5-1-1973

# A Study of the Nickel Catalyzed Rearrangement of 1,4-Dienes

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# A STUDY OF THE NICKEL CATALYZED REARRANGEMENT OF 1,4-DIENES

by
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Bachelor of Science, Southern University 1966

A Dissertation
Submitted to the Faculty
of the
University of North Dakota
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy

Grand Forks, North Dakota

May
1973

This Dissertation submitted by Harry James Golden in partial fulfillment of the requirements for the Degree of Doctor of Philosophy from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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# ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. Roy G. Miller, Jr. for suggesting the research problem and for his helpful advice, guidance, and support throughout its pursuance. He would also like to express his appreciation to Professors R. G. Severson, R. J. Baltisberger, J. R. Waller, and N. Kulevsky for their help and cooperation. In addition, he would like to acknowledge the encouragement of his family. The author would also like to extend thanks to Mrs. M. A. Garay who typed this dissertation.

The author is grateful to the National Science Foundation for traineeships (1967-1969) and Graduate Teaching Assistantships which were provided through the UND Chemistry Dept. Acknowledgement is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research through grants to Dr. Miller.

Finally, he would like to thank his fellow graduate students, who contributed to this work with helpful suggestions. Special thanks are due to Dr. Richard Stauffer who, while working on a similar project, supplied many helpful suggestions.

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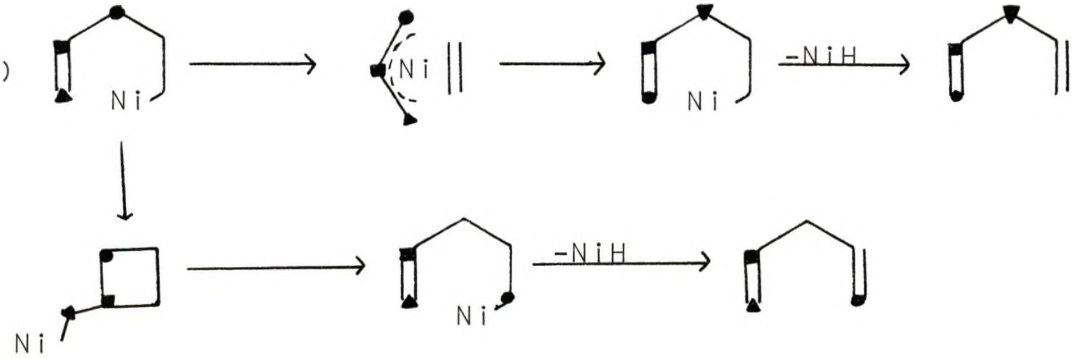
# ABSTRACT

Two types of rearrangement are afforded by the reaction of 1,4-dienes with a catalyst formed from trans-dichlorobis(tri-n-butylphosphine)Ni(II) and diisobutylaluminum chloride. Type I is exemplified by the rearrangement of 1,4-pentadiene to 2-methyl-1,3-butadiene. Type II is exemplified by the rearrangement of 3-methyl-1,4-pentadiene to 1,4-hexadienes. The catalyst is thought to be a nickel hydride or its chemical equivalent.

This study was primarily concerned with the type II rearrangement. Two possible routes for the type II rearrangement were considered. (1) A 1,2-nickel hydride addition to the terminal unsubstituted double bond of the diene followed by β-elimination of ethylene to form a π-allylnickel(II)ethylene complex (fragmentation) which could reform to afford products. (2) A 1,2-nickel hydride addition to the diene followed by cyclization to form a cyclobutylcarbinylnickel(II) species which could then rearrange to form products (equation 1).

(1)

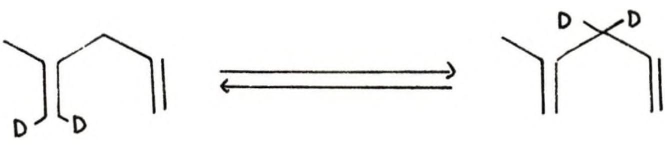


1,1-Dideutero-2-methyl-1,4-pentadiene was prepared by the pyrolysis of 1,1-dideutero-2-methyl-4-pentenylacetate. The main precursor of the acetate was 2-methyl-4-pentenoic acid which was prepared by the reaction of allyl chloride with diethylmethyl malonate. The resulting diester was hydrolyzed and decarboxylated by heating it at low pressures. 2-Methyl-4-pentenoic acid was esterified with ethanol and reduced with lithium aluminum deuteride to form 2-methyl-4-pentenol-1-$D_2$. The acetate was formed by treating the alcohol with acetyl chloride.

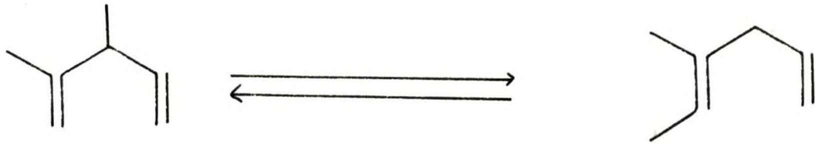
2,3-Dimethyl-1,4-pentadiene was prepared by codimerizing ethylene and 2-methyl-1,3-butadiene with the nickel catalyst formed from _trans_-dichlorobis(tri-n-butylphosphine)Ni(II) and diisobutylaluminum chloride.

1,1-Dideutero-2-methyl-1,4-pentadiene when treated with the nickel catalyst resulted in the reappearance of hydrogen at C-1 as indicated by the pmr spectrum of recovered dideutero-2-methyl-1,4-pentadienes. The pmr spectrum was consistent with the presence of 3,3-dideutero-2-methyl-1,4-pentadiene in recovered unisomerized diene (equation 2).

(2)



The rearrangement of 2,3-dimethyl-1,4-pentadiene with the catalyst resulted in the formation of (4E)-4-methyl-1,4-hexadiene as the only isomeric 1,4-diene product (equation 3).

(3) 

The type II rearrangement of 1,1-dideutero-2-methyl-1,4-pentadiene and 2,3-dimethyl-1,4-pentadiene were consistent with the fragmentation route.

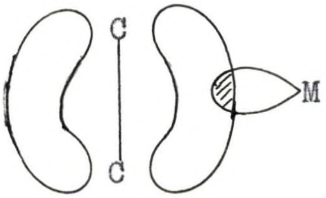
Polar solvents increase the rate of conversion of 1,4-dienes to isomeric products.

It was also possible to generate the nickel catalyst by different methods. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II), 1, in tetrachloroethylene resulted in the formation of trans-chloro(trichlorovinyl)bis(triethylphosphine)Ni(II), 2, and indene as major products. One of the minor products was trans-chloro(2-propenylphenyl)bis(triethylphosphine)Ni(II), 3. The main product during the thermolysis of 1 in benzene was 3. Allylbenzene was isomerized to trans-1-phenyl-1-propene and cis-1,4-hexadiene was rearranged to trans-2-methyl-1,3-pentadiene when present during the thermolysis of 1 in benzene. The catalyst formed during the thermolysis of 1 was not a nickel(0) complex since ethylenebis(triphenylphosphine)Ni(0) did not isomerize allylbenzene without the addition of HCl.

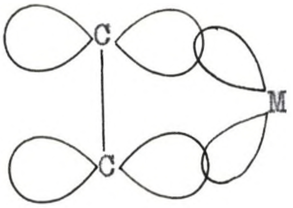
# PART I. INTRODUCTION

The field of organometallic transition metal chemistry has grown rapidly since the report of the first organotransition metal complex in 1830, $K^+ [PtCl_3C_2H_4]^- \cdot H_2O$[1], known as Zeise's salt. The major impetus occurred in the 1950's with the discovery of Reppe's oligomerization catalyst[2] and the Zeigler-Natta[3,4] catalysts for the polymerization of olefins. These practical applications illustrated the potential uses of related soluble complexes as homogenous catalysts. The discovery of bis(cyclopentadienyl)iron(II)[5,6] in 1951 also created considerable interest when it was discovered that this stable compound was actually a sandwich of the iron atom between two cyclopentadienyl molecules which were found to be π-bonded rather than σ-bonded. The compound was named ferrocene because it undergoes reactions typical of benzene.

The current molecular orbital description[7,8] of bonding in metal to olefin complexes consists of two parts: (a) overlap of the π-electron density of the olefin with a σ-type acceptor orbital on the metal atom; (b) a backbond resulting from the flow of electron density from a filled metal d orbital into antibonding π-orbitals on the carbon atoms.



**a**

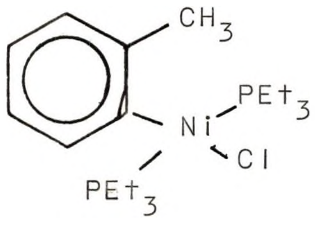


**b**

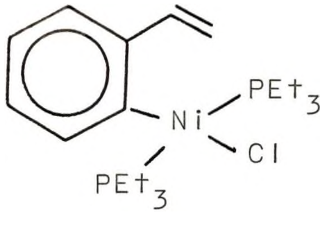
The polarity of the donor bond is thus $R^{+}$—$M^{-}$, whereas in the backbond it is in the opposite direction so that these modes of donor bonding reinforce each other electrostatically and can lead to electroneutrality.

The x-ray structure[9, 10] of Zeise's salt has been determined and shows that the C-C bond is perpendicular to the bonding plane. This orientation would allow backbonding with the $d_{xz}$ or $d_{yz}$ orbitals. However nmr studies of ethylene-Rh complexes[11, 12] show that the barrier to rotation in coordinated complexes is usually small and the ethylene in Zeise's salt[13] has been shown to oscillate. When the C-C bond is in the bonding plane, backbonding can occur with the $d_{xy}$ orbital.

The inability to undergo backbonding may be the reason that localized alkyl C-M σ-bonds are relatively unstable. However, Chatt and Shaw[14] were able to synthesize a series of stable ortho substituted aryl nickel complexes containing a Ni-C σ-bond which were stable in solution or when exposed to air. One example was trans-chloro (2-methylphenyl) bis-(triethylphosphine) nickel(II), 1.



