tion of the residue afforded a mixture of ethyl cis-2-butenoate, 6.6 g (12%), and cis-2-buten-1-ol-1-d₂, 26.6 g (84%), bp 120–123°.

d. 1-Chloro-2-butene-1-d₂. cis-2-Buten-1-ol-1-d₂, 21.1 g (0.285 mol), and 6.3 g of the ester precursor were dissolved in a solution of purified tri-n-butylamine,[15] 54.3 g (0.285 mol), in 500 ml of ether and the resulting mixture was cooled to −5°. Thionyl chloride, 35 g (0.290 mol), in 100 ml of ether was slowly added to the well stirred, cold solution over a 3-hr period. The reaction mixture was then stirred at room temperature for 3 hr after which the volatile components were flash distilled (40° (1 mm)). Distillation of the flash distillate at atmospheric pressure then removed most of the SO₂ and ether from the product mixture. The remaining solution was then treated with 4 ml of water and then was stirred over 3 g of K₂CO₃ for 3 hr. The mixture was again subjected to flash distillation (40° (1 mm)) and the distillate was dried over CaCl₂. Atmospheric pressure distillation then afforded a mixture containing the ester impurity (5.8 g, 92% recovered) and 1-chloro-cis-2-butene-1-d₂ (17.8 g, 67% product yield), bp 83–87° (lit.[15] bp 84–85°). The mixture was characterized by examination of its pmr and infrared spectra.

e. cis-1,4-Hexadiene-3-d₂. A solution of 0.187 mol of vinylmagnesium chloride in 94 ml of tetrahydrofuran was added to a solution (cooled to −50°) of 12.3 g (0.131 mol) of 1-chloro-cis-2-butene-1-d₂ and 4.0 g of the ester (derived from step d) in 94 ml of tetrahydrofuran which contained 6.6 g (0.066 mol) of heptane, employed as an internal standard for glpc analysis.[16] After the addition was complete, the solution was warmed to room temperature and stirred for 8 hr after which it was stirred at 50° for 8 hr. Analysis by glpc gave the following product yields: cis-1,4-hexadiene-3-d₂, 27%; trans-1,4-hexadiene-3-d₂, 4%; and 3-methyl-1,4-pentadiene-1-d₂, 13%. The product mixture was flash distilled (45° (1 mm)) and the distillate was washed with NaCl solution until the volume of the organic layer did not change (removal of THF). After being dried with calcium chloride, 4 ml of a mixture of dienes in residual THF, which distilled below 96°, was collected. Preparative glpc separation using a 20 ft × ³/₈ in. TCEP column at 80° (to remove the THF), followed by use of a 15 ft × ³/₈ in. β,β′ column at 60° to separate the dienes afforded cis-1,4-hexadiene-3-d₂, 1.38 g, 12.5% yield, trans-1,4-hexadiene-3-d₂, 0.10 g, 1–2% yield,

and 3-methyl-1,4-pentadiene-1-d₂, 0.68 g, 6.2% yield. Spectral identification: cis-1,4-hexadiene-3-d₂, infrared spectrum (neat) essentially the same as that of cis-1,4-hexadiene but with additional peaks at 2190, 2120, and 2090 cm⁻¹; pmr spectrum in Figure 3. Structures of the other diene products were also confirmed by examination of their pmr and infrared spectra.

Rearrangement of cis-1,4-Hexadiene-3-d₂. A 17.35 ml solution of trans-dichlorobis(tri-n-butylphosphine)nickel(II), 0.103 g (0.192 mmol), and 1-3-d₂, 0.192 g (2.31 mmol), in toluene was treated with a 25% toluene solution of diisobutylaluminum chloride (0.65 ml, 0.78 mmol) at 25°. After 2 min elapsed, the reaction was terminated by the addition of 2 ml of 2-propanol. Glpc analysis indicated that 55% of the 1-3-d₂ had been converted to products. The usual work-up afforded a diene-rich toluene solution from which the products and unisomerized starting material were recovered by preparative glpc. The pmr spectra of recovered deuterio-1 and the deuterio-2 are described in Results. Since the amounts of 2,4-hexadiene products collected were small, they were analyzed as a mixture, affording the following pmr spectrum (CCl₄): δ 6.2–4.9 (broad multiplet, 2.91 H, vinylic protons) and 1.7 (sharp multiplet, 6.00 H, CH₃ protons).

An analogous experiment was conducted in which 90% of the 1-3-d₂ was converted to products during 2 hr. The pmr spectra of recovered deuterio-1 and the deuterio-2 are described in Results. The pmr spectrum (CCl₄) of the deuterio-2,4-hexadienes collected as a mixture: δ 6.2–4.9 (2.85 H, vinylic protons) and 1.7 (6.00 H, CH₃ protons).

Rearrangement of a Mixture of 1 and 1-3-d₂. A solution of trans-dichlorobis(tri-n-butylphosphine)nickel(II), 0.092 g (0.17 mmol), and 0.23 ml (2.06 mmol) of 1 and 1-3-d₂ (Table I), total volume, 16.7 ml, was treated with a 25% toluene solution of diisobutylaluminum chloride, 0.57 ml (0.69 mmol). The amber solution was stirred for 2 min at 25° after which the reaction was terminated (55% conversion) with 2-propanol. The products were isolated and identified in the usual manner.

