Nickel-Promoted Skeletal Rearrangements of 1,4-Dienes by a Fragmentation Process. Mechanistic Relationship to an Alkene-1,3-Diene Addition Reaction[1,2a]

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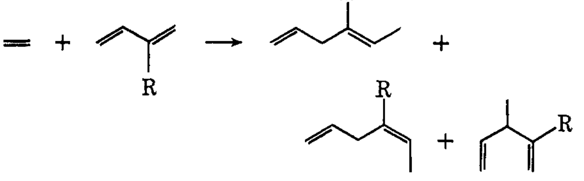
Abstract: 2-Methyl-1,4-pentadiene-*1*-d_2 has been synthesized and was isomerized in toluene, chlorobenzene, and *o*-dichlorobenzene by a catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride. The isomeric products in chlorobenzene and toluene were 2-methyl-1,4-pentadiene-*3*-d_2, *trans*-2-methyl-1,3-pentadiene-*1*-d_2, and 2,3-dimethyl-1,3-butadiene-*1*-d_2. Under the same conditions, 2,3-dimethyl-1,4-pentadiene was isomerized to predominantly (*E*)-4-methyl-1,4-hexadiene. Treatment of a mixture of (*E*)- and (*Z*)-4-methyl-1,4-hexadiene with the catalyst in chlorobenzene afforded small amounts of 2,3-dimethyl-1,4-pentadiene along with (2*E*,4*Z*)-, (2*Z*,4*E*)-, and (2*E*,4*E*)-3-methyl-2,4-hexadiene as products. 3-Methyl-1,4-hexadiene and 4-methyl-1,4-hexadiene were isolated from product mixtures derived from treatment of 1,4-pentadiene with the catalyst. Treatment of 3-methyl-1,4-pentadiene with the catalyst in the presence of propylene afforded 2-methyl-1,4-hexadiene and 1,4-hexadienes as products. The results are interpreted in terms of a diene rearrangement mechanism which involves a carbon–nickel β-elimination reaction of an alkenylnickel intermediate.

Carbon–carbon bond formation associated with alkene linear oligomerization reactions is an energetically favorable process. It has been noted, for instance, that $-\Delta G°$ for the conversion of ethylene to butene is very large and the equilibrium constant has a value of *ca.* 10^{11}.[3,4] Processes such as this have high activation energies, however, and require some form of catalysis or chain initiation in order to provide reasonably high reaction rates under mild experimental conditions. The introduction of Ziegler–Natta type transition metal coordination catalysts[5,6] provided a very practical low energy route to transformations in the linear polymerization class. The role of the transition metal in these reactions has been discussed at length and it has been concluded that, in many cases, the propagation step involves a carbon–metal addition to a coordinated alkene (eq 1).[7-9] Recent work lends support to this hypothesis.[10] The process has been described as an electronic rearrangement accompanied by only small nuclear displacements,[7,8] thus accounting for its low activation energy. To our knowledge, the reverse transformation in eq 1, a carbon–transition metal β elimination, has never been observed in a system possessing an acyclic hydrocarbon ligand.

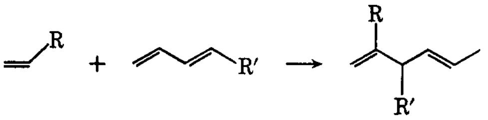
$$\begin{array}{c} CH_2{=}CH_2 \\ | \\ R{-}M \end{array} \rightleftharpoons \begin{array}{c} CH_2{-}CH_2 \\ / \qquad / \\ R \qquad M \end{array} \qquad (1)$$

One type of transition metal catalyzed alkene addition reaction where carbon–carbon bond formation is believed to occur as in eq 1 is exemplified by the rhodium-[11] and nickel-[12] promoted reactions of alkenes with 1,3-dienes. The primary hydrocarbon products are 1,4-dienes, and product studies from reactions of substituted hydrocarbon precursors[12a] indicate that the nickel-catalyzed reaction generates the products described in eq 2 and 3. These results, along with studies



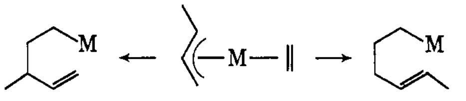
(2)

R = H, CH$_3$, Cl



(3)

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



(4)

II I III

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(1) Some of these results were reported in preliminary communications: (a) R. G. Miller, *J. Amer. Chem. Soc.*, **89**, 2785 (1967); (b) R. G. Miller, H. J. Golden, D. J. Baker, and R. D. Stauffer, *ibid.*, **93**, 6308 (1971).

(2) (a) Taken in part from the Ph.D. Theses of D. J. Baker, 1970, and H. J. Golden, 1973, University of North Dakota; (b) NSF Predoctoral Trainee, 1967–1970; (c) NDEA Predoctoral Fellow, 1965–1968.

(3) (a) J. E. Kilpatrick, *et al.*, *J. Res. Nat. Bur. Stand.*, **36**, 610 (1946).

(4) R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965).

(5) K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

(6) G. Natta and I. Parquon, *Advan. Catal.*, **11**, 1 (1959).

(7) P. Cossee, *J. Catal.*, **3**, 80 (1964), and references cited therein.

(8) See R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968), for a discussion of olefin oligomerization reactions.

(9) F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968).

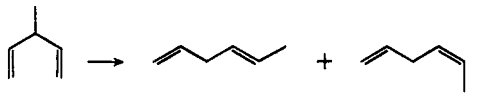
(10) (a) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3116 (1963); (b) R. Cramer, *ibid.*, **87**, 4717 (1965); (c) K. Sonogashiva and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1178 (1966); (d) A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 5989 (1967); (e) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968); (f) W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969); (g) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, **92** (1970); (h) H. Yawazaki and N. Hagihara, *J. Organometal. Chem.*, **21**, 431 (1970).

(11) (a) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965); (b) R. Cramer, *ibid.*, **89**, 1633 (1967).

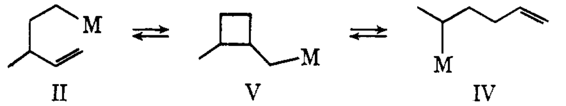
(12) (a) R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, **89**, 3756 (1967); (b) C. A. Tolman, *ibid.*, **92**, 6777 (1970); (c) A. C. L. Su and J. W. Collette, *J. Organometal. Chem.*, **36**, 177 (1972); (d) B. Bogdanovic, B. Henc, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem.*, **84**, 1070 (1972).

reported by other workers,[11b,12b–d] suggest that the growth step occurs by a carbon–metal addition of a methylallylmetal moiety to coordinated alkene (eq 4). A proton nmr study has provided direct evidence for an intermediate such as I where M = $\mathrm{Ni[P(OEt)_3]_2^+}$.[12b]

One of these catalyst systems also accomplishes two types of skeletal isomerization of 1,4-dienes.[13] These rearrangements have only been observed in the absence of high concentrations of 1,3-dienes.[12a,13] The mechanism of the type I rearrangement has been discussed elsewhere.[14] The type II rearrangement, exemplified by the conversion of 3-methyl-1,4-pentadiene to 1,4-hexadiene (eq 5), is related to the alkene–1,3-diene addition reaction in the structural sense that the reactant and products in eq 5 are all formed in the ethylene–1,3-butadiene reaction (eq 2, R = H).


(5)

Arguments have been presented that the combination of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride in the presence of alkenes leads to the generation of catalysts that act as hydridonickel complexes.[13,14a] A 1,2-addition of a nickel hydride to 3-methyl-1,4-pentadiene and to 1,4-hexadiene would afford II and III, eq 4, respectively, where M represents the nickel atom and its auxiliary ligands. The alternative 2,1-additions are believed to generate alkenylnickel complexes of the kind which undergo the type I skeletal change.[14] Two modes of reaction of II which seemed most reasonable as candidates for the type II skeletal change were: (1) conversion of II to III *via* a methylallylnickel intermediate, I, as in eq 4, and (2) conversion of II to IV *via* a cyclobutylcarbinylnickel derivative, V, eq 6. Both paths 1 and 2 involve C–Ni elimination reactions in the C–C bond breaking step. The first evidence for path 2 was found in organomagnesium,-sodium and-lithium chemistry.[15] This route has also recently been proposed to account for the formation of vinylcyclobutanes from alkenes and 1,3-dienes in a process afforded by a titanium-based catalyst.[16] We know of no precedent in the transition metal catalysis of hydrocarbon reactions for path 1, a transformation which is closely related to the reversal of the propagation step in metal-catalyzed alkene oligomerization reactions.



