) (5%), *trans*-2-methyl-2,4-hexadiene (**24**) (45%), and *cis*-2-methyl-2,4-hexadiene (**25**) (21%) in 73% overall yield after 2 days at 80 °C. The products were isolated and identified by ^1H NMR spectral comparison with authentic samples. No intermediates were detected by gas liquid phase chromatographic (GLC) analysis during the rearrangement. Zero-order kinetics were observed for both product appearance and for disappearance of the starting vinylcyclopropane **21** (Figure 1).

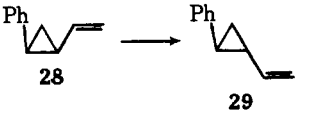


Importantly, control experiments with authentic samples of the rearrangement products showed that they are stable and not interconverted under the reaction conditions. Furthermore, other isomers, 2-methyl-1,3-hexadiene (**26**) and 2-methyl-3,5-hexadiene (**27**), also yielded no **22, 23, 24,** or **25** under the reaction conditions. Thus the latter are all primary products of the rhodium(I) catalyzed rearrangement of **21.**

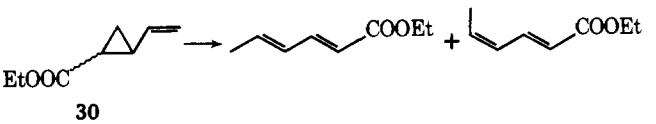
1-Phenyl-2-vinylcyclopropane. Thermal rearrangement of 1-phenyl-2-vinylcyclopropane[12] gives 4-phenylcyclopentene.[13] In the presence of dicarbonylrhodium(I) chloride dimer (8 mol %), however, no vinylcyclopropane to cyclopentene rearrangement occurs. Rather, ring cleavage is again observed with formation of *trans,trans*- and *trans,cis*-1-phenyl-1,3-pentadiene in 50–60% overall yield after 24 h at 80 °C. The catalyzed rearrangement was retarded, but not stopped, in the presence of sodium carbonate or 1,8-bis(dimethylamino)-naphthalene.[14]



A novel rhodium(I) catalyzed epimerization was discovered during the rearrangement of *cis*-1-phenyl-2-vinylcyclopropane (**28**). Thus, the trans isomer (**29**) was rapidly formed as an intermediate in the rearrangement of **28,** building up to a maximum of 50% of the mixture of products and vinylcyclopropanes (Figure 2).



1-Carboethoxy-2-vinylcyclopropane (30). Similar ring cleavage to give ethyl *trans,cis*-2,4-pentadienoate and ethyl *trans,trans*-2,4-pentadienoate (1:8 ratio) and cis-trans epimerization was observed in the rearrangement of *cis*- and *trans*-1-carboethoxy-2-vinylcyclopropanes. However, the overall reaction proceeded very slowly even in the presence of a relatively large mole percent of catalyst.



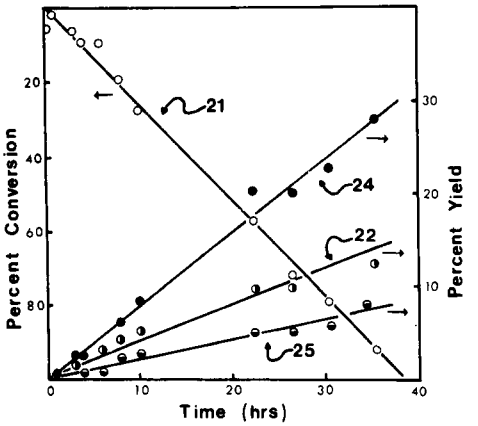


Figure 1. Rearrangement of 1,1-dimethyl-2-vinylcyclopropane (**21**) in the presence of dicarbonylrhodium(I) chloride dimer (**16**).

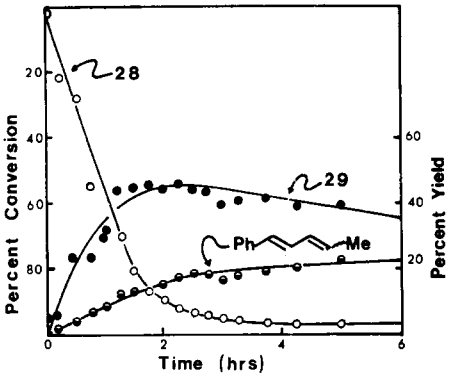
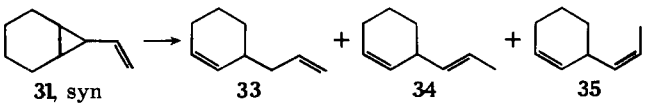


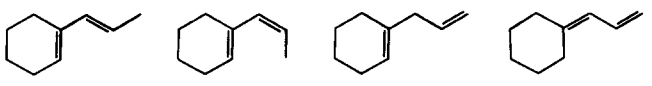
Figure 2. Rearrangement of *cis*-1-phenyl-2-vinylcyclopropane (**28**) in the presence of dicarbonylrhodium(I) chloride dimer (**16**).

7-Vinylbicyclo[4.1.0]heptane. Both *syn*- (**31**) and *anti*-7-vinylbicyclo[4.1.0]heptane (**32**) undergo rearrangement with cleavage of the cyclopropane ring in the presence of dicarbonylrhodium(I) chloride dimer. The syn isomer (**31**) gives 3-allylcyclohexene (**33**), 3-(*trans*-propenyl)cyclohexene (**34**), and 3-(*cis*-propenyl)cyclohexene (**35**) in overall yields of 40, 21, and 19%, respectively. The anti isomer (**32**) gave the same products in overall yields of 56, 39, and 4%, respectively. These products are stable and not interconverted under the reaction conditions. Other isomeric dienes *trans*-propenyl-1-cyclo-



31, syn
32, anti
33 **34** **35**

hexene (**36**), *cis*-propenyl-1-cyclohexene (**37**), 1-allylcyclohexene (**38**), and propenylidenecyclohexane (**39**), are not produced. The dienes **37**, **38**, and **39** are slowly converted into **36** under the conditions for rearrangement of vinylcyclopropanes **31** and **32**. However, **36**, **37**, **38**, and **39** are not transformed into **33**, **34**, or **35** under these conditions.



36 **37** **38** **39**

The rate of disappearance of the anti isomer (**32**) is about eight times that of the syn isomer (**31**). Also, a novel epimerization of **31** into **32** was detected by careful monitoring of the reaction mixture composition (Figure 3), and **32** was isolated from the rearrangement of **31**. The rearrangement of **32** follows zero-order kinetics for at least 2 half-lives (Figure 4), and

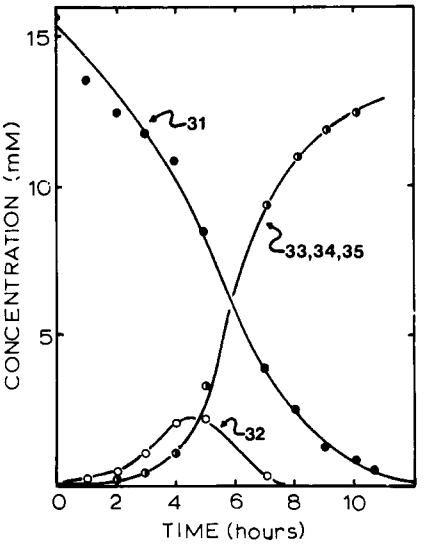


Figure 3. Rearrangement of **31** at 78 °C in benzene solution in the presence of 4.5 mol % of **16**.

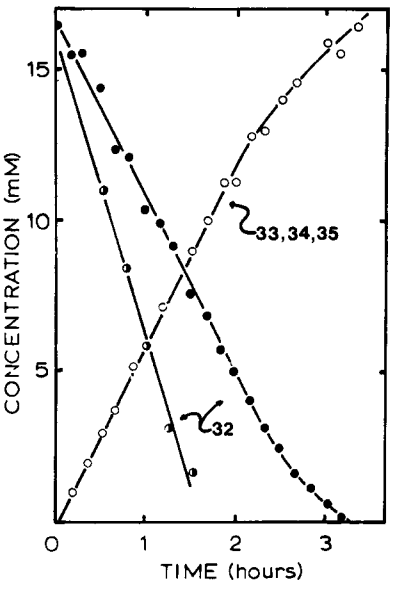


Figure 4. Rearrangement of **32** at 78 °C in benzene solution in the presence of 2.2 (○, ◑) and 4.5 (●) mol % of **16**.

doubling the catalyst concentration doubles the rate of rearrangement. The rearrangements of **31** and **32** are not significantly affected by the presence of anhydrous sodium carbonate in the reaction mixture. No rearrangement occurs with *p*-toluenesulfonic acid as catalyst in the absence of rhodium(I). As expected, *syn*-7-vinylbicyclo[4.1.0]heptane (**31**) gave 3-(*cis*-propenyl)cyclohexene (**35**) at 375 °C in a vapor-phase flow pyrolysis.[5] Since a cyclic 1,5-homodienyl hydrogen shift is geometrically precluded for the anti isomer **32**, the latter did not give ring-cleaved diene under the same conditions. However, at 490 °C, **32** rearranged cleanly to a single product, **35**.

Stereospecifically Deuterium-Labeled 7-Vinylbicyclo[4.1.0]heptanes. A mechanism (see Discussion) which we favored for the catalyzed rearrangement of vinylcyclopropanes into ring-cleaved dienes reported above could also account for the catalyzed epimerization and predicts that epimerization is coupled with cis–trans isomerization about the vinyl π bond. In order to test this prediction, *endo*-7-(*trans*-β-deuteriovinyl)bicyclo[4.1.0]heptane (**14**) was rearranged in the presence of **16**. The vinyl proton region of the ^{1}H NMR spectrum of the

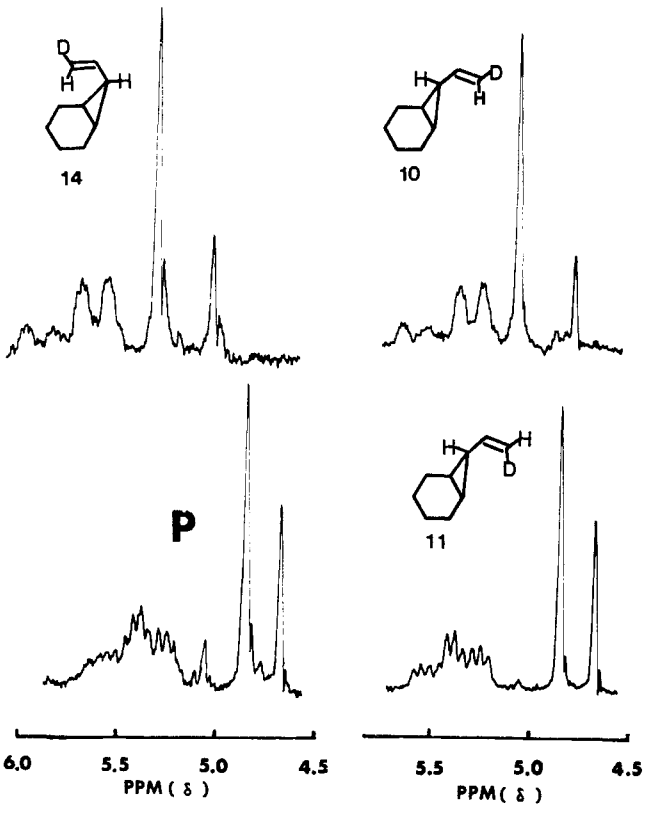
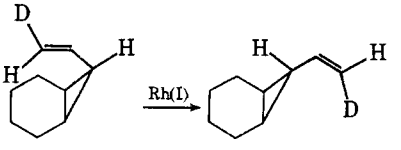


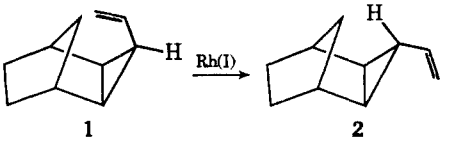
Figure 5. ^{1}H NMR spectra (60 MHz, $CDCl_3$ solutions).

deuterium-labeled *exo*-7-vinylbicyclo[4.1.0]heptane (P) produced by epimerization is presented in Figure 5 together with spectra of authentic samples of *endo*-7-(*trans*-β-deuteriovinyl)bicyclo[4.1.0]heptane (**14**), *exo*-7-(*trans*-β-deuteriovinyl)bicyclo[4.1.0]heptane (**10**), and *exo*-7-(*cis*-β-deuteriovinyl)bicyclo[4.1.0]heptane (**11**). The spectrum of the product (P) of epimerization is identical with that of **11.** Thus, endo-exo epimerization is coupled with trans-cis isomerization about the vinyl C-C π bond.