Nickel-Promoted Methylvinylcyclopropane Rearrangements. Mechanistic Relevance to the cis-1,4-Hexadiene to 2-Methyl-1,3-pentadiene Isomerization[1,2]

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Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201. Received October 15, 1973
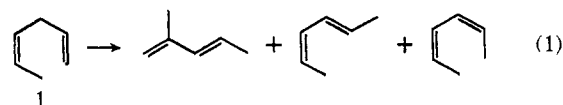
Abstract: trans- and cis-2-methylvinylcyclopropanes were skeletally isomerized by catalysts derived from trans-dichlorobis(tri-n-butylphosphine)nickel(II) and diisobutylaluminum chloride and from ethylenebis(tri-o-tolyl phosphite)nickel(0) and hydrogen chloride. Both catalyst systems afforded trans-2-methyl-1,3-pentadiene, and trans,-trans- and trans,cis-2,4-hexadienes as rearrangement products at 25° in toluene solution. The introduction of ethylene to solutions containing the 2-methylvinylcyclopropanes and the (n-Bu₃P)₂NiCl₂/i-Bu₂AlCl catalyst caused pronounced increases in the rates of isomerization. The rates of isomerization of trans- and cis-1,4-hexadiene by the catalyst were also increased when ethylene was present. The isomeric product distributions afforded by the methylvinylcyclopropanes at −22° in the presence of ethylene were substantially different from the product compositions obtained at 25° in the absence of ethylene. The results are interpreted in terms of the intervention of cyclopropylcarbinylnickel derivatives and the stereochemistry of each intermediate is discussed.

W̲e have presented arguments that the skeletal change and the hydrogen transfer associated with the nickel-catalyzed cis-1,4-hexadiene to trans-2-

(1) Most of these results were reported in preliminary communications: (a) R. G. Miller and P. A. Pinke, J. Amer. Chem. Soc., 90, 4500 (1968); (b) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, J. Organometal. Chem., 29, C42 (1971).
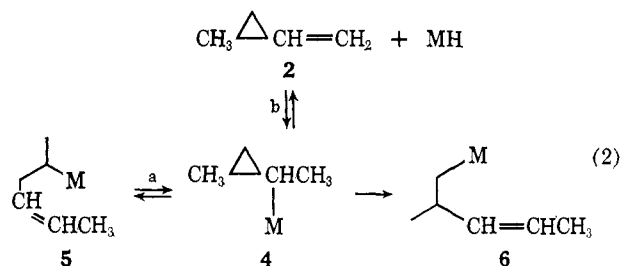
(2) Taken in part from the Ph.D. Theses of P. A. Pinke, 1970, and R. D. Stauffer, 1972, University of North Dakota.

methyl-1,3-pentadiene rearrangement, eq 1, are con-

sistent with a mechanism involving the intervention of a cyclopropylcarbinylnickel complex derived from isom-

erization of an alkenylnickel species, eq 2.[3] Prec-

$$CH_3 \triangle CH{=}CH_2 \ + \ MH$$
2

$$\mathbf{b} \Updownarrow$$

(2)

5   **4**   **6**

edent for this reaction path was found in studies by Roberts and coworkers[4] who demonstrated that inter-conversions of allylcarbinyl Grignard reagents involved the intervention of cyclopropylcarbinylmagnesium species. Subsequently, the preparation of a cyclo-propylcarbinyllithium reagent was disclosed.[5] Although no examples of this type of reaction existed in transition metal catalysis, the possibility that the nickel-promoted cis-1,4-hexadiene rearrangement involved the corresponding organonickel intermediates, eq 2, was considered. We further recognized that the transition metal analog of this reaction must be a very low energy process relative to the allylcarbinylmagnesium inter-conversion. Whereas a half-life of 30 hr at 27° and an activation energy of ca. 26 kcal/mol were characteristic of the equilibration of allylcarbinyl Grignard reagents,[4c] the half-life for the *catalytic* conversion of cis-1,4-hexa-diene to isomeric products was <2 min at 25° when a diene:nickel molar ratio of 12:1 was employed.[6]

In order to further test this postulated mechanism for the diene rearrangement, answers to two crucial ques-tions were sought. (a) Is the chemistry of a cyclo-propylcarbinylnickel species consistent with its postu-lated role in our mechanistic scheme? (b) Can an inter-mediate of this type account for the observed steric course of the cis-1,4-hexadiene rearrangement? We re-port herein the results of experiments designed to af-ford the *in situ* synthesis of the proposed intermediate. In order to maintain the closest possible resemblance between the experimental conditions used to accomplish the nickel-catalyzed diene rearrangement and those conditions employed for our examination of the pro-posed intermediate, we have employed the nickel cata-lyst in the synthesis of the intermediate by an indepen-dent route. Our picture of the catalyst system[3,6] pre-dicted that treatment of a 2-methylvinylcyclopropane isomer[7] with the catalyst precursors would generate a cyclopropylcarbinylnickel derivative through addition of nickel hydride to the double bond, eq 2, step b. The use of both cis- and trans-2-methylvinylcyclopropanes would afford the opportunity to synthesize all four stereoisomers of the dimethylcyclopropylcarbinylnickel intermediate (two cis diastereomers and two trans

(3) P. A. Pinke and R. G. Miller, *J. Amer. Chem. Soc.*, **96**, 4221 (1974).

(4) (a) M. S. Silver, P. A. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); (c) M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).

(5) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *J. Amer. Chem. Soc.*, **86**, 2247 (1964).

(6) R. G. Miller, P. A. Pinke, R. D. Stauffer, H. J. Golden, and D. J. Baker, *J. Amer. Chem. Soc.*, **96**, 4211 (1974).

(7) Thermal isomerizations of these compounds have been studied: (a) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc., London*, 221 (1964); (b) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964); (c) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).

diastereomers), thus allowing a comparison of their behavior with that of the intermediate which is re-sponsible for the determination of product structures in the cis-1,4-hexadiene rearrangement.

