

A Mechanistic Study of the Nickel-Promoted 1,4-Pentadiene to Isoprene Rearrangement. Isomerization of Deuterio-*cis*-1,4-hexadienes^{1,2}

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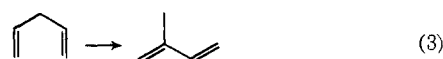
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Abstract: A series of deuterio-*cis*-1,4-hexadienes has been synthesized and each compound was isomerized by a catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride. *cis*-1,4-Hexadiene-3-*d*₂, -4(5)-*d*, and -6-*d*₃ were transformed into *trans*-2-methyl-1,3-pentadiene-1-*d*₂, -3(4)-*d*, and -5-*d*₃, respectively. The determinations of the deuterium compositions and locations in these products and in the 2,4-hexadiene by-products have provided information concerning the nature of the skeletal change and the accompanying hydrogen transfer. No deuterium isotope effect on the *trans*-2-methyl-1,3-pentadiene/2,4-hexadiene product ratio was observed when *cis*-1,4-hexadiene and its -3-*d*₂ counterpart were treated with the catalyst. The results are interpreted in terms of a mechanism for the skeletal rearrangement involving the participation of alkenylnickel and dimethylcyclopropylcarbinylnickel intermediates.

During the past 5 years, attention has been focused by a number of workers on the catalysis by transition metals of hydrocarbon transformations involving the cleavage and formation of C-C σ bonds.³ Some of these reactions attracted immediate interest because, aside from their novelty in the realm of hydrocarbon chemistry, they offered the opportunity of extending the concept of orbital symmetry conservation⁴ into the field of transition metal catalysis.⁶ The transformations of presumably greatest potential in this respect were related to the metal-promoted 2 + 2 cycloreversion and cycloaddition reactions, eq 1, and disrotatory cyclobutene to 1,3-butadiene conversions, eq 2, all symmetry restricted processes as concerted thermal reactions in the absence of a transition metal.⁵ With two notable exceptions,^{1a,7} each of the early examples^{6c,8} of transition metal catalysis of C-C σ bond cleavage—including the olefin metathesis reaction⁶—fell, conceptually, into one of these two classes. Although sharing the most novel and significant feature associated with all of these catalytic reactions—namely C-C σ bond fission—the nickel-promoted diene rearrangements⁷ and vinylcyclopropane isomerizations^{1a} have received less attention by workers in the field, apparently because the hydrocarbon reactants and products were not formally related by a symmetry restricted process. The pos-

sibility that nickel-promoted diene rearrangements such as that in eq 3 might possess mechanistic features in common with certain metal-induced isomerizations of strained small ring hydrocarbons has, apparently, rarely been considered. Our preliminary ideas regarding the mechanisms of the diene rearrangements, which invoked the intervention of organometallic intermediates possessing carbon-metal σ bonds, were published in 1967 and 1968.^{1a,7} Subsequent reports have indicated that a number of known metal-induced hydrocarbon transformations related to eq 1 and 2 proceed *via* organometallic intermediates.¹⁰ In addition, much information has been accumulated which indicates that the metal-catalyzed isomerizations of bicyclobutane, bicyclopentane, and various cubane derivatives occur by multistep processes involving the generation of organometallic complexes.¹¹

In this paper we wish to present evidence that nickel-induced transformations such as that in eq 3 are indeed mechanistically related, in certain respects, to some strained small ring hydrocarbon rearrangements and that they also bear a close mechanistic resemblance to transition metal-catalyzed olefin oligomerization reactions.



(1) Some 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, and D. J. Baker, *ibid.*, **92**, 4490 (1970).

(2) Taken from the Ph.D. Thesis of P. A. Pinke, University of North Dakota, 1970.

(3) References to the pertinent literature can be found in ref 4.

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

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(6) (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967); (c) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); (d) F. D. Mango, *Advan. Catal.*, **20**, 291 (1969); (e) F. D. Mango, *Tetrahedron Lett.*, 4813 (1969); (f) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **93**, 1123 (1971), and references cited therein.

(7) R. G. Miller, *J. Amer. Chem. Soc.*, **89**, 2785 (1967).

(8) (a) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); (b) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).

(9) N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972).

(10) (a) T. J. Katz and S. A. Cereface, *J. Amer. Chem. Soc.*, **91**, 2405 (1969); (b) *ibid.*, **91**, 6519 (1969); (c) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970); (d) J. Wristers, L. Brenner, and R. Pettit, *ibid.*, **92**, 7499 (1970); (e) T. J. Katz and S. A. Cereface, *ibid.*, **93**, 1049 (1971); (f) R. H. Grubbs and T. K. Brunck, *ibid.*, **94**, 2540 (1972); (g) L. G. Cannell, *ibid.*, **94**, 6867 (1972); (h) R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *ibid.*, **95**, 1674 (1973); (i) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *ibid.*, **95**, 597 (1973).

(11) See the following for leading references: (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); (d) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