1



2

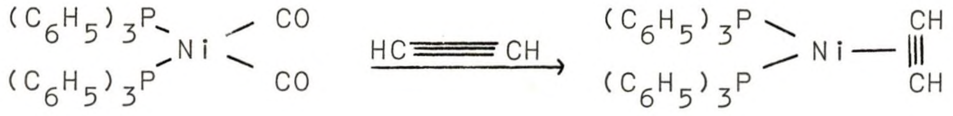
The stability of such complexes was attributed to several factors: (1) the ortho substituent prevents rotation about the Ni-C bond because of interference by the bulky tertiary phosphines on each side of the nickel atom. This allows backbonding of aromatic antibonding $\pi$-orbitals with the filled $d_{xy}$ orbital of the nickel atom. This bonding could cause an increase in the energy difference of the $d_{xy}$ and $d_{x^2-y^2}$ orbitals by lowering the energy level of the $d_{xy}$ orbital;[14, 15] (2) the ortho substituent protects one of the octahedral positions of the nickel atom by shielding it from attack by other reagents. That the ortho substituent was held above the nickel atom was shown by the low field shift of the protons on the ortho substituent in ortho-styrylnickel complexes such as <u>2</u> when compared to styrene.[16]

Coordination of olefins with transition metal complexes can usually be studied by observing the change in the C=C stretching frequency in the infrared or raman. The C=C stretching frequency of $K^+ [C_3H_6PtCl_3]^- \cdot H_2O$ and was $(C_3H_6PtCl_2)_2$ showed strong absorption at 1504 $cm^{-1}$ which was 143 $cm^{-1}$ lower than observed in uncoordinated propylene. Silver complexes[17] of trans-2-butene showed that the C=C stretching frequency was lowered by about 65 $cm^{-1}$ than in free trans-2-butene. Palladium complexes[18] of 1,5-hexadiene showed that the C=C stretching frequency was 118 $cm^{-1}$ lower than in free diene. The much greater lowering of the stretching frequency in Pt complexes compared with those of Ag was attributed to olefins being coordinated more strongly to Pt.[7] A similar trend was noted in (acrylonitrile)$_2$nickel and (acrolein)$_2$nickel. Acrolein complexes were less stable than their acrylonitrile analogs. The C=C stretching frequency in (acrolein)$_2$nickel[19,20,21] was only slightly lower than in free acrolein whereas in (acrylonitrile)$_2$nickel[19,20,22] the C=C stretching frequency was 164 cm$^{-1}$ lower than in free acrylonitrile. The C=C stretching frequency in (acrolein)$_2$nickel was lowered by 157 cm$^{-1}$ indicating that coordination may be occurring through the carbonyl functional group.

Olefin coordination is one of the processes necessary in the reaction of olefins catalyzed by transition metal complexes. Oxidation addition and *cis*-ligand addition or insertion are other processes which are also important.

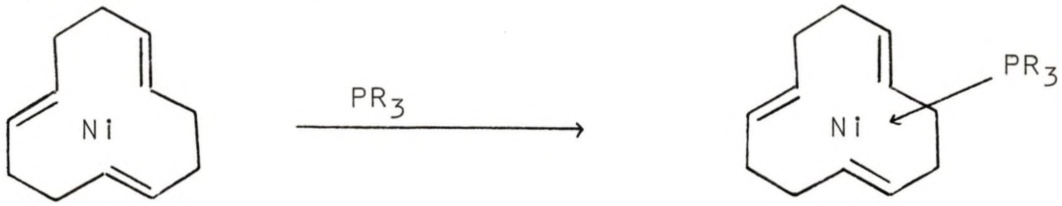
For olefin coordination to occur, there must be a vacant coordination site available. For this reason, a vacant coordination site has been called the single most important property of a homogeneous catalyst.[23] If the coordination site is not available, it may become available by several methods. (1) Ligand dissociation may occur. Induction periods,[24] and the requirement of thermal[25,26] or photochemical stimulation[27] may be indications that the active site is formed by expelling ligands. $NiL_4$ (L is phosphine or phosphite) solutions are known to dissociate.[28,29] (2) The vacant coordination site may become available by displacement of other ligands. The preliminary step in the trimerization of acetylenes may be the formation of a π-complex by displacement of carbonyl ligands[30] (equation 1).

(1)

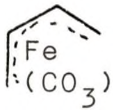


(3) The metal may increase its coordination number. Cyclododecatrienenickel(0) was stabilized by forming a 1:1 adduct with tertiary phosphines[31] (equation 2). This stabilizing effect was thought to be due to bonding of the filled $d_{xy}$ orbital of the nickel atom with the empty $d_{xy}$ orbital of the phosphorus atoms.

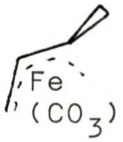
(2)



Although alkenes and unconjugated dienes usually form π-complexes with transition metals, conjugated dienes may also form π-allyl complexes. One of the first examples of such a complex was formed in 1930 by treating pentacarbonyliron(0) with butadiene.[32] The product at first was thought to contain two Fe-C σ-bonds at C-1 and C-4. Reinvestigation[33,34] has shown it to be a π-allyliron complex with a *syn* structure.



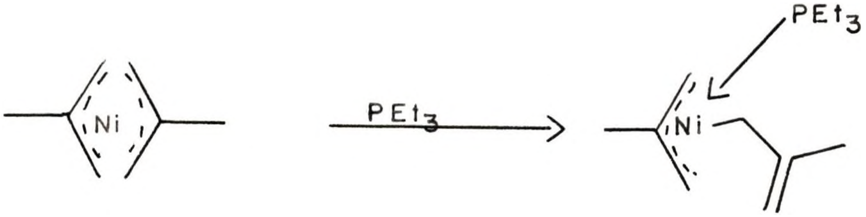
*anti*



*syn*

The bonds in π-allyls were intermediate between a σ-bond and a π-bond. Two ligand positions were occupied in the coordination complexes. The stability of π-allyl nickel compounds as compared to the unstable compounds with localized C-metal σ-bonds may be due to the π-bond character. Nickel π-allyls, of which many are now known, have recently been reviewed by Wilke.[35] One of the more interesting π-allyl compounds covered in the review was bis-(methylallyl) nickel(II) which forms a stable 1:1 adduct with triethylphosphine. The adduct contained both a σ-allyl and a π-allyl [36](equation 3).

(3)

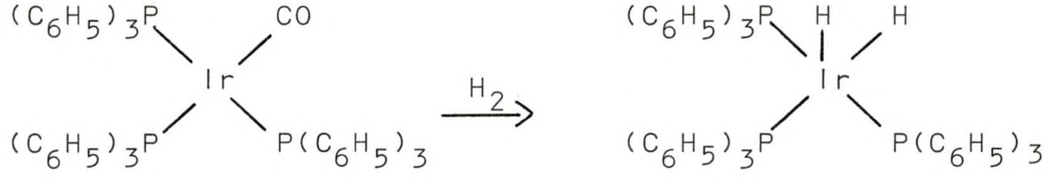


The oxidation number and the coordination number of a metal ion may be increased by insertion into a bond A-B (equation 4).

$$(4) \quad M^{v} + A{-}B \longrightarrow A{-}M^{v+2}{-}B$$

Attention was drawn to these addition reactions by Vaska's[37] discovery of a planar iridium complex, 3, which underwent a number of oxidative addition reactions ($d^8$ to $d^6$) which may be conveniently followed by the shift in the infrared band of the carbonyl ligand (equation 5).

(5)



3

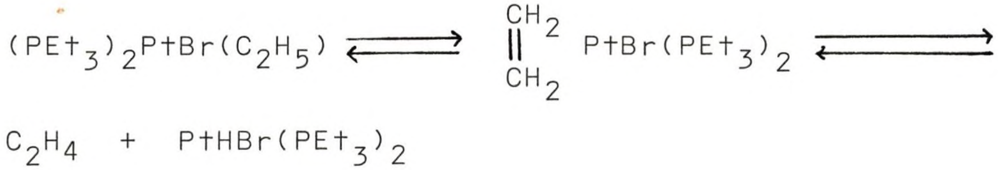
This reaction[38-40] had recently been used to prepare stable organonickel complexes containing localized Ni-C σ-bonds. Ethylenebis(triethylphosphine)Ni(0) formed *in situ* oxidatively ($d^{10}$ to $d^8$) added to tetrachloroethylene to form *trans*-chloro(trichlorovinyl)bis(triethylphosphine)Ni(II). Oxidative addition reactions have been the subject of several excellent reviews and will not be covered further here.[41-43]

Metal hydrides were thought to be intermediates in the isomerization of olefins,[44-50] dimerization of olefins,[51] codimerization of olefins and diolefins,[52-61] skeletal isomerization of diolefins,[62-65] hydrosylation of olefins,[66-68] and hydrogenation of olefins.[69-72] The most pertinent oxidative addition reactions to this study were those involving transition metals with hydrogen and strong acids.

Oxidative addition reactions were not the only method of producing metal hydrides. A variety of reducing agents have been used.[53,73-76] However, the stable hydrides were not very good catalysts and the hydrides which were good homogeneous catalyst systems were not very stable. The elements nickel and platinum illustrated this point very well. Platinum hydrides were stable but were not very good catalysts since high temperatures were usually necessary to activate them. Most nickel hydrides were unstable and must be used *in situ* under anaerobic conditions. Recently, several stable nickel hydrides have been synthesized.[74,75] These complexes were very unreactive however, and could not be used as homogeneous catalysts.

The reactions of metal hydrides must therefore be studied by indirect methods. *cis*-Ligand addition or insertion of platinum hydride and ethylene have been studied.[76-78] Ethylene reversibly added to *trans*-[$PtHBr(PEt_3)_2$], *4*. Studies with *trans*-[$Pt(CD_2CH_3)Br(PEt_3)_2$] showed that either the methylene or methyl of the ethyl was capable of supplying the hydride (equation 6). Recovered platinum hydride contained deuterium (PtH/PtD = 2.3/1).

(6)



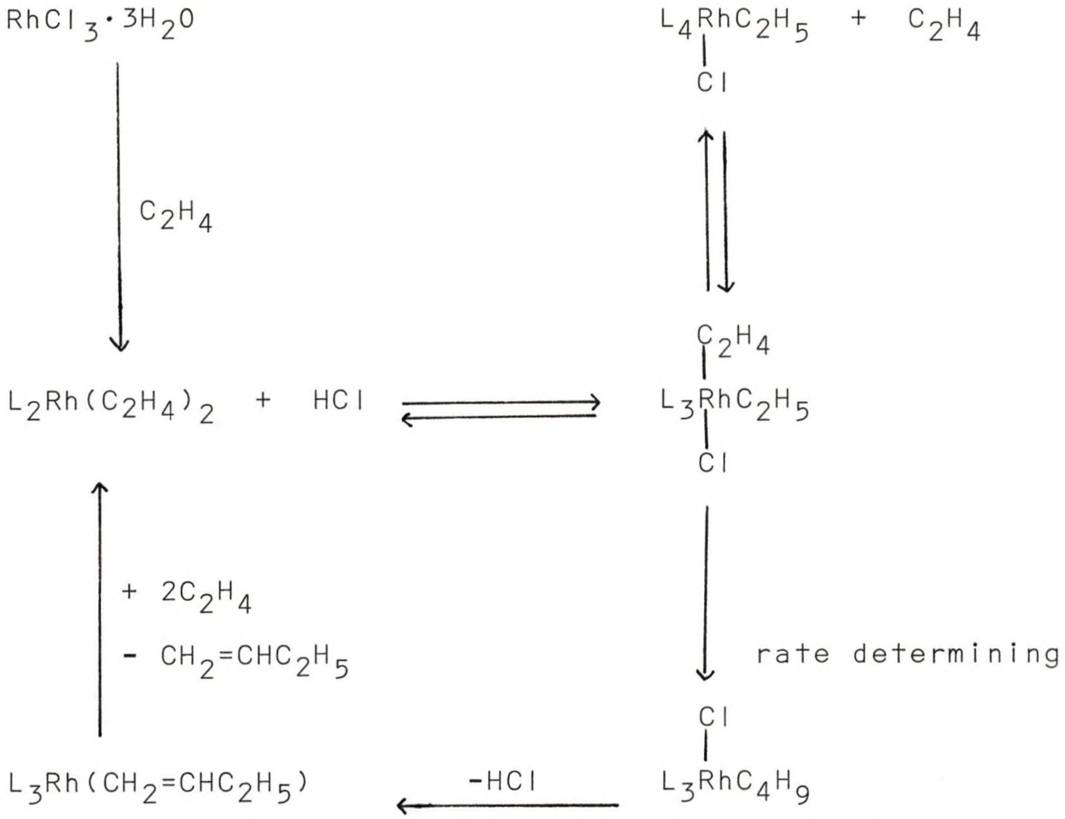
$$(PEt_3)_2PtBr(C_2H_5) \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} PtBr(PEt_3)_2 \rightleftharpoons C_2H_4 + PtHBr(PEt_3)_2$$

*4*

Propylene also reacted with 4 via a 1,2-platinum hydride addition to form the n-propyl complex. This was verified by the observation that treatment of the n-propyl complex with HCl resulted in only $CH_3CH_2CH_2D$.