14 11

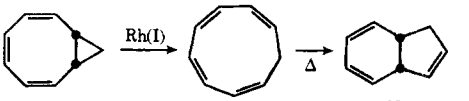
***syn*- and *anti*-3-Vinyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane.** For comparison with the structurally related vinylbicycloheptanes **31** and **32,** the vinyltricyclooctanes **1** and **2** were heated in the presence of dicarbonylrhodium(I) chloride dimer (**16**). The syn isomer **1** gives the anti isomer **2** (84%) as the sole volatile product. No trace of ring-cleaved products is formed. The vinylcyclopropane **2** is consumed upon prolonged heating in the presence of **16.** However, no volatile isomers were produced.



1 2

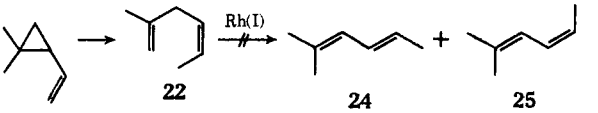
Discussion

A. Ring Cleavage Rearrangement. Catalysis by dicarbonylrhodium(I) chloride (**16**) of a vinylcyclopropane rearrangement was first observed in the quantitative conversion of bicyclo[6.1.0]nonatriene (**40**) into *cis*-8,9-dihydroindene (**41**) in 2 h at 35 °C.[1] The results of the present study demonstrate that this synthetically interesting catalysis of vinylcyclopropane to cyclopentene rearrangements by **16** is not general. Rather, **16** generally catalyzes a rearrangement of vinylcyclopropanes involving cleavage of the three-membered ring to give 1,3-, 1,4- and 1,5-dienes.[15] Moreover, it is possible that the **40** to **41** rearrangement is not simply a rhodium(I) catalyzed vinylcyclopropene to cyclopentene rearrangement. Rather, the reaction may involve a rhodium(I) catalyzed ring cleavage rearrangement to give 1,3,5,7-cyclononatetraene, followed by an uncatalyzed electrocyclic rearrangement of the latter to give **41.**[16]



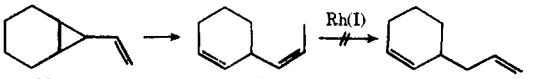
40 41

The ring cleavage rearrangements cannot be accounted for by a mechanism involving rhodium(I) catalysis of orbital symmetry allowed 1,5-homodienyl hydrogen shifts followed in some cases by allylic rearrangements of initially formed 1,4-dienes. Thus, we have shown that the 1,3-dienes **24** and **25** are *primary* rearrangement products formed directly from **21,** and not by secondary rhodium(I) catalyzed rearrangements of **22,** the expected product of a 1,5-homodienyl hydrogen shift.



21 22 24 25

Similarly, we have shown that the 1,5-diene **33** is formed directly from *syn*- and *anti*-7-vinylbicyclo[4.1.0]heptane, and not by a secondary rhodium(I) catalyzed rearrangement of **35,** the exclusive product of *thermal* 1,5-homodienyl hydrogen shift. Moreover, the anti epimer (**32**) is geometrically precluded from undergoing a concerted cyclic 1,5-homodienyl hydrogen shift. Thus, the thermal rearrangement of **32** to **35**

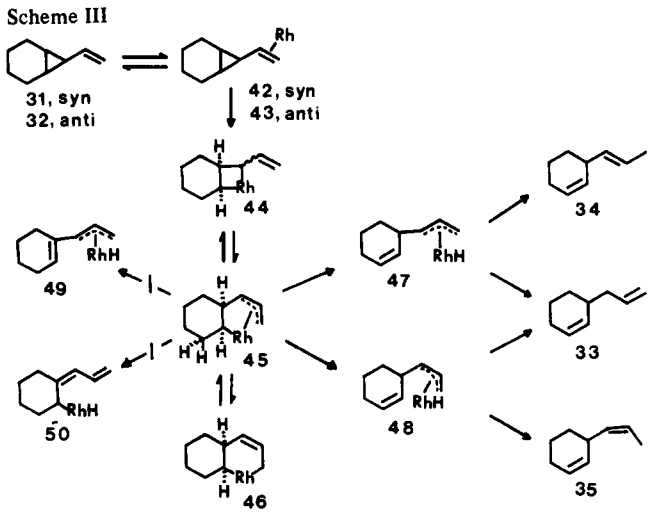


31, syn
32, anti
35 33

occurs at considerably higher temperatures than needed for the **31** to **35** rearrangement, presumably via initial epimerization to give **31.**[33a,b] In contrast, the rhodium(I) catalyzed rearrangement of **32** is eight times *faster* than that of the syn isomer **31.**

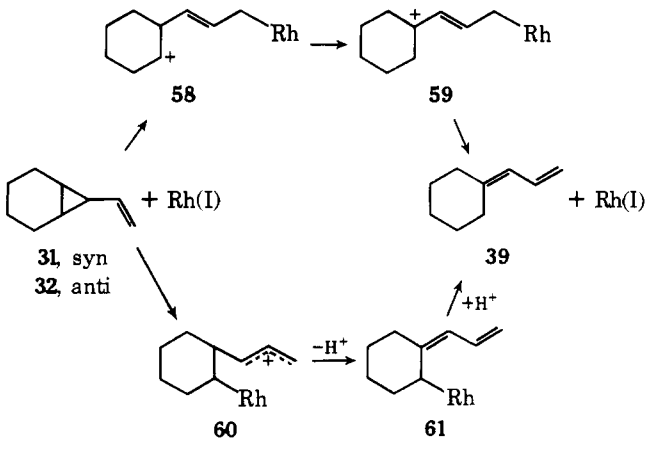
Conjugated 1,3-dienes are generally produced in ring cleavage rearrangements of vinylcyclopropanes catalyzed by rhodium(I).[15] The complete absence of such products in the rearrangements of **31** and **32** is thus interesting and significant. This novel product selectivity is readily explained (Scheme III) by a stringent cis stereochemical requirement for β-hydride elimination,[17a] giving allylrhodium(III) hydride[17] intermediates **47** and **48** from metallocyclic allylrhodium(III) alkyl intermediates **44, 45,** or **46.** The latter arise by oxidative addition to rhodium(I) of a strained C-C σ bond of the cyclopropyl ring.[18] The alternative rhodium hydrides **49** and **50,** which would be the progenitors of **36, 37, 38,** and **39,** are not formed, since the tertiary hydrogen in **44-46** is geometrically precluded[19] from attaining the syn periplanar relationship to rhodium(III) required for β-hydride elimination. Furthermore, this simple mechanism, which involves well-precedented intermediates, explains all known rhodium catalyzed rearrangements of vinylcyclopropanes. The distribution of isomeric products from **42** and **43** is not identical. Thus, the syn and anti

Scheme III

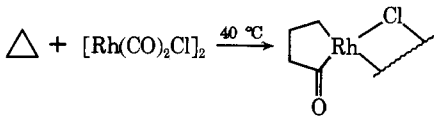


isomers of **44** (cf. Scheme VI) derived from **42** and **43**, respectively, must not be fully equilibrated (vide infra), and lead to different amounts of the isomeric allylrhodium(III) hydrides **47** and **48**.

Scheme IV

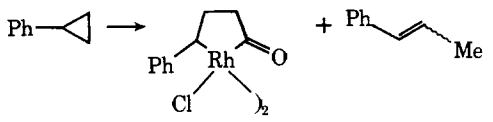


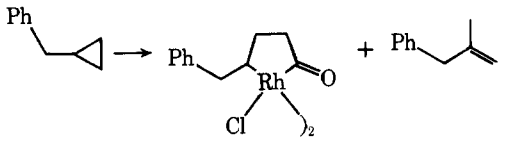
Oxidative cleavage of a cyclopropyl σ bond occurs in stoichiometric reactions of cyclopropanes with palladium or platinum complexes, which yield ring-opened transition metal complexes.[20] Practical use of this reaction has been made in palladium catalyzed hydrogenation of cyclopropanes[21] and aqueous oxidation of substituted cyclopropanes[22] to give ring opened ketones. Rhodium chloride dicarbonyl dimer (**16**) reacts with cyclopropane, giving the rhodiocyclopentanone **51**.[23]



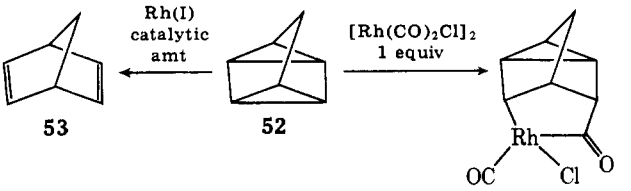
51

There are few reports of catalytic reactions of transition metals with cyclopropanes to give olefins. Powell and McQuillin mention some minor olefin products along with ring insertion products in the reactions of a variety of aryl and alkyl cyclopropanes with rhodium.[18a] Strain facilitates reaction of



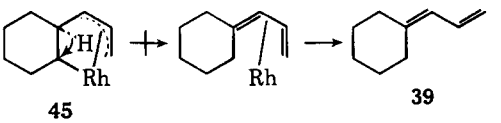


cyclopropanes with transition metals.[24] The ring opening reactions of bicyclobutanes have been extensively studied in the past few years.[25] Rhodium complexes are very active catalysts for this reaction. Quadricyclane (**52**) gives norbornadiene (**53**) upon treatment with catalytic amounts of rhodium(I) complexes,[26a] and product (**54**) containing rhodium and carbonyl has been isolated from the reaction of **52** with a stoichiometric quantity of **16**.[26b]



54

The *metallocyclic* structures of intermediates such as **44**, **45**, or **46** (Scheme III) readily account for the regiospecificity observed for β-hydride elimination and the coupling of trans-cis isomerization with syn-anti epimerization of **31** to give **32** (vide infra). Mechanisms involving *acyclic* intermediates such as **58** or **60** were suggested previously to account for rhodium(I) catalyzed ring cleavage rearrangements of vinyl cyclopropanes.[15b,c] However, the complete absence of **39** as well as **36**, **37**, and **38** from the reaction product mixture is not readily explained by such mechanisms. For example, **58** is expected to give **39** via **59**, and **60** is expected to give **39** via **61** (Scheme IV). Different mechanisms, which have been proposed for rearrangements of vinylcyclopropanes induced by metals other than rhodium, are similarly inadequate. An intermediate analogous to **45** was postulated for the rearrangement of vinylcyclopropanes induced by iron carbonyls.[27] However, the postulated subsequent hydrogen shift toward the terminal carbon atom, σ-bonded to the metal, would be expected to yield **39**, which is not observed. Such a mechanism



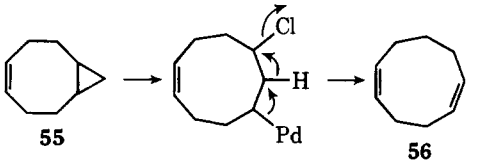
45 39

is therefore improbable in the rhodium catalyzed rearrangements. In nickel catalyzed rearrangements of vinylcyclopropanes, initial 1,2-addition of a nickel hydride to yield a cyclopropylcarbinyl nickel intermediate is followed by isomerization to an allyl carbinyl nickel intermediate, which eliminates nickel hydride to give dienes.[6c] Applied to the rearrangement of **31** or **32**, such a mechanism cannot account for the direct formation of **33**, the major product.