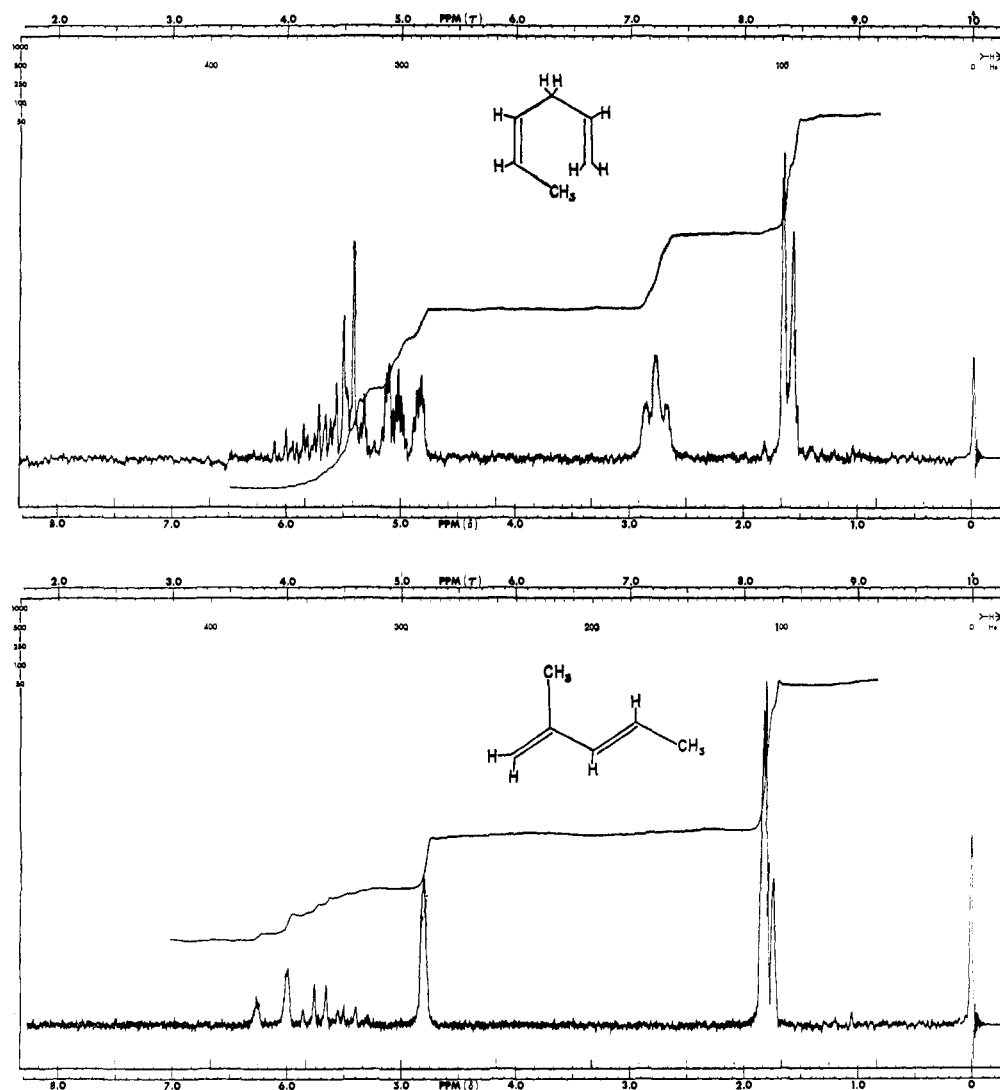


Figure 1. PMR spectra of 1 and 2 in CCl_4 solution, recorded at ambient temperature.

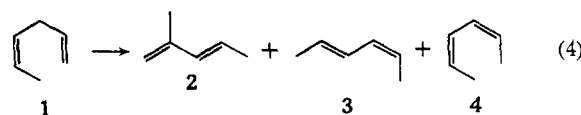
Results

Since there was no precedent for the transition metal catalysis of a transformation such as that in eq 3, the answers to some very elementary questions were sought. Of highest priority was the determination of the fate of each carbon atom in the reacting diene system. Associated with this problem was the question of whether the carbon skeletal change was an intramolecular or intermolecular process. Information concerning the hydrogen transfer associated with the skeletal change was also wanted. Only after the answers to these questions became available could the role of the transition metal be defined and could the number of mechanistic possibilities be limited.

Synthesis and Rearrangement of Deuterio-1,4-dienes.

In order to determine the fate of each carbon in the 1,4-diene reactant as it was transformed into the type 1⁴ rearrangement product by the catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride, a series of deuterio-1,4-dienes was synthesized and then treated with the catalyst. The isotopic composition and the location of the deuterium in each isomerization product were determined. The isomerization of *cis*-1,4-hexadiene (1) to *trans*-2-methyl-1,3-pentadiene (2) and *trans,cis*- (3) and *cis,cis*-

2,4-hexadiene (4) (eq 4) was examined in the most detail



because of the relatively high yields of skeletal rearrangement product afforded in this case.⁴

The relationship of the *cis*-1,4-hexadiene rearrangement to that of 1,4-pentadiene, eq 3, was defined by treatment of *cis*-1,4-hexadiene-6- d_3 , synthesized by the method of Roth and König,¹² with the catalyst in toluene solution at 25°. In an experiment in which a diene:Al:Ni molar ratio of 77:4.5:1.0 was employed, 72% of 1-6- d_3 (98.5 ± 2 atom % D at C-6 by pmr integration) was converted to products affording a C-6 isomer yield of 63%; 57% of the C-6 product mixture consisted of *trans*-2-methyl-1,3-pentadiene-5- d_3 (98 ± 2 atom % D at C-5 by pmr integration), 25% was *cis,cis*-2,4-hexadiene-1- d_3 , and 18% was *cis,cis*-2,4-hexadiene-1- d_3 (eq 5). PMR spectra of 1, 2, 1-6- d_3 , and 2-5- d_3 are given in Figures 1 and 2. The position of the deuterium in the deuterio-2 could be unambiguously

(12) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).

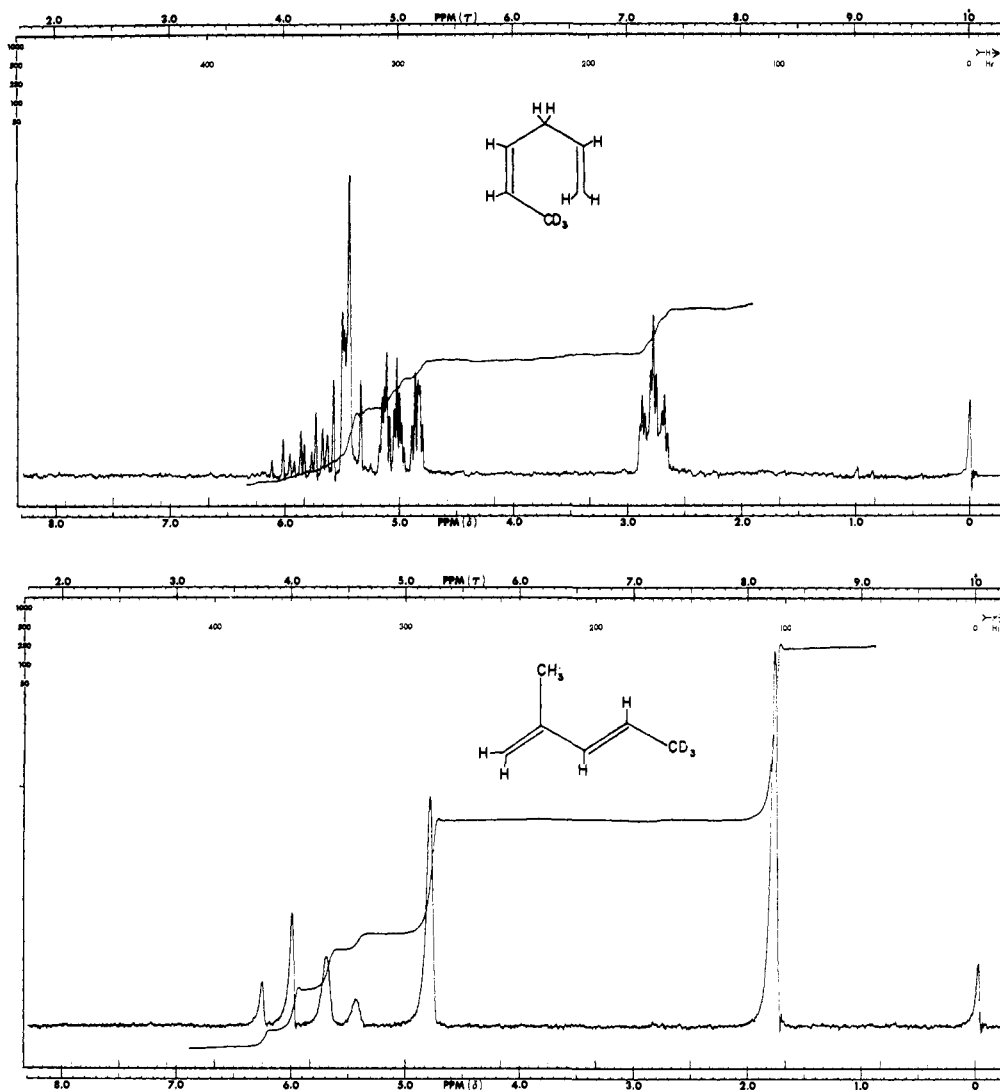
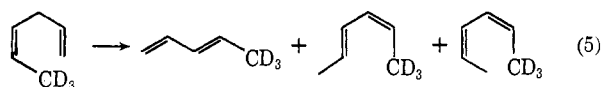