Results

Action of Nickel Catalysts on Methylvinylcyclopro-panes. The cis- and trans-2-methylvinylcyclopropanes (**2a** and **2b**) were prepared by the thermolysis of a 1:1 mixture of cis- and trans-3-methyl-5-vinylpyrazolines. The pyrazoline mixture was afforded by the addition of diazoethane to butadiene according to the general procedure of Crawford.[8] The resulting 1:1 mixture of **2a** and **2b** was resolved and each compound was col-lected *via* preparative glpc. The structural assignments for **2a** and **2b** were confirmed by comparison of the pmr and infrared spectra with those reported by Roth and König.[7c]

The addition of diisobutylaluminum chloride to toluene solutions containing trans-dichlorobis(tri-n-butylphosphine)nickel(II) and either **2a** or **2b** (diene: Al:Ni molar ratio = 18:4.5:1) at 25° resulted in the skeletal isomerization of each to the same C-6 diene products, eq 3. During 120 min, 58% of **2a** was con-

2a

2b

(3)
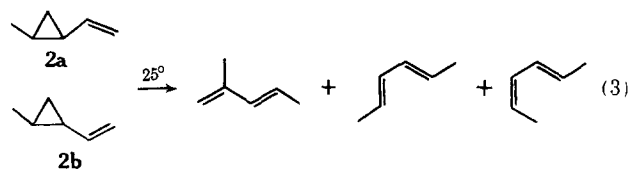
verted to products with a C-6 isomer yield of 68%. The isomeric product mixture consisted of trans-2-methyl-1,3-pentadiene (79%), trans,trans-2,4-hexadiene (13.4%), and trans,cis-2,4-hexadiene (7.6%). During 120 min 68% of **2b** was converted to products, the C-6 isomers being afforded in 53% yield, and the mixture consisted of 63.5% trans-2-methyl-1,3-pentadiene, 24.0% trans,trans-2,4-hexadiene, and 12.7% trans,cis-2,4-hexadiene. The half-life for the conversion of each isomer of **2** to products was ca. 60 min. A similar ex-periment in which vinylcyclopropane was treated with the catalyst afforded a mixture of trans- and cis-1,3-pentadienes in low yield.

The addition of hydrogen chloride to a toluene solu-tion of ethylenebis(tri-o-tolyl phosphite)nickel(0) and **2a** (olefin:Ni:HCl molar ratio = 12:1.0:0.78, 0.11 *M* in **2a**) at 25° resulted in the rapid isomerization of **2a** to a C-6 mixture consisting of trans-2-methyl-1,3-penta-diene (65%), trans,trans-2,4-hexadiene (10%), trans,cis-2,4-hexadiene (25%), and a trace of a component with a glpc retention time identical with that of cis,cis-2,4-hexadiene. During 1.5 min, 50% of **2a** was converted to products which included a 60% yield of the C-6 iso-mers. Extending the reaction period to 10 min af-forded a 70% yield of the isomeric products at 70% con-version. The C-6 isomer product ratio remained at ca. the same value throughout these reaction periods and on extended contact with the catalyst for 3.5 hr.

Treating a toluene solution of **2b** and ethylenebis-(tri-o-tolyl phosphite)nickel(0) with hydrogen chloride (olefin:Ni:HCl ratio = 12:1.0:0.74, 0.14 *M* in **2b**) at 25° caused the rapid isomerization of **2b** to trans-2-methyl-1,3-pentadiene (54%), trans,cis-2,4-hexadiene

(8) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

(30%), trans,trans-2,4-hexadiene (13%), and a minor component with a glpc retention identical with that of cis,cis-2,4-hexadiene (2%). During 2.5 min, 56% of **2b** was converted to products and the C-6 isomers were formed in 80% yield. During 5 min more than 70% of **2b** had been converted to products.

No cis-2-methyl-1,3-pentadiene was detected in product mixtures from either **2a** or **2b**. Control experiments demonstrated that hydrogen chloride, alone, did not cause isomerization of **2a** or **2b** during a 5-hr period. When **2a** and **2b** were treated with ethylenebis(tri-o-tolyl phosphite)nickel(0) (olefin:Ni molar ratio = 10:1) in toluene solution at 25° in independent experiments, essentially no loss of either **2a** or **2b** was observed during a 2-hr period. Two very minor hydrocarbon products (<1% yield) of unknown identity were formed when the temperature of the reaction mixtures was raised to 58°. During the period of time during which the temperature was raised, the solutions slowly darkened from their normal yellow color and large quantities of solid were deposited on the walls of the flask.

Rearrangements of Methylvinylcyclopropanes and 1,4-Hexadiene in the Presence of Ethylene. The introduction of ethylene to solutions containing **2a** or **2b** and the catalyst derived from trans-dichlorobis(tri-n-butylphosphine)nickel(II) and diisobutylaluminum chloride caused a pronounced rate enhancement in the formation of isomeric products. In order to satisfactorily monitor the formation of products, a relatively large methylvinylcyclopropane:nickel ratio was employed (**2a** or **2b**:Al:Ni = 212:14:1). The magnitude of the rate enhancement—when the above ratio was employed—was illustrated in experiments conducted at −22°. When the nickel and aluminum catalyst precursors were mixed in the presence of **2a** and **2b** in independent experiments at −22°, <2% of each methylvinylcyclopropane was converted to products during a 3-hr period. However, the addition of 1 atm of ethylene to these reaction mixtures had a remarkable effect on the rate of formation of isomeric products. For instance, 51% of **2b** was converted to products during 5 min and a 99% yield of a C-6 isomer mixture was obtained which consisted of trans- and cis-2-methyl-1,3-pentadiene and trans,trans-, trans,cis-, and cis,cis-2,4-hexadiene. The percentage composition of this product mixture is given in Figure 1. An experiment conducted under almost identical conditions at 25° afforded an 89% conversion of **2b** to products during 4 min with a C-6 isomer yield of 90%. The composition of the C-6 product mixture obtained at this higher temperature was substantially different; trans-2-methyl-1,3-pentadiene (37.0%), cis-2-methyl-1,3-pentadiene (36.0%), trans,trans-2,4-hexadiene (16.0%), and trans,cis-2,4-hexadiene (11.0%).