The greater reactivity observed for **32** compared to **31** indicates that the rhodium catalyst coordinates initially with the C-C π bond rather than inserting directly into the strained C-C σ bond of the cyclopropyl ring (Scheme III). Thus, one face of the cyclopropyl ring in **31** is unsubstituted. Direct insertion by rhodium approaching the cyclopropane from this sterically uncongested face of **31** should occur more readily than direct insertion into the more sterically congested cyclopropane in **32**. Yet **32** reacts significantly faster than **31**. Coordination of rhodium by the C-C π bond of **32** prior to oxidative insertion is also supported by the zero-order kinetics at constant catalyst concentration and by the proportionality of rate to total catalyst concentration observed for the disappearance of **32**. Formation of the complex **43** is *not* rate de-

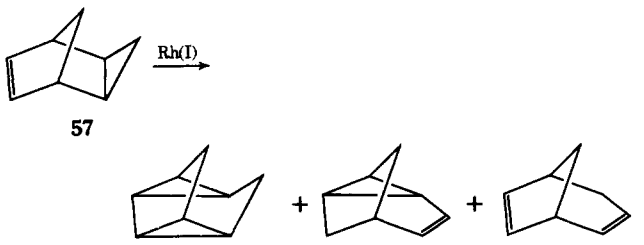
termining. The rate of reaction depends only on the concentration of olefin–rhodium π complex **43**, which is constant and is equal to the total catalyst concentration. The reaction products apparently do not compete effectively for coordination sites of the catalyst for at least several half-lives. Though further evidence is clearly warranted, this behavior might be construed to indicate a significant enhancement by a cyclopropyl substituent of the coordinating ability of an olefin.

The presence of remote unsaturation in the molecule apparently provides bonding sites which facilitate cyclopropyl ring opening. Thus, palladium complexes isomerize bicyclo[6.1.0]non-4-ene (**55**) to 1,5-cyclononadiene (**56**).[28] The reaction proceeds by addition of PdCl across the cyclopropyl bond followed by 1,2-hydrogen migration and elimination of PdCl. In a careful series of studies,[29] Katz examined the ring



55 **56**

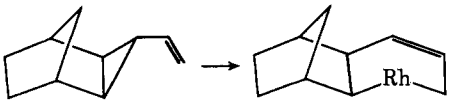
opening of **57** catalyzed by rhodium complexes and found evidence for a rhodiocyclobutane intermediate and for the involvement of a rhodium(III) hydride intermediate in the hydrogen migration. Several other structurally very similar hy-



57

drocarbon rearrangements have been studied.[30]

Since no syn periplanar elimination of rhodium and hydride is geometrically feasible for the allylrhodium(III) alkyl (**62**) derived from **2**,[19] no ring-cleaved dienes were observed from **2**. On the other hand, the rearrangement of 1,1-dimethyl-2-

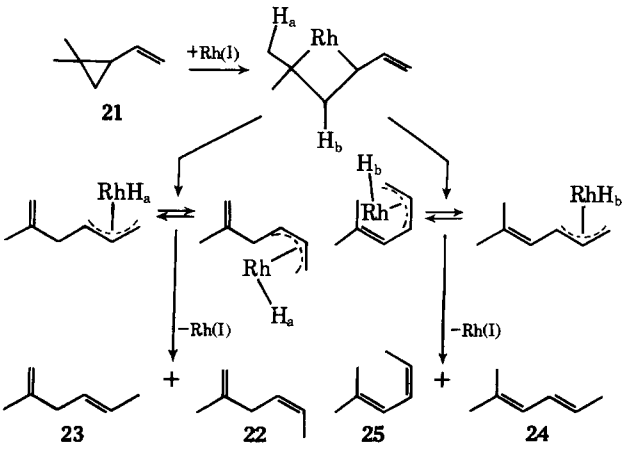


2 **62**

vinylcyclopropane (**21**) gives a mixture of products resulting from elimination of hydrogens both from the methyl group and from the cyclopropyl methylene. Since all products were stable under reaction conditions, the mixture of isomers formed is an accurate depiction of the reaction pathway. This is the only case which allows direct comparison of the two modes of hydrogen loss: from exocyclic or endocyclic positions. As shown in Scheme V, the 1,4-diene products (33%) all arise from exocyclic elimination of H_a, while all the 1,3-diene products (67%) arise from endocyclic elimination of H_b. These results, contrasted with the complete absence of endocyclic β-hydride elimination during rhodium(I) catalyzed cleavage of **31** and **32**, support the proposed operation of a special constraint, i.e., syn periplanar β elimination, in these rearrangements.

The ring cleavage rearrangements of 1-carboethoxy-2-vinylcyclopropane and 1-phenyl-2-vinylcyclopropane give similar products. 1,5-Homodienyl hydrogen migrations are not possible for any of these vinylcyclopropanes, but rearrangement still proceeds, particularly readily in the phenyl case. The rearrangement products all have a 1,3-diene conjugated with the substituent, indicating that hydride is ultimately delivered at the terminal position of the intermediate allyl complex.

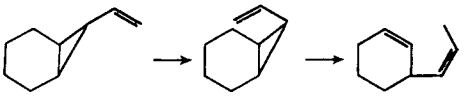
Scheme V



21 **23** **22** **25** **24**

Under certain conditions, acid is generated during the reaction of bicyclobutanes with rhodium(I) complexes. It was shown that different products may be obtained under these conditions in comparison with reactions observed under scrupulously nonacidic conditions.[31] In the present study the presence of acid scavangers or added acid does not significantly affect the reaction rate or products.

B. Epimerization. Epimerization of vinylcyclopropanes is an unprecedented reaction in transition metal catalysis. Base-catalyzed epimerization of certain cyclopropanes is known, although strenuous conditions are required.[12,32] Ring deuterated vinylcyclopropane undergoes a thermal epimerization reaction at 360 °C for which diradical intermediates were suggested.[33a,b] Similarly, 1-phenyl-2-vinylcyclopropane undergoes epimerization at lower temperatures (150 °C) than required for rearrangement to 4-phenylcyclopentene.[33c,d] The thermal rearrangement of **32** in a flow system presumably involves preliminary epimerization to give **31** at 490 °C, followed by conversion of **31** to the 1,4-diene **35**, which occurs readily in the same flow system at lower temperatures (375 °C).

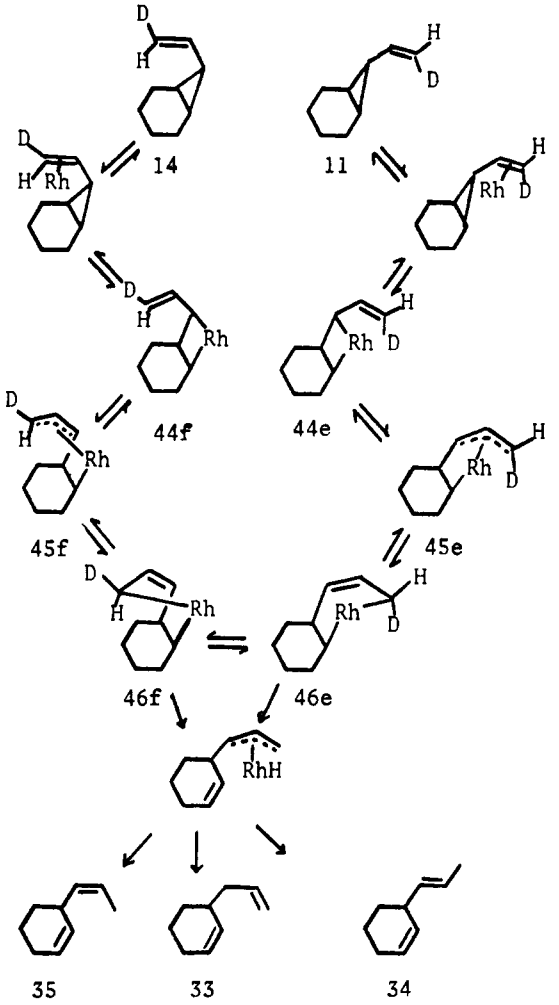


32 **31** **35**

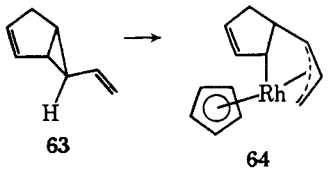
A mechanism which can account for the epimerization of vinylcyclopropanes which is catalyzed by rhodium(I) is outlined in Scheme VI. Thus, the metallocyclic allylrhodium(III) intermediates such as **44**, **45**, and **46** postulated above for the ring cleavage rearrangements of vinylcyclopropanes can provide a pathway for epimerization. The key intermediate for this epimerization mechanism is a η^1-allylrhodium(III) alkyl metallocycle **46**. This rhodiocyclohexene derivative can adopt either a folded conformation **46f** or an extended conformation **46e**. The η^1- and η^3-allylrhodium(III) alkyls **44f** and **45f** derived from **14** are in equilibrium with **46f**, while the η^1- and η^3-allylrhodium(III) alkyls **44e** and **45e**, which lead to **11**, are in equilibrium with **46e**. Thus the conformational reorganization of **46f** to **46e** provides a link between **14** and **11**. During the conformational change a rotation occurs about the C–C bond between the monodeuterated methylene and vinyl carbons in **46f** and **46e**. This rotation provides a pathway for trans–cis isomerization about the vinyl C–C π bond, which is thus coupled with epimerization.

The intermediacy of η^3-allylrhodium(III) derivatives such as **45** in rhodium(I) catalyzed ring cleavage rearrangement and epimerization reactions of vinylcyclopropanes is strongly supported by the recent *isolation* of the η^3-allylrhodium(III) complex (**64**) from a reaction of *exo*-6-vinyl-

Scheme VI



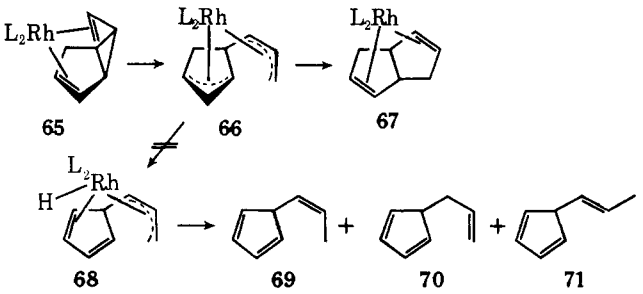
bicyclo[3.1.0]hex-2-ene (**63**) with bisethylenerhodium(I) chloride and thallium cyclopentadienide.[34]



It is important to note that the η^3- to η^1-allyl change decreases the coordinative saturation of the rhodium(III) alkyl. Thus, **44** and **46** are coordinatively unsaturated. There is mounting evidence that coordinative saturation discourages β-hydride elimination for metal alkyls.[35a,b] In other words, coordinative unsaturation may be a prerequisite for facile β-hydride elimination, which leads to ring-cleaved dienes (vide infra). It is thus noteworthy that while formation of the coordinatively unsaturated intermediates **44** or **46** is likely to precede and facilitate β-hydride elimination and subsequent formation of ring-cleaved dienes, these intermediates do not always undergo β-hydride elimination. There is apparently a delicate balance between β-hydride elimination and reductive elimination of rhodium to give a vinylcyclopropane. This is most remarkable when it is recognized that re-formation of a highly strained three-membered ring is a thermodynamically unfavorable process. Clearly kinetic factors, such as the requirement of a syn periplanar geometry for β-hydride elimination, are crucial for the successful competition to form an epimerized vinylcyclopropane instead of ring-cleaved dienes.