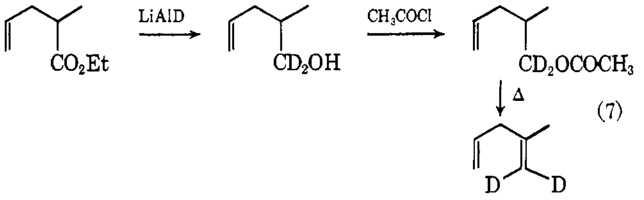
(6)

With this background in mind, we sought to investigate the following aspects of the type II rearrangement: (1) the fate of each carbon in the 1,4-diene reactant as it is transformed into the skeletally isomerized product; (2) the nature of the hydrogen transfer associated with the skeletal change; (3) whether the rearrangement is intramolecular or intermolecular with respect to the hydrocarbon moiety; (4) the roles of the metal components in the catalyst system.

Results

Labeling Experiments. The fate of each carbon atom in the 1,4-diene reactant, as it was transformed into the type II rearrangement product, was determined in experiments in which deuterium and methyl labels were attached to the 1,4-pentadiene carbon skeleton. We realized that the employment of a labeled diene reactant possessing double bonds which were *both* susceptible to nickel hydride transfer from the catalyst could lead to competing isomerization reactions. This would have greatly complicated the interpretation of the results. This consideration, for instance, made the isotopic labeling and subsequent isomerization of 1,4-pentadiene an impractical exercise. Our studies of the type I diene rearrangement indicated that the elements of nickel hydride were not readily transferred to a methyl-substituted double bond.[14a] We therefore chose to examine the rearrangements of some dienes which possessed only one terminal, unsubstituted vinyl group to which the metal hydride could be added.

A. Synthesis and Rearrangement of 1,1-Dideuterio-2-methyl-1,4-pentadiene (1-*1*-d_2). The 1,1-dideuterio-2-methyl-1,4-pentadiene (**1**-*1*-d_2) was synthesized in a number of steps from the ethyl ester of 2-methyl-4-pentenoic acid (eq 7). Reduction of the ester with lithium aluminum deuteride afforded 1,1-dideuterio-2-methyl-4-penten-1-ol in 85% yield. The dideuterio alcohol was then treated with acetyl chloride producing 1,1-dideuterio-2-methyl-4-pentenyl acetate in similar yield. Pyrolysis of the acetate at 600° afforded **1**-*1*-d_2 in 17% yield. The position of the deuterium was unambiguously verified by the near absence of the C-1 proton resonance at τ 5.32 (Figure 1). The C-2 methyl proton resonance was used as an internal standard for the determination of the relative peak intensity of the C-1 proton resonance (C-2 $\mathrm{CH_3}$:C-1:C-3:C-4:C-5 = 3.00:0.043:1.99:1.11:2.07). This method indicated a 98% deuterium composition at C-1. Mass spectral analysis of a typical sample prepared in the above manner showed the deuterium composition to be 1.2% d_0, 2.78% d_1, 96.0% d_2, and 0.02% d_3.



(7)

The **1**-*1*-d_2 was treated with the catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and diisobutylaluminum chloride in toluene solution for 6.5 hr at 24–26°. During this period of time, 42% of the deuterio-**1** was converted to structurally different products. The isomeric products were 1,1-dideuterio-2,3-dimethyl-1,3-butadiene and 1,1-dideuterio-*trans*-2-methyl-1,3-pentadiene, present in 11.5 and 10.2% yields, respectively. The deuterium locations in these products were unambiguously identified by examination of their pmr spectra. The pmr spectrum of recovered deuterio-2-methyl-1,4-pentadiene showed that part of the C-1

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

(14) (a) P. A. Pinke and R. G. Miller, *J. Amer. Chem. Soc.*, **96**, 4221 (1974); (b) P. A. Pinke, R. D. Stauffer, and R. G. Miller, *ibid.*, **96**, 4229 (1974).

(15) (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).

(16) L. G. Cannell, *J. Amer. Chem. Soc.*, **94**, 6867 (1972).

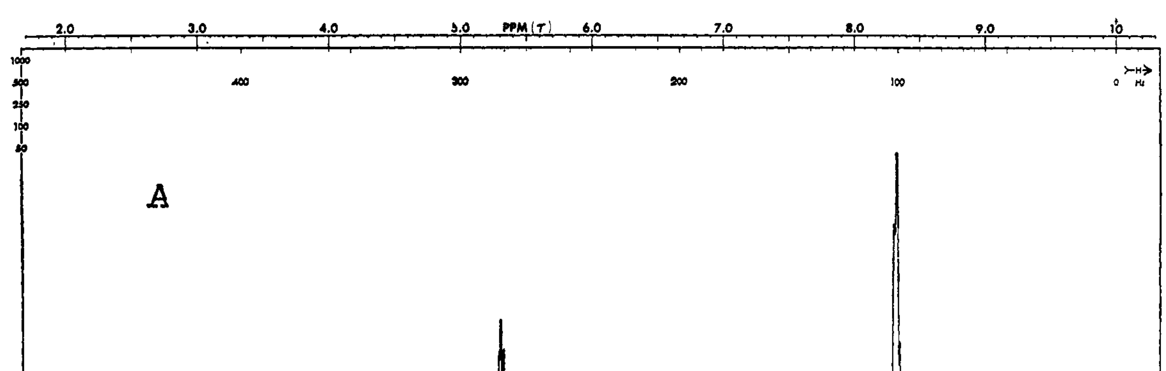


Figure 1. The 60-MHz pmr spectra of 2-methyl-1,4 pentadiene, A, and 1,1-dideuterio-2-methyl-1,4-pentadiene, B, recorded in carbon tetrachloride solution at ambient temperature.

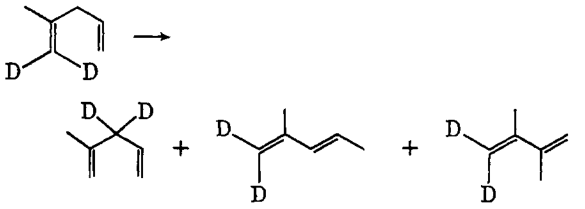
proton resonance at τ 5.32 had reappeared, accompanied by a decrease in the intensity of the C-3 allylic proton resonance at τ 7.29. Pmr integration (C-2 CH_3: C-1:C-3:C-4:C-5 = 3.00:0.38:1.70:1.06:2.06) indicated a 16.8% decrease in deuterium content at C-1 and a 15% gain at C-3. Mass spectral analysis of the recovered deuterio-**1** showed that it contained 2.9% d_1, 95.5% d_2, and 1.6% d_3.

When **1**-*1*-d_2 was treated with the catalyst in chlorobenzene for 2 hr at 25°, 56% was consumed and deuterio-2,3-dimethyl-1,3-butadiene and deuterio-*trans*- and deuterio-*cis*-2-methyl-1,3-pentadiene were afforded in 22.3, 34.5, and 3.8% yields, respectively. Pmr analysis of recovered starting material indicated that 19.9% of the deuterium at C-1 had been lost and an 18.5% increase in deuterium content at C-3 had occurred. These values derive from very careful integration of the proton peak areas which gave a C-1:C-2 CH_3:C-3:C-4:C-5 proton ratio of 0.43:3.00:1.62:1.07:2.02. Integration of the peak areas in the pmr spectrum of the deuterio-2,3-dimethyl-1,3-butadiene product demonstrated a methyl:vinyl proton ratio of 2.95:1.00. Similar analysis of the deuterio-*trans*-2-methyl-1,3-pentadiene using the C-4 vinyl proton resonance as an internal standard of relative peak intensity 1.0 gave a C-1:C-3:total CH_3 proton ratio of 0.24:0.89:5.33. The per cent deuterium compositions of these products are listed in Table I. The pmr and mass spectral data indicate that the major deuteriodiene products are those described in eq 8.