The addition of HCl to π-cyclopentadienylbis(ethylene)-rhodium(I) at -80°C occurred rapidly to form a π-cyclopentadienylethylethylenerhodium(III)chloride.[51] The reaction was rapid and reversible. Use of HCl resulted in extensive deuteration of added ethylene. Raising the temperature to 10°C resulted in insertion of coordinated ethylene into the $RhC_2H_5$ bond to form a $RhC_4H_6$ complex. Insertion of ethylene into the $RhC_2H_5$ bond was the rate determining step in the dimerization of ethylene (Scheme I; L = acetylacetone).

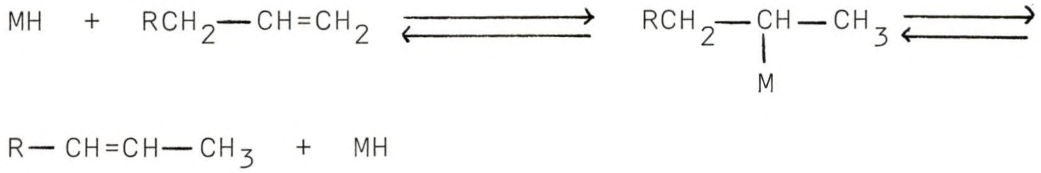
The 1-butene initially formed in the above reaction was 70% isomerized to 2-butene. This appeared to be caused by competition between kinetic and thermodynamic control. Isomerization was much faster than dimerization so the 1-butene would be expected to isomerize as it was formed. However, coordination of substrate for dimerization (ethylene) was favored by a factor of 1000 over the isomerization substrate (1-butene), so thermodynamics favored dimerization.



Scheme I. --Dimerization of ethylene to butenes.

The isomerization of 1-butene to 2-butenes indicated that the rhodium hydride was also capable of isomerizing alkenes. A variety of other transition metals are capable of producing homogeneous catalysts which isomerize alkenes. The majority of these catalysts were thought to cause isomerization via a metal hydride (equation 7).

(7)

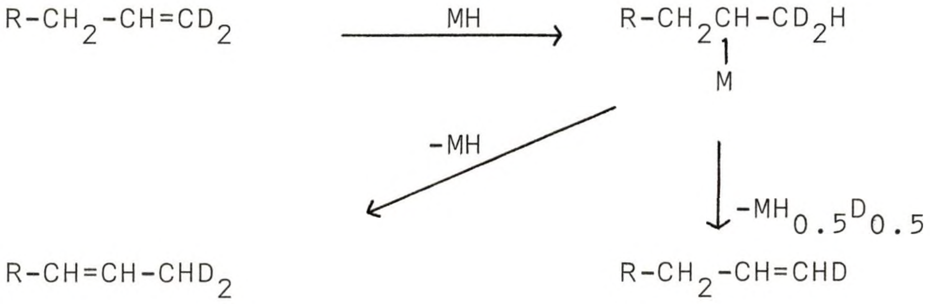


$$MH + RCH_2{-}CH{=}CH_2 \rightleftarrows RCH_2{-}\underset{\displaystyle M}{\underset{|}{CH}}{-}CH_3 \rightleftarrows R{-}CH{=}CH{-}CH_3 + MH$$

Supporting evidence included the following: (1) isomerizations carried out in deuterated solvents resulted in deuterium being incorporated into the products; (2) alkenes deuterated in allylic positions of terminal olefins resulted in deuterium being incorporated in the vinylic positions; (3) the metal hydrides were mild reducing agents which were capable of reducing dienes to monoalkenes;[69] (4) hydrogenations carried out using platinum hydrides usually resulted in the isomerization of unconjugated dienes to conjugated dienes before hydrogenation occurred;[79] and (5) only olefin isomerization occurred with the platinum hydride under low hydrogen pressure.[80]

Treatment of terminal alkenes, deuterated in vinylic positions, with the Rh catalyst resulted in scrambling of deuterium which could not be explained adequately employing a mechanism involving simple metal hydride addition-elimination. However, when a 2,1-metal hydride addition and 2,1-metal deuteride elimination was taken into account, the results were consistent with a metal hydride catalyst[24] (equation 8). It was also used to account for the isomeriz-

(8)

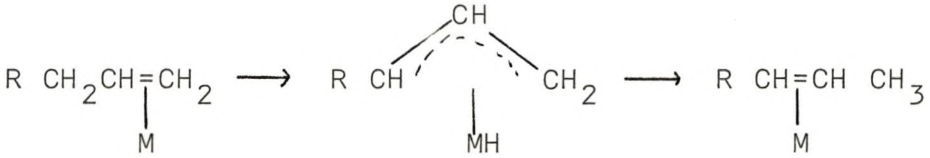


$$\begin{tikzcd} R\text{-}CH_2\text{-}CH{=}CD_2 \arrow[r, "MH"] & R\text{-}CH_2\underset{\underset{M}{|}}{CH}\text{-}CD_2H \arrow[dl, "-MH"'] \arrow[d, "-MH_{0.5}D_{0.5}"] \\ R\text{-}CH{=}CH\text{-}CHD_2 & R\text{-}CH_2\text{-}CH{=}CHD \end{tikzcd}$$

ation of 1-butene in a deuterated solvent using a rhodium hydride catalyst which resulted in extensively deuterated 1-butene but only partially deuterated 2-butene.[48]

Cobalt and palladium homogeneous catalysts appear to isomerize alkenes via an intramolecular π-allyl metal hydride (equation 9).

(9)

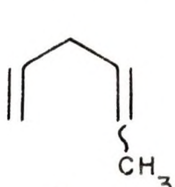


$$R\ CH_2\underset{\substack{|\\ M}}{CH}{=}CH_2 \longrightarrow R\ CH\overset{CH}{\underset{\substack{|\\ MH}}{\cdots}}CH_2 \longrightarrow R\ \underset{\substack{|\\ M}}{CH}{=}CH\ CH_3$$

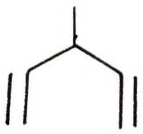
The results, however, were not entirely consistent with this mechanism. The isomerization of 3,3-dideutero-1-octene using a palladium catalyst[81,82] produced very little of the expected 1,3-dideutero-2-octene. The isomerization of 1-octene in deuterated solvents resulted in no deuterium incorporation in any of the products.[81] The isomerization of deuterated terminal olefins in both vinylic and allyic positions resulted in products containing scrambled deuterium which was markedly different from the same products produced using a metal hydride catalyst.[46] Treatment of allylbenzene with $DCo(CO)_4$[70] resulted in only a small amount of deuterium being incorporated in the <u>trans</u>-1-phenyl-1-propene produced.

Extensive deuteration occurred in the minor product propylbenzene however. $HCo(CO)_4$ will also reduce butadiene to butenes[69] and stable alkylcobalt compounds are also produced using cobalt carbonyls.[83]

One of the more interesting reactions is the codimerization of 1,3-dienes and ethylene. The codimerization has been carried out using homogeneous catalysts formed from Rh[52,61] Ni,[28,31,53] Fe,[54-56,84-87] Co,[57-59,88-92] and Pd[93]. Most of the work has been carried out using butadiene to produce 1,4-hexadiene. Except for one of the cobalt catalyst systems,[88] codimerization of ethylene and butadiene resulted in the formation of *cis* or *trans*-1,4-hexadiene, 5, as the major product. Minor products included 3-methyl-1,4-pentadiene, 6, 2,4-hexadiene, 7, and 1,3-hexadiene, 8.



5



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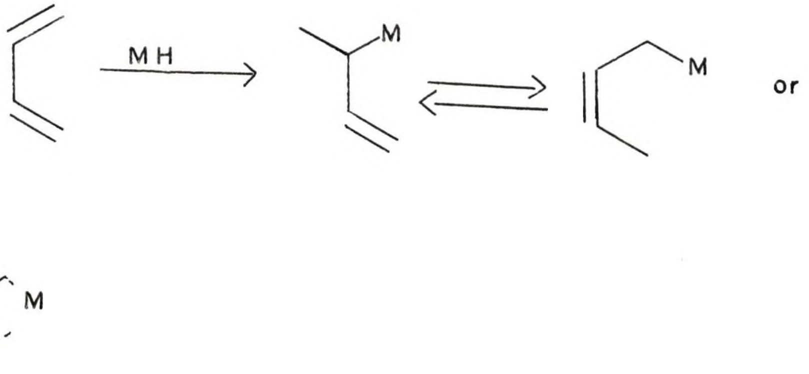
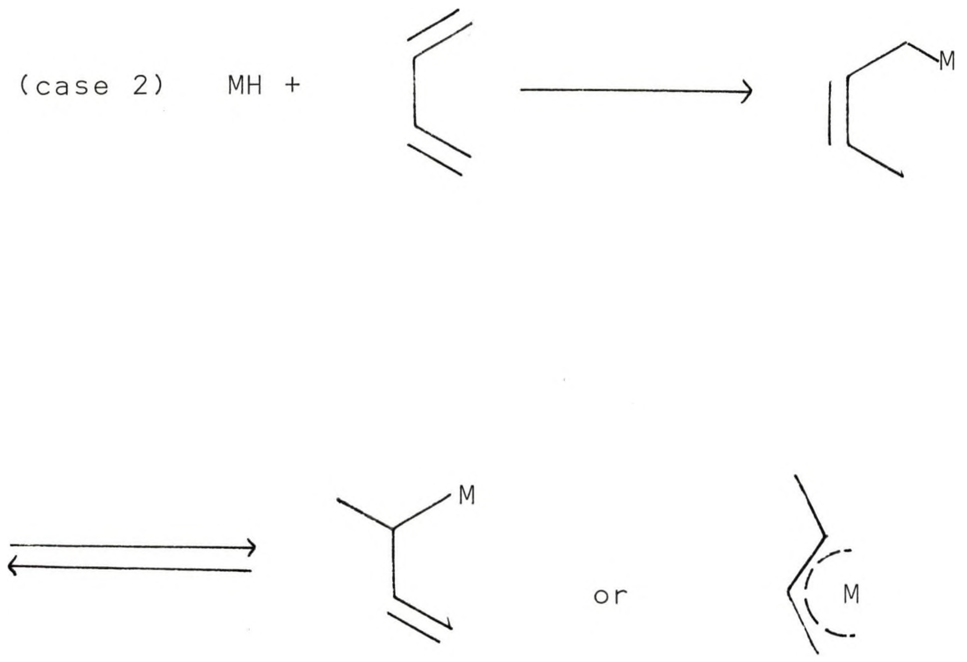
8