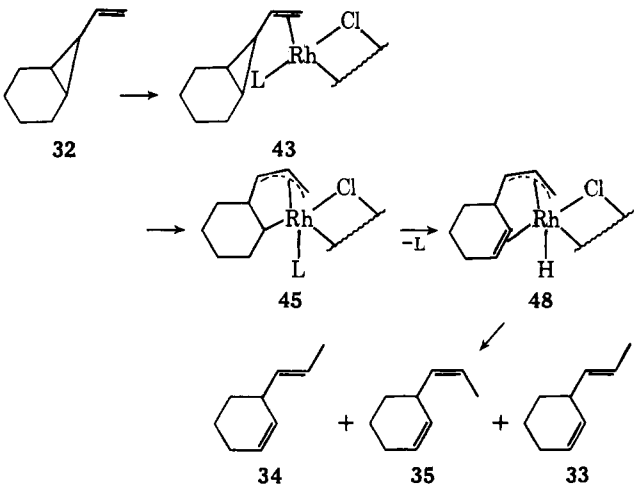
The vinylcyclopropane to cyclopentene rearrangement which occurs with the stoichiometric complex **65** is unusual[4] (Scheme VII). The rhodium(III) complex **66**, proposed as an intermediate in the **65** to **67** rearrangement,[4] possesses a geometrically suitable β-hydrogen for syn periplanar β-hydride elimination to form complex **68**, the precursor of ring-cleaved products **69**, **70**, or **71**. It should be noted that one of the ligand

Scheme VII

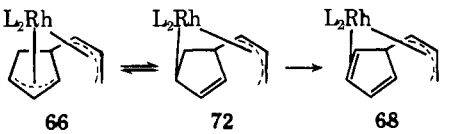


C-C π bonds is not coordinated to Rh in complex **68**, since the complex as indicated is coordinatively saturated. Thus, β-hydride elimination is accompanied by dissociation of a two-electron ligand. Similarly, rearrangement of the olefin complex **43** derived from **32** to the complex **48** must be accompanied by dissociation of a ligand (either CO or the C-C π bond of a second olefin molecule) (Scheme VIII). If it is assumed that

Scheme VIII



these dissociations of a two-electron ligand *must* precede β-hydride elimination, then the anomalous reluctance of **66** to undergo β-hydride elimination is readily explained. The C-C π bond in **66** which must dissociate is part of a *chelating* ligand. This militates against the formation of the required coordinatively unsaturated intermediate such as **72.** On the other



L_2 = hexafluoroacetylacetonate

hand, loss of a ligand from **45** is not similarly obstructed. Stability of alkyl derivatives of other metals towards β-hydride elimination has been similarly ascribed to the inaccessibility of coordinatively unsaturated intermediates.[35a,b] Coordinative unsaturation was kinetically shown to be a prerequisite for facile β-hydride elimination of platinum[35c] and palladium[35d] alkyls. The vacant coordination site evidently assists in cleaving the β-C-H bond by accepting electron density from it, eventually leading to a new M-H bond. Simultaneously, the σ-M-C bond is replaced by a π^2-olefin-metal interaction.

Conclusions

Epimerization of vinylcyclopropanes and rearrangement

to ring-cleaved dienes are catalyzed by rhodium(I). These transformations are both accounted for by initial reversible formation of an allylrhodium(III) alkyl intermediate through oxidative addition to rhodium(I) of a strained C–C σ bond of the three-membered ring. The η^1-allyl form of this intermediate, a rhodiocyclohexene, must have sufficient lifetime to allow conformational reorganization, which gives epimerized vinylcyclopropane through reductive elimination of rhodium(I). The allylrhodium(III) intermediate may alternatively undergo stereospecific cis-β-hydride elimination, leading to ring-cleaved dienes via allylrhodium(III) hydrides.

Experimental Section

General. All IR spectra are neat films, and all NMR spectra (reported in δ units) were performed in carbon tetrachloride unless otherwise noted. Benzene and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. Analytical vapor-phase chromatography was done on a Varian 1400 instrument, and preparative work was done on a Varian 202 instrument. VPC columns used: A, 10 ft × ⅛ in. 20% FFAP on 80/100 Chromosorb P; B, 5 ft × ¼ in. 20% FFAP on 60/80 Chromosorb P; C, 3 ft × ¼ in. 40% saturated silver nitrate in glycerine on 30/60 Chromosorb P; D, 15 ft × ¼ in. 20% Apiezon L on 60/80 Chromosorb W; E, 10 ft × ¼ in. 20% FFAP on 60/80 Chromosorb P; F, 15 ft × ¼ in. 20% Carbowax 1540 on 60/80 Chromosorb P; G, 15 ft × ¼ in. 20% SE 30 on 60/80 Chromosorb P; H, 15 ft × ¼ in. 15% FFAP on 60/80 Chromosorb P (NAW); I, 13 ft × ⅛ in. 20% FFAP on 80/100 Chromosorb P.

A. Synthesis of Rearrangement Substrates and Products. 3-Vinyltricyclo[3.2.1.0^{2,4}]octanes (1 and 2). A solution of vinyldiazomethane (0.16 mol) in pentane (1.2 l.) was added to a suspension of cupric triflouromethane sulfonate (0.5 g) in a solution of norbornylene (0.47 mol) in pentane (200 ml).[8] The addition rate was adjusted so that the red diazo compound was consumed as it was added. After the completion of the addition, nitrogen evolution ceased and the reaction mixture was a light yellow clear solution. The solution was decanted from the catalyst and solvent was removed by rotary evaporation. Distillation of the residual oil under reduced pressure through a 20-cm vacuum-jacketed Vigreux column gave the title compound as a 1:2 mixture of syn (**1**) and anti (**2**) isomers, respectively, bp 83–88 °C (20 mm) (4.9 g, 23%). The isomers were separated by liquid phase chromatography on column F at 150 °C. Relative retention times were 1.00 and 1.11 for the syn and anti isomers, respectively.

The assignment of structures of these isomers was confirmed by an independent multistep synthesis starting with the addition of ethyl diazoacetate to norbornene. The procedure of Sauers et al. was employed except that cupric trifluoromethane sulfonate was employed as a catalyst, and the ratio of syn to anti isomers obtained was 3:7 rather than 1:9 obtained with CuCN as catalyst.[9] The ester mixture was reduced with lithium aluminum hydride as described previously. The resulting diols were oxidized by the general procedure of Ratcliffe and Rodehorst[36] to give a 3:7 mixture of aldehydes (71%). The major isomer exhibited a ^{1}H NMR spectrum identical with that reported previously for *exo*-tricyclo[3.2.1.0^{2,4}]octane-3-*anti*-carboxaldehyde.[9] The minor product is therefore the syn isomer *exo*-tricyclo-[3.2.1.0^{2,4}]octane-3-*syn*-carboxaldehyde: NMR ($CDCl_3$) δ 0.6–1.7 (7 H), 2.57 (1 H, s, C-1,5), 9.90 (1 H, m, aldehyde).

Treatment of these aldehydes with methylene triphenylphosphorane in tetrahydrofuran gave the respective vinyl tricyclooctanes in agreement with the structures assigned above.

***syn*-3-Vinyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane (1):** NMR ($CDCl_3$) δ 0.5–1.6 (9 H), 2.37 (2 H, s, C-1,5), 4.8–5.3 (2 H, m, vinyl-CH_2), 5.95 (1 H, ddd, J = 4, 10, 17 Hz, vinyl-CH). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.43; H, 10.45.

***anti*-3-Vinyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane (2):** NMR ($CDCl_3$) δ 0.5–1.2 (4 H), 1.2–1.7 (5 H), 2.28 (2 H, s, C-1,5), 4.78 (1 H, dd, J = 3, 9 Hz, terminal vinyl), 4.9–5.6 (2 H, m, vinyl). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.52; H, 10.60.

7-Carboethoxybicyclo[4.1.0]heptane.[37] To a 2-l. flask equipped with magnetic stirring bar, condenser, 250-ml dropping funnel, and containing cyclohexene (250 g, 6.1 mol) and cupric triflate (0.2 g) was added a solution of ethyl diazoacetate (100 g, 0.96 mol) in cyclohexene (250 g). A 25-ml portion of this solution was added to initiate the reaction, after which the solution was added dropwise to maintain a gentle reaction (exothermic with gas evolution). The addition takes 5–6 h with vigorous stirring continued overnight. Before workup, additional triflate was added to ensure complete destruction of the diazoacetate. Excess crude product was distilled through a 15-cm Vigreux column, bp 60–70 °C (1–2 mm), and redistilled to give the product as a mixture of endo-exo isomers **12** and **3**, respectively (138 g, 87%), bp 63–71 °C (1.5 mm). Spinning band distillation gave a fraction enriched in the endo isomer (80:20) as analyzed by VPC (column G, 195 °C), relative retention endo-exo = 0.92:1.00, and a fraction consisting of pure exo isomer **3**: NMR ($CDCl_3$) δ 1.1–2.1 (14 H, ring protons and ester CH_3), 4.11 (4 H, q, J = 7 Hz, ester CH_2).

7-Hydroxymethylnorcarane (4). To a dry 3-l. three-necked flask, equipped with reflux condenser, dropping funnel, and mechanical stirrer was added lithium aluminum hydride (16 g, 0.42 mol) and anhydrous ether (300 ml). The esters **12** and **3** (vide supra) (99 g, 0.59 mol) in ether (300 ml) were added dropwise under N_2 at a rate to maintain gentle reflux (1–2 h). The resulting mixture was then refluxed for an additional 2 h and quenched by the cautious addition of H_2O (16 ml), 15% NaOH (16 ml) and H_2O (30 ml). The salts were filtered and washed with ether (three 150-ml portions). The ether was removed by rotary evaporation and the material distilled through a 15-cm Vigreux column to give a mixture of endo-exo isomers (30:70), bp 84–86 °C (4.5 mm) (63 g, 85%), VPC relative retention exo-endo = 1.00:1.24 (column G, 195 °C).

Spinning band distillation provided fractions of enriched endo (>75%) and exo (>90%) isomers: NMR ($CDCl_3$) exo (**4**), δ 0.78 (2 H, t, cyclopropyl), 1.0–2.2 (9 H, ring protons), 2.94 (1 H, s, hydroxyl), 3.41 (2 H, d, J = 6 Hz, hydroxyl CH_2); endo, 3.75 (2 H, d, hydroxyl CH_2).