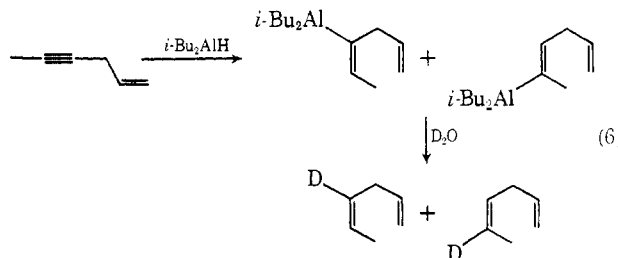
Figure 2. Pmr spectra of 1-6- d_3 before treatment with the catalyst and of the deuterio-2 rearrangement product, recorded at ambient temperature in CCl_4 solution.



determined. The doublet proton resonance present at δ 1.8 (CCl_4) (C-5 CH_3) in the spectrum of **2** which overlaps with the 2-methyl proton resonance at 60 MHz was absent, and the complex C-4 olefinic proton resonance in **2** had become the high field half of an AB quartet. Broadening of the C-4 proton resonance as compared to the C-3 proton resonance due to weak D-H coupling was further evidence that the C-5 position contained the deuterium label. The pmr spectrum of recovered starting material indicated that no detectable H-D exchange or deuterium scrambling had occurred. Integration of the pmr spectrum of the deuterio-2,4-hexadiene products (CH_3 :vinyl proton ratio = 3.0:4.0) indicated that the deuterium resided on a methyl carbon. The CH_3 - $\text{CH}=\text{C}$ coupling constant, $J = 6.0$ Hz, of the deuterio-*cis,trans*-2,4-hexadiene product may be compared to values of 5.9 and 6.5 Hz for the analogous coupling in *trans,trans*- and in *cis,cis*-2,4-hexadiene, respectively. These comparisons implied that the CH_3 group was attached to the double bond with the *trans* or *E* configuration, and the CD_3

group was attached to the double bond with the *cis* or *Z* configuration in the deuterio-*cis,trans*-2,4-hexadiene product.

In an effort to determine the extent of hydrogen transfer taking place at the internal double bond of **1**, the C-4 and C-5 carbon atoms were labeled with deuterium. *Cis* addition of diisobutylaluminum hydride to the triple bond of 1-hexen-4-yne according to the general procedure of Eisch and Kaska,¹³ followed by treatment with D_2O , afforded a mixture of 1-4- d and 1-5- d , eq 6. The



pmr spectrum of the deuterio-**1** mixture exhibited a C-6 methyl proton resonance at δ 1.5 (CCl_4) which consisted

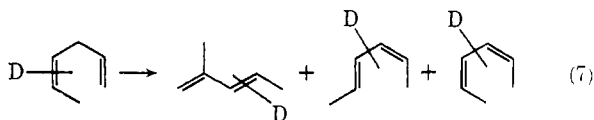
(13) J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, 85, 2765 (1963).

of a singlet in the center of a doublet, and a poorly resolved multiplet for the C-3 methylene proton resonance at δ 2.7.

Integration of the peak areas gave a CH_3 :C-1 vinyl:C-2, -4, and -5 vinyl proton ratio = 3.0:2.0:2.05 which, in combination with the synthetic scheme, eq 6, demonstrated that the deuterium label in each molecule resided on the C-4 or C-5 carbon atom. A 100-MHz spectrum of the mixture did not separate the C-4 and C-5 proton resonances well enough to allow determination of the relative amount of deuterium at each position.

Treatment of 1-4-*d*(5-*d*) with the nickel catalyst in toluene at 25° (diene:Al:Ni molar ratio = 12:4.5:1) afforded a 65% conversion of starting material to products during 3 min, with a C-6 isomer yield of 71%. The isomer product mixture consisted of deuterio-2, 74%, deuterio-3, 20%, and -4, 6%, the deuterio-2:deuterio-3 + -4 ratio being 2.7:1. The location of the deuterium in the deuterio-2 product was established to be at C-3 and C-4 by the decrease in the intensity and resolution of the C-3 (δ 6.1) and C-4 (δ 5.6) proton resonances relative to those in 2. Integration of the peak intensities indicated a CH_3 :C-1 vinyl:C-3 + C-4 vinyl proton ratio of 6.00:2.00:1.09. Pmr integration also indicated that an almost even distribution of deuterium at C-3 and C-4 resulted, the ratio of the peak intensities being C-3:C-4 = 1.1:1.0. Examination of the pmr spectrum of the recovered starting material indicated that no detectable amount of deuterium scrambling or H-D exchange had occurred. Mass spectral analysis of the 1-4-*d*(5-*d*) before (1.4% d_0 , 98.6% d_1) and after its treatment with the catalyst (1.8% d_0 , 97.2% d_1 , 1.0% d_2) demonstrated that very little intermolecular H-D exchange occurred during the reaction period.

Integration of the pmr spectrum of the mixture of deuterio-*trans*, *cis*- and -*cis*, *cis*-2,4-hexadienes isolated from the product mixture gave a CH_3 :vinyl proton ratio = 6.00:3.06, indicating that $94 \pm 2\%$ of the sample had a deuterium atom at a vinyl position. However, the specific location(s) of the vinyl deuterium could not be determined from the pmr spectrum.



The synthesis of *cis*-1,4-hexadiene-3- d_2 was accomplished in the following manner. An ether solution of ethyl *cis*-2-butenate was treated with aluminum tri-deuteride according to the general procedure of Jorgenson¹⁴ to afford *cis*-2-buten-1-ol- d_2 . Treatment of the butenol- d_2 with thionyl chloride in the presence of tri-*n*-butylamine¹⁵ in ether gave 1-chloro-*cis*-2-butene-1- d_2 which was then coupled with vinylmagnesium chloride¹⁶ in tetrahydrofuran. This procedure afforded a mixture of *cis*-1,4-hexadiene-3- d_2 (27%), 3-methyl-1,4-pentadiene-1- d_2 (13%), and a small amount of *trans*-1,4-hexadiene-3- d_2 . The pure compounds were separated and collected *via* preparative glpc.

The location of the deuterium in each of the 1,4-diene- d_2 products was verified by comparison of their pmr

(14) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

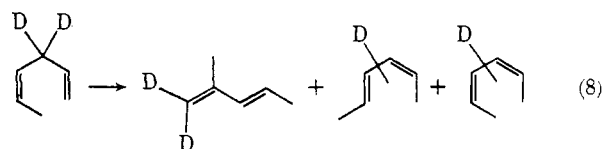
(15) W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, 82, 1376 (1960).