The catalyst was thought to be a metal hydride or some system capable of transferring hydrogen. Aluminum alkyls are quite often used as cocatalysts. These are thought to function as reducing agents in the formation of metal hydrides. Studies with dichlorobis(diphenylphosphino)ethane cobalt(II), 9, and hydrido bis(diphenylphosphino)ethane cobalt(I), 10, showed that triethylaluminum was the more effective catalyst for **9** and diethylaluminum chloride was more effective with **10**.[57] If the diene contained a substituted or an internal double bond, addition occurred to the unsubstituted end. The catalyst formed from iron(II)acetylacetonate and triethylaluminum[84,85] however, formed products by addition of ethylene to either end of the diene. Studies with nickel(II)acetylacetonate and aluminum alkyls indicated that the more probable catalyst was also a metal hydride.[94] The iron catalyst[84,85] was also stereospecific in that only *cis*-1,4-dienes were produced. Rhodium and nickel catalysts produced predominately *trans*-1,4-dienes.

The first step in the codimerization was generally believed to be the reaction of the catalyst with the 1,3-diene to form either a π-allyl or σ-allyl metal complex. Addition of metal hydride to 1,3-dienes was thought to occur in either of two manners: (1) 2,1-metal hydride addition to form the π-allyl or equilibrating σ-allyls (equation 8); or (2) 1,4-addition of metal hydride via Markonikoff's rule to form the π-allyl or rapidly equilibrating σ-allyl metal complexes.

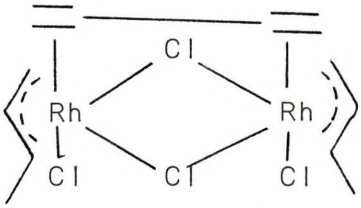
(Case I)





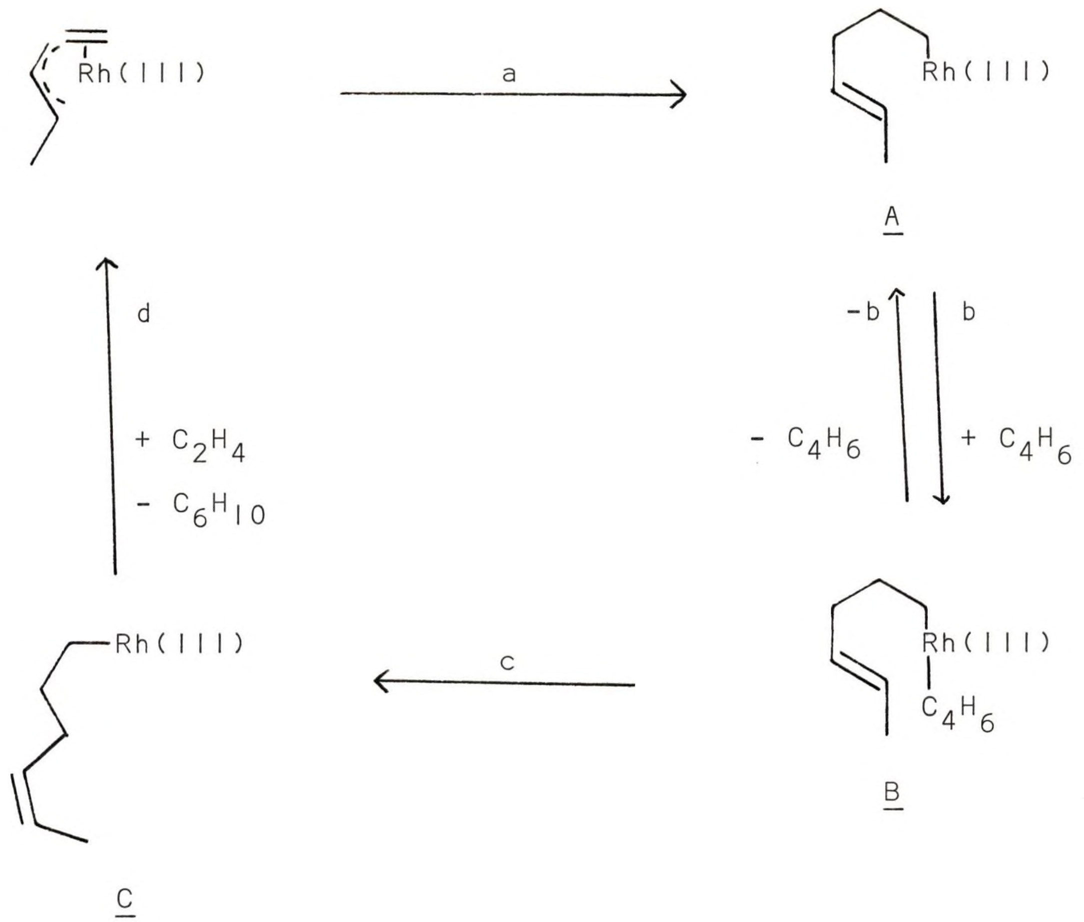
In case (1), insertion of ethylene into the M-C bond to form a 4-hexenylmetal chelate was thought to be followed by β-elimination of metal hydride to form the 1,4-diene. In case (2), addition of ethylene was postulated to proceed by addition of a hydrogen atom to form a coordinated ethylene complex with the simultaneous addition of the residual ethylene molecule and expulsion of the catalyst.

The only catalyst in which the codimerization has been extensively studied is the one involving rhodium hydride. Bis(ethylene)Rh(I) compounds react with HCl to produce the intermediate $[C_2H_5Rh(III)Cl_3s_2]^-$ (s = solvent) from which ethylene may be displaced by an excess of butadiene to give the stable π-crotylrhodium(III) complex, II.[61] This compound which has been independently synthesized[95-96] has been well characterized using both chemical and physical means.



II

That II is the intermediate formed from the RhH catalyst was indicated by the observation that addition of ethylene to II which was sparingly soluble in methanol resulted in it being rapidly dissolved with 2.4 moles of ethylene being absorbed. Further absorption of ethylene did not occur. Analysis showed that the products were 5 and 7. Thus ethylene rapidly displaced the π-bonded butadienes as expected and insertion of ethylene was not rate determining. Kinetic studies showed that release of 5 was the rate determining step. One reason may be due to the stability of chelate B. Other examples of such stable chelates similar to B are known.[87,97-102] Another reason may be due to the higher stability of A when compared to localized σ-alkylmetal complexes.



Scheme 2. --Codimerization of ethylene and butadiene.

Five processes appear to occur in the reaction of alkenes with homogeneous transition metal catalysts.[103] These are: (1) C-H bond formation; (2) C-H bond cleavage; (3) C=C π-bond cleavage; (4) C=C π-bond formation; and (5) C-C σ-bond formation. A sixth process, C-C σ-bond cleavage has been reported with a nickel catalyst.[62] The nickel catalyst skeletally rearranged <u>cis</u>-1,4-hexadiene to <u>trans</u>-2-methyl-1,3-pentadiene and 3-methyl-1,4-pentadiene to 1,4-hexadienes.

Several other examples of skeletal rearrangement via σ-bond cleavage are known. These usually involve the reaction of strained hydrocarbons. Katz[104] and Hogeveen[105] were able to rearrange exo-tricyclo [3.2.1.$0^{2,4}$] octene to a variety of products using a rhodium catalyst. The isomerization of cubane to syn-tricyclooctadiene with a rhodium catalyst is another example of rearrangement occurring via C-C σ-bond fission.[106] The olefin disproportionation reaction[107-110] is also another example of skeletal rearrangement of olefins (equation 10).

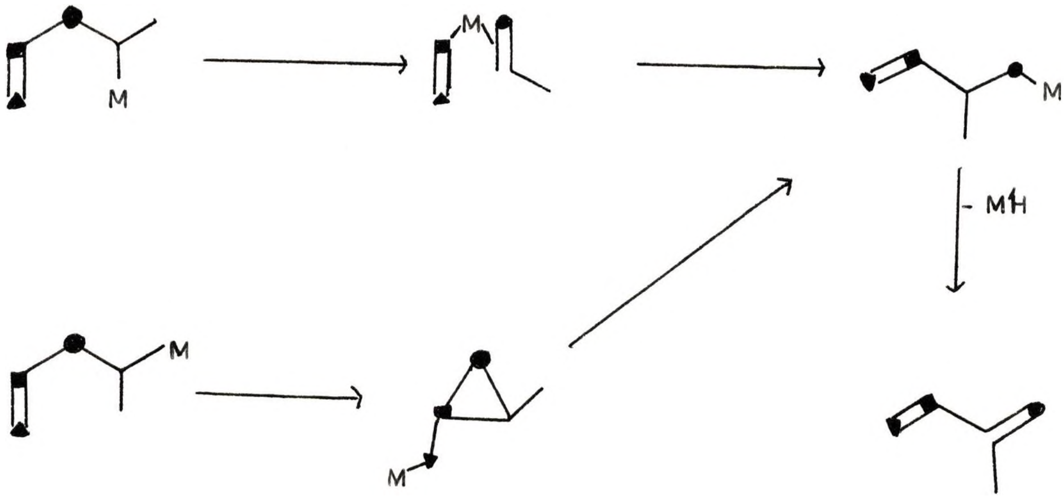
$$(10)\quad RCH{=}CHR' \longrightarrow RCH{=}CHR \;+\; R'CH{=}CHR'$$

The nickel catalyst is the only one capable of dimerizing 1-olefins, isomerizing 1-olefins, codimerizing 1-olefins and 1,3-dienes, and skeletally rearranging 1,4-dienes.

Two types of skeletal rearrangement are afforded by the nickel catalyst.[63] Type I is exemplified by rearrangement of 1,4-pentadiene to 2-methyl-1,3-butadiene. Type II is exemplified by rearrangement of 3-methyl-1,4-pentadiene to 1,4-hexadienes.

The catalyst which is formed by the reaction of dichlorobis(triethylphosphine)nickel(II) and diisobutylaluminum chloride is thought to be a nickel hydride or its chemical equivalent.