When ethylene was introduced to a solution of **2a** and the catalyst at −22° under the above conditions, 64% of the methylvinylcyclopropane was converted to products during 30 min and a 96% yield of C-6 isomers was afforded. The per cent composition of the mixture is described in Figure 1.

When cis-1,4-hexadiene (**1**) was treated with the nickel and aluminum catalyst precursors in toluene at −22° (diene:Al:Ni = 211:14:1), no loss of the diene was observed during a 3-hr period. However, when ethylene was passed through this solution, **1** was rapidly
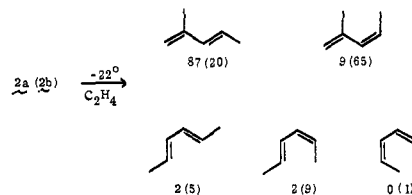

Figure 1. Percentage compositions of C-6 isomer mixtures derived from **2a** and **2b** in the presence of ethylene.

converted to a mixture composed of trans,cis-2,4-hexadiene (64.0%), cis,cis-2,4-hexadiene (26.1%), trans,trans-2,4-hexadiene (4.2%), and trans-2-methyl-1,3-pentadiene (5.7%). The total yield of C-6 isomers was 99% and the half-life for the conversion of **1** to these products was ca. 14–15 min. Treatment of **1** with the catalyst components in toluene at 25° (diene:Al:Ni = 140:4.6:1.0, **1** = 0.12 M) in the presence of an atmosphere of ethylene caused its isomerization to the same C-6 isomers (trans-2-methyl-1,3-pentadiene:2,4-hexadiene ratio = 1:2) and the half-life for the conversion of **1** to products was ca. 2 min.

Reaction of trans-1,4-hexadiene with the catalyst under the conditions employed in the above cis-1,4-hexadiene experiment resulted in essentially no conversion of starting material to products during 3 hr at −22° in the absence of ethylene. However, the addition of ethylene to this solution caused 75% of the 1,4-diene to be converted during 30 min to trans,trans- and trans,cis-2,4-hexadienes in nearly quantitative yield.

Discussion

The results demonstrate that the same nickel catalysts which accomplish the type I skeletal rearrangement of 1,4-dienes[6] also cause the isomerization of the methylvinylcyclopropanes. It is significant that ethylenebis(tri-o-tolyl phosphite)nickel(0) does not, by itself, catalyze the isomerization of **2a** and **2b**. In view of the demonstrated reactivity of cyclopropane[9] and its derivatives[10,11] toward coordinatively unsaturated[12] transition metal compounds, one might presume that the nickel-promoted vinylcyclopropane rearrangements would occur either via the oxidative addition of a carbon–carbon bond[9,10c,d,13] in the three-membered ring to the nickel(0) complex, or by some alternate route[11,14] also involving direct reaction of the metal with the cyclopropane ring. Oxidative addition mechanisms have recently been postulated to account for the reactions of other nickel(0) complexes with some highly strained hydrocarbons containing three-membered

(9) (a) D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, J. Chem. Soc., 738 (1961); (b) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, Chem. Commun., 396 (1966); (c) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, J. Chem. Soc. A, 845 (1968); (d) K. G. Powell and F. J. McQuillin, Chem. Commun., 931 (1971).

(10) (a) R. J. Ouellette and C. Levin, J. Amer. Chem. Soc., 90, 6889 (1968); (b) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, ibid., 91, 2137 (1969); (c) T. J. Katz and S. A. Cerefice, ibid., 91, 2405 (1969); (d) ibid., 91, 6519 (1969).

(11) For leading references to bicyclobutane and bicyclopentane chemistry, see (a) P. G. Gassman, T. J. Atkins, and J. T. Lumb, J. Amer. Chem. Soc., 94, 7757 (1972); (b) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, ibid., 93, 4611 (1971); (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, ibid., 94, 7780 (1972).

(12) J. P. Collman, Accounts Chem. Res., 1, 136 (1968).

(13) L. Cassar, P. E. Eaton, and J. Halpern, J. Amer. Chem. Soc., 92, 3515 (1970).

(14) J. Wristers, L. Brener, and R. Pettit, J. Amer. Chem. Soc., 92, 7499 (1970).

rings.[15] The observations that neither **2a** and **2b** nor *cis*-1,4-hexadiene was skeletally isomerized by ethylene-bis(tri-*o*-tolyl phosphite)nickel(0) until hydrogen chloride was added to the nickel(0) compound support our supposition[3,6] that one of the first steps in each skeletal isomerization reaction path involves the addition of the elements of nickel hydride to the hydrocarbon substrate. A report in the literature which appears to be closely related to these isomerizations is the recent investigation by Heathcock and Poulter[16] of the hydrogenation of vinylcyclopropane derivatives employing a rhodium-based catalyst. These workers observed the formation of saturated ring-opening products, and a reaction path involving the addition of a rhodium hydride to the vinylcyclopropane double bond can account for the product structures.