Table I. Deuterium Per Cent Compositions of **1**-*1*-d_2 and Its Isomerization Products[a]

	d_0	d_1	d_2	d_3
1 (reactant)	1.2	2.78	96.0	0.02
1 (recovered)	1.23	3.11	93.2	2.45
trans-2-Me-1,3-PD	0.57	9.1	89.5	0.86
2,3-Me_2-1,3-BD	1.83	3.93	92.8	1.4

[a] The experiment was conducted at 25° in chlorobenzene solution, diene:Al:Ni ratio = 11:3.2:1.0.



(8)

Less skeletal rearrangement and more extensive hydrogen transfer occurred when **1**-*1*-d_2 was treated with the catalyst in 1,2-dichlorobenzene. During 1.5 hr, 56% of the deuterio-**1** was consumed and deuterio-

trans-2-methyl-1,3-pentadiene, deuterio-*cis*-2-methyl-1,3-pentadiene, and deuterio-2,3-dimethyl-1,3-butadiene were afforded in 38.7, 4.8, and 4.6% yields, respectively. Pmr analysis of recovered deuterio-**1** indicated a loss of 17% of the deuterium originally residing at C-1, and an increase of only 11.5% deuterium at C-3. The sample contained 2.12% d_0, 8.17% d_1, and 89.7% d_2 by mass spectrometry. An analogous analysis of the deuterio-*trans*-2-methyl-1,3-pentadiene showed a proton ratio of 0.28:0.88:4.23 for C-1:C-3:total CH_3, employing the C-4 proton resonance as an internal standard of relative intensity 1.0. The deuterium composition was found to be 1.54% d_0, 11.2% d_2, 85.2% d_3, 1.02% d_4, and 0.44% d_4.

B. Synthesis and Isomerization of 2,3-Dimethyl-1,4-pentadiene (2) and 4-Methyl-1,4-hexadiene (3). We have mentioned briefly in another report that a catalyst derived from *trans*-dichlorobis(tri-*n*-butylphosphine)-nickel(II) and diisobutylaluminum chloride was found to isomerize 2,3-dimethyl-1,4-pentadiene to 4-methyl-1,4-hexadiene.[13] This result was very pertinent to the mechanistic study of the type II rearrangement so the reaction has been the subject of further investigation and a more detailed report of results is included here.

The syntheses of 2,3-dimethyl-1,4-pentadiene and 4-methyl-1,4-hexadiene were accomplished by adding ethylene to isoprene (eq 2, R = CH_3), using the $(n\text{-}Bu_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ catalyst.[12a] The reaction was conducted in ethylene-saturated chlorobenzene solution under 1 atm of ethylene, employing an isoprene:Ni:Al molar ratio of 146:1.0:3.5. These conditions were different from those used in the previously reported synthesis[12a] where ethylene pressures of *ca.* 100 psi were employed. During 1 hr under the low-pressure conditions, 63% of the isoprene was converted to products affording 54 and 12% yields (based on glpc analyses) of 4-methyl-1,4-hexadiene and 2,3-dimethyl-1,4-pentadiene, respectively. Glpc and pmr analysis showed that both isomers of 4-methyl-1,4-hexadiene were present, with the isomer exhibiting the longer retention time on a β,β'-oxydipropionitrile on firebrick column being the major product.

The skeletal rearrangement of **2** to **3** was carried out in toluene, chlorobenzene, and *o*-dichlorobenzene solvents. During 3 hr in toluene, 52% of **2** was converted to products and **3** was afforded in 60% yield. Two minor products (<5% yield) were shown to be conjugated isomers of **3**, formally derived from double bond migration. Significantly, no other 1,4-diene isomers were detected and 2-methyl-1,4-hexadiene and 2-methyl-1,5-hexadiene were specifically shown to be absent. The same products were formed in chlorobenzene and *o*-dichlorobenzene and the rate of formation of isomeric products appeared to be greater in the more polar solvents. The geometric isomer which exhibited the longer retention time on the β,β'-oxydipropionitrile column composed >95% of the **3** isomer mixture formed in each of these experiments. This isomer was designated as (*E*)-4-methyl-1,4-hexadiene[17] (**3a**) based upon the following observations. (1) The same isomer of **3** predominated in product mixtures derived from the rearrangement of **2**, and from the addition of ethylene to isoprene, when the $(Bu_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ catalyst was employed. (2) All previous alkene–1,3-diene addition reactions and 1,4-diene skeletal rearrangements catalyzed by the $(Bu_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ system at 25° have afforded predominantly *trans*-1,4-diene products. (3) Treatment of a 2.6:1.0 mixture of the geometric isomers of **3** (afforded by the nickel catalyzed addition of ethylene to isoprene) with diisobutylaluminum hydride, followed by hydrolysis, gave (*E*)-3-methyl-2-hexene as the major product. (4) Analogous diisobutylaluminum hydride reduction of the 4-methyl-1,4-hexadiene product afforded by an iron-catalyzed addition of ethylene to isoprene gave (*Z*)-3-methyl-2-hexene.[18]

The identifications of the two minor conjugated isomeric products derived from **3** were facilitated by an experiment in which a mixture of (*E*)- and (*Z*)-**3** (*E*:*Z* = 2.4) in chlorobenzene was treated with the catalyst for 3 hr. During this period, 54% of **3** was converted to products. Four isomeric dienes were detected in the product mixture and were collected by preparative glpc. Analyses of the pmr spectra of these products showed them to be 2,3-dimethyl-1,4-pentadiene (**2**) (2% yield), (2*E*,4*Z*)-3-methyl-2,4-hexadiene (**4**) (8%), (2*Z*,4*E*)-3-methyl-2,4-hexadiene (**5**) (10%), and (2*E*,4*E*)-3-methyl-2,4-hexadiene (**6**) (55%). The configuration of the least-substituted double bond in each product could be determined from the magnitudes of the –C*H*=C*H*–vinyl proton spin coupling constants. Coupling constants of protons trans to one another in alkenes have been demonstrated to be substantially greater than the corresponding cis coupling.[19] This coupling was found to be 15.5 and 16.0 Hz in the isomers which were ultimately assigned structures **5** and **6**, respectively, and was measured at 12.0 Hz in isomer **4**. The C-4 vinyl proton resonance in isomer **5** is expected to occur at lower field than the C-4 proton resonances in **4** and **6** due to "steric deshielding" by the C-1 methyl group.[20] The observation of this resonance at τ 3.60 in **5** relative to 4.23 and 3.87 in isomers **4** and **6** supports the configuration assignment in **5**. The absence of the deshielding of the C-4 proton in **4** confirms the 2*E*,4*Z* configuration here. It is noteworthy that the unobserved fourth isomer possessing the 2*Z*,4*Z* configuration should exhibit "steric deshielding" of its C-4 proton.

The isomers which were assigned structures **4** and **6** possessed glpc retention times identical with the two minor products afforded on isomerization of **2** by the catalyst. These were the double bond migration products which were expected to be generated by reaction of the catalyst with **3a**,[14a] the isomer which composed >95% of the **3**–isomer mixture derived from **2**, and 70% of the **3**–isomer mixture which was treated with the catalyst independently. These isomerization reactions are summarized in eq 9.