7-Norcaranecarboxaldehyde (5). Chromium trioxide (48.0 g, 480 mmol) was added slowly in small portions to a mechanically stirred solution of pyridine (76 g, 960 mmol) in CH_2Cl_2 (1 l. distilled from P_2O_5) in a dry 2-l. three-necked flask. The burgundy colored solution was then stirred an additional 30 min.[36]

The above alcohol (10.1 g, 80 mmol) in CH_2Cl_2 (20 ml) was added in one portion via an addition funnel under an atmosphere of dry N_2. After the addition, the funnel was rinsed with CH_2Cl_2 (5 ml). Immediately on addition, the solution turned a black color and a blackish tar accumulated on the bottom. After 30 min, the mixture was decanted into a 2-l. flask and the tarry residue extracted (triturated) with boiling ether (six 100-ml portions). The reaction mixture and extracts were combined and filtered. The solution was washed with 4% NaOH (three 100-ml portions), saturated aqueous $CuSO_4$ (two 100-ml portions), H_2O (100 ml), saturated aqueous NaCl (two 100-ml portions), and dried (Na_2SO_4). Solvent removal and distillation through a 15-cm Vigreux column afforded the product as a mixture of endo-exo isomers (20:80), bp 68–70 °C (4.5 mm) (7.5 g, 75%).

Oxidation of the 90+% exo alcohol gave a 68% yield: NMR ($CDCl_3$) exo (**5**), δ 1.0–2.3 (11 H, ring protons), 9.90 (1 H, d, J = 5 Hz, CHO); endo, 1.1–2.4 (11 H, ring protons), 10.53 (1 H, d, J = 5 Hz, CHO).

***β,β*-Dibromo-7-ethenylnorcarane (6).**[11] Triphenylphosphine (31.2 g, 118 mmol) was slowly added to a magnetically stirred solution of carbon tetrabromide (39.8 g, 118 mol) and dry CH_2Cl_2 (300 ml) in a 500-ml flask with condenser. To the resulting orange solution, zinc (7.8 g, 118 mmol) is added slowly with cooling. Addition of the zinc generates first a green colored solution which then turns to a light tan color after stirring 48 h. The aldehyde (7.3 g, 59 mmol) in CH_2Cl_2 (30 ml) is added dropwise to this ylide and after 15 min, the resulting solution turns black. After 1–2 h, to the reaction mixture, transferred to a 2-l. Erlenmeyer flask, is added 1000 ml of pentane. The resulting precipitate is filtered via a sintered glass funnel. The insoluble tarry residue is reworked three more times by CH_2Cl_2 extraction (100 ml) and pentane (400 ml) to remove all the olefinic product. The solvent was removed from the combined extracts and the residue distilled, bp 75–77 °C (1.3 mm) (14.2 g, 86%). The 90% exo isomer and 76% endo isomer gave yields of 86 and 60%, respectively: NMR ($CDCl_3$) exo (**6**), δ 0.95–2.3 (11 H, ring protons), 5.80 (1 H, d, J = 8 Hz, vinyl CH); endo, 0.95–2.3 (11 H, ring proton), 6.30 (1 H, d, J = 5 Hz, vinyl CH).

***exo*-7-(Deuterio-7-ethynyl)norcarane (9).**[11] The vinyl dibromide (5.0 g, 117.8 mmol) and dry THF (85 ml) in a 250-ml flask was cooled to −78 °C and under an atmosphere of N_2 was slowly treated with a solution of *n*-BuLi in hexane (1.67 N, 23.4 ml, 39 mol). The clear yellowish solution was stirred 1 h at −78 °C and 1 h at 25 °C. The

resulting lithio alkyne was then quenched with D_2O (2 ml, 100 mmol, 99.8% *d*). The added D_2O gave a cloudy solution, which was allowed to stir 2-3 h. Pentane (100 ml) was added and the solution washed with H_2O (50 ml) and saturated aqueous NaCl (two 50-ml portions), dried (Na_2SO_4), and the solvent removed via rotary evaporation. Short path distillation provided the deuterated alkyne (**9**), bp 44-46 °C (5.5 mm) (1.1 g, 61%). Reaction of the 76% endo isomer (4.0 g, 14.3 mol) and the 90% exo isomer (14.0 g, 50 mol) gave yields of 77 and 67%, respectively: IR (neat film, mixture) 2600 (≡CD) and 1990 cm^{-1} (C≡C), no absorptions at 3300 or 2100 cm^{-1} (vide infra).

7-Ethynylnorcarane (8 and 13). The same procedure was utilized in preparing the undeuterated analogues except that the intermediate lithio alkynes were quenched with distilled H_2O. Hence the *endo*-vinyl dibromide (76% endo, 4.0 g, 14.3 mol) and *n*-BuLi (21.0 ml, 35 mmol) in THF (80 ml) was quenched with distilled H_2O (2 ml, 100 mmol) to yield the *endo*-alkyne (**13**) on workup (1.3 g, 77%). The *exo*-vinyl dibromide (90% exo, 14.0 g, 50 mmol), *n*-BuLi (72 ml, 120 mmol), THF (150 ml), and H_2O (3 ml, 150 mol) yielded the corresponding *exo*-7-ethynylnorcarane (**8**) (4.0 g, 67%): IR (neat film, mixture) 3300 (≡CH) and 2100 cm^{-1} (C≡C); NMR ($CDCl_3$) exo (**8**), δ 1.79 (1 H, d, J = 2 Hz, acetylenic); endo (**13**), 2.02 (1 H, d, J = 2 Hz, acetylenic).

7-(*cis*-β-Deuteriovinyl)bicyclo[4.1.0]heptane (11).[10] To a dry 100-ml flask containing the deuterated alkyne **9** 0.93 g, 7.7 mol) and dry hexane (30 ml) under N_2 was slowly added neat diisobutylaluminum hydride (DIBAL) (1.10 g, 7.7 mol) via a dry preweighed syringe. The solution was kept below 40 °C during the addition, stirred for 30 min afterward, and finally heated at 50 °C for 3 h.

The reaction was quenched by *cautious* addition of distilled H_2O (600 μl), (32 mmol) and vigorous stirring. The resulting reaction gelled solidly in most cases, but was transformed to a milky slurry by adding extra hexane (20 ml). The mixture was vacuum filtered after stirring 2 h and the filter cake washed with pentane (three 50-ml portions). The crude product was dried (Na_2SO_4) and concentrated via rotary evaporation to give the cis-deuterated endo-exo isomers. The endo-exo isomers of the crude cis-deuterated vinylcyclopropanes were easily separated and purified via VPC (column F, 130°), relative retention exo-endo = 1.00:1.29. Exo (**11**): NMR ($CDCl_3$) δ 0.75-1.08 (2 H, cyclopropyl), 1.08-2.3 (9 H, ring proton), 4.77 (1 H, d, J = 10 Hz, β-vinyl CH) 5.20-5.67 (1 H, m, J = 2.5 Hz, α-vinyl CH).

7-(*trans*-β-Deuteriovinyl)bicyclo[4.1.0]heptane (10 and 14). A similar procedure was used on the corresponding undeuterated alkyne except that the resultant alkane generated from the alkyne (2.4 g, 20 mmol) in hexane (60 ml) and DIBAL (3.0 g, 21 mmol) was hydrolyzed with D_2O (2.0 ml, 75 mmol, 99.8% *d*). This hydroalumination-deuteriolysis provided the corresponding trans-deuterated endo-exo isomers, which were subsequently separated and purified via VPC (column F, 130°), Exo (**10**): NMR ($CDCl_3$) δ 0.75-1.08 (2 H, cyclopropyl), 1.08-2.3 (9 H, ring protons), 4.90 (1 H, d, J = 17 H, β-vinyl CH), 5.44 (1 H, dd, J = 17, 8 Hz, α-vinyl CH). Endo (**14**): NMR ($CDCl_3$) δ 0.7-2.2 (11 H, ring protons), 5.17 (1 H, d, J = 17 Hz, β-vinyl CH), 5.77 (1 H, complex dd, J = 17, 8 Hz, α-vinyl CH).

***cis*- and *trans*-3-Propenylcyclohexene.**[38] A stock solution of 1-propenylmagnesium bromide was prepared from 1-propenyl bromide (36.3 g, 300 mmol, mixture of isomers) and magnesium turnings (6.8 g, 280 mmol) in THF (70 ml). THF was added after the reaction was complete to make the total volume 100 ml (2.8 M). To a slurry of anhydrous CuI (6.6 g, 35 mmol) in THF (30 ml) under N_2 was added a solution of the above stock solution (25 ml) in THF (30 ml) at 0 °C. After stirring 1 h to effect formation of the cuprate, a solution of 3-bromocyclohexene (3.0 g, 18.6 mmol) in THF (25 ml) was added dropwise at 0 °C. After vigorous stirring overnight at room temperature, the product was isolated by careful addition of H_2O and extraction with pentane. The extracts were washed with H_2O and saturated aqueous NaCl, dried (Na_2SO_4), concentrated, and distilled. The product (1.9 g, 83%) was shown by NMR to be a 60:40 mixture of cis (**35**) and trans (**34**) isomers, bp 65-80 °C (20 mm): NMR (**34**), δ 1.05-2.34 (9 H, m), 2.47-2.92 (1 H, m), 4.94-5.83 (4 H, m); (**35**), 1.13-2.40 (9 H, m), 2.76-3.33 (1 H, m), 4.93-5.83 (4 H, m). The products were collected by preparative VPC (column C, 70 °C).

***cis*- and *trans*-1-Propenylcyclohexene (36 and 37).** Cyclohexanone (0.05 mol) in ether (40 ml) was added rapidly dropwise with stirring and cooling (ice water bath) to a solution of 1-propenylmagnesium bromide (0.05 mol) in tetrahydrofuran (50 ml). The mixture was allowed to stand at room temperature 4 h and then poured into ice cold dilute HCl. The alcohol product was extracted with ether (100 ml) and the extracts were washed with water (three 100-ml portions) and the solvent removed. The residue was distilled under nitrogen in the presence of *p*-toluenesulfonic acid (100 mg) to yield the diene and water. The distillate was dissolved in pentane (20 ml), dried ($MgSO_4$), and redistilled to give a mixture of *cis*- and *trans*-1-propenylcyclohexene (4.1 g, 67%). The products are readily separable by preparative VPC on column B (110 °C) and identified by comparison of their NMR spectra with those published.[39]

Bicyclo[6.1.0]non-2-ene (15). 9,9-Dibromobicyclo[6.1.0]non-2-ene was prepared from 1,3-cyclooctadiene by the literature procedure.[40] Lithium (2 g, 0.28 mol) was added to a solution of dibromo compound (10 g, 0.036 mol) and dry *tert*-butyl alcohol (10.5 g, 0.14 mol, distilled from sodium) in anhydrous ether (100 ml) under nitrogen. After 0.5 h of stirring, the reaction started and spontaneously refluxed. After the reaction subsided, the mixture was stirred under reflux for 3 days (shorter reaction times led to recovery of considerable amounts of starting material). The solution was cooled, filtered with suction, and the solid washed with ether. The filtrate was washed with water (100 ml) and saturated salt solution (100 ml). The organic layer was dried ($MgSO_4$), concentrated at atmospheric pressure, and distilled (bp 65-70 °C (20 mm)) to yield 3 g (68%) of final product **15:** NMR δ −0.03 to −0.31 (1 H, m), 0.47-1.11 (2 H, m), 1.11-2.86 (9 H, m), 5.42 (1 H, d, J = 11 Hz), 5.52-5.87 (1 H, m).