Although the isomerization products derived from the methylvinylcyclopropanes possessed the same carbon skeletons as those generated in the *cis*-1,4-hexadiene rearrangement, some striking differences were seen in the double bond configurations of the diene products. The determination of the reason(s) for these differences is essential in establishing the degree of mechanistic relevance of the methylvinylcyclopropane reactions to the *cis*-1,4-hexadiene rearrangement. The facts which must be accommodated are the following. (a) At 25° in the absence of ethylene, **1**, **2a**, and **2b** all afforded *trans*-2-methyl-1,3-pentadiene as the only methylpentadiene product. However, the *only* 2,4-hexadienes afforded by **2a** and **2b** were the trans,trans and trans,cis isomers. All of our experiments with **1**[6] at 25° have afforded *trans,cis*- and *cis,cis*-2,4-hexadienes with only traces of the trans,trans isomer being detected. (b) At −22° in the presence of ethylene, the predominant 2-methyl-1,3-pentadiene obtained from **2a** was the trans isomer (trans:cis ratio = 9.6), and the product mixture consisted almost entirely of methylpentadienes (MePD:2,4HD = 24). (c) At −22° in the presence of ethylene, **2b** gave a more balanced distribution of products with the cisoid double bond configuration predominating (*trans*-MePD:*cis*-MePD = 0.31). The MePD:2,4HD ratio of 6.0 was much smaller than that afforded in the reaction of **2a**.

Are the contrasting product compositions obtained from treatment of **1**, **2a**, and **2b** with the nickel catalyst compatible with the postulate that the intervention of a cyclopropylcarbinylnickel derivative is responsible for the product structures derived from all three reactants? A careful analysis of these data reveals that they are consistent with this postulate. Our interpretation of the data was induced by careful examination of molecular models of each of the four dimethylcyclopropylcarbinyl-nickel stereoisomers, **4**, which could be formed on treatment of **2a** and **2b** with the catalyst. This study revealed that (1) severe steric restrictions on concerted ring-opening and ring-closing processes involving certain of the stereoisomers of **4** would exist, eq 2, and (2) the configurations of the internal double bond in each ring opening product, **5** and **6**, eq 2, would be determined by the configurations of the carbinyl carbon in **4**

(15) (a) R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, 92, 5780 (1970); (b) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, 93, 5894 (1971); (c) R. Noyori, T. Suzuki, and H. Takaya, *ibid.*, 93, 5896 (1971); (d) R. Noyori, Y. Kumagai, I. Umeda, and H. Takaya, *ibid.*, 94, 4018 (1972).

(16) C. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969).

if the ring opening were a concerted process. The principle of microscopic reversibility dictates that the configuration of the internal double bond in **5** or **6** would in turn determine which stereoisomer of **4** is generated on concerted ring closure.

Scheme I elucidates the stereochemical relationships

Scheme I
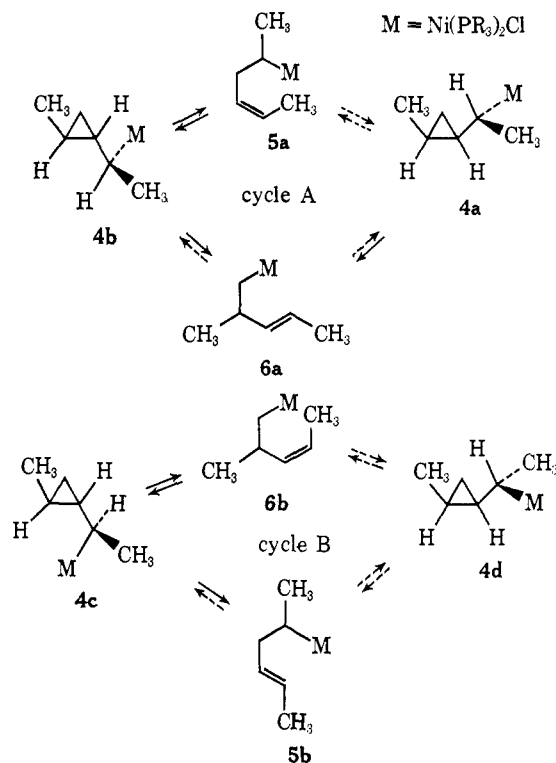
of all possible stereoisomers of **4**, **5**, and **6** as they are interconverted *via* concerted reactions. The branched products arise from metal migration to the unalkylated carbon of the cyclopropane ring while linear products come from metal migration to the methylated carbon. The following points are significant. (1) Based upon consideration of the configuration at the carbinyl carbon in each cyclopropylcarbinylnickel derivative, **5a** and **6a** can only be generated from **4a** and **4b** and *vice versa* (cycle A), if the metal is transferred from carbon to carbon in a concerted fashion. In an analogous manner, **5b** and **6b** can only be generated directly from **4c** and **4d** and *vice versa* (cycle B). Crossover between cycle A and cycle B would come only from a nickel hydride elimination–addition sequence involving the formation of a 2-methylvinylcyclopropane followed by generation of the diastereomer of the dimethylcyclopropylcarbinylnickel species in the original cycle, *i.e.*, **4b** ⇌ **4c** and **4a** ⇌ **4d**. (2) Based upon our observation that the catalyst does not skeletally rearrange 1,4-dienes possessing a trans internal double bond (*i.e.*, *trans*-1,4-hexadiene),[6] conversions of **4c** and **4d** to **5b** and of **4a** and **4b** to **6a** are considered to be essentially irreversible. (3) Examinations of molecular models of **4a**, **4b**, **4c**, and **4d** reveal that the conformations required in the transition states for the concerted interconversions of **4a** and **5a** and of **5b** or **6b** and **4d** should be very high in energy due to methyl–methyl and metal–methyl repulsions. Thus, these interconversions should have low rates relative to analogous transformations where these steric interactions are less severe, such as the