Evidence for Fragmentation of the Diene Reactant. In an attempt to determine whether the diene reactant was cleaved into two hydrocarbon fragments during the skeletal rearrangement, experiments designed to

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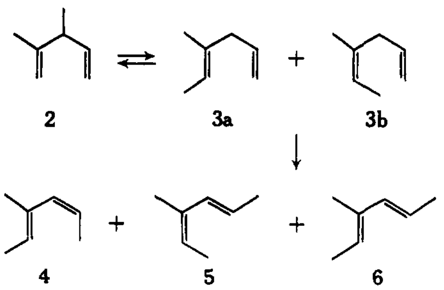
[17] See F. D. Greene, *J. Org. Chem.*, **35**, 2849 (1970), regarding the nomenclature of these diene isomers.

[18] G. Hata and D. Aoki, *J. Org. Chem.*, **32**, 3754 (1967). This iron-based catalyst affords *cis*-1,4-dienes exclusively.

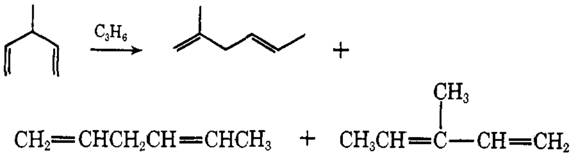
[19] See C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); we have consistently observed the same phenomena in spectra of other dienes. For instance, the proton–proton spin couplings in the internal double bonds of *trans*- and *cis*-2-methyl-1,3-pentadiene are 15.7 and 12.4 Hz, respectively.

[20] C. G. Cardenas, *Tetrahedron Lett.*, 4013 (1969).



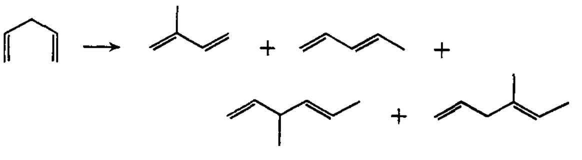
(9)

trap species such as I (eq 4), were conducted. 3-Methyl-1,4-pentadiene was treated with a toluene solution of the catalyst in the presence of a large excess of propylene. The reaction was conducted in a pressure vessel and the conditions employed were those which were necessary to add propylene to butadiene, using the same catalyst system.[12a] During 19 min at 86–90°, a significant quantity of 2-methyl-1,4-hexadiene (predominately trans) was produced (9% yield) along with 1,4-hexadiene (trans:cis = 4, 4.5% yield) and 3-methyl-1,3-pentadiene (10%). These compounds accounted for *ca.* 98% of the products which distilled from the product mixture in the 64–94° boiling point range. The yields were based upon a 52% recovery of 3-methyl-1,4-pentadiene. Thus, a C-7 diene was generated from C-3 and C-6 precursors (eq 10).



$$\mathrm{CH_2{=}CHCH_2CH{=}CHCH_3} + \mathrm{CH_3CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \qquad (10)$$

A careful examination of product mixtures derived from treatment of 1,4-pentadiene with the catalyst at 24–26° for relatively long periods of time provided further evidence for a fragmentation process. It was found that in addition to the isomerization products isoprene and 1,3-pentadiene, substantial quantities of two C-7 dienes were present. These were identified as 3-methyl-1,4-hexadiene and 4-methyl-1,4-hexadiene by comparison of their pmr and infrared spectra with those of authentic samples. In a typical experiment conducted in toluene in which a diene:Ni molar ratio of 12:1 was employed, 64% of the 1,4-pentadiene was converted to products during 3.5 hr and 3-methyl-1,4-hexadiene and 4-methyl-1,4-hexadiene were afforded in 11 and 6% yields, respectively. Under these conditions, the yield of isoprene was 30%. C-7 dienes were also formed from 1,4-pentadiene when tetrachloroethylene and xylene were employed as solvents. Glpc analyses demonstrated that the reactants and solvents were free of ethylene and it was determined that the maximum amount of ethylene that could have been liberated from the trace ethylaluminum impurity in the diisobutylaluminum chloride was insignificant compared to the amounts of C-7 dienes produced. It should be noted that no ethylene was detected in any of the reaction aliquots or in the distillates. Therefore, the C-7 dienes must have been generated from the C-5 precursor (eq 11).



(11)

Formation of Hydrogenation Products. Two attempts to conduct diene isomerization reactions at slightly elevated temperatures resulted in reduced yields of isomeric dienes and in the generation of hydrogenation products. 2-Methyl-1,4-pentadiene was treated with the catalyst in toluene at 50–55° and aliquots were removed periodically during a 6.5-hr period and were analyzed by glpc. During 4 hr, 68% of the reactant was consumed and 2,3-dimethyl-1,3-butadiene and *trans*-2-methyl-1,3-pentadiene were afforded in 1.6 and 4.1% yields, respectively. The major monomeric hydrocarbon product was shown to be 2-methyl-1-pentene, 22% yield, by comparison of its pmr spectrum with that of an authentic sample.

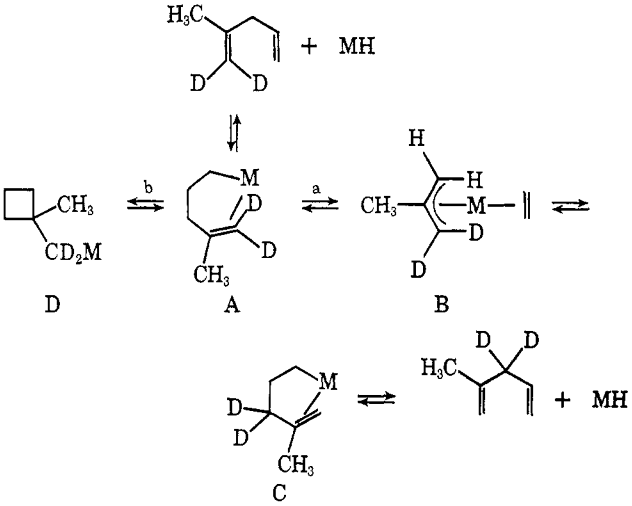
When *trans*-1,4-hexadiene was treated with the catalyst precursors at 85° for 17 min, the only C-6 product, other than 2,4-hexadiene, was shown to be *trans*-2-hexene by comparison of its pmr and infrared spectra with those of authentic samples.

Discussion

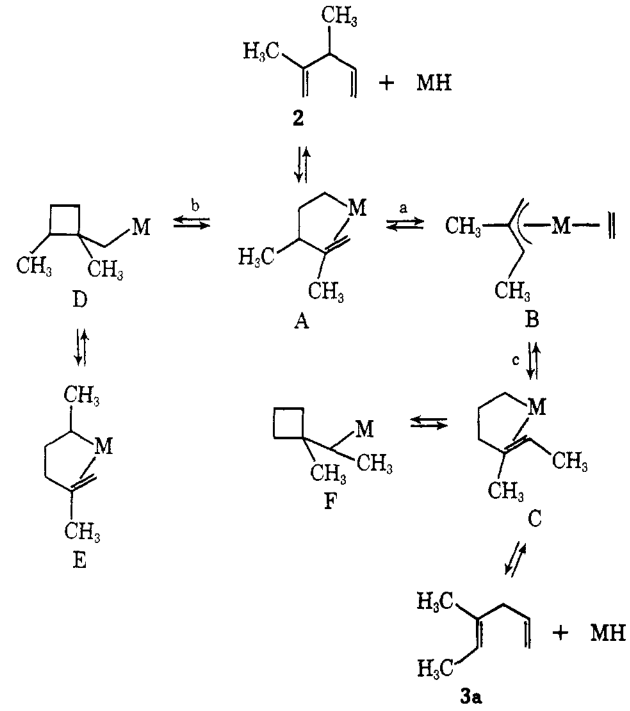
Nature of the Skeletal Change. The observed fates of labels at C-1 and C-3 relative to that of a label at C-2 in the 1,4-pentadiene skeleton elucidate the nature of the skeletal change in the type II rearrangement. The experimental results are explained by a rearrangement mechanism which interconverts alkenylnickel compounds by path a in Schemes I and II. An alternative route involving the intervention of cyclobutylcarbinylnickel derivatives, path b, is inconsistent with our observations. The alkenylnickel species, A, are generated by nickel hydride addition to the unsubstituted double bond in **1**-*1*-d_2 and **2**. Rearrangement of A derived from **1**-*1*-d_2 *via* path b in Scheme I would generate a chemically symmetrical cyclobutylcarbinylnickel derivative, D, which on ring opening through cleavage of either C–C bond on the ring and adjacent to the incipient double bond could only regenerate A. Isomerization of A *via* path a would afford the methylallylnickel complex B which should give a nearly 50:50 mixture of A and C on its collapse. Nickel hydride elimination from A and C would regenerate the catalyst and afford the mixture of **1**-d_2 isomers observed on recovery of deuterio-**1** from the product mixture.