Two routes[63,111] were suggested as mechanistic possibilities for the type I rearrangement. A 2,1-metal hydride addition to form an allylcarbinylmetal complex was thought to be a preliminary step in both. For the first fragmentation of the hydrocarbon occurs. Alternatively, a 2,1-metal hydride addition is followed by cyclization to produce a cyclopropylcarbinylnickel species followed by rearrangement to form the products (Scheme 3).

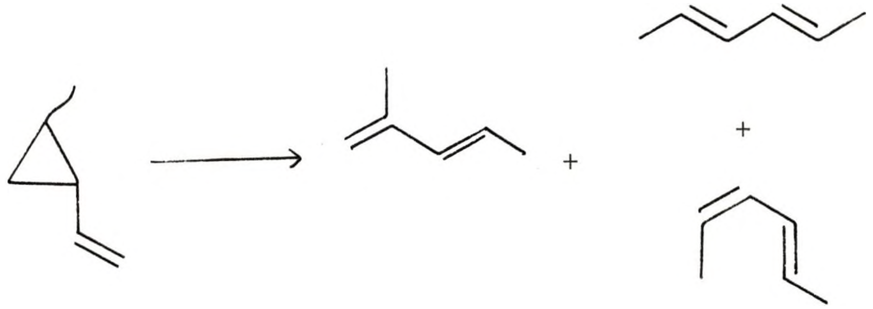


Scheme 3. --Possible routes for the type I rearrangement.

The catalyst in both routes is regenerated by β-elimination of nickel hydride to form the diene product. Several examples of β-elimination of metal hydride to form alkenes have already been discussed.

Treatment of methylvinylcyclopropanes[112] with the nickel catalyst resulted in the formation of trans-2-methyl-1,3-pentadiene as the major product and trans,trans-2,4-hexadiene and cis,trans-2,4-hexadiene as minor products (equation 11). These products possessed the same carbon skeletons in similar proportions as those formed when cis-1,4-hexadiene was treated with the nickel catalyst.

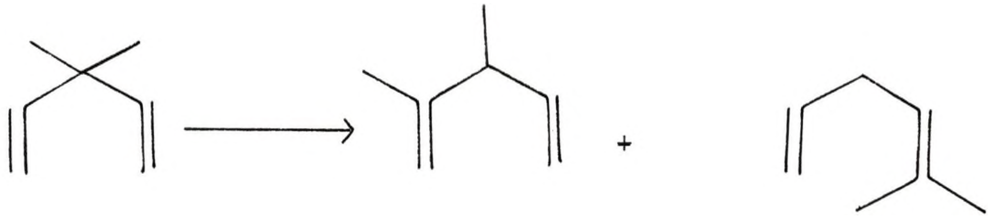
(11)



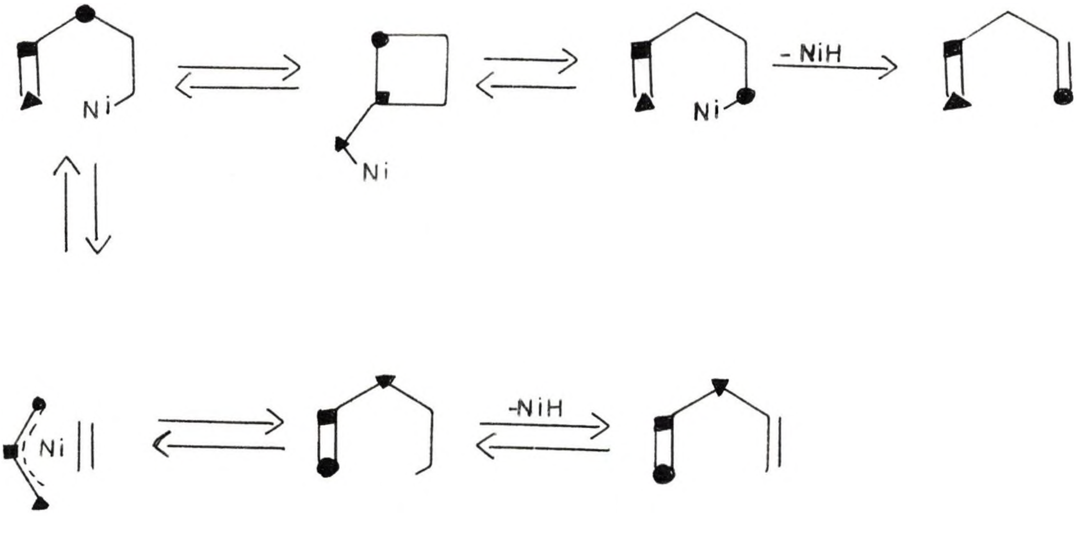
The type I rearrangement was also studied[63,111] using deuterated cis-1,4-hexadienes. The deuterated trans-2-methyl-1,3-pentadienes formed were also consistent with the cyclopropylcarbinylnickel route. Allylcarbinyl complexes of other metals were thought to rearrange via the cyclopropylcarbinyl route. Grignards formed from allylcarbinyl chlorides such as 4-chloro-1-pentene resulted in a mixture of 1-pentenyl-4-magnesium chloride and 3-methyl-1-butenyl-4-magnesium chloride.[113] Cyclopropylchloromethane when treated with magnesium afforded 1-butene from the hydrolyzed solution.[114] Cyclopropane derivatives have also been isolated from some substituted 4-chloro-1-butenes.[115]

Substitution and stereochemistry apparently affected both the rate and the reaction pathway of the 1,4-dienes. Although _cis_-1,4-hexadiene rapidly rearranged via the type I rearrangement, _trans_-1,4-hexadiene only underwent double bond migration.[62] The rearrangement of _cis_-1,4-hexadiene was as rapid as that of 1,4-pentadiene but the rearrangement of 2-methyl-1,4-pentadiene to 2,3-dimethyl-1,3-butadiene and _trans_-2-methyl-1,3-pentadiene was considerably slower. 3-Methyl-1,4-pentadiene may undergo both the type I and type II rearrangements. However, only the type II rearrangement would generate a new carbon skeleton. Thus, the type I rearrangement could not be detected during the transformation. The rearrangement of 3,3-dimethyl-1,4-pentadiene produced distinct products by both the type I and type II rearrangements. It formed 2,3-dimethyl-1,4-pentadiene by the type I rearrangement and 5-methyl-1,4-hexadiene by the type II rearrangement (equation 12).

(12)



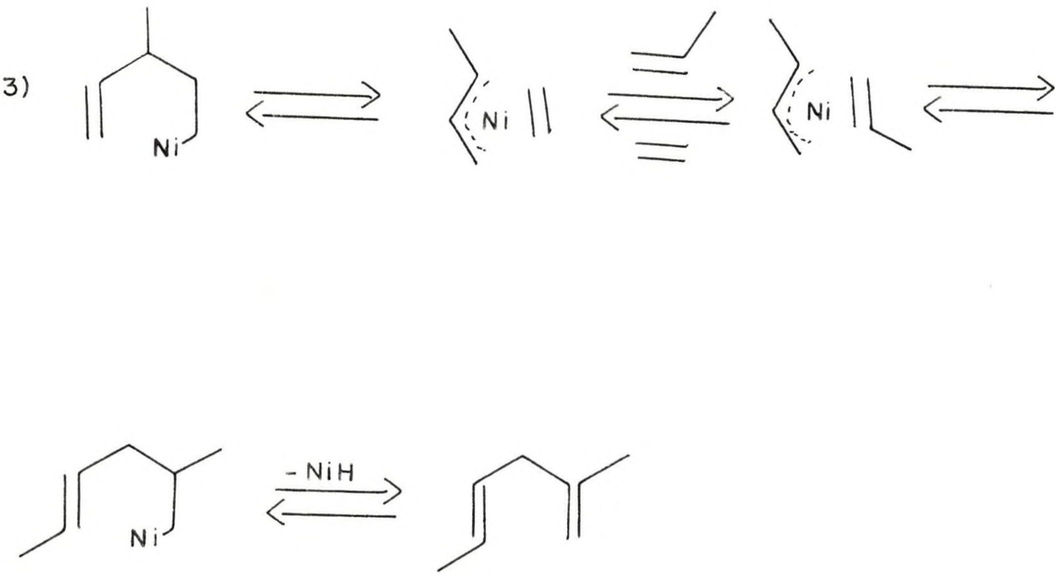
The type II rearrangement was thought to proceed via a 1,2-nickel hydride addition to the terminal double bond of the diene to form a 4-enylnickel complex. Cyclization could then occur to afford a cyclobutylcarbinylnickel species which could then rearrange to produce products. Alternatively, β-elimination of ethylene might occur to afford an allyl nickel-ethylene complex. Recombination of the fragments would result in the formation of products (scheme 4).



Scheme 4. -- Possible routes for the type II rearrangement.

The available data tend to favor the fragmentation route. The rearrangement of 3-methyl-1,4-pentadiene under a propene atmosphere resulted in the formation of 2-methyl-1,4-hexadiene.[62] This could result from displacement of ethylene by propene if the rearrangement was occurring via the fragmentation route (equation 13).

(13)



During the rearrangement of 1,4 pentadiene to 2-methyl-1,3-butadiene and 1,3-pentadiene via the type I rearrangement, two minor products were formed.[116] These minor products were identified by pmr and infrared spectra to be a 4-methyl-1,4-hexadiene and 3-methyl-1,4-hexadiene. These are the same products formed during the codimerization of 2-methyl-1,3-butadiene and 1,3-pentadiene respectively with ethylene.[53] The ethylene can only come from fragmentation of 1,4-pentadiene. The fragmentation route is essentially the reverse of the growth step in the codimerization process.

Prior to the present study, however, the cyclobutylcarbinyl route could not be ruled out. Either route could be used to satisfactorily explain the formation of 1,4-hexadienes from 3-methyl-1,4-pentadiene. Cyclobutylcarbinyl derivatives of lithium, sodium, and magnesium are known to undergo ring opening to form carbinylmetal complexes. The reaction is apparently reversible since 4-enylcarbinyl complexes will rearrange to form cyclobutylcarbinyl intermediates.[117]

Scheme 4 demonstrated that labelled 1,4-dienes could be used to distinguish between the two pathways. One problem however, was that in the 1,4-dienes used to date, both double bonds were unsubstituted. As a result, utilization of deuterated dienes would result in scrambling since addition of catalyst could occur at either end of the diene. This would tend to confuse the results. Labelling one end of the diene with methyl groups would avoid this since available evidence indicated that metal hydride addition to methyl substituted double bonds was not favored. Three such dienes are 2,3-dimethyl-1,4-pentadiene, 4-methyl-1,4-hexadiene, and 1,1-dideutero-2-methyl-1,4-pentadiene. These dienes were prepared and studied.