(16) H. Normant, *C. R. Acad. Sci.*, 239, 1811 (1954).

spectra with those of the nonlabeled compounds. The spectrum of 1-3- d_2 showed the absence of the resonance at δ 2.8 (CCl_4) due to the C-3 proton resonance in 1, and also exhibited a simplification of the C-2 and C-4 proton resonances centered at δ 5.5 (Figure 3). The CH_3 :vinyl proton ratio was 3.0:5.0 by integration. Mass spectral analysis demonstrated a deuterium content of 0.3% d_0 , 2.0% d_1 , and 97.7% d_2 .

A toluene solution of 1-3- d_2 was then treated with the catalyst for *ca.* 2 min at 25° (diene:Al:Ni ratio = 12:4:1) affording a 55% conversion to products with a C-6 isomer yield of 77%. The isomeric product mixture consisted of *trans*-2-methyl-1,3-pentadiene-1- d_2 (74%), *trans*, *cis*-2,4-hexadiene-*d* (18%), *cis*, *cis*-2,4-hexadiene-*d* (5.7%), and a component with a glpc retention time of *trans*, *trans*-2,4-hexadiene (2.3%). The ratio of 2-1- d_2 -deuterio-2,4-hexadienes was 2.7:1.0. The pmr spectrum of the skeletal rearrangement product (Figure 3) demonstrated that the deuterium label was at C-1 as evidenced by the absence of the C-1 proton resonance, present at δ 4.8 (CCl_4) in the nonlabeled analog. Integration of peak intensities in the spectrum (methyl:vinyl proton ratio = 6.0:2.0) gave a ratio of 1.0:260 for residual proton at C-1 to total proton present at other positions. This result not only demonstrated that very little hydrogen remained at C-1, but indicated that the amount of deuterium at other positions was negligible. Mass spectral analysis of the deuterio-2 product demonstrated a deuterium content of 0.1% d_0 , 1.6% d_1 , 93.1% d_2 , and 5.3% d_3 . The pmr spectrum of the recovered starting material was essentially identical with that of the original 1-3- d_2 employed, indicating that little if any H-D exchange at the C-3 position had occurred. However, the mass spectrum of the recovered starting material indicated a deuterium content of 1.1% d_0 , 2.7% d_1 , 86.6% d_2 , 9.2% d_3 , and 0.4% d_4 , which demonstrated that about 10% of the molecules contained an excess of deuterium. Pmr integration of the peak intensities in the spectrum of a mixture of the deuterio-2,4-hexadiene products gave a methyl:vinyl proton ratio = 6.00:2.94, indicating that the deuterium label was on a vinylic carbon. The specific location could not be determined, however.

A comparable experiment employing nonlabeled 1 afforded a 54% conversion to products during 2 min with a C-6 isomer yield of 65%. The C-6 product



mixture consisted of 2 (71%), 3 (21.4%), and 4 (7.6%). The 2:3 + 4 product ratio was 2.7:1.0 at 54% conversion. Comparison of the *trans*-2-methyl-1,3-pentadiene-2,4-hexadiene product ratios in reactions of 1 and 1-3- d_2 indicated that no deuterium isotope effect on this ratio was evident.

Integration of peak intensities in the pmr spectra of recovered starting material and of the deuterio-2 afforded when 1-3- d_2 was treated with the catalyst for 1 hr (90% conversion) at 25° in toluene solution (diene:Al:Ni = 8-9:4:1) suggested that the amount of excess deuterium present had increased significantly over that found at 55% conversion in other experiments. A C-6

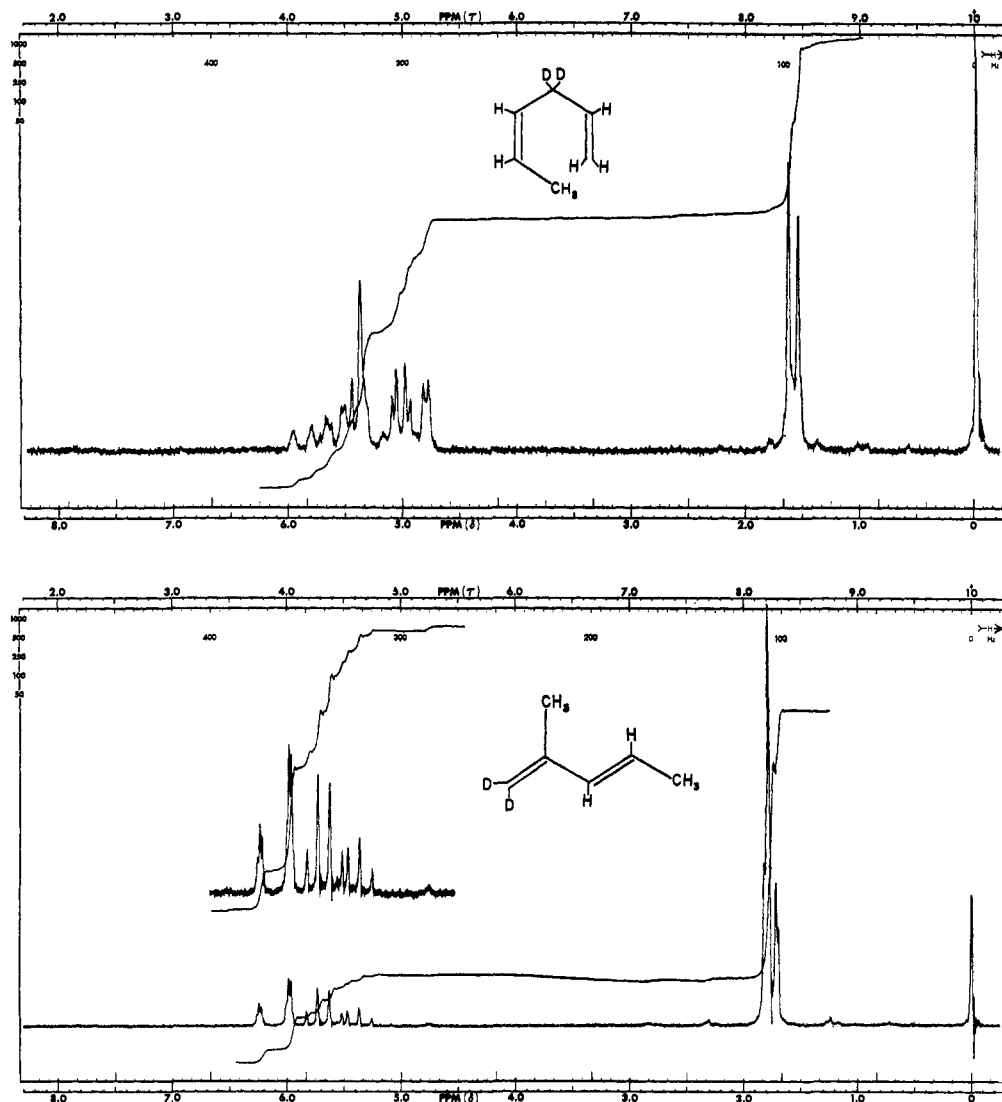


Figure 3. PMR spectra of 1-3- d_2 before treatment with the catalyst and of the deuterio-2 rearrangement product, recorded at ambient temperature in CCl_4 solution.

isomer yield of 60% with a deuterio-2:deuterio-3 + -4 = 3.3:1.0. Integration of the peak areas in the pmr spectrum of the deuterio-2 product showed a slightly more intense C-1 proton resonance (residual proton at C-1:total proton at other positions = 2.7:260). No detectable amount of H-D exchange at C-3 in recovered starting material had occurred. However, integration of the pmr spectrum indicated that a significant amount of deuterium was present on vinylic carbons (methyl:vinyl proton ratio = 3.00:4.68).