***cis*- and *trans*-1-Phenyl-2-vinylcyclopropane (28 and 29).** The phenylcyclopropanes were prepared by the zinc chloride catalyzed addition of phenyldiazomethane to butadiene.[12] Separation of the isomers proved difficult, as VPC chromatography on QF-1 (13 × ¼ in. 135 °C) (the column used by Closs[12]) gave ring opening. After a considerable search, column D at 150 °C was found to give adequate separation and no rearrangement. *cis*-1-Phenyl-2-vinylcyclopropane (**28**) had a shorter retention time on this column.

***cis*- and *trans*-2-Methylhexa-1,4-diene (22 and 23).** 2-Methyl-4-hydroxyhexene (Chemical Samples, 0.105 mol, 12 g), dimethylaniline (14.6 g, 0.15 mol), and ether (25 ml) were heated to reflux. The source of heat was removed and acetyl chloride (10.2 g, 0.13 mol) was added with stirring dropwise over 30 min. The reaction became cloudy after half addition, and solid slowly precipitated. The solution was heated under reflux for 2 h, cooled, and water (25 ml) added. The ether layer was separated and washed with 10% sulfuric acid (six 25-ml portions), saturated $NaHCO_3$ (25 ml), and water (25 ml). The organic layer was dried ($MgSO_4$), the solvent removed, and the product distilled, bp 50-53 °C (~ 10 mm) (13.5 g, 83%).

The acetate (5.4 g) was added dropwise at a rate of 1 drop/2 s via syringe through a quartz pyrolysis column (22-cm length, packed with quartz chips) heated at 470 °C. The nitrogen flow through the column was 1 ml/s. The product was collected in a dry ice-acetone cooled receiver. The crude product, containing acetic acid, was washed with saturated Na_2CO_3 to remove the acid, dried ($MgSO_4$), and distilled, bp 90-110 °C (1.84 g, 52%). The product was examined by VPC (column E, 40 °C). The product was a mixture of five components identified by NMR and IR: *cis*-2-methylhexa-1,4-diene[41a] (13%, IR cis double bond 10.3), *trans*-2-methylhexa-1,4-diene[41c] (4%, 10.3 IR band absent), *trans*-2-methylhexa-1,3-diene (66%), *cis*-2-methylhexa-2,4-diene (**25**) (13%), and *trans*-2-methylhexa-2,4-diene (**24**) (4%); NMR cis-1,4, δ 1.68 (6 H, narrow m), 2.53-2.83 (2 H, br d, J = 5 Hz), 4.72 (2 H, narrow m), 5.23-5.58 (2 H, m); trans 1,4, 1.67 (6 H, narrow m), 2.50-2.87 (2 H, m), 4.69 (2 H, narrow m), 5.30-5.57 (2 H, finely split m); *trans*-2-methylhexa-1,3-diene, 1.03 (3 H, t, J = 7 Hz), 1.80 (3 H, slightly split s), 2.15 (2 H, quintet, J = 7 Hz), 4.86 (2 H, slightly broadened s), 5.63 (1 H, d t, J = 16, 6 Hz), 6.18 (1 H, d, J = 16 Hz, trans olefin).

***cis*- and *trans*-2-methylhexa-2,4-diene (25 and 24).** The title compounds were prepared by pyrolysis of the acetate (obtained from 2-methyl-3-hydroxyhex-4-ene—Chemical Samples) as in the synthesis above.[41b] The products were examined by VPC (column E, 40 °C), the mixture consisting of 2-methylhexa-3,5-diene (60%), *trans*-2-methylhexa-2,4-diene (**24**) (25%), and *cis*-2-methylhexa-2,4-diene (**25**) (15%).

The trans compound was also made by the Wittig reaction of *trans*-2-butenal with isopropylide:[41b] NMR 2-methylhexa-3,5-diene, δ 1.0 (6 H, d, J = 7 Hz), 2.27 (1 H, heptet with fine splitting, J = 7 Hz), 4.6-5.25 (2 H, m), 5.25-6.56 (3 H, m).

B. Rhodium Catalyzed Rearrangements. General Rearrangement Procedure. In a dry round-bottom flask fitted with a condenser and magnetic stirring bar was placed the vinylcyclopropane, VPC internal standard, and dry solvent (normally benzene). The solution was heated

to reflux under nitrogen and the catalyst added. Periodically, aliquots were removed and analyzed by VPC. In preparative scale reactions, when rearrangement was complete, the mixture was cooled and washed with dilute aqueous ammonia until the aqueous washes were colorless. The organic layer was dried, the solvent removed, and the residue distilled. The products were separated by preparative VPC.

Attempted Rearrangements of 15. The general procedure was followed using **15** (20 mg), benzene (5 ml), and various catalysts (3 mg). The reactions were followed on VPC column A (85 °C). No reaction was observed with tetrakis(triphenyl phosphite)nickel, norbornadiene rhodium chloride dimer, diiron nonacarbonyl, chromium hexacarbonyl, bis(benzonitrile)palladium dichloride, silver fluoroborate, molybdenum hexacarbonyl, rhodium trichloride dihydrate, palladium chloride, mercuric trifluoroacetate, cupric hexafluoroacetylacetonate, ferrocene, bis(cyclopentadiene)titanium dichloride, or bis(cyclopentadiene)vanadium dichloride. Tris(triphenylphosphine)rhodium chloride after 2 days gave 10% reaction to a new product (1,4-cyclononadiene). A preparative scale reaction was done with this catalyst (60 mg) and **15** (500 mg) in toluene (100 ml). The reaction was stopped after 1 month reflux. VPC analysis (column B, 110 °C) indicated the presence of three compounds, relative retention time 1 (70%), 1.16 (15%), and 1.35 (15%). All products were collected by preparative VPC on column B and analyzed by NMR. The major product was starting material, the second 1,5-cyclononadiene,[42] and the third, 1,4-cyclononadiene (**17**). Pyrolysis of **15** at 165 °C for 3 days in the liquid phase gave an authentic sample of 1,4-cyclononadiene.[43a] The 1,5-cyclononadiene is a secondary product arising from 1,4-cyclononadiene and rhodium over extended reaction times:[43b] NMR 1,4-cyclononadiene, δ 1.33–1.80 (4 H, m), 2.00–2.50 (4 H, m), 2.80 (2 H, t with fine splitting, J = 7 Hz), 5.16–5.70 (4 H, m). A yield (76%) was obtained after 29 h of reflux using $[RhCl(CO)_2]_2$[44] (12 mg), **15** (8.87 mg, 0.72 mmol), and benzene (3 ml) with tetradecane as an internal VPC standard. The sole product in this case was 1,4-cyclononadiene.

Rearrangement of 7-Vinylbicyclo[4.1.0]heptane (31 and 32). Syn **31** and anti **32** were prepared by the literature procedure.[8] A mixture of the isomers (ca. 1:1) (7 mg) in refluxing benzene (2 ml) was treated with various catalysts (1 mg). No products were observed by VPC (column A, 75 °C) after several days with bis(benzonitrile)palladium dichloride, tetrakis(triphenylphosphite)nickel, dirhodium tetraacetate dimethanol, pyridine (1 drop), pyridinium hydrochloride, rhodium trichloride dihydrate, diiron nonacarbonyl, cupric hexafluoroacetylacetonate dihydrate, or bis(diphenylmethylphosphine)platinum dibromide. After 2 days of reflux, rearrangement (disappearance of starting materials) was 99% complete with $[RhCl(CO)_2]_2$, 60% complete with tris(triphenylphosphine)rhodium chloride, and 10% complete with norbornadiene rhodium chloride dimer. By VPC, the same products were also obtained using THF or cyclohexane as the reaction solvent. A preparative reaction was done with a mixture of **31** and **32** (500 mg), $[Rh(CO)_2Cl]_2$ (20 mg), and anhydrous benzene (125 ml). Rearrangement was complete by VPC after 6 days of reflux. The products were isolated by preparative VPC on column C (70 °C). Three products were isolated: **34** (relative retention time 1); **35** (relative retention time 3.4); and **33**[45] (relative retention time 5.6). The products were identified by comparison with independently made samples (see above). Pure **31** and pure **32** were also rearranged to obtain yields and product compositions using *cis*-decalin as an internal standard and analyzing on both column A and column C. Relative retention times of isomers on column A are **33** (1), **34** and **35** (1.07), **32** (1.33), *cis*-2-propenylcyclohexene (1.6), **31** and allylidene cyclohexane (1.8), *cis*-decalin (2.05), and *trans*-2-propenylcyclohexene (2.4). From **32** 99% yield of **34:35:33** 0.68:0.065:1, and from **31** 80% yield of **34:35:33** 0.52:0.48:1 was obtained.

The kinetic studies were carried out in refluxing benzene with internal standard *cis*-decalin under nitrogen with stirring. Small (0.2 ml) samples were removed periodically and examined by VPC (column A and C). The amounts of the various starting materials and products were determined by peak weighing relative to the standard. For the kinetic runs, 0.5–1 mg of catalyst was used with 6–15 mg of starting material in 3–7 ml of benzene.

Isolation of Intermediate from the Rearrangement of Syn 31. Syn **31** (200 mg) and $[RhCl(CO)_2]_2$ (15.5 mg) in benzene (80 ml) were heated under reflux and the reaction progress was followed by VPC on column A (85 °C). After 4 h, the intermediate had built up to a maximum. The reaction was then quenched by shaking with dilute aqueous ammonia and worked up by the general procedure. Preparative VPC of the intermediate (column B, 110°) gave pure anti **32**, identified by the NMR spectrum.

Thermal Rearrangement of Syn 31 and Anti 32. A 10:1 solution of pentane–mixture of **31** and **32** was passed through a 10-in. heated quartz tube (filled with quartz chips) dropwise at a rate of 1 drop/s with a nitrogen flow of 2 ml/s. The temperature was slowly raised and the extent of reaction was followed by analytical VPC (column A, 90 °C). No rearrangement occurred below 250 °C. At 375 °C syn **31** is completely rearranged, but anti **32** is rearranged very little. At 490 °C anti **32** is 90% rearranged. Two preparative scale rearrangements were done on 100 mg of starting material, one at 340 °C and the other at 540 °C. The products from both rearrangemetts were collected by preparative VPC (column B, 110 °C) and shown by NMR to be identical with **35** obtained from the rhodium catalyzed rearrangement above. Cis double bond stereochemistry was assigned to **35** because a cis product is expected in the thermal rearrangement (compare with the thermal rearrangement of 1,1-dimethyl-2-vinylcyclopropane, which gives a cis product),[41a] and because **35** has a longer retention time[45] on the silver nitrate VPC column than **34**, which is assigned the trans stereochemistry.

Control Reactions for the 31 and 32 Reaction Series. All reactions were analyzed on column A (90 °C). Relative retention times are given above.

A. 3-Allylcyclohexene (33) was prepared by the literature procedure.[46] A benzene solution (6 ml) of 3-allylcyclohexene (24 mg), *cis*-decalin (VPC standard, 24 mg), and $[RhCl(CO)_2]_2$ (2 mg) was heated under reflux for 41 h. No new products formed.

B. Allylidenecyclohexene[47] (11.5 mg), $[RhCl(CO)_2]_2$ (1.5 mg), and *cis*-decalin (10.5 mg) in benzene (2.5 ml) were heated under reflux 2 days. No **34, 35,** or **33** was formed. There was a yield of 91% starting material and 9% *trans*-1-propenylcyclohexene (the latter identified by NMR after preparative VPC on column B, 110 °C, on a large scale reaction). A mixture of **31** and **32** (20 mg) was added to the reaction mixture along with an additional 2 mg of catalyst. After 3 days, although **31** and **32** had completely rearranged, the starting material and *trans*-1-propenylcyclohexene remained in 100% yield.