The stable nickel compound trans-chloro(2-allylphenyl)-bis(triethylphosphine)Ni(II) will also be studied. It is an example of a stable 4-enylnickel complex. Pmr studies had shown that the allyl group was situated above the nickel atom. Heating this compound in tetrachloroethylene resulted in the formation of trans-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II) and indene as major products. Minor products were allylbenzene, 1-phenyl-1-propene, trans-chloro-

(2-propenylphenyl)bis(triethylphosphine)nickel(II), and dichlorobis(triethylphosphine)nickel(II).[40] An active catalyst may be formed during the thermolysis which affords the variety of products. The reaction will be carried out in other solvents and in the presence of dienes to determine if the catalyst is also a nickel hydride.

# PART II. RESULTS

## PREPARATION OF LABELLED 1,4-DIENES

The 1,4-dienes prepared were labelled with deuterium; 1,1-dideutero-2-methyl-1,4-pentadiene, 12a, and methyl groups; 2,3-dimethyl-1,4-pentadiene, 13, and 4-methyl-1,4-hexadiene, 14.

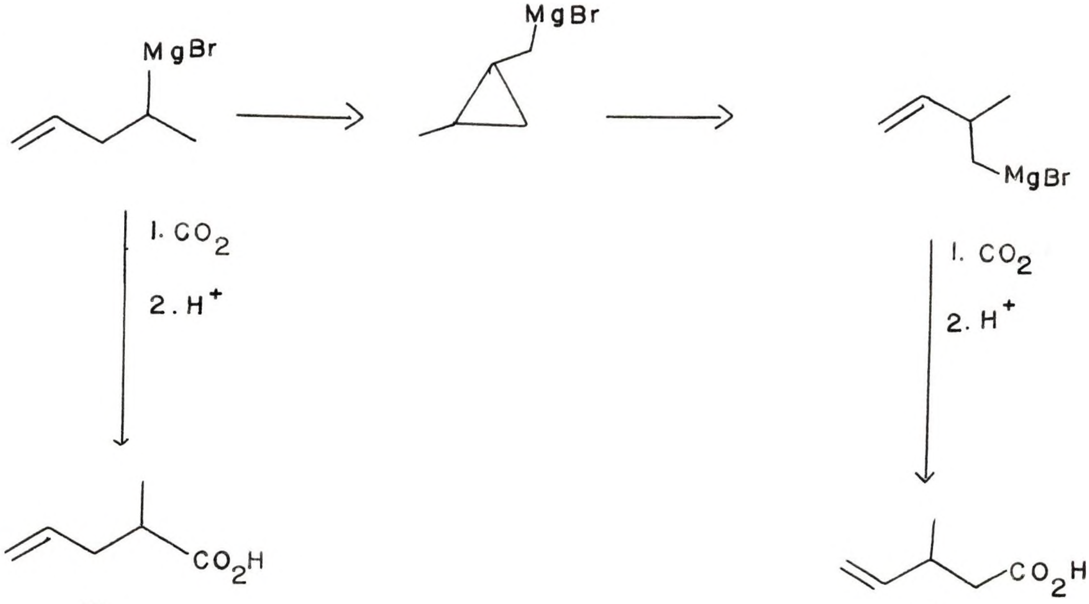
### A. THE SYNTHESIS AND REARRANGEMENT OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE

The synthesis of 1,1-dideutero-2-methyl-1,4-pentadiene, 12a, presented the most difficulties. The synthesis had previously been unsuccessfully attempted using 4-penten-2-one and dideuteromethylene triphenylphosphine.[116] The method finally utilized was the pyrolysis of 1,1-dideutero-2-methyl-4-pentenyl acetate, 15a.

The main precursor for the acetate, 15a, is 2-methyl-4-pentenoic acid, 16. The first attempt to prepare 16 was by the reaction of 1-pentenyl-4-magnesium bromide, 17, with carbon dioxide. Compounds such as 17, however, are known to rearrange *via* a cyclopropylcarbinyl metal intermediate[113] to produce a mixture of intermediates which can react with carbon dioxide yielding a mixture of acids (equation 14). The desired product 16 would be contaminated with 3-methyl-4-pentenoic acid, 18. These would be difficult to separate and were also formed in poor yields. This method was therefore abandoned.

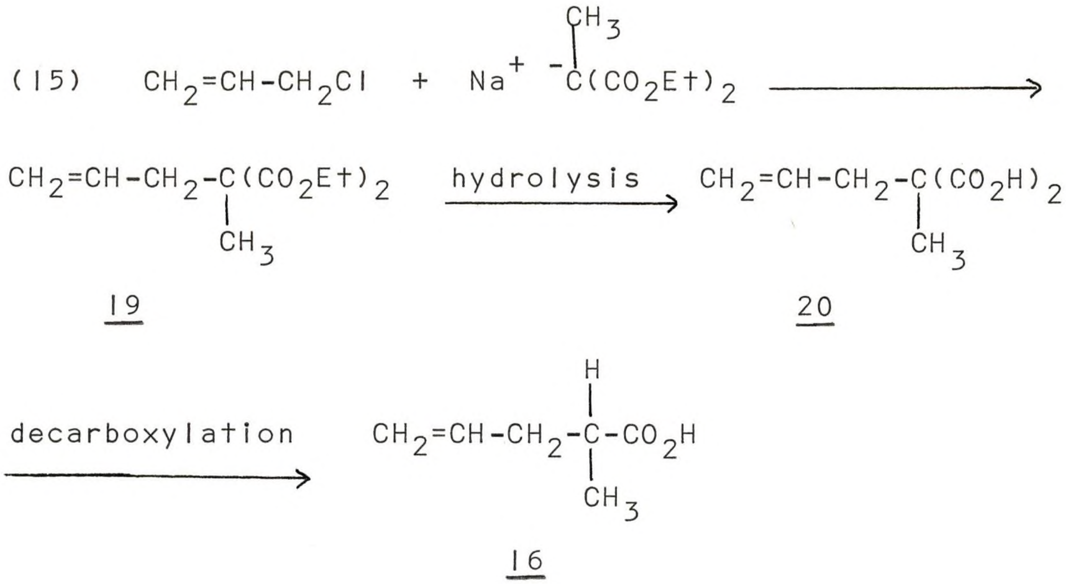
The method of preparation of 16 finally used was that of Stenhagen.[118] According to Stenhagen, diethyl-1-penten-4,4-dicarboxylate, 19, could be prepared in 85-89% yield. Hydrolysis of 19 to produce 1-penten-4,4-dicarboxylic acid, 20 followed by decarboxylation of 20 resulted in a 92% yield of 16 based upon 19.

(14)



16 18

The ester 19 was prepared in 79% yield from allyl chloride and sodio-diethylmethyl malonate. Hydrolysis of 19 however produced poor yields of 20. It was found that by varying the hydrolysis conditions, the highest yields of 20 could be obtained by gently refluxing the solution for 45 minutes after the initial exothermic reaction had subsided. The product was then collected by liquid-liquid extraction with ether. Decarboxylation of 20 at 150-170°C resulted in a 68% yield of 16 (equation 15).



$$(15)\quad CH_2{=}CH{-}CH_2Cl \;+\; Na^+\;{}^-\overset{\displaystyle CH_3}{\overset{|}{C}}(CO_2Et)_2 \longrightarrow$$

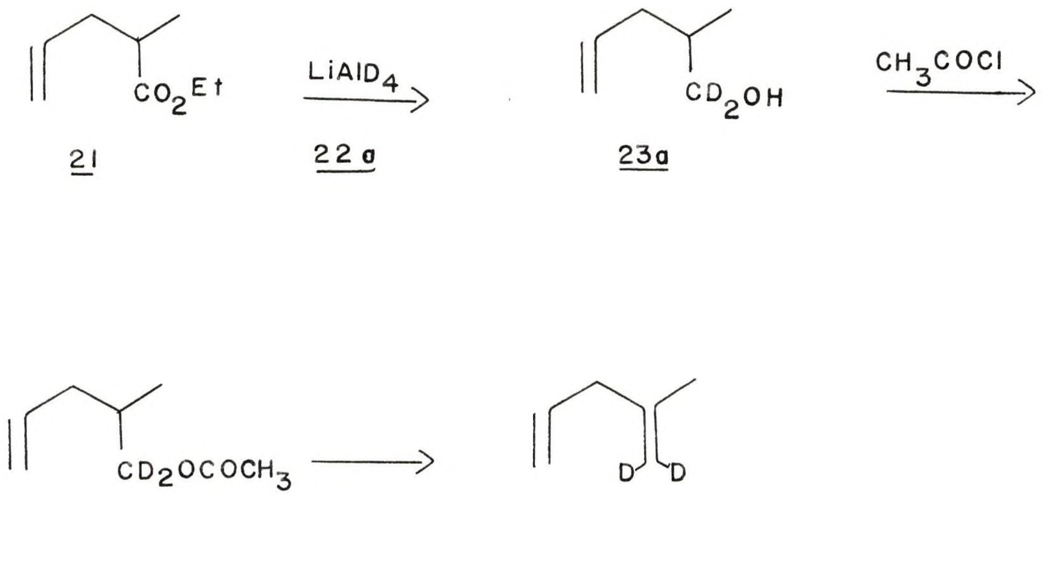
$$\underset{\underline{19}}{CH_2{=}CH{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(CO_2Et)_2} \xrightarrow{\text{hydrolysis}} \underset{\underline{20}}{CH_2{=}CH{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(CO_2H)_2}$$

$$\xrightarrow{\text{decarboxylation}} \underset{\underline{16}}{CH_2{=}CH{-}CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CO_2H}$$

Ethyl-2-methyl-1,4-pentenoate, 21, was prepared in 75% yield by refluxing 16 and ethanol in benzene for 11 hours using sulfuric acid as a catalyst. Refluxing the solution longer resulted in higher yields of 21 but sometimes caused double bond migration to produce ethyl-2-methyl-3-pentenoate.

The reduction of the ester 21 with lithium aluminum hydride, 22, to produce 2-methyl-4-penten-1-ol, 23, in 85% yield utilized the method of Fray and Polgar[119] for the reduction of 16 with 22. The reduction of 21 with lithium aluminum deuteride, 22a, produced 1,1-dideutero-2-methyl-4-penten-1-ol, 23a, in 85% yield (equation 16).

(16)



21 22a 23a

15a 12a

Comparison of the pmr spectra of 23 and 23a resulted in the expected disappearance of the doublet at τ6.6 in 23a for the two C-1 protons. The reaction of acetyl chloride with 23a produced 1,1-dideutero-2-methyl-4-pentenyl acetate, 15a in similar yields.

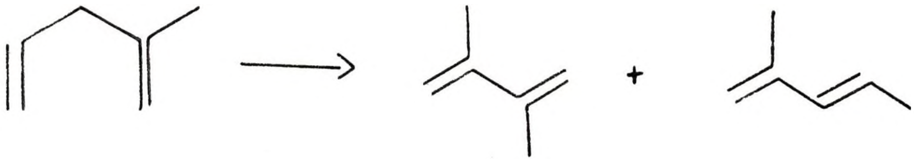
Pyrolysis of 15 at 600°C produced 12 in 20% yield. The suggestion[120] that pyrolysis of primary acetates should be carried out at 500-525°C with the unreacted product recycled to increase yields and prevent charring and secondary reactions can not be applied to 15 since very little product is produced below 570°C. Pyrolysis of 15a in the same manner resulted in the formation of 17% of 12a. Comparison of the pmr spectra of 12 and 12a resulted in the expected disappearance of the singlet at τ5.32 in 12a (Figures 1 and 2).