In an effort to obtain a more accurate measurement of the effect of deuterium at the C-3 position in **1** on the methylpentadiene-2,4-hexadiene product ratio, a mixture of **1** and 1-3- d_2 was treated with the catalyst and the products were analyzed by mass spectrometry. Table I lists the deuterium compositions of the reactant mixture employed and of the products obtained in the experiment.

Discussion

Functions Required of the Catalyst. Our results rigorously define the nature of the skeletal change and of the hydrogen transfer processes associated with the type I rearrangement. They also establish the nature

Table I. Deuterium Per Cent Compositions of Reactants and of Isomerization Products from Treatment of **1** and 1-3- d_2 with the $(n\text{-Bu}_3\text{P})_2\text{NiCl}_2\text{-}i\text{-Bu}_2\text{AlCl}$ Catalyst^{a,b}

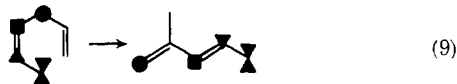
	<i>cis</i> -1,4-HD (reactant)	<i>cis</i> -1,4-HD (recovered)	<i>trans</i> -2-Me- 1,3-PD	2,4-HD's
d_0	56.0	53.5	52.9	59.2
d_1	1.1	4.1	5.2	38.7
d_2	42.9	40.3	40.9	2.1
d_3		2.1	1.0	<0.1

^a The experiment was conducted at 25° in toluene (diene:Al:Ni ratio = 12:4:1) and carried to a 55% conversion during *ca.* 2 min. The C-6 isomer yield was 75% and the isomeric product mixture consisted of *trans*-2-Me-1,3-PD, 73%, *trans,cis*-2,4-HD, 20.6%, and *cis,cis*-2,4-HD, 6.4%, Me-1,3-PD:2,4-HD ratio = 2.7. ^b PD, pentadiene; HD, hexadiene; Me, methyl.

of the hydrogen transfer which accompanies the formation of the double bond migration products. The findings thus define the functions required of the catalyst and, in conjunction with the established chemistry of the catalyst precursors,⁴ allow some conclusions regarding its probable structure to be drawn.

The origins of four of the six carbon atoms in the *trans*-2-methyl-1,3-pentadiene product are unambig-

ously identified on examination of the positions of the deuterium labels in the deuterio-2 derived from the various deuterio-1 reactants, eq 5, 7, 8, and of the positions of the methyl labels^{1b,4} in type I products derived from 2-methyl-1,4-pentadiene (2,3-dimethyl-1,3-butadiene) and 3,3-dimethyl-1,4-pentadiene (2,3-dimethyl-1,4-pentadiene). Thus, C-5 in 2 originates from C-6 in 1, C-4 in 2 from C-5 in 1, C-3 in 2 from C-4 in 1, and C-1 in 2 from C-3 in 1, eq 9. Carbon 2 and its



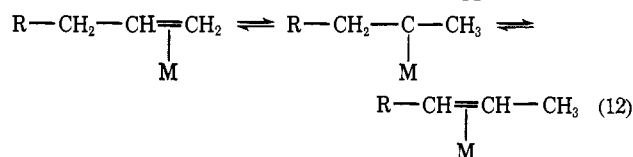
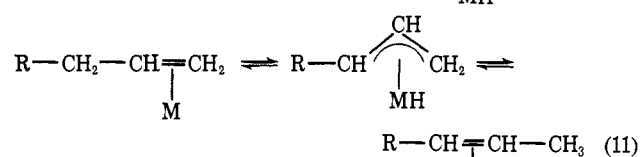
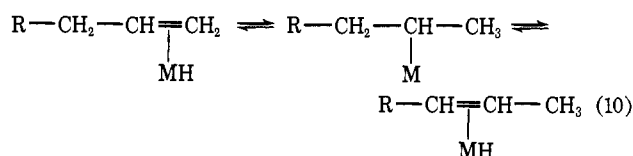
methyl substituent in 2 thus derive from C-1 and C-2 in 1. The results require a reaction path which involves the cleavage of the σ bond between C-3 and C-4 in 1, and the formation of a σ bond between what were originally C-2 and C-4 in 1. The findings indicate that hydrogen exchange does not occur to any significant extent at carbons 3, 4, 5, or 6 in 1 nor in their counterparts, carbons 1, 3, 4, or 5 in 2. Therefore, the hydrogen transfer process associated with the skeletal rearrangement must only involve carbons originating at positions 1 and 2 in 1. The simplest interpretation would involve transfer of hydrogen to the carbon originating at C-1 in 1 and from the carbon originating at C-2. This would dictate that C-1 in 1 would transform into the methyl carbon attached to C-2 in 2, and C-2 in 1 would transform into C-2 in 2.

Examination of the deuterium composition and the location of residual deuterium in the 2,4-hexadienes derived from isomerization of the deuterio-*cis*-1,4-hexadienes, eq 5, 7, and 8, reveals the nature of the hydrogen transfer process in 2,4-hexadiene formation, and these results are pertinent to the hydrogen transfer accompanying the skeletal rearrangement. The previously proposed mechanisms for transition metal induced double bond migrations in alkenes fall into three main classes exemplified by the following specific cases: (1) an intermolecular hydrogen transfer process involving a metal hydride addition-elimination sequence,¹⁷ eq 10, (2) intramolecular 1,3-hydrogen transfer via a π -allylmetal hydride complex,^{17,18} eq 11, and (3) intramolecular 1,2-hydrogen transfer via a carbene-metal complex,¹⁹ eq 12. Our results clearly eliminate "intramolecular" processes, such as those in eq 11 and 12, from consideration as mechanisms for the 2,4-hexadiene formation. The data in Table I demonstrate that one atom of deuterium per molecule was lost on conversion of 1-3-*d*₂ to deuterio-3 and -4. The pmr data indicate that the remaining deuterium in the 3-*d*₁ and 4-*d*₁ products resided on a vinylic carbon. The observations that 1 was isomerized by the catalyst to *trans,cis*- and *cis,cis*-2,4-hexadienes whereas *trans*-1,4-

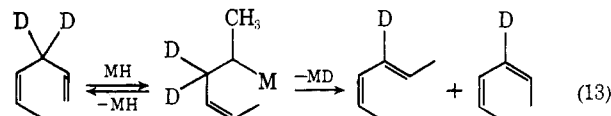
(17) (a) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4023 (1961); (b) J. F. Harrod and A. J. Chalk, *ibid.*, **86**, 1776 (1964); (c) G. C. Bond and M. Hellier, *Chem. Ind. (London)*, 35 (1965); (d) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966); (e) R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966); (f) J. F. Harrod and A. J. Chalk, *ibid.*, **88**, 3491 (1966); (g) H. Itatani and J. C. Bailar, Jr., *ibid.*, **89**, 1600 (1967).