The predicted fates of **2** on being transformed by paths a and b are described in Scheme II. Path a would

Scheme I



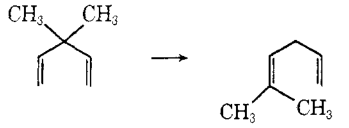
Scheme II



generate 4-methyl-1,4-hexadiene (**3**), the product actually observed. Path b predicts the formation of 2-methyl-1,4-hexadiene and 2-methyl-1,5-hexadiene, neither of which were detected in product mixtures derived from **2**. It is also interesting to note that the rearrangement of **3** *via* a dimethylallylnickel derivative B should afford **2**, an observed product, but the generation of a cyclobutylcarbinylnickel complex, F, would not lead to a skeletal change.

While a label at C-3 in the 1,4-pentadiene skeleton cannot provide a distinction between path a and path b, the structures of the isomerization products derived from 3,3-dimethyl-1,4-pentadiene and 3-methyl-1,4-pentadiene (5-methyl-1,4-hexadiene and 1,4-hexadiene, respectively[13]) are consistent with path a. 2-Methyl-1,5-hexadiene and 1,5-hexadiene, products also expected from path b reactions of 3,3-dimethyl- and 3-methyl-1,4-pentadiene were not detected in the product mixtures.[13]

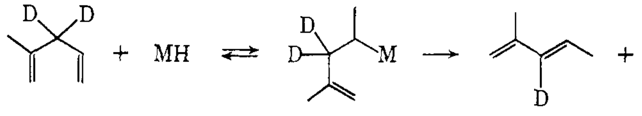
The Hydrogen Transfer. The proposed hydrogen transfer reactions in Schemes I and II are consistent with the results obtained in toluene and chlorobenzene solution. The isomerization of 3,3-dimethyl-1,4-pentadiene to 5-methyl-1,4-hexadiene[13] (eq 12) demonstrated



(12)

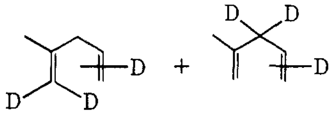
that hydrogen transfer at C-3 of the 1,4-pentadiene skeleton is not required in the type II rearrangement. Our experimental results support the supposition that nickel hydride addition to methyl-substituted double bonds in the 1,4-diene reactants is not favored. Factors in support of this contention include: (a) our failure to detect the formation of type I skeletal rearrangement products or double bond migration products derived from initial addition of metal hydride to a methyl-substituted double bond;[13] (b) geometric isomerism of *trans*- or *cis*-1,4-hexadienes was not observed;[13] (c) significant exchange of deuterium at C-4 and C-5 in *cis*-1,4-hexadiene with hydrogen in the catalyst pool was not observed;[14c] (d) treatment of *trans*-1,4-hexadiene and 2-methyl-1,4-pentadiene with the catalyst at elevated temperatures afforded hydrogenation products *trans*-2-hexene and 2-methyl-1-pentene, respectively, but hydrogenation of the methyl-substituted double bonds was not observed.

The data in Table I indicate that treatment of **1**-*1*-d_2 with the catalyst in chlorobenzene did not cause appreciable H–D exchange. The deuterium compositions of the reactant and of recovered deuterio-**1** were essentially identical with the exception of the small decrease in % d_2 and a corresponding increase in % d_3 found in recovered **1**. An analogous result was observed in the isomerization of 3,3-dideuterio-*cis*-1,4-hexadiene.[14a] The excess deuterium found in recovered deuterio-**1** can be explained by a release of deuterium into the catalyst hydrogen pool through isomerization of **1**-*3*-d_2 derived from rearrangement of **1**-*1*-d_2 (eq 13 and 14). The



MD (13)

MD + 1–1d_2 + 1–3-d_2 ⇌



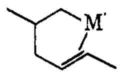
+ MH (14)

observation of a 6% increase in d_1 composition in the deuterio-2-methyl-1,3-pentadiene product (Table I) is consistent with the formation of 2-methyl-1,3-pentadiene-*3*-d_1 (eq 13). This result, along with the respective *ca.* 19% increase and decrease in deuterium at C-3 and C-1 in recovered deuterio-**1** relative to the **1**-*1*-d_2 reactant, allows the assignment of a lower limit on the amount of deuterio-**1** which underwent fragmentation *via* path a, Scheme I, in chlorobenzene. For every molecule of **1**-*1*-d_2 which was converted to **1**-*3*-d_2, *ca.* two molecules would have fragmented *via* intermediate B, Scheme I. The data therefore indicate that *ca.* 38% of the recovered deuterio-**1**, and 12% of the deuterio-1,4-diene that eventually became deuterio-2-methyl-1,3-pentadiene, fragmented *via* intermediate B. The relative amounts of the type I rearrangement product, dideuterio-2,3-dimethyl-1,3-butadiene, which derive from **1**-*1*-d_2 *vs.* from **1**-*3*-d_2 could not be determined. Mechanistic considerations[14a] indicate that 1,1-dideuterio-2,3-dimethyl-1,3-butadiene should be formed from both compounds and the pmr and mass spectral data indicate that this was the major deuterio-2,3-dimethyl-1,3-butadiene formed in toluene and chlorobenzene.

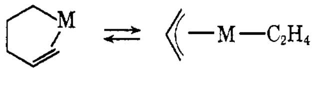
While the above interpretations appear valid for rearrangements conducted in toluene and chlorobenzene, more facile hydrogen transfer and accompanying H–D exchange were observed when **1**-*1*-d_2 was treated with the catalyst in the more polar *o*-dichlorobenzene. The interpretation of results in this case does not appear to be as clear-cut.

Evidence for the Fragmentation Route. A more direct type of evidence for the participation of allylnickel intermediates in the type II rearrangements was provided in the experiments where C-7 dienes were generated from 1,4-diene reactants possessing five and six carbon atoms. The formation of 2-methyl-1,4-hexadiene on treatment of 3-methyl-1,4-pentadiene with the catalyst in the presence of propylene can be explained by the reaction of propylene with a methylallylnickel-ethylene complex, I, generated from 3-methyl-1,4-pentadiene (eq 15). 2-Methyl-1,4-hexadiene was the major diene product afforded on treatment of propylene and 1,3-butadiene with the $(R_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ catalyst system (eq 3b).[12a] The proposed mechanism for this addition reaction involves the generation of a methylallylnickelpropylene complex.[12] The C-7 dienes derived from treatment of 1,4-pentadiene with the catalyst are believed to be formed by reaction of ethylene—generated by fragmentation of 1,4-pentadiene, eq 16—with the conjugated isomers formed from 1,4-pentadiene. The nickel catalyst system has been employed for the synthesis of 3-methyl-1,4-hexadiene and 4-methyl-1,4-hexadiene from reactions of ethylene with 1,3-pentadiene and isoprene, respectively (eq 3a and 2, R = CH_3). We suggest, therefore, that the organometallic intermediates in the type II rearrangement are similar in structure to, or possibly identical with, those which participate in the nickel catalyzed alkene-1,3-diene addition reaction.