The C-2 methyl protons were used as an internal standard for calculating integral ratios from the pmr spectrum of 12a. This method of analysis resulted in 97.8% $D_2$ at C-1. Mass spectral analysis of 12a showed 1.2% $D_o$, 2.78% $D_1$, 96.0% $D_2$, and 0.02% $D_3$.

The rearrangement of 12 and 12a were carried out in deoxygenated solvents. In a typical experiment, 8.52 mmoles of 12 were added to a side arm flask under a nitrogen atmosphere containing 70 ml of deoxygenated toluene and 0.71 mmoles of *trans*-dichlorobis(tri-n-butylphosphine)Ni(II), 24. A 0.15 ml aliquot was removed and shaken with 0.05 ml of 2-propanol in a stoppered test tube for gas liquid phase chromatography (glpc) analysis. To the flask was quickly added 2 ml (2.48 mmoles) of a 25% solution of diisobutylaluminum chloride (DIBAC) in toluene (diene:Ni:Al mole ratio = 12:1:3.5). The resulting amber solution was stirred at 24-26°C for 6.5 hours with 0.15 ml of solution periodically removed and treated as before. The reaction was terminated with 2 ml of 1-butanol.

The glpc analysis was carried out using a 20 ft. x 3/8 inch 20% β,β'-oxydipropionitrile (β,β') on firebrick 60/80 column at 60°C with a helium flowrate of 170 ml/minute. The analysis showed two peaks immediately following the air peak. The first was identified as isobutane and the second as isobutene by mass spectrometry. The third peak was identified as unreacted 12. Two peaks eluted after 12 were collected by preparative glpc and identified by comparing the pmr spectra with known compounds. The first was identified as 2,3-dimethyl-1,3-butadiene, 25,[116,121] and the second product was identified as *trans*-2-methyl-1,3-pentadiene, 26[111,122] (equation 17).

(17)



12 25 26

Glpc analysis also showed that after 6.5 hours, 35% of 12 had isomerized with 7.8% of the amount isomerized converted to 25 and 6.8% to 26.

In an attempt to increase the yields of products, the rearrangement of 12 was carried out at 50-55°C. Glpc analysis showed a much reduced yield of 25 (1.6%) and 26 (4.3%). The major product was a new compound with a retention time less than that of 12. The new compound was collected and identified as 2-methyl-1-pentene, 27, from its pmr spectrum.[123] The rearrangement of 12 was then carried out in the more polar solvent chlorobenzene (dielectric constant at 25°C is 5.62 compared to 2.38 for toluene).[124] The reaction was much faster in chlorobenzene. The increase in the rate of reaction was due to the increase in the formation of 26 and a higher rate of conversion of 12 to products.

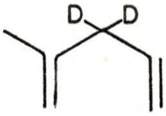
The amount of 25 formed is comparable to the amount formed in toluene. During 6.5 hours, 74% of 12 had reacted with 10.7% of the amount reacted converted to 25 and 21.3% to 26. In addition, a new product with a retention time intermediate between 12 and 25 was produced in about 3% yield. It was identified by comparative pmr to be *cis*-2-methyl-1,3-pentadiene, 28.[111] Since using a more polar solvent seemed to increase the amount of 12 that reacted and the amount of 26 formed, the rearrangement of 12 was carried out in the more polar solvent 1,2-dichlorobenzene (dielectric constant at 25°C is 9.93).[124] During two hours, 61.8% of 12 had reacted with 5.6% of the amount reacted converted to 28, 4% to 25, and 43.3% to 26. The amount of 12 reacted was slightly higher than the reaction in chlorobenzene and the amounts of 26 and 28 also increased relative to the amounts formed in chlorobenzene but the amount of 25 decreased.

1,1-Dideutero-2-methyl-1,4-pentadiene, 12a, was treated with the nickel catalyst formed from DIBAC and 24 in toluene, chlorobenzene, and 1,2-dichlorobenzene. Treatment of 12a with the nickel catalyst in toluene was carried out for 6.5 hours. During this time, 42.3% of 12a reacted with 11.5% of the amount reacted converted to 1,1-dideutero-2,3-dimethyl-1,3-butadiene, 25a, and 10.2% to 1,1-dideutero-*trans*-2-methyl-1,3-pentadiene, 26a. The pmr spectrum of recovered dideutero-2-methyl-1,4-pentadiene showed that the singlet at $\tau$ 5.32 had reappeared (Figure 3). There was a decrease of 16.8% $D_2$ at C-1 and a gain of 15.0% $D_2$ at C-3. This indicated that an average of 15.9% 3,3-dideutero-2-methyl-1,4-pentadiene, 12b was produced in the reaction. Mass spectral analysis of recovered dideutero-2-methyl-1,4-pentadiene, 12a showed that it contained 2.9% $D_1$, and 95.5% $D_2$ as compared with 2.2% $D_1$ and 97.8% $D_2$ in pure 12a.

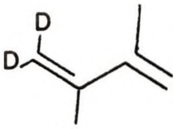
TABLE I

THE RATIO OF 2-METHYL-1,3-PENTADIENES TO 2,3-DIMETHYL-1,3-BUTADIENE FORMED IN DIFFERENT SOLVENTS

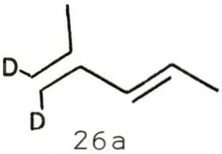
| Time (Minutes) | Toluene | Chlorobenzene | 1,2-dichlorobenzene |
|---|---|---|---|
| 30 | 0.91 | 2.96 | 11.15 |
| 60 | 1.0 | 2.64 | 13.9 |
| 120 | 0.9 | 2.54 | 12.3 |
| 390 | 0.9 | 2.26 | - |



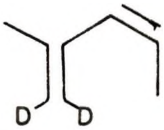
12b



25a



26a



28a

Treatment of 12a with the nickel catalyst in chlorobenzene was carried out for two hours. During this time, 56.3% of 12a had isomerized with 3.8% of the amount isomerized converted to 28a, 22.3% to 25a, and 34.5% to 26a. Pmr analysis of recovered dideutero-2-methyl-1,4-pentadiene indicated that 19.9% $D_2$ was lost at C-1 and 18.5% $D_2$ gained at C-3. Thus, there was an average of 19.2% 12b in the recovered 12a. Mass spectral analysis showed 1.23% $D_o$, 3.11% $D_1$, 93.2% $D_2$, and 2.45% $D_3$.

Pmr analysis of 25a showed a ratio of 2.95:1 for the methyl:vinyl protons which was 98.3% of the theoroetical ratio of 3:1. The mass spectral analysis of 25a showed 1.83% $D_o$, 3.93% $D_1$, 92.8% $D_2$, and 1.4% $D_3$. The pmr analysis of 26a was carried out using the vinylic proton at C-4 as an internal standard. The integral ratios were 0.885 (11.5% $D_2$) at C-3; 0.24 (10.7% $H_2$) at C-1; and 5.33 for the six methyl protons (11% D). Mass spectral analysis showed that 26a contained 9.1% $D_1$, 0.57% $D_o$, 89.5% $D_2$, and 0.86% $D_3$ (Figures 4 and 5).

Treatment of 12a with the nickel catalyst in 1,2-dichlorobenzene was carried out for 1.5 hours. During this time, 56.4% of 12a isomerized with 4.82% of the amount isomerized converted to 28a, 4.64% to 25a, and 38.71% to 26a. Pmr analysis of recovered 12a showed a loss of 17.1% $D_2$ at C-1 and a gain of only 11.5% $D_2$ at C-3. There was a minimum of 11.5% 12b in recovered 12a. Mass spectral analysis of recovered 12a showed 2.12% $D_o$, 8.17% $D_1$, and 89.7% $D_2$.

The pmr analysis of 26a showed a ratio of 0.88 (12% D) at C-3; 0.283 (14.2% $H_2$) at C-1; and 4.23 (29.5% D) for the six methyl protons. Mass spectral analysis showed 1.54% $D_o$, 11.2% $D_1$, 85.2% $D_2$, 1.02% $D_3$, and 0.44% $D_4$.

The ratio of <u>26a</u> and <u>28a</u> to <u>25a</u> was similar to the ratio of <u>26</u> and <u>28</u> to <u>25</u> in toluene. The ratio decreased slightly in chlorobenzene. The ratio of <u>26a</u> and <u>28a</u> to <u>25a</u> decreased sharply in 1,2-dichlorobenzene. The decrease was about 75%.

TABLE 2

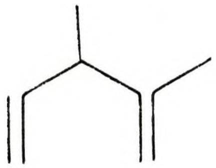
THE RATIO OF 2-METHYL-1,3-PENTADIENES-1-$D_2$ TO 2,3-DIMETHYL-1,3-BUTADIENE-1-$D_2$ IN DIFFERENT SOLVENTS

| Time (Minutes) | Toluene | Chlorobenzene | 1,2-Dichlorobenzene |
|---|---|---|---|
| 15 | 1.0 | 2.06 | 8.65 |
| 30 | 0.89 | 2.87 | - |
| 60 | 0.95 | 2.5 | 9.8 |
| 90 | - | 2.5 | 9.5 |
| 390 | 0.9 | - | - |

## B. THE SYNTHESIS AND REARRANGEMENT OF 2,3-DIMETHYL-1,4-PENTADIENE AND 4-METHYL-1,4-HEXADIENE

The synthesis[53] of 2,3-dimethyl-1,4-pentadiene, <u>13</u> and 4-methyl-1,4-hexadiene, <u>14</u>, had been carried out by codimerizing ethylene and 2-methyl-1,3-butadiene (isoprene) using a catalyst formed from DIBAC and <u>24</u>. The codimerization was carried out at high temperature and high ethylene pressures.

Since apparatus for such reaction conditions was not available, the codimerization was carried out in ethylene saturated chlorobenzene under one atmosphere of ethylene (isoprene:Ni:Al mole ratio = 146:1:3.5). The reaction was terminated after one hour with 1-butanol. Glpc analysis showed that 63% of isoprene had reacted with 12% of the amount reacted converted to 2,3-dimethyl-1,4-pentadiene (Figure 6), 13, and 54% to 4-methyl-1,4-hexadiene, 14 (Figure 7). Glpc analysis also showed that both geometric isomers of 14 were formed with the isomer having the longer retention time on the β,β' column being the major product.