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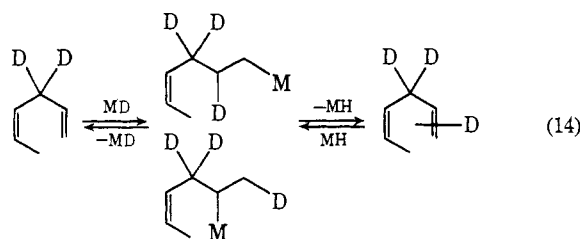
(19) (a) N. R. Davis, *Nature (London)*, 201, 490 (1964); (b) N. R. Davis, *ibid.*, 205, 281 (1965).



hexadiene afforded only *trans,cis*- and *trans,trans*-2,4-hexadienes^{4,7} demonstrate that the geometry of the internal double bond in the 1,4-hexadiene reactants was not altered during the isomerization to 2,4-dienes. All of these results can be accommodated by a metal hydride addition-elimination mechanism, eq 13, where M



represents the nickel atom and its auxiliary ligands. According to this scheme, metal hydride is transferred only to the terminal double bond in 1. The entry into the catalyst hydrogen pool of deuterium eliminated as metal deuteride, eq 13, provides the source of the excess deuterium found in recovered 1, 2, and in 3 and 4. Calculations based on the values in Table I and on the per cent conversion and per cent yield data in footnote a indicate that the deuterium lost on formation of the 2,4-hexadienes-*d*₁ was quantitatively reincorporated into the isomeric products and recovered starting material. The results indicate that this occurs via the addition of MD to the terminal double bond in 1-3-*d*₂, eq 14. Subsequent isomerization of 1-*d*₃, generated in this



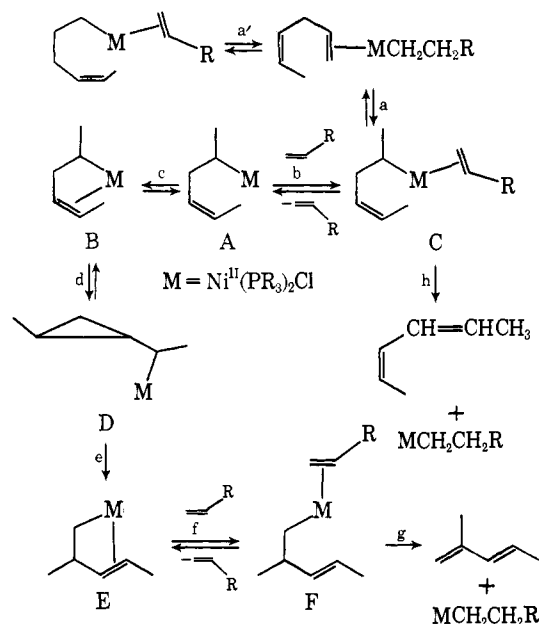
manner, accounts for the excess deuterium found in 2, 3, and 4.

A conclusive demonstration that the hydrogen transfer associated with the rearrangement of 1 to 2 does not involve hydrogen on C-3 in 1 is provided by the data in Table I. The results indicate that 1-3-*d*₂ and 1-3-*d*₀ were converted to 2-*d*₂ and 2-*d*₀, respectively. The findings eliminate from consideration any mechanism which would involve the formation and subsequent rearrangement of 2,4-hexadienes to 2, in agreement with our observations that conjugated dienes were not skeletally rearranged by the catalyst.⁴ The second step in eq 13 must be essentially irreversible since no deu-

terium loss was observed in recovered deuterio-1 or in deuterio-2 derived from 1-3- d_2 . Subsequent reaction of metal hydride with 3- d_1 or 4- d_1 should have generated substantial amounts of 1- d_1 and 2- d_1 . The amounts of these products which were observed can be accommodated by reaction of 1- d_0 with metal deuteride as in eq 14. The absence of appreciable H-D exchange at the internal double bond on treatment of 1-4(5)- d with the catalyst indicates that metal hydride addition to the internal double bond is either nonexistent, or is very slow relative to its rate of addition to and elimination from the terminal double bond.

Mechanism of the Skeletal Rearrangement. Our mechanistic interpretation of results bearing on the skeletal rearrangement is outlined in Scheme I. Central

Scheme I



to this scheme is the formation of a d^8 coordinatively unsaturated²⁰ alkenylnickel(II) species, **A**, derived from additive transfer of the elements of nickel hydride to the terminal double bond in **1**. The hydrogen transfer process requires a coordinated alkene as the ultimate hydride acceptor in accord with reactions in steps a, a', h, and g. Intermediate **A** is transformed by competitive intramolecular and intermolecular alkene coordination into the coordinatively saturated²⁰ alkenylnickel chelate **B** and into **C**, respectively. The intermolecular alkene coordination initiates the hydrogen transfer that leads to 2,4-hexadiene formation, step h.²¹ Intramolecular carbon-nickel addition to the coordinated double bond in **B** would generate a cyclopropylcarbinylnickel derivative, **D**. Ring opening of **D** via a carbon-nickel β elimination to generate **E** accounts for the observed skeletal change. The hydrogen transfer from **E** via steps f and g would give **2** and the regenerated hydrogen transfer agent. Steps e, h, and g are believed to be irreversible. The cyclopropyl-

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

(21) The role of coordinated alkene in initiating hydrogen transfer is not known. The results are consistent with the hypothesis that transformations (a), (a'), (h), and (f) are multistep processes involving the intervention of hydridonickel complexes. For prior discussions of this problem in related systems, see ref 22.

(22) (a) R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965); (b) F. Faraday, L. Benze, and L. Marko, *J. Organometal. Chem.*, **17**, 107 (1969).

carbinylnickel derivative, **D**, is believed to possess the trans configuration. Arguments supporting this assignment and elucidating other stereochemical features of this rearrangement are presented elsewhere.²³

Scheme I explains why no deuterium isotope effect on the product ratio of *trans*-2-methyl-1,3-pentadiene-2,4-hexadienes was observed when **1** and 1-3- d_2 , either as a mixture, or in separate experiments, were treated with the catalyst. If intermolecular alkene coordination, step b, is slow relative to C-H bond cleavage in step h, no isotope effect on the above product ratio should be observed. The dramatic rate enhancement in hydrogen transfer observed when **1** was treated with the catalyst in the presence of ethylene,²³ and the pronounced effect of the original 1,4-diene concentration on the 2:3 + 4 product ratio,⁴ support this conclusion. Cramer²⁴ and Wilkinson and coworkers²⁵ have demonstrated that the formation constants for ethylene-Rh(I) complexes are orders of magnitude greater than complexes of propylene or other longer-chained alkenes. We suggest that the specific rate of alkene-nickel coordination, step b, and the magnitude of the formation constant for the alkene-nickel coordination complex are much greater when $RCH=CH_2$ is C_2H_4 than when this alkene is **1**.