conversion of **4a** to **6a** and the conversions involving the *trans*-**4** diastereomers. (4) The –CH=CH₂ functional group has been demonstrated to participate in the hydrogen transfer reactions,[3,6] the most dramatic effect being the tremendous rate enhancement of hydrogen transfer caused by the presence of ethylene. Therefore, in the presence of ethylene, the rates of nickel hydride addition to **2a** and **2b** and the rates of nickel hydride β elimination from **4**, **5a**, **5b**, **6a**, and **6b** are believed to be high relative to the rates of all other processes in Scheme I. (5) Based upon our observations that none of the *conjugated* dienes derived from nickel hydride elimination from **5a**, **5b**, **6a**, and **6b** are isomerized by the catalyst,[3,6] hydrogen transfer (conjugated diene formation) from each of these intermediates is considered to be irreversible.

In light of the above considerations, the conversions in Scheme I which are joined by dashed arrows are considered to be reactions with relatively high $\Delta G^{\ddagger}$'s, whereas the solid arrow conversions should be lower in energy.

We propose the following interpretations of the results obtained in reactions of **2a** and **2b** with the catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)-nickel(II) and diisobutylaluminum chloride. (1) At −22° in the presence of ethylene, the products derived from treatment of **2a** and **2b** with the catalyst are determined by kinetic control. The primary ring-opening products, **5** and **6**, derived from the appropriate **4** stereoisomers, are trapped by rapid and irreversible nickel hydride elimination therefrom to generate the diene products observed. Thus, although **2a** reacts rapidly and reversibly to form both **4a** and **4d**, most of the diene product (*trans*-2-methyl-1,3-pentadiene in this case) is derived from the **4a** → **6a** conversion, the one relatively low energy skeletal change available to the system. In the case of **2b**, all ring opening reactions of **4b** and **4c** are available, affording the more balanced distribution of products. (2) At 25° in the absence of ethylene, the hydrogen transfer steps—formation of isomers **4** and nickel hydride elimination from **5** and **6**—become the rate-determining steps. Equilibration in both cycle A and cycle B can occur and the products are siphoned off in the irreversible formation of **6a** and **5b**, products with the trans internal double bond.

The relevance of these results to the *cis*-1,4-hexadiene rearrangement is clear. Addition of the elements of nickel hydride to *cis*-1,4-hexadiene at 25° in the absence of ethylene would afford **5a**.[17] Therefore, the diene products must come from cycle A. Cycle A can only generate *trans*-2-methyl-1,3-pentadiene, *trans,cis*-2,4-hexadiene, and *cis,cis*-2,4-hexadiene, the products actually observed. It seems reasonable to conclude that the major product-determining intermediate in the *cis*-1,4-hexadiene rearrangement is **4b** due to the higher $\Delta G^{\ddagger}$ predicted for **4a** formation. We have no way of estimating how much of the hydrocarbon pool that becomes **5a** eventually becomes 2,4-hexadiene *via* an

isomer of **4** and how much goes directly to 2,4-hexadienes *via* nickel hydride elimination without ever forming **4**. The results would indicate that at −22° in the presence of ethylene, very little **4** is generated and rapid hydrogen transfer from **5a** to form 2,4-hexadienes occurs, since *trans*-2-methyl-1,3-pentadiene was a very minor product under these conditions.

Experimental Section

All operations involving organometallic compounds were conducted under a nitrogen or argon atmosphere in deoxygenated solvents. Boiling points and melting points were uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Proton magnetic resonance (pmr) spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. The spectral data are reported in units of δ (ppm downfield from TMS). The infrared spectra were recorded on a Beckman IR-12 spectrometer.

Hydrocarbon yields were determined by glpc as described previously.[6] Relationships between the recorder signal areas and sample quantities were determined using standard mixtures of the dienes. A 20 ft × ³/₈ in. 20% β,β'-oxydipropionitrile on Firebrick 60/80 column operated at 60° with a helium flow rate of 170 ml/min effectively separated the C-6 isomeric products. The ratios of the recorder peak areas for a standard mixture containing equal molar amounts of the hydrocarbons were: *cis*-1,4-hexadiene, 1.00; *trans*-1,4-hexadiene, 0.96; *trans*-2-methylvinylcyclopropane, 1.01; *cis*-2-methylvinylcyclopropane, 1.01; *cis*-2-methyl-1.3-pentadiene, 0.99; *trans*-2-methyl-1,3-pentadiene, 1.01; *trans,trans*-2,4-hexadiene, 0.94; *trans,cis*-2,4-hexadiene, 1.00; *cis,cis*-2,4-hexadiene, 1.03.

The relative retention times in minutes of the dienes on the above column under the conditions listed were: *trans*-1,4-hexadiene, 8.8; *trans*-2-methylvinylcyclopropane, 9.2; *cis*-1,4-hexadiene, 9.4; *cis*-2-methylvinylcyclopropane, 11.4; *cis*-2-methyl-1,3-pentadiene, 12.0; *trans*-2-methyl-1,3-pentadiene, 13.2; *trans,trans*-2,4-hexadiene, 15.6; *trans,cis*-2,4-hexadiene, 17.9; *cis,cis*-2,4-hexadiene, 19.5. All of the glpc analyses were performed on a Varian Aerograph Model 90-P3 instrument.