C. *trans*-1-Propenylcyclohexene (21.8 mg), prepared as described above, catalyst (2 mg), and *cis*-decalin (25.8 mg) were heated under reflux in benzene (6 ml) for 2 days. No new products were formed, 87% of the starting material remained. A mixture of **31** and **32** (20 mg) and additional catalyst (2 mg) was added and the mixture was heated another 4 days. At this time, rearrangement of **31** and **32** was complete, but the *trans*-1-propenylcyclohexene remained (70%).

D. *cis*-1-Propenylcyclohexene (8.2 mg), prepared as described above, catalyst (1 mg), and *cis*-decalin (10 mg) were heated under reflux in benzene (3 ml) for 2 days. At this time, some rearrangement to *trans*-1-propenylcyclohexene (25%) occurred, but no other products formed. A mixture of **31** and **32** (10 mg) and additional catalyst (1 mg) was added and the mixture refluxed another 4 days. Only further cis to trans rearrangement of *cis*-1-propenylcyclohexene occurred, even though rearrangement of **31** and **32** was complete.

E. 1-Allylcyclohexene (Chemical Samples, 21.8 mg), catalyst (2 mg), and *cis*-decalin (21.2 mg) were heated under reflux in benzene (6 ml) for 27 h, yielding 83% starting material and 10% *trans*-1-propenylcyclohexene (the latter identified by NMR after preparative VPC of a large scale reaction).

F. *cis*-3-Propenylcyclohexene (34) (20 mg, prepared by thermolysis of **31** and **32**), catalyst (3 mg), and *cis*-decalin (24.6 mg) were heated under reflux in benzene (6 ml) for 4 days. VPC analysis on both column A and C (70 °C) indicated that 81% starting material was present, with no additional products being formed.

G. *trans*-3-Propenylcyclohexene (35) (21 mg), catalyst (2.5 mg), and *cis*-decalin (26 mg) were heated under reflux in benzene (5 ml) for 3 days. Most of the starting material remained (87%), but another product was formed whose retention time on column C corresponded to **34** (this possibly could have arisen from one of the impurities in the starting material, which was only 75% pure).

H. Effect of Na_2CO_3 on the Rearrangement of 31 and 32. Pulverized anhydrous sodium carbonate (110 mg), **31** and **32** (10.2 mg), catalyst (1 mg), and *cis*-decalin (10.2 mg) were heated under reflux. The rearrangement still proceeded readily, reaching completion in 6 h. The same products were obtained, **33** (48%), **34** (27%), and **35** (25%).

I. Effect of Acid on the Rearrangement of 31 and 32. *p*-Toluenesulfonic acid (2 mg), **31** and **32** (17.2 mg), *cis*-decalin (20.6 mg), and benzene (5 ml) gave no rearrangement after 2 days of reflux. If catalyst (2 mg) is added to the above mixture, the rearrangement pro-

ceeds rapidly at a rate roughly 1.2 times rearrangement in the absence of acid.

Rearrangement of *cis*- and *trans*-1-Phenyl-2-vinylcyclopropane (28 and 29). A mixture of *cis*- and *trans*-1-phenyl-2-vinylcyclopropane (2 g), and $[RhCl(CO)_2]_2$ (50 mg) was heated under reflux in benzene (250 ml) for 4 days. VPC analysis (column A, 135 °C) showed starting materials still present (25%), but a new product (75%) of longer retention time also present. The products were collected by preparative VPC on column B (205 °C). By NMR comparison with independently made authentic samples,[48] the product is a mixture of *trans,cis*-1-phenylpenta-1,3-diene and *trans,trans*-1-phenylpenta-1,3-diene, with the trans,trans compound predominating. No reaction occurs in the absence of catalyst, although the reaction proceeds readily in the absence of solvent.

The kinetic analyses of the rearrangement of pure **28** and **29** were carried out on the same scale and with similar amounts as described above for **31** and **32** above. Hexadecane was used as an internal standard, and the relative retention time of the compounds are tetradecane (1), cis **28** (1.22), trans **29** (1.31), and *trans,cis*- and *trans,trans*-1-phenylpenta-1,3-diene (3.1). Trans **29** gave a 78% yield after 85% completion. In the rearrangement of cis **28**, trans **29** built up to a maximum of 51%. Trans **29** was isolated from cis **28** in a large scale reaction carried out to partial completion (monitored by VPC as in the isolation of the intermediate from syn **31**).

Control Reactions with Cis 28 and Trans 29. A mixture of cis **28** and trans **29** (19.8 mg), rhodium catalyst (1 mg), and hexadecane (18.2 mg, VPC standard) in benzene (4 ml) was heated under reflux in the absence and in the presence of either pulverized anhydrous sodium carbonate (100 mg) or "proton sponge" (50 mg, Aldrich, 1,8-bis(dimethylamino)naphthalene). The reaction done in the absence of base was five times as fast as the proton sponge reaction, and two times as fast as the sodium carbonate reaction, although all reactions gave both cis-trans isomerization and the ring opening reactions.

Rearrangement of 1,1-Dimethyl-2-vinylcyclopropane (21). Compound **21** (300 mg), prepared as described in the literature,[8] and $[RhCl(CO)_2]_2$ (30 mg) in dry *m*-xylene (distilled from sodium, 50 ml) were heated at 80 °C in an oil bath under nitrogen. The reaction was monitored by VPC (column A, 35 °C). After 3 days, rearrangement was complete, and the products were worked up as usual, except that the products (and some xylene) were distilled away from the higher boiling solvent at atmospheric pressure. Preparative VPC (75 °C, column E) gave two peaks, both of which were collected. Each peak was a mixture of two compounds (cis-trans isomers) whose composition could be analyzed for on column B (40 °C). By NMR, the first peak was 2-methylhexa-1,4-diene, and the second was 2-methylhexa-2,4-diene. All of the possible isomers of the 1,4- and 2,4-dienes were independently synthesized (see above), and their NMR and VPC retention times compared with the products obtained in the rearrangement. A yield for the rearrangement was obtained with cyclooctane as an internal VPC standard: **21** (10.4 mg), the catalyst (2.1 mg), and cyclooctane (10 mg) were dissolved in *m*-xylene (1 ml), and 50-μl samples were sealed in tubes and placed in an oil bath at 80 °C. Rearrangement was complete in 48 h. The relative retention times (column A, 35 °C) for the various isomers were **21** (1), *trans*-2-methylhexa-1,4-diene (1.06), *trans*-2-methylhexa-3,5-diene (1.09), *cis*-2-methylhexa-1,4-diene (1.14), *trans*-2-methylhexa-1,3-diene (1.4), *trans*-2-methylhexa-2,4-diene (1.72), *cis*-2-methylhexa-2,4-diene (1.83), and cyclooctane (2.66).

For the kinetic study, the reaction was carried out with stirring in a screw top vial (to avoid evaporation of starting material or products), since rearrangements in the sealed tubes gave inconsistent results (probably because they were not stirred or heated at exactly the same temperature). Thus, for the kinetic run, **21** (20.8 mg), catalyst (20 mg), and cyclooctane (20 mg) were heated at 78 °C in dry *m*-xylene (4 ml), samples being removed periodically for analysis.

Control Experiments in the 1,1-Dimethyl-2-vinylcyclopropane Series. A. *cis*-2-Methylhexa-1,4-diene (22) (14.6 g), rhodium catalyst (10.2 g), and cyclooctane VPC standard (11.9 mg) in *m*-xylene (anhydrous, 2 ml) were heated at 85 °C for 48 h with stirring in a screw top vial. No **23, 24,** or **25** was formed. Starting material (75%) remained along with a new product X (25%) of longer retention time than **25.** This unknown compound formed in many of the controls (see below), but its formation was not reproducible.

B. *trans*- and *cis*-2-Methylhexa-1,4-diene (23 and 22). A 7:3 mixture of **23:22** was treated with rhodium as in A above. After 48 h, the mixture consisted of 26% **23,** 14% **22,** and 60% X.

C. *trans*-2-Methylhexa-2,4-diene (24) was treated with rhodium as in A above. After 48 h, the mixture was composed of **24** (58%) and X (2%).

D. *cis*- and *trans*-2-Methylhexa-2,4-diene (25 and 24). A mixture of **25** (53%) and **24** (47%) was treated with rhodium as in A above. After 48 h, the mixture consisted of **25** (46%) and **24** (41%).

E. *trans*-2-Methylhexa-1,3-diene was treated with rhodium as in A above. After 48 h, the mixture consisted of starting material (87%) and X (6%).

F. 2-Methylhexa-3,5-diene was treated with rhodium as in A above. After 48 h, the mixture consisted of starting material (36%), a new product whose retention time corresponds to *cis*-2-methylhexa-1,4-diene (7%), and X (11%).

***cis*- and *trans*-1-Carboethoxy-2-vinylcyclopropane (30).** The title compounds were prepared by the addition of ethyl diazoacetate[49] to butadiene catalyzed by cupric triflate.[37] Obtained was a mixture of trans (60%) and cis (40%) cyclopropanes[50] which were separable on column E (110 °C), the trans compound having the shorter retention time. Treatment of the isomer mixture (200 mg) with the dicarbonyl rhodium chloride dimer (24 mg) in refluxing benzene (anhydrous, 30 ml) for 7 days gave partial (ca. 50%) rearrangement to two new products, C and D (1:3). Compared to trans starting material, C had a relative retention time of 2.0, and D of 2.3. Both products were collected by preparative VPC and identified by comparison of their NMR with those published.[51] C is *trans,cis*-ethylhexa-2,4-dienoic acid, and D is *trans,trans*-ethylhexa-2,4-dienoic acid.

Experiments conducted with pure *cis*-1-carboethoxy-2-vinylcyclopropane with internal standard bicyclohexyl indicated that cis-trans isomerization was occurring, but the reaction was very sluggish, requiring large amounts of catalyst.

Rearrangement of *endo*-7-(*trans*-β-deuteriovinyl)bicyclo[4.1.0]-heptane (14). The endo isomer **14** (215 mg, 1.745 mmol) and $[Rh(CO)_2Cl]$ catalyst (17.1 mg, 0.088 mmol) were rearranged under the usual conditions in refluxing benzene (80 ml). The olefin was thrice purified via preparative VPC (column F or H, 130 °C), and the composition analyzed to be 99.924% endo and 0.076% exo isomers.

The reaction progress was followed by VPC during the course of 60 min, at which time the intermediate exo isomer had rearranged to a maximum amount. The reaction was then worked up by washing successively with 9% aqueous ammonia (four 30-ml portions), H_2O (50 ml), saturated aqueous NaCl, and then dried (Na_2SO_4). The solvent was removed by careful rotary evaporation and the resulting solution of endo-exo isomers was easily purified and isolated via VPC. Both isolated isomers were then reanalyzed as to their purity (column E, 90 °C). NMR analysis of the endo fraction showed no change from the original endo-trans-deuterated material; however the exo fraction was identical with the spectrum of authentic exo-cis-deuterated material **11,** but seemed to contain a small amount (5%) of what appeared to be the exo-trans-deuterated isomer.

Acknowledgment is made to the Research Corporation and to the National Science Foundation for support of this research.