$$\underset{\text{I}}{C_4H_7MC_2H_4} \xrightarrow{C_3H_6} C_4H_7MC_3H_6 + C_2H_4 \longrightarrow$$

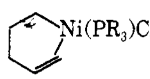


(15)

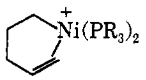


(16)

Driving Force for the Fragmentation. A major difference in the organonickel complexes believed to be generated in the C–C σ bond breaking steps in the type I[14a] and type II rearrangements is the number of coordination sites occupied by the hydrocarbon ligand. Whereas complexes B (Schemes I and II) require the availability of three coordination sites to accommodate the hydrocarbon moieties, the generation of a cyclopropylcarbinylnickel complex[14a]—a process analogous to path b, Schemes I and II—requires only two coordination sites on the metal. The type I rearrangement is catalyzed by the $(R_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ system but can also be accomplished in the absence of an aluminum Lewis acid compound. For instance, conbinations of nickel(0) compounds with HCl,[13] and of nickel(II) complexes with $NaBH_4$,[21] have generated effective catalysts. We have not observed the type II reaction in the absence of a fairly strong Lewis acid such as the alkylaluminum cocatalyst. We propose that the aluminum component plays a more extensive role in catalyst generation in the type II rearrangement and that in addition to its alkylation of the nickel(II) complex,[13] it participates in the creation of additional coordination sites on the nickel. This could be accomplished by complexation with phosphine or halide ligands. Evidence for this role of the aluminum cocatalyst in the alkene-1,3-diene addition reaction has been reported.[12c,d] The most effective Lewis acid species derived from the $(R_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ system would be isobutylaluminum dichloride, the expected aluminum product from alkylation of the Ni(II) complex.[12c,13] We picture the organometallic precursor to the π-allylnickel–alkene intermediate as a coordinatively unsaturated alkenylnickel complex such as i or ii.



i



ii

The driving force for the C–C bond cleavage is the energetic demand of nickel for the creation of an additional electron pair donor ligand. This factor, along with the generation of the delocalized electronic structure of the π-allyl system, would be responsible for the relatively low activation energy of the fragmentation step.

Experimental Section

All experiments involving organometallic catalyst systems were conducted in deoxygenated solvents under a nitrogen atmosphere. Solvents were purified as described previously.[13] Infrared spectra were recorded on a Beckman IR-12 instrument and pmr spectra were recorded on a Varian A-60 spectrometer using neat samples or carbon tetrachloride solutions. Tetramethylsilane was employed as an internal standard. Mass spectra were recorded by Morgan Shaffer Corp., Montreal, Canada, or on a Du Pont 21-491 mass spectrometer in our laboratory.

Product yields from the diene rearrangements were determined by gas–liquid phase chromatography (glpc) as described previously.[13] Diene separations were accomplished by a Varian Aerograph 90-P3 instrument utilizing a 20 ft × 3/8 in. 20% β,β′-oxydipropionitrile on Firebrick 60/80 column. The alkenes were analyzed on a 15 ft × 0.25 in. 20% silicon rubber (SE-30) on Chromosorb P 60–80 column.

Synthesis of 2-Methyl-1,4-pentadiene-*1*-d_2(1-*1*-d_2). (a) **Ethyl 2-Methyl-4-pentenoate.** 2-Methyl-4-pentenoic acid,[22] 35 g (0.31 mol), was added to a flask containing 40 ml of absolute ethanol, 75 ml of dry benzene, and 3 ml of sulfuric acid. The solution was then refluxed for 11 hr under a nitrogen atmosphere at 94–97° and the water was removed by a Dean-Stark trap as it was formed. The mixture was then cooled and was shaken with a 15% aqueous solution of sodium chloride. The organic layer was then washed with an aqueous 10% sodium chloride–10% sodium carbonate solution and then dried over anhydrous magnesium sulfate. Distillation afforded 32.4 g, 75% yield, of ethyl 2-methyl-4-pentenoate: bp 80–82° (71 mm).

The pmr spectrum of the product: multiplet at τ 3.87–4.53 (1 H), multiplets at 4.88 and 5.10 (2 H), quartet at 5.82 (2 H), multiplet at 7.33–8.28 (3 H), and multiplet from 8.68 to 8.92 (6 H). The infrared spectrum showed characteristic peaks at 3090, 1740, 1650, 1000, and 920 cm^{-1}.

(b) **2-Methyl-4-penten-1-ol-*1*-d_2.** Lithium aluminum deuteride, 3.0 g (0.07 mol), was placed in the reaction flask under a nitrogen atmosphere in a glove bag. Anhydrous diethyl ether, 50 ml, was then added to the flask and the mixture was stirred for 5 min. A solution of ethyl 2-methyl-4-pentenoate, 19.1 g (0.135 mol), in 60 ml of anhydrous ether was added to the flask at a rate which maintained a gentle reflux of the ether. An additional 100 ml of ether was then added and the resulting solution was stirred for 1 hr. The excess aluminum deuteride was then destroyed by the careful addition of water. The mixture was then added to 200 ml of 12.5% sulfuric acid and ice. The ether layer was then separated and the aqueous layer was extracted three times with 50-ml portions of ether. The combined ether extracts were washed twice with an aqueous 10% sodium chloride–10% sodium carbonate solution and then dried over magnesium sulfate. The resulting solution was filtered and then distilled to afford 13.7 g, 100% yield, of 2-methyl-1-penten-1-ol-*1*-d_2, bp 114–116° (146 mm). The pmr and infrared spectra of the product were entirely consistent with the structure assignment.

(c) **2-Methyl-4-pentenyl Acetate-*1*-d_2.** The 2-methyl-4-penten-1-ol-*1*-d_2, 13.7 g (0.134 mol), was treated with 100 ml of anhydrous

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[21] L. W. Gosser and G. W. Parshall, *Tetrahedron Lett.*, 2555 (1971).

[22] S. Stallberg-Stenhagen, *Ark. Kemi, Mineral. Geol.*, A23, 1 (1946).

ether and 12 g of pyridine. The resulting solution was cooled to 0° and acetyl chloride, 13.2 g (0.168 mol), was added to the mixture during 20 min under a nitrogen atmosphere. The solution was then warmed to room temperature and stirred for 3 hr. It was then refluxed for an additional 2 hr. The solution was then treated with 50 ml of cold water; the ether layer was washed successively with 100 ml of 10% hydrochloric acid, 100 ml of water, and 100 ml of 10% sodium chloride–10% sodium carbonate solution and then dried over magnesium sulfate. Distillation afforded 19.3 g, 80%, of 2-methyl-4-pentenyl acetate-*1*-d_2: bp 99–102° (111 mm); pmr multiplet at τ 3.95–4.5 (1 H), multiplets centered at 4.88 and 5.10 (2 H), multiplet at 7.77–8.32 (3 H), singlet at 8.03 (3 H), and a doublet at 6.58 (3 H).

(d) **2-Methyl-1,4-pentadiene-*1*-d_2.** The 2-methyl-4-pentenyl acetate-*1*-d_2, 8.3 g (0.098 mol), was pyrolyzed by slowly passing it, in a nitrogen stream, through a 10-in. column of glass ringlets heated to 600°. The nitrogen flow rate was *ca.* 5 l./hr. The product was collected in two traps immersed in Dry Ice–acetone baths. The diene product was separated from the acetic acid by distillation and unreacted ester was recycled. Preparative glpc of the product mixture afforded 1.4 g, 17%, of 2-methyl-1,4-pentadiene-*1*-d_2. Pmr and mass spectra of the product are described in Results.

This entire sequence of reactions was first employed in the synthesis of 2-methyl-1,4-pentadiene and the spectra of each nondeuterio intermediate aided in the characterization of the corresponding dideuterio compound.

Rearrangement of 2-Methyl-1,4-pentadiene-*1*-d_2. The general experimental procedure employed in the diene rearrangement reactions has been described elsewhere.[13] Details of the application of the procedure to the diene reactions in this study are presented here. In each case, the progress of the reaction was monitored by glpc analysis of aliquots which were removed periodically.