Materials. Solvents were purified as described previously.[6] Diisobutylaluminum chloride, as a 25% wt/wt solution in toluene, was purchased from Texas Alkyls, Inc., Houston, Texas. *trans*-Dichlorobis(tri-*n*-butylphosphine)nickel(II) and ethylenebis(tri-*o*-tolyl phosphite)nickel(0) were prepared by procedures described previously.[6] *cis*-1,4-Hexadiene was prepared according to the procedure of Hata.[19] The ethylene and hydrogen chloride (C.P. Grade) were purchased from Matheson Gas Products, Joliet, Ill.

Synthesis of cis- and trans-2-Methylvinylcyclopropanes. a. *N*-Nitroso-*N*-ethylurea. A procedure similar to that used in the preparation of *N*-nitroso-*N*-methylurea by Arndt[20] was employed. An aqueous solution prepared from ethylamine hydrochloride, 360 g, 4.5 mol, and potassium cyanate, 454 g, 5.5 mol, in 1.8 l. of water was brought to a mild boil for 15 min. The hot solution was filtered and the filtrate was added to a solution of 300 g (4.1 mol) of sodium nitrite in 600 ml of water. The resulting solution was divided into three equal portions and each portion was carried through the remainder of the procedure separately.

Each solution was cooled to *ca.* 0° and then slowly added to a 4-l. beaker which contained a well-stirred mixture of ice, 600 g, and concentrated sulfuric acid, 100 g. The addition required *ca.* 1 hr. The foamy precipitate which formed was filtered, washed with cold water, and partially dried on the filter. The slightly moist urea, 402 g, was kept under refrigeration prior to use.

b. Diazoethane. The general procedure of Arndt[21] was employed. A suspension of *N*-nitroso-*N*-ethylurea, 100 g (*ca.* 1.0 mol), in 500 ml of ether was slowly added to a vigorously stirred aqueous solution of potassium hydroxide (200 ml of a 50% solution) at 50°. The suspension was added at such a rate that the diazoethane bubbled into three collection tubes cooled to 0° at a moderate rate. An all glass standard taper arrangement was used successfully. All of the standard taper joints were liberally greased to eliminate any rough surfaces since diazoalkanes have been known to detonate on such rough surfaces.[21] An aliquot of the orange-red

(17) 1,2-Addition of a nickel hydride to the terminal double bond of *cis*-1,4-hexadiene would afford an alkenylnickel species possessing a terminal C–Ni σ bond. Although, in the case of **1**, this mode of addition does not lead to isomerization products, some 1,4-dienes do isomerize *via* an intermediate of this type affording what we have labeled as the type II skeletal change.[6,18]
(18) (a) R. G. Miller, H. J. Golden, D. J. Baker, and R. D. Stauffer, *J. Amer. Chem. Soc.*, **93**, 6308 (1971). (b) H. J. Golden, D. J. Baker, and R. G. Miller, *ibid.*, **96**, 4229 (1974).

(19) G. Hata, *J. Amer. Chem. Soc.*, **86**, 3903 (1964).
(20) F. Arndt, *Org. Syn.*, **18**, 48 (1938).
(21) F. Arndt, *Org. Syn.*, **15**, 3 (1935).

ether solution of the diazoethane was reacted with benzoic acid to determine the diazoethane concentration. The excess benzoic acid was titrated with standardized sodium hydroxide solution to a phenolphthalein end point. The yield of diazoethane from 400 g of the urea was 1.06 mol, 26%.

c. *cis-* and *trans-3-vinyl-5-methylpyrazolines.* The procedure employed was similar to that reported by Crawford and Cameron[8] for the preparation of 3-vinylpyrazoline. A solution of 1.06 mol of diazoethane in 700 ml of ether was treated with 320 g (6.0 mol) of 1,3-butadiene. The reaction flask, kept in the dark at room temperature, was connected to a Dry Ice–acetone cooled dewar condenser. The orange-red color of the diazoethane disappeared during a 4-hr period. The ether and excess 1,3-butadiene were then removed by distillation through a packed column. Distillation of the residue under reduced pressure afforded a 1:1 mixture of the *cis-* and *trans-3-vinyl-5-methylpyrazolines*, 82 g (74% yield), bp 62–64° (15–20 mm); infrared spectrum (neat) included peaks at 1640 cm^{-1} (vinylic C=C stretching frequency), 1550 cm^{-1} (–N=N– stretch), and 910 and 1000 cm^{-1} (vinyl C–H out of plane deformation vibration); pmr (CCl$_4$) 6.40–5.40 (m, 1 H, C-2 vinylic proton), 5.3 and 5.12 (2 m, 2 H, C-1 vinylic protons), 4.95–4.0 (m, 2 H, CH ring protons), 2.35–1.65 and 1.1–0.5 (m, 2 H, CH$_2$ ring protons) and 1.45 and 1.3 (d, 3 H, $J = 7.7$ Hz, methyl protons).

d. *cis-* and *trans-2-Methylvinylcyclopropanes*, **2a** and **2b**. Pyrolysis of the 3-vinyl-5-methylpyrazoline mixture, 82 g (0.75 mol), at atmospheric pressure employing an oil bath at 100–110° for *ca.* 5 hr followed by a gradual increase of the bath temperature to 160° afforded 50 g of a yellow liquid. Distillation of this liquid afforded a 1:1 mixture of the *cis-* and *trans-2-methylvinyl-cyclopropanes*, bp 34–36°. The isomers were separated and collected *via* preparative glpc from a 15 ft β,β'-oxydipropionitrile on Firebrick column operated at 60° with a helium flow rate of 100 ml/min.

Anal. Calcd for C$_6$H$_{10}$: C, 87.73; H, 12.27. Found: **2a**, C, 87.53; H, 12.27. **2b**, C, 87.47; H, 12.38. Structural assignments were confirmed by comparison of the pmr and infrared spectra with those reported by Roth and König[7c] who synthesized **2a** and **2b** by a different route.