References and Notes

(1) R. Grigg, R. Hayes, and A. Sweeney, *Chem. Commun.*, 1248 (1971).
(2) (a) B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95,** 5311 (1973), and references cited therein, especially footnote 18; (b) J. P. Marino and T. Kaneko, *Tetrahedron Lett.*, 3975 (1973); (c) *ibid., J. Org. Chem.*, **39,** 3175 (1974); (d) J. R. Neff, R. R. Gruetzmacher, and J. E. Nordlander, *ibid.*, **39,** 3814 (1974).
(3) J. M. Brown, *Chem. Commun.*, 226 (1965).
(4) (a) V. Aris, J. M. Brown, and B. T. Golding, *J. Chem. Soc., Chem. Commun.*, 1206 (1972); (b) V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and D. H. Williamson, *J. Chem. Soc., Perkin Trans. 2,* 4 (1975).
(5) (a) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966); (b) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc. London,* 276 (1963); (c) E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiwa, *J. Am. Chem. Soc.*, **92,** 6635 (1970); (d) M. J. Jorgenson and A. F. Thacher, *Tetrahedron Lett.*, 4651 (1969); (e) G. Ohloff, *ibid.*, 3795 (1965); (f) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970.
(6) (a) R. G. Miller and P. A. Pinke, *J. Am. Chem. Soc.*, **90,** 4500 (1968); (b) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organomet. Chem.*, **28,** C42 (1971); (c) P. A. Pinke, R. D. Stauffer, and R. G. Miller, *J. Am. Chem. Soc.*, **96,** 4229 (1974).
(7) (a) R. Ben-Shoshan and S. Sarel, *Chem. Commun.*, 883 (1969); (b) S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Am. Chem. Soc.*, **87,** 2517 (1965); (c) R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4253 (1970); (d) C. H. DePuy, V. M. Kobal, and D. H. Gibson, *J. Organomet. Chem.*, **13,**

266 (1968); (e) R. Aumann, *ibid.*, **47,** C29 (1973); (f) W. E. Billups, L.-P. Lin, and O. A. Gansow, *Angew. Chem., Int. Ed. Engl.*, **11,** 637 (1972); (g) R. Aumann, *J. Am. Chem. Soc.*, **96,** 2631 (1974); (h) S. Sarel, A. Felzenstein, R. Victor, and J. Yovell, *J. Chem. Soc., Chem. Commun.*, 1025 (1974).
(8) R. G. Salomon, M. F. Salomon, and T. R. Heyne, *J. Org. Chem.*, **40,** 756 (1975).
(9) R. R. Sauers, S. B. Schlosberg, and P. E. Pfeffer, *J. Org. Chem.*, **33,** 2175 (1968).
(10) (a) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88,** 2213 (1966); (b) G. F. Zweifel and R. B. Steele, *ibid.*, **89,** 2754 (1967).
(11) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).
(12) J. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, **34,** 25 (1969).
(13) I. G. Bolesov, U. I. Sein, A. S. Koz'min, and R. Ya. Levina, *J. Org. Chem. USSR*, **5,** 1655 (1969).
(14) R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. Winterman, *Chem. Commun.*, 723 (1968).
(15) (a) M. F. Salomon and R. G. Salomon, *J. Chem. Soc., Chem. Commun.*, **89** (1976); (b) H. W. Voigt and J. A. Roth, *J. Catal.*, **33,** 91 (1974); (c) R. K. Russell, R. E. Wingard, and L. A. Paquette, *J. Am. Chem. Soc.*, **96,** 7483 (1974); (d) K. W. Barnett, D. L. Beach, D. L. Garin, and L. A. Kaempfe, *ibid.*, **96,** 7129 (1974).
(16) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *J. Am. Chem. Soc.*, **94,** 5845 (1972).
(17) (a) T. J. Katz and S. A. Cerefice, *J. Am. Chem. Soc.*, **93,** 1049 (1971); **91,** 2405 (1969); A. Stefani, G. Consiglio, C. Botteghi, and P. Pino, *ibid.*, **95,** 6504 (1973); J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **95,** 4451 (1973); H. Horino, M. Arai, and N. Inoue, *Tetrahedron Lett.*, 647 (1974); J. Schwartz, D. W. Hart, and B. McGiffert, *J. Am. Chem. Soc.*, **96,** 5613 (1974). (b) For a review see: W. Keim in "Transition Metals in Homogeneous Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971.
(18) (a) K. G. Powell and F. J. McQuillin, *Chem. Commun.*, 931 (1971); (b) K. B. Wiberg and K. C. Bishop III, *Tetrahedron Lett.*, 2727 (1973); (c) B. F. G. Johnson, J. Lewis, and S. W. Tam, *ibid.*, 3793 (1974); (d) A. deMeijere, *ibid.*, 1845 (1974).
(19) Such a transition state for elimination would be excessively strained and would lead to a trans C–C π bond in a six-membered ring from **44–46** or a anti-Bredt bridgehead olefin from **62.**
(20) (a) D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *Proc. Chem. Soc. London*, 179 (1960); (b) *ibid., J. Chem. Soc.*, 738 (1961); (c) P. W. Hall, R. J. Puddephatt, and C. F. H. Tipper, *J. Organomet. Chem.*, **71,** 145 (1974); (d) D. B. Brown, *ibid.*, **24,** 787 (1970); (e) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Commun.*, 396 (1966); (f) S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 1227 (1969).
(21) J. A. Roth, *J. Am. Chem. Soc.*, **92,** 6658 (1970).
(22) R. J. Ouellette and C. Levin, *J. Am. Chem. Soc.*, **93,** 471 (1971).
(23) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968).
(24) (a) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (b) R. J. Roth and T. J. Katz, *J. Am. Chem. Soc.*, **94,** 4770 (1972); (c) H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 3667 (1973); (d) P. G. Gassman and E. A. Armour, *ibid.*, 1431 (1971); (e) S. F. Nelsen, J. P. Gillespie, P. J. Hintz, and E. D. Seppanen, *J. Am. Chem. Soc.*, **95,** 8380 (1973); (f) W. E. Billups, W. Y. Chow, and C. V. Smith, *ibid.*, **96,** 1979 (1974).
(25) (a) P. G. Gassman and T. Nakai, *J. Am. Chem. Soc.*, **94,** 2877 (1972); (b) P. G. Gassman and F. J. Williams, *ibid.*, **94,** 7733 (1972); (c) P. G. Gassman, G. R. Meyer, and F. J. Williams, *ibid.*, **94,** 7741 (1972); (d) P. G. Gassman and T. J. Atkins, *ibid.*, **94,** 7748 (1972); (e) P. G. Gassman, T. J. Atkins, and J. T. Lumb, *ibid.*, **94,** 7757 (1972); (f) P. G. Gassman and R. R. Reitz, *ibid.*, **95,** 3057 (1973); (g) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93,** 1288, 2335 (1971); **94,** 7771, 7780 (1972); (h) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *ibid.*, **94,** 7761 (1972); (i) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *ibid.*, **94,** 9222 (1972); (j) L. A. Paquette and J. S. Ward, *Tetrahedron Lett.*, 4909 (1972); (k) L. A. Paquette and G. Zon, *J. Am. Chem. Soc.*, **96,** 203, 215, 224 (1974); (l) W. G. Dauben and A. J. Kielbania, *ibid.*, **94,** 3669 (1972); (m) W. G. Dauben, A. J. Kielbania, and K. N. Raymond, *ibid.*, **95,** 7166 (1973); (n) R. Noyori, T. Suzuki, T. Kumagai, and H. Takaya, *ibid.*, **93,** 5894 (1971); (o) R. Noyori, *Tetrahedron Lett.*, 1691 (1973); (p) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *J. Am. Chem. Soc.*, **93,** 1043 (1971); (q) M. Sakai and S. Masamune, *ibid.*, **93,** 4610 (1971); (r) M. Sakai, H. H. Westberg, Y. Yamaguchi, and S. Masamune, *ibid.*, **93,** 4611 (1971).
(26) (a) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89,** 2486 (1967); (b) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).
(27) S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Am. Chem. Soc.*, **87,** 2517 (1965).
(28) G. Albelo and M. F. Rettig, *J. Organomet. Chem.*, **42,** 183 (1972).
(29) T. J. Katz and S. Cerefice, *J. Am. Chem. Soc.*, **91,** 2405, 6519 (1969); **93,** 1049 (1971).
(30) (a) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Am. Chem. Soc.*, **91,** 218, 2137 (1969); (b) T. J. Katz and S. A. Cerefice, *Tetrahedron Lett.*, 2509, 2561 (1969); (c) R. Grigg and G. Shelton, *Chem. Commun.*, 1247 (1971).
(31) (a) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Am. Chem. Soc.*, **94,** 9222 (1972); (b) P. G. Gassman and R. R. Reitz, *ibid.*, **95,** 3057 (1973); (c) H. Hogeveen and W. F. J. Huurdeman, *Tetrahedron Lett.*, 1255 (1974).
(32) (a) R. A. Moss, *J. Org. Chem.*, **30,** 3261 (1965); (b) F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, 3837 (1966).
(33) (a) M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89,** 723 (1967); (b) *ibid.*, **91,** 4310 (1969); (c) J. M. Simpson and H. G. Richey, *Tetrahedron Lett.*, 2545 (1973); (d) E. N. Marvell and C. Lin, *ibid.*, 2679 (1973).
(34) N. W. Alcock, J. M. Brown, J. A. Conneely, and D. H. Williamson, *J. Chem. Soc., Chem. Commun.*, 792 (1975).
(35) (a) G. Albelo, G. Wiger, and M. F. Rettig, *J. Am. Chem. Soc.*, **97,** 4510 (1975); (b) T. J. Marks and W. A. Wachter, *ibid.*, **98,** 703 (1976); (c) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *ibid.*, **94,** 5258 (1972); (d) D. E. James and J. K. Stille, *ibid.*, **98,** 1810 (1976).
(36) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35,** 4000 (1970).
(37) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95,** 3300 (1973).
(38) Cf.: E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89,** 3911 (1967); C. Casey and R. Boggs, *Tetrahedron Lett.*, 2455 (1971).
(39) (a) E. N. Marvell and J. Tashiro, *J. Org. Chem.*, **30,** 3991 (1965); (b) J. C. Hamlet, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951).
(40) (a) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, **87,** 3158 (1965); (b) W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **2,** 115 (1963).
(41) (a) H. M. Frey and R. K. Solly, *Int. J. Chem. Kinet.*, **1,** 473 (1969); (b) P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, 1409 (1971); (c) R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Am. Chem. Soc.*, **89,** 3756 (1967); (d) R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, *ibid.*, **92,** 6345 (1970).
(42) G. Nagendrappa and D. Devaprabhakara, *J. Organomet. Chem.*, **15,** 225 (1968).
(43) (a) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966); (b) M. Bhagwat and D. Devaprabhakara, *J. Organomet. Chem.*, **52,** 425 (1973).
(44) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8,** 211 (1966).
(45) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84,** 4697 (1962).
(46) P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron, Suppl.*, **No. 8,** 399 (1966).
(47) E. J. Corey and D. E. Cane, *J. Org. Chem.*, **34,** 3053 (1969).
(48) K. Alder and M. Schumacher, *Justus Liebigs Ann. Chem.*, **571,** 122 (1951).
(49) N. E. Searle, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 424.
(50) (a) J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, **33,** 1173 (1968); (b) H. Weitkamp and F. Korte, *Tetrahedron*, **20,** 2125 (1964).
(51) F. Näf and P. Degen, *Helv. Chim. Acta.*, **54,** 1939 (1971); Sadtler NMR Index Spectrum, No. 18 700M.