(a) **Toluene Solvent.** *trans*-Dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.083 g (0.15 mmol), and **1**-*1*-d_2, 1.7 mmol, in 14 ml of toluene were treated with 0.4 ml of a 25% wt/wt solution of diisobutylaluminum chloride in toluene, 0.50 mmol. The resulting amber solution was stirred for 6.5 hr at 24–26° after which the mixture was treated with 2 ml of 1-butanol. The diene products were distilled from the toluene and each component was collected *via* preparative glpc.

(b) **Chlorobenzene Solvent.** *trans*-Dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.242 g (0.453 mmol), and **1**-*1*-d_2, 0.425 g (5.06 mmol), in 43 ml of chlorobenzene were treated with 1.2 ml of a 25% solution of diisobutylaluminum chloride in toluene, 1.49 mmol. The mixture was stirred for 2 hr at 24–26° after which it was treated with 2 ml of 1-butanol. The products were isolated as in a.

(c) **1,2-Dichlorobenzene Solvent.** The same procedure as in (a) and (b) was employed. The quantities of reactants were: *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.30 g (0.56 mmol), **1**-*1*-d_2, 6.75 mmol, *o*-dichlorobenzene, 55 ml, and 1.6 ml of a 25% solution of diisobutylaluminum chloride in toluene, 1.98 mmol. The reaction was terminated after 1.5 hr at 24–26°.

Analogous experiments employing 2-methyl-1 4-pentadiene were conducted for comparison with the reactions of **1**-*1*-d_2.

Rearrangement of 2,3-Dimethyl-1,4-pentadiene (2). The rearrangement was conducted in toluene, chlorobenzene, and *o*-dichlorobenzene solvents. The following procedure is typical.

trans-Dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.10 g (0.19 mmol), and **2**, 0.22 g (2.26 mmol), in 20 ml of toluene, were treated with 0.54 ml of a 25% solution of diisobutylaluminum in toluene, 0.67 mmol. The mixture was stirred for 5 hr at 24–26° after which it was treated with 2 ml of 1-butanol. The course of the reaction was monitored by the periodic removal and glpc analysis of small aliquots. The 4-methyl-1,4-hexadiene geometric isomer mixture was isolated by distillation from the product mixture, followed by collection *via* preparative glpc. 4-Methyl-1,4-hexadiene was the only 1,4-diene detected in the product mixture and the isomer mixture was identified by comparison of its pmr spectrum with that of an authentic sample.[12a] The major component, which composed >95% of the mixture, exhibited the longer retention time on a β,β'-oxydipropionitrile column. An assignment of the *E* configuration to the internal double bond of the major component was based upon the pmr analyses of the 3-methyl-2-hexenes which were generated from a mixture of the isomeric 4-methyl-1,4-hexadienes using the procedure of Hata.[18] Since larger quantities of a 4-methyl-1,4-hexadiene isomer mixture were available through the reaction of ethylene with isoprene, catalyzed by the $(Bu_3P)_2NiCl_2$/*i*-Bu_2AlCl system, a sample prepared in this manner was used in the analysis. The ratio of the longer:shorter retention time isomer in this sample was 2.6:1.0.

Synthesis of 4-Methyl-1,4-hexadiene (3) and 2,3-Dimethyl-1,4-pentadiene (2) by Addition of Ethylene to Isoprene. *trans*-Dichlorobis(tri-*n*-butylphosphine)nickel(II), 1.09 g (2.05 mmol), was dissolved in 200 ml of chlorobenzene and the resulting solution was purged with nitrogen. The solution was then saturated with ethylene, after which 20 g (300 mmol) of isoprene was added. As ethylene was continuously passed through the solution at 23–25°, 6 ml of a 25% solution of diisobutylaluminum chloride in toluene, 7.45 mmol, was added and the resulting mixture was stirred for 30 min. The mixture was then treated with 5 ml of 1-butanol. Glpc analysis of the crude product mixture indicated that 63% of the isoprene had been converted to products and **2** was afforded in 12% yield, whereas **3** was present in 54% yield. Most of the butenes, afforded by ethylene dimerization,[12a] were then removed by distillation. A fraction boiling at 70–96° on a short column was collected and redistilled on a 36-in. spinning band column affording a fraction, bp 77–82°, which consisted mainly of **2**. A fraction collected at 90–95° was composed of the geometric isomers of **3**. The products were further purified by preparative glpc. The geometric isomers of **3** could not be completely resolved and were collected as a mixture. The (*E*)-**3**:(*Z*)-**3** ratios in product mixtures prepared in this manner were in the 2.4–2.6 range. The pmr spectra of **2** and of the **3** isomer mixture served as an unambiguous identification when compared to those reported previously.[12a]

Reduction of the 4-Methyl-1,4-hexadienes by Diisobutylaluminum Hydride. A mixture of the 4-methyl-1,4-hexadienes, 2.9 g (0.03 mol), prepared as described above, and 5.6 ml (0.033 mol) of diisobutylaluminum hydride was stirred at 70° in a sealed tube for 16 hr. The mixture was then cooled to *ca.* 0° and the tube was opened under a nitrogen atmosphere. Water was carefully added to the mixture until the vigorous reaction ceased. The mixture was then treated with a 12.5% sulfuric acid solution, and then the hydrocarbon layer was separated, washed with water, and then dried over molecular sieves. The 3-methyl-2-hexenes were separated from unreacted 4-methyl-1,4-hexadienes on the β,β'-oxydipropionitrile column after which the individual isomers of 3-methyl-2-hexene were collected from a 15-ft SE-30 on Chromosorb P column, operated at 45° with a helium flow rate of 60 ml/min. The structure assignments were based upon the observation of Bates[23] that the methyl proton resonance in the *cis*-$CH_2C(CH_3){=}CHCH_2$ unit is found at lower field than that in the trans unit and on the extension of this analysis by Hata[18] to the 3-methyl-2-hexenes. The pertinent methyl proton resonance of the major 3-methyl-2-hexene isomer formed in our reduction experiment was at τ 8.43 while the analogous resonance in the minor component was found at τ 8.35, both values being obtained with the aid of spin decoupling. (The literature values for (*E*)- and (*Z*)-3-methyl-2-hexene are reported to be τ 8.40 and 8.33, respectively.[18])

Rearrangement of 4-Methyl-1,4-hexadiene (3). The general procedure for the rearrangement of dienes was followed and 0.479 g (0.71 mmol) of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 0.82 g (8.5 mmol) of a 2.4:1.0 mixture of (*E*)-**3**:(*Z*)-**3**, 2 ml of a 25% solution of diisobutylaluminum chloride, 2.5 mmol, and 70 ml of chlorobenzene solvent were employed. The reaction was terminated after 3 hr at 24–26° by the addition of 2 ml of 1-butanol. The products were separated from the solvent by distillation, after which they were collected *via* preparative glpc. Four isomers of **3** were identified. A product possessing a retention time on the β,β-oxydipropionitrile column which was shorter than that of **3** was shown to be **2** (2% yield) by comparison of its glpc retention time and pmr spectrum with those of an authentic sample. In addition, three of the four possible geometric isomers of 3-methyl-2,4-hexadiene were isolated. Two of these products—the first and third components eluted after **3**—possessed glpc retention times identical with those of the two "minor" products derived from treatment of **2** with the catalyst.

The pmr spectrum of the first component eluted after **3** (8% yield) exhibited a doublet centered at τ 4.23, J = 12.0 Hz (1 H), the low field half of an AB spectrum assigned to the C-4 vinyl proton. The other two vinyl proton resonances consisted of complex multiplets found from τ 4.3 to 5.0. The CH_3 proton resonances consisted of an apparent triplet of peaks (9 H) with a strong center peak at τ 8.28 and with different line separations between the center

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(23) R. B. Bates and D. M. Gales, *J. Amer. Chem. Soc.*, **82**, 5749 (1960).

and outer peaks, the separation between the two outer peaks being *ca.* 11.4 Hz.