Rearrangements of the 2-Methylvinylcyclopropanes, 2a and 2b. The following descriptions are typical of the procedures employed in the many experiments which were conducted.

a. **Utilization of the (R$_3$P)$_2$NiCl$_2$/i-Bu$_2$AlCl catalyst.** A solution of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.130 g (0.24 mmol), and either **2a** or **2b**, 0.35 g (4.25 mmol), in 35 ml of toluene was treated with a 25% toluene solution of diisobutylaluminum chloride, 0.77 ml (0.93 mmol). The amber colored solution was stirred at 25° under a nitrogen atmosphere and small aliquots were removed periodically. They were quenched with 2-propanol, and then they were analyzed by glpc. The reaction was terminated after 2 hr by the addition of 2 ml of 2-propanol to the reaction mixture. Under these conditions, the reactions had proceeded to 58 and 68% conversions of **2a** and **2b**, respectively, to products. The product mixture was then washed with water, and then dried over calcium chloride after which the mixture was fractionally distilled to afford a diene-rich toluene solution. The products were then collected *via* preparative glpc. The diene products were identified by comparison of their pmr spectra and glpc retention times with those of authentic samples.

b. **Utilization of the (R$_3$P)$_2$NiCl$_2$/i-Bu$_2$AlCl Catalyst in the Presence of Ethylene.** A solution of *trans*-dichlorobis(tri-*n*-butyl-phosphine)nickel(II), 0.011 g (0.02 mmol), and **1**, **2a**, **2b**, or *trans*-1,4-hexadiene, 0.35 g (4.25 mmol), olefin:Ni = 211:1, at −22° (Dry Ice–CCl$_4$ bath) in 35 ml of toluene was treated with a 25% solution of diisobutylaluminum chloride in toluene (0.2 ml, 0.24 mmol). The resulting amber solution was stirred at −22° under a

nitrogen atmosphere for 3 hr. Glpc analysis of aliquots removed after 3 hr indicated that, in each case, <2% of the olefin reactant had disappeared. Ethylene was then rapidly bubbled into the solution, at −22°, and small aliquots were removed periodically for glpc analysis. The reaction was terminated after 30 min of ethylene treatment by addition of 2 ml of 2-propanol. The hydrocarbon products were isolated and characterized as described previously.

Other experiments in which **2a** and **2b** were treated with the catalyst in the presence of ethylene at −22°, without any time lag between catalyst addition and ethylene addition, resulted in the same very rapid conversion of the **2a** or **2b** to the same products in near quantitative yield.

In experiments conducted in the presence of ethylene at 25°, the same general procedure as that described above was employed with the exception that the diisobutylaluminum chloride was added to an ethylene-saturated toluene solution containing the olefin under investigation and the *trans*-dichlorobis(tri-*n*-butylphosphine)nickel-(II).

In all of these experiments, the diene isomerization product formation was accompanied by the formation of butenes derived from dimerization of ethylene.

c. **Utilization of the (R$_3$P)$_2$NiC$_2$H$_4$/HCl Catalyst.** Ethylenebis-(tri-*o*-tolyl phosphite)nickel(0),[6] 0.105 g (0.13 mmol), and **2a**, 0.13 g (1.60 mmol), dissolved in 14.5 ml of toluene, were treated with 0.4 ml of toluene which was saturated with hydrogen chloride (0.10 mmol) at 25°. Aliquots were withdrawn from the resulting orange-amber solution at frequent intervals; they were quenched by exposure to air, and then analyzed by glpc. The reaction was terminated after 3.5 hr and the isomeric products along with recovered **2a** were collected *via* preparative glpc and were identified by comparison of their pmr spectra and glpc retention times with those of authentic samples. A component with a glpc retention time identical with that of *cis,cis*-2,4-hexadiene was present in only trace amounts and was tentatively identified by glpc retention time alone. All of the major products, along with yield and conversion data, are described in Results.

Treating 14.5 ml of a toluene solution of ethylenebis(tri-*o*-tolyl phosphite)nickel(0),[6] 0.134 g (0.17 mmol), and **2b**, 0.17 g (2.10 mmol), at 25° with 0.5 ml of toluene, saturated with hydrogen chloride (0.13 mmol), resulted in the rapid conversion of **2b** to C-6 isomers. The reaction was quenched and the products were isolated and identified as described in the experiment with **2a**. Product description, yield, and conversion data are given in Results.

d. **Treatment of 2a and 2b with HCl.** A toluene solution (14.5 ml) of **2a**, 0.17 g (2.10 mmol), at 25° was treated with 0.5 ml of toluene saturated with hydrogen chloride (0.126 mmol). Similarly, a toluene solution (7.5 ml) of **2b**, 0.086 g (1.05 mmol), at 25° was treated with 0.25 ml of toluene saturated with hydrogen chloride (0.06 mmol). Aliquots analyzed by glpc during a 5.5-hr period indicated that neither **2a** or **2b** was being converted to isomeric products and there was essentially no decrease in the amount of either of the starting materials.

e. **Treatment of 2a and 2b with Ethylenebis(tri-*o*-tolyl phosphite)-nickel(0).** Fifteen milliliters of a toluene solution of ethylenebis-(tri-*o*-tolyl phosphite)nickel(0),[6] 0.192 g (0.24 mmol), and **2b**, 0.15 g (1.8 mmol), was stirred at 25° for 5 min. Only a very small amount of **2b** had disappeared and no isomeric products were detected. The temperature then was raised to 58°. Only trace amounts of two unknown products were detected by glpc during a 2-hr period. An analogous experiment with **2a** afforded no C-6 isomerization products