With the exception of step e, each of the reactions in Scheme I has a counterpart in certain olefin oligomerization processes which are catalyzed by metal hydride transfer agents.²⁶ The steps up to and including step d of Scheme I may be considered as an "intramolecular" analog of an olefin dimerization mechanism. Step d represents the intramolecular analog of the growth step, namely, carbon-metal addition to coordinated alkene. A yet closer relationship exists between the type II diene rearrangement and some alkene-1,3-diene addition reactions.²⁷

Experimental Section

All operations involving organometallic compounds were conducted under an argon or nitrogen atmosphere in deoxygenated solvents as described elsewhere.⁴

Mass spectral analyses and deuterium content interpretations were provided by Dr. R. Schaffer of Morgan-Schaffer Corp., Montreal, Canada. The proton magnetic resonance (pmr) spectra were recorded on a Varian A-60 spectrometer and tetramethylsilane was employed as an internal standard. The spectral data are reported in δ units (ppm downfield from TMS). The multiplicity of the resonance signal, the relative number of protons corresponding to peak areas, the line separation in Hz for doublets, and the spectral assignments are given in parentheses. The abbreviations used to describe the resonances are: (s) singlet, (d) doublet, (t) triplet, (q) quartet, and (m) multiplet. The infrared spectra were recorded on a Beckman IR-12 spectrometer.

Hydrocarbon yields were determined by glpc as described previously.⁴ Separations were accomplished by a Varian Aerograph 90-P3 instrument utilizing a 20 ft \times $\frac{3}{8}$ in. 20% β,β' -oxydipropionitrile on Firebrick 60-80 column.

Materials. Solvents were purified as described previously.⁴ Diisobutylaluminum chloride and diisobutylaluminum hydride (neat or as 25% wt/wt solutions in toluene) were purchased from Texas Alkyls Inc., Houston, Texas. Vinylmagnesium chloride was purchased from Alfa Inorganics as a 2 M solution in tetrahydrofuran. Deuterium oxide and methyl- d_3 iodide were purchased

(23) P. A. Pinke, R. D. Stauffer, and R. G. Miller, *J. Amer. Chem. Soc.*, **96**, 4229 (1974).

(24) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).

(25) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(26) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(27) H. J. Golden, D. J. Baker, and R. G. Miller, *J. Amer. Chem. Soc.*, **96**, 4235 (1974).

from Merck, Sharpe and Dohme of Canada. Lithium aluminum deuteride (99% minimum deuterium) was obtained from E. Merck AG, Darmstadt, Germany. The tetrahydrofurfural chloride,²⁸ 4-pentyn-1-ol,²⁸ and 4-pentyne 1-acetate²⁹ which were precursors to 1-penten-4-yne were prepared by literature methods. The sources of other reagents employed were reported previously.⁴

Syntheses and Rearrangements of Deuterio-1,4-dienes. **Synthesis of *cis*-1,4-Hexadiene-6-*d*₃.** **a. 1-Penten-4-yne.**²⁹ The slow addition of 4-pentyne 1-acetate, 202 g (1.77 mol), to a flask which contained a layer of glass beads at 560–580°, heated by a molten lead bath, afforded a yellow liquid which was condensed in two traps in series at –78°. The liquid was then washed with dilute aqueous sodium bicarbonate solution after which the organic layer was dried over magnesium sulfate. Distillation of the product afforded 1-penten-4-yne, 44 g (38%), bp 41–43° (lit.²⁹ bp 42–43°), along with recovered starting material, 68 g (33%). The recovered starting material was recycled. Identification of the product was verified by examination of its infrared and pmr spectra.

b. 1-Hexen-4-yne-6-*d*₃.¹² A tetrahydrofuran solution of ethylmagnesium bromide, prepared from 0.30 mol of bromoethane and 0.3 mol of magnesium turnings, was slowly added to a solution of 1-penten-4-yne, 16.5 g (0.25 mol), in 150 ml of tetrahydrofuran. A rapid evolution of ethane gas accompanied the addition. The resulting solution was then stirred at 40° for 8 hr. Methyl-*d*₃ iodide, 20 g (0.14 mol), was then slowly added to this red solution at 0°, after which the resulting mixture was stirred at room temperature for 4 hr, followed by warming at 45° for 12 hr. The cooled product mixture was then hydrolyzed with dilute HCl solution and then extracted several times with pentane. The pentane extract was washed twice with dilute sodium bicarbonate solution, dried over calcium chloride, and then distilled, affording 3.4 g of a yellow oil bp 40–45° (140 mm). This distillate was purified by preparative glpc on a 15 ft × 3/8 in. 20% β,β'-oxydipropionitrile on Firebrick 60–80 column at 80°, flow rate 100 ml/min. Pmr and infrared spectral analysis showed that the sample collected, 2.4 g, 21% yield, was a mixture of *cis*-2-hexen-4-yne-6-*d*₃ (40%) and 1-hexen-4-yne-6-*d*₃ (60%).

c. *cis*-1,4-Hexadiene-6-*d*₃. Using an atmospheric pressure hydrogenation apparatus as described by House,³⁰ the mixture of 1-hexen-4-yne-6-*d*₃ and *cis*-2-hexen-4-yne-6-*d*₃, 2.4 g (0.03 mol), in 3 ml of pentane was hydrogenated at room temperature employing 5% palladium on barium sulfate (60 mg) and synthetic quinoline, 2 drops. The rate of the hydrogenation was followed by glpc and the reaction was terminated at an optimum yield of the desired product. The product mixture was carefully removed from the catalyst and after most of the pentane was removed by distillation, the diene products were collected by preparative glpc on a 20 ft × 3/8 in. 1,2,3-tris(2-cyanoethoxy)propane on 60–80 Chromosorb P column operated at 110° with a helium flow rate of 70 ml/min. The glpc-collected liquid was found to be a mixture which could be resolved on the 15 ft β,β' column at 60°, 60 ml/min flow rate. This second separation afforded two compounds: *cis*-1,4-hexadiene-6-*d*₃, 0.70 g; the infrared spectrum (neat) was essentially the same as that of *cis*-1,4-hexadiene but with additional peaks at 2230, 2201, 2211, and 2077 cm⁻¹ (C–D stretching vibrations); pmr spectrum (CCl₄), Figure 2. The second component was *cis,cis*-2,4-hexadiene-1-*d*₃, 0.21 g; the infrared spectrum (neat) was the same as that of *cis,cis*-2,4-hexadiene but with additional peaks at 2240, 2203, 2120, and 2070 cm⁻¹; pmr spectrum (CCl₄) δ 6.5–6.0 and 5.8–5.1 (m, 4 vinylic protons) and 1.72 (d, *J* = 6.5 Hz, 3 methyl protons).