The vinyl pmr spectrum of the second product eluted after **3** (10% yield) showed a doublet centered at τ 3.60, J = 15.5 Hz, the low field half of an AB spectrum assigned to the C-4 vinyl proton. The other two vinyl proton resonances consisted of multiplets centered at τ 4.27 and near 4.69. The CH_3 proton resonances appeared as a triplet of peaks (9 H) with the intense center peak at τ 8.26 and with different line separations between the central and outer peaks. The line separation between the two outer peaks was 13.4 Hz.

The vinyl proton spectrum of the third product eluted after **3** (55% yield) consisted of a doublet, low field half of an AB spectrum, centered at τ 3.87, J = 16.0 Hz (C-4 vinyl proton). The other two vinyl proton resonances consisted of multiplets at τ 4.33 and from τ 4.46 to 4.8. The methyl proton resonances consisted of an unresolved multiplet with an intense peak at τ 8.30. The infrared spectrum showed a characteristic peak at 840 cm^{-1}, the C–H out-of-plane deformation vibration associated with the trisubstituted double bond.

Treatment of 3-Methyl-1,4-pentadiene with the Catalyst in the Presence of Propylene. The experiment was conducted in a 1.9-l. stainless steel autoclave which has been described previously.[12a] 3-Methyl-1,4-pentadiene, 41.3 g, which was 99.7% pure by glpc analysis and which was specifically shown to contain no ethylene or butadiene within the glpc detection limits, was placed in 400 ml of toluene which contained 0.534 g (1 mmol) of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II). Propylene, 81 g (99.4% pure by glpc analysis, no butadiene detected), was then distilled into the reactor. The mixture was then warmed to 86° and diisobutylaluminum chloride, 1.2 ml (6 mmol), was added. The mixture was stirred at 86–90° for 19 min, after which the reaction was terminated by addition of 3.0 ml of 2-propanol. Distillation afforded 21 g of recovered 3-methyl-1,4-pentadiene and a second fraction, bp 54–93°, which contained 5.8 g of a mixture of C-6 and C-7 dienes. Glpc analysis of this fraction indicated the following per cent compositions in order of their elution from the glpc column given as component, %: 3-methyl-1,4-pentadiene, 8.4; unknown, 0.7; *trans*-1,4-hexadiene, 12.4; *cis*-1,4-hexadiene, 3.2; unknown eluted after *cis*-1,4-hexadiene, 0.7; 2-methyl-1,4-hexadiene, 32.0; 3-methyl-1,3-pentadienes, 42.6. The 1,4-hexadienes were isolated as a mixture and their identification was confirmed by the infrared and pmr spectra. The sample was contaminated with a small amount of the unknown substance eluted after *cis*-1,4-hexadiene which possessed vinylidene unsaturation. (Subsequent work suggests that this material was *trans*-2-methyl-1,3-pentadiene.) The 2-methyl-1,4-hexadiene was isolated in the same manner and was identified conclusively by comparison of its pmr spectrum and glpc retention time with those of an authentic sample.[12a] The 3-methyl-1,3-pentadienes were collected as a mixture and were identified by their pmr and infrared spectra.

An accurate detemination of the amount of ethylene present in the product mixture could not be determined. Glpc analysis of the recovered propylene showed the presence of a component with a glpc retention time of ethylene in amounts *ca.* 20–30 times that present in the reagent propylene. Butadiene was not detected in the product mixture or in the reagents.

The above experiment was repeated under the same conditions and afforded the same product mixture. The 2-methyl-1,4-hexadiene was isolated in this case also, and was identified by its pmr and infrared spectra.

Treatment of 1,4-Pentadiene with the Catalyst. Five experiments were conducted in which the treatment of 1,4-pentadiene with the nickel catalyst led to the formation of C-7 diene products. The general procedure employed in each case was the same as that described above for the diene rearrangements conducted at atmospheric pressure. The following experiments afforded the highest yields of C-7 products. (a) When 0.354 g (0.667 mmol) of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and 1.9 ml of a 25% solution of diisobutylaluminum chloride, 2.36 mmol, were employed as cocatalysts in 75 ml of toluene at 25° (1,4-pentadiene:Ni ratio = 12), a 44.5% conversion of the diene to products was obtained during 63 min. The yields of diene products afforded were: isoprene, 25%; *cis*-1,3-pentadiene, 2.4%; *trans*-1,3-pentadiene, 6.2%; 3-methyl-1,4-hexadiene (predominantly trans), 13%; 4-methyl-1,4-hexadiene, 3%. (b) Utilizing of 0.187 g (0.350 mmol) of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II), 1.0 ml of a 25% solution of diisobutylaluminum chloride in toluene (1.2 mmol), and 1,4-pentadiene, 0.143 g (2.10 mmol), in 34 ml of toluene at 25° (diene:Ni ratio = 6), 60% of the 1.4-pentadiene was converted to products during 3 hr. The yields of diene products were: isoprene, 30%; 1,3-pentadiene, 6%; 3-methyl-1,4-hexadiene, 30%; 4-methyl-1,4-hexadiene 15%. After 5.5 hr at 78% conversion, the yields were isoprene, 19%; 1,3-pentadiene, 7%; 3-methyl-1,4-hexadiene, 14%; and 4-methyl-1,4-hexadiene, 9%. (c) Utilization of 1.96 g (3.67 mmol) of the nickel compound, 13.8 mmol of diisobutylaluminum chloride, 3.00 g (44 mmol) of 1,4-pentadiene, and 240 ml of toluene gave a 33% conversion of diene to products during 1.5 hr. The yields of isoprene, 1,3-pentadiene and 3-methyl-1,4-hexadiene were 63, 13, and 17%, respectively. During 3.5 hr, 64% conversion, the corresponding yields were 30, 2, and 11%. The yield of 4-methyl-1,4-hexadiene was not determined in this experiment.

The diene products were collected *via* preparative glpc and identified by comparison of their pmr spectra with those of authentic samples.[12a] The relationships between recorder signal areas and sample quantities in the glpc analyses were determined by analysis of a standard mixture and these relationships were used to calculated the yields. The following relative values in mmol/unit area were determined for use in analyses employing 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: 1,4-pentadiene (1.158×10^{-4}); 2-methyl-1,3-butadiene (1.219×10^{-4}); 3-methyl-1,4-hexadiene (1.185×10^{-4}); 4-methyl-1,4-hexadiene (0.989×10^{-4}); *cis*- and *trans*-1,3-pentadiene (1.179×10^{-4}). This essentially 1:1 correspondence of peak areas of equimolar mixtures has been found to be true for other diene product mixtures we have analyzed.[13]

Formation of Hydrogenation Products. A solution of 0.116 g (0.21 mmol) of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and 2.53 mmol of 2-methyl-1,4-pentadiene in 40 ml of toluene was warmed to 50°. A 25% solution of diisobutylaluminum chloride, 0.6 ml, 0.74 mmol, was then added and the mixture was stirred at 50–55° for 6.5 hr, after which 2 ml of 1-butanol was added. The volatile products were separated from the solvent by distillation and were then collected by preparative glpc. The major component of the product mixture (75% conversion) was 2-methyl-1-pentene, 25% yield, identified by comparison of its pmr spectrum with that of an authentic sample.[24] The minor products were 2,3-dimethyl-1,3-butadiene, 1.3% yield, and *trans*-2-methyl-1,3-pentadiene, 4.3% yield.

A similar experiment employing *trans*-1,4-hexadiene in toluene at 85° for 17 min led to the formation of *trans*-2-hexene as the major C-6 product. The product was collected *via* preparative glpc and was identified by comparison of its infrared spectrum with that of an authentic sample.[25]

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(24) C. Agani and S. Combrisson, *Bull. Soc. Chim. Fr.*, 2139 (1968).

(25) API Catalogue, 1955. Spectrum No. 620.