Rearrangement of *cis*-1,4-Hexadiene-6-*d*₃, 1-6-*d*₃. Nine milliliters of a toluene solution of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.041 g (0.070 mmol), and 1-6-*d*₃, 0.60 g (5.4 mmol), was treated with a toluene solution of diisobutylaluminum chloride, 0.2 ml (0.24 mmol), affording an amber solution. The mixture was stirred at 25° for 8 hr with periodic removal of aliquots which were analyzed by glpc. During this time, 72% of the starting material was converted to products with a C-6 isomer yield of 63%. The aliquots and the final reaction mixture were quenched with small amounts of 2-propanol. 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 and unisomerized starting material were then

collected *via* preparative glpc and were identified by their pmr spectra which are described in Results.

Synthesis of a *cis*-1,4-Hexadiene-4-*d* and -5-*d* Mixture. **a. 1-Hexen-4-yne.** Propyne, 0.60 mol, was slowly bubbled into a 250-ml tetrahydrofuran solution of ethylmagnesium bromide (prepared from 12.2 g (0.5 mol) of magnesium and 54.5 g (0.50 mol) of ethyl bromide). A Dry Ice–acetone dewar condenser was employed to keep the propyne in the system. The deep red solution was stirred for 2 hr after which freshly distilled allyl iodide, 75.5 g (0.45 mol), in 50 ml of tetrahydrofuran was added slowly. The mixture was then stirred at 40° for 24 hr, then cooled to 0° and hydrolyzed with hydrochloric acid. The aqueous layer was washed several times with ether and the organic portions were then combined and dried over magnesium sulfate. Distillation on a spinning band column afforded 10.5 g, 26%, of 1-hexen-4-yne, bp 86–88°, the structure being confirmed by pmr and infrared spectra.

b. The *cis*-1,4-Hexadiene-4-*d* and -5-*d* Mixture. Diisobutylaluminum hydride,¹³ 19.7 ml (0.10 mol), was slowly added to a well-stirred solution of 8.18 g (0.10 mol) of 1-hexen-4-yne in 80 ml of heptane at –5°. After the addition was complete, the mixture was warmed to room temperature. The progress of the reaction was followed by glpc analysis of reaction aliquots, after their treatment with 2-propanol. After stirring the mixture for 5 days, 9 ml (0.50 mol) of D₂O was added slowly to the mixture which was then stirred at room temperature for 3 hr. Flash distillation at 40° (1 mm) afforded an organic layer which was dried over calcium chloride. Distillation on a spinning band column afforded a slightly impure mixture of *cis*-1,4-hexadiene-4-*d* and *cis*-1,4-hexadiene-5-*d*, 4.0 g, 49% yield. The product was purified *via* preparative glpc. The pmr spectrum is described in Results.

Rearrangement of *cis*-1,4-Hexadiene-4-*d* and -5-*d*. *trans*-Di-chlorobis(tri-*n*-butylphosphine)nickel(II), 0.172 g (0.32 mmol), and 0.32 g (3.85 mmol) of the *cis*-1,4-hexadiene-4-*d* and -5-*d* mixture in 29 ml of toluene was treated with 1.09 ml of a 25% solution of diisobutylaluminum chloride in toluene (1.3 mmol) affording an amber solution. The solution was stirred at 25° and aliquots were removed for glpc analysis. After 3 min, the reaction was terminated by addition of 4 ml of 2-propanol. A 65% conversion of 1,4-diene to products was achieved during this period. After the regular work-up, the unisomerized starting material and the diene products were collected by preparative glpc. Pertinent spectral data are given in Results.

Synthesis of *cis*-1,4-Hexadiene-3-*d*₂. **a. *cis*-2-Butenoic Acid.**³¹ A mixture of potassium bicarbonate, 200 g (2.0 mol), and 80 g (0.57 mol) of 1,3-dibromo-2-butanone in 2 l. of water was stirred for 8 hr. The resulting solution was then acidified with hydrochloric acid, saturated with sodium chloride, and then extracted several times with ether. Removal of the ether afforded 22.4 g of the impure acid, 50% yield.

b. Ethyl *cis*-2-Butenoate. A solution of the crude *cis*-2-butenic acid, 60 g (0.69 mol), prepared as in step a in 100 g (2.0 mol) of absolute ethanol and 200 ml of benzene containing 6 ml of concentrated sulfuric acid was heated to reflux. The lower layer of the water–ethanol–benzene azeotrope was removed with the aid of a Dean–Stark trap. The reaction was terminated when the theoretical amount of water was removed from the reaction mixture. The ethanol and benzene were then distilled from the black product mixture after which the organic residue was washed with water, and then with dilute base solution and then dried over calcium chloride. Distillation of the organic residue afforded a 20:80 mixture of ethyl *trans*-2-butenate and ethyl *cis*-2-butenate, 40 g, 50% yield, bp 136–141°. Redistillation of the isomeric mixture through a 36-in. spinning band column using a 20:1 reflux ratio afforded the lower boiling *cis* isomer in greater than 96% purity, bp 125–126°.

c. *cis*-2-Buten-1-ol-1-*d*₂. Ethyl *cis*-2-butenate, 54 g (0.475 mol, 96% *cis*), in 125 ml of ether was slowly added to a well-stirred mixture of lithium chloride and aluminum trideuteride¹⁴ (generated from LiAlD₄, 10 g, 0.24 mol, and AlCl₃, 21.3 g, 0.16 mol) in 600 ml of ether at room temperature. The addition required 3 hr, after which the mixture was refluxed for 8 hr. The mixture was then cooled by an ice bath and then treated with 10 ml of water, then with 10 ml of 15% NaOH solution and then with 30 ml of water. The resulting white precipitate was filtered from the ether solution and then washed twice with ether after which the combined ether solution was dried over magnesium sulfate and then the ether was removed by distillation through a glass-packed column. Distilla-

(28) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 901.

(29) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 417 (1953).

(30) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p. 3.

(31) C. Rappe, *Acta Chem. Scand.*, 17, 2766 (1963).

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

d. 1-Chloro-2-butene-*I-d*₂. *cis*-2-Buten-1-ol-*I-d*₂, 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-*I-d*₂ (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-*d*₂. 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-*I-d*₂ 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-*d*₂, 27%; *trans*-1,4-hexadiene-3-*d*₂, 4%; and 3-methyl-1,4-pentadiene-*I-d*₂, 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-*d*₂, 1.38 g, 12.5% yield, *trans*-1,4-hexadiene-3-*d*₂, 0.10 g, 1–2% yield,

and 3-methyl-1,4-pentadiene-*I-d*₂, 0.68 g, 6.2% yield. Spectral identification: *cis*-1,4-hexadiene-3-*d*₂, 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-*d*₂. A 17.35 ml solution of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.103 g (0.192 mmol), and 1-3-*d*₂, 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-*d*₂ 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-*d*₂ 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-*d*₂. 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-*d*₂ (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.

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

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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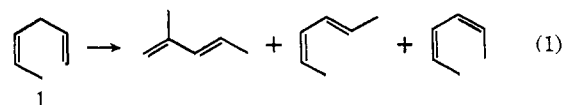
Abstract: *trans*- and *cis*-2-methylvinylcyclopropanes were skeletally isomerized by catalysts derived from *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride and from ethylenebis(tri-*o*-tolyl phosphite)nickel(0) and hydrogen chloride. Both catalyst systems afforded *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.

We 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-