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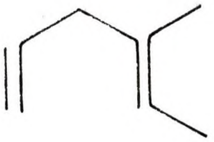
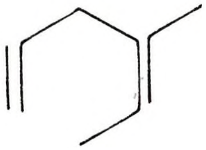


14a



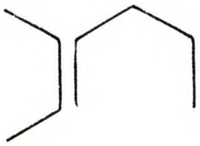
14b

The rearrangement of 13 was carried out using the same general procedure as for the rearrangement of 12. The reaction was carried out in toluene, chlorobenzene, and 1,2-dichlorobenzene. Only one major product was produced in toluene. Two minor products with long retention times were produced in less than 5% yield. Comparative pmr spectra showed the product to be 4-methyl-1,4-hexadiene. During three hours, 51.8% of 13 reacted with 60% of the amount reacted converted to 14. No 2-methyl-1,4-hexadiene or 2-methyl-1,5-hexadiene were detected.

The rate of reaction of 13 and the rate of formation of 14 were much faster in chlorobenzene than in toluene. After 30 minutes, 36.4% of 13 had reacted with 91% of the amount reacted converted to 14. The amount of 14 could not be accurately determined after this time since it underwent double bond migration rapidly to form the minor products mentioned above. The rearrangement of 13 in 1,2-dichlorobenzene was slightly faster than in chlorobenzene. The reaction of 14 to form minor products was much more rapid. After 15 minutes, 27% of 13 had isomerized with 57% of the amount isomerized converted to 14. Accurate determination of the amount of 14 initially formed was not possible at long reaction times because of it's rapid reaction to form minor products.

Gas liquid phase chromatographic analysis of recovered 14 showed that the geometrical isomer having the longest retention time on the β, β' column was being produced in greater than 95% yield. This isomer was identified using the procedure of Hata[85] for the identification of the cis isomer of 14b which is (Z)-4-methyl-1,4-hexadiene by the new rules of nomenclature (IUPAC).[125] Diisobutylaluminum hydride preferentially added to the terminal unsubstituted double bond of 14. Hydrolysis produced a mixture of cis and trans-methyl-2-hexenes (Figure 8). Bates and Gales[126] had found experimentally that the τ values for the methyl protons in a cis $CH_2-CH=C(CH_3)-CH_2$-unit were lowered by approximately 0.07 ppm than in the trans unit.

Since the dimerization of ethylene and isoprene produced 14 with the same geometric isomer as the major product, this mixture was treated with diisobutylaluminum hydride. The product mixture was resolved using a Se-30 column which showed that the isomer having the longest retention time, 3-methyl-2-hexene, was the major product. The decoupled pmr spectrum of the minor product showed two peaks for the methyl groups. The downfield singled was also sharply spit into a doublet which had a $\tau$value of 8.35 (Figure 9). The decoupled pmr spectrum of the major product showed only a singlet with a $\tau$value of 8.43 (Figure 10). Thus, the major isomer form the hydrogenation of the mixture of isomers of 14 was (2E)-3-methyl-2-hexene, 29, and the minor product was (2Z)-3-methyl-2-hexene, 30. The major product form the rearrangement of 13 was therefore (4E)-4-methyl-1,4-hexadiene, 14a.



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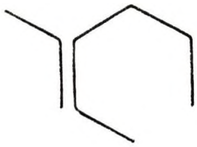
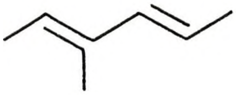


30

The minor products formed during the rearrangement of 13 came from the reaction of 14 formed during the reaction. The rearrangement of the mixture of *cis*,*trans*-4-methyl-1,4-hexadiene, 14 was carried out using the general procedure for the rearrangement of 12. The reaction was terminated after three hours. Glpc analysis on the β,β' showed four new products. The first was a small peak eluted before unreacted 14, the second was eluted after 14, the third product was a small peak followed immediately by the fourth which was the major product. All four products were collected by preparative glpc. The largest peak was identified by its infrared and pmr spectrum to be (2E, 4E)-3-methyl-2,4-hexadiene, 31. The small peak before unreacted 14 was identified by its pmr spectrum to be 2,3-dimethyl-1,4-pentadiene, 13. Glpc analysis of the time zero aliquot showed that the small amount of 13 was not an impurity. The second peak was identical to the third except that the vinylic proton coupling constant (J=12 Hz) showed it to be cis. The coupling constant of the third peak (J=15 Hz) showed it to be trans. The second and fourth products had retention times identical with products formed by the isomerization of 14 prepared during the rearrangement of 13. The second was therefore assigned to (2E, 4Z)-3-methyl-2,4-hexadiene, 32, and the third was assigned to (2Z, 4E)-3-methyl-2,4-hexadiene, 33. The expected type I product was 2,3-dimethyl-1,3-pentadiene, 34. The pmr spectrum of 34 has been published[127] and the pmr spectra of the four products were not similar to it.



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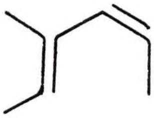

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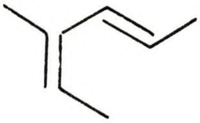

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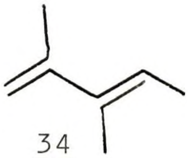


34

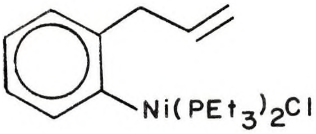
## C. THE THERMOLYSIS REACTION OF *TRANS*-CHLORO(2-ALLYLPHENYL)BIS(TRIETHYLPHOSPHINE)NICKEL(II)

*Trans*-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II), 35, is a very interesting compound. It is a model 4-enylnickel complex. It also contains a stable Ni-C σ-bond. It is prepared by the reaction of *trans*-dichlorobis(triethylphosphine)nickel(II), *36*, with an excess of 2-chloro-1-allylphenylmagnesium chloride[128]. It is a yellow air stable solid with a planar structure. The stability is thought to arise from the fixed geometry of the system.[14] Non bonding steric repulsions of the *trans*-phosphine ligands with the ortho substituent force the phenyl group to assume a position perpendicular to that of the bonding system. This also places the allyl group directly above the nickel atom. That this is the case is shown by the down field shift of the benzylic protons in the pmr spectrum of 35[16].

Solutions of 35 were heated in deoxygenated solvents under an inert gas atmosphere. Generally one gram of 35 (2.2 mmoles) was dissolved in 10-15 ml of nitrogen purged solvent. Solutions of 35 in benzene were heated from 16-26 hours at 50-70°C and in tetrachloroethylene at 80-90°C from 2.5-24 hours. The products were separated by a column chromatography on an 18 inch column of acid washed alumina through which nitrogen purged hexane had been passed several times. The column was then left under a nitrogen atmosphere overnight before being used. The conditions used were necessary since unreacted 35 and products undergo decomposition on unpurged columns.

The solvent collected from the column before any of the organo nickel compounds were eluted was concentrated. It was then analyzed by glpc for aromatic hydrocarbons using the 20 ft. x 3/8 in. 20% 1,2,3-tris(2-cyanoethoxy)propane(TCEP) on 60/80 Chromsorb P column.

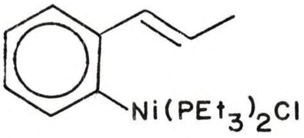
Thermolysis of 35 in tetrachloroethylene had previously been carried out by Miller and Fahey[40]. A large amount of 35 was used in order to obtain products from an unpurged alumina column. Under these conditions, three products were collected and identified. The major product formed in 40% yield was trans-chloro(trichlorovinyl)bis(triethylphosphine)-nickel(II), 37. Two minor products were trans-chloro(2-propenylphenyl)bis(triethylphosphine)nickel(II), 38, and 36 formed in 11 and 2% yields respectively. Glpc analysis of hydrocarbons showed that 46% indene, 39 and 3% each of allylbenzene, 40, and *trans*-1-phenyl-1-propene, 41 were formed. A similar experiment in benzene[128] resulted in 31% 39, 11% 42, and 5% 41. No products containing the nickel moeity were isolated because of decomposition on the unpurged alumina column.



35

$C_2Cl_3Ni(PEt_3)_2Cl$

37



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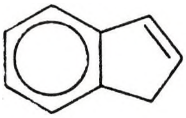

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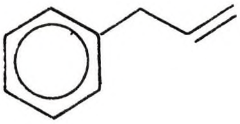

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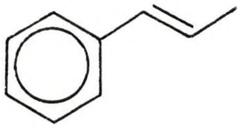


41

When 35 was heated in tetrachloroethylene for 2.5 hours and chromatographed on the nitrogen purged alumina column, similar yields of products were obtained. No new products were found. Pmr analysis of the chromatographed products showed that 96% of 35 was converted to products with 48.1% of the amount reacted converted to 37 and 6.4% to 38. Glpc analysis showed that 53.3% of 39, 5.1% of 40, and 2% of

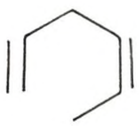
41 were produced.

The thermolysis of 35 was carried out for 16 hours in benzene before the solution was chromatographed on the nitrogen purged column of alumina. The major product was 38. Analysis showed that 56% of 35 had reacted with 39.09% of the amount reacted converted to 38. Glpc analysis showed that the amount of indene, 39, had decreased to 11% and only 1.4% of 40 and 1.6% of 41 were formed.

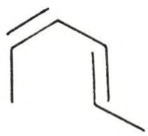
The thermolysis of *trans*-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), 35, was carried out in benzene containing tetrachloroethylene (Ni:tetrachloroethylene mole ratio = 3:1) in order to determine if there were two separate reactions occurring. Analysis after 24 hours indicated that 96.4% of 35 had reacted with 24.31% of the amount reacted converted to 38, 28.4% to 39, 1.05% to 40, and 8.5% to 41. The amount of trichlorovinylnickel complex, 37, formed was 75% of the theoretical amount possible.

The thermolysis of 35 was also carried out in benzene containing allylbenzene (allylbenzene:Ni mole ratio = 2:1) in order to determine whether the double bond migration occurring in 35 is intramolecular or intermolecular. During 26 hours, 78.7% of 35 reacted with 53.5% of the amount reacted converted to 38 and 22% to 39. Glpc analysis showed that 97.4% of the allylbenzene had reacted with 63.7% converted to *trans*-1-phenyl-1-propene, 41. The thermolysis of 35 was also carried out in tetrachloroethylene containing allylbenzene, 40 (allylbenzene:Ni mole ratio = 5:1). No detectable isomerization of allybenzene occurred during 24 hours.

The thermolysis of 35 was also carried out in toluene containing *cis*-1,4-hexadiene, 5a (diene:Ni mole ratio = 2.45:1). Glpc analysis on the $\beta,\beta'$ column showed that two products were eluted after 5a. These were collected *via* preparative glpc and identified by comparative pmr spectra[62,111] to be *trans*-2-methyl-1,3-pentadiene, 26, *cis*,*trans*-2,4-hexadiene, 42 and *cis*, *cis*-2,4-hexadiene, 43. The reaction was terminated after 41 hours. During this time, 25.5% of 5a had reacted with 58.7% of the amount reacted converted to 26, 21.1% to 42, and 20.7% to 43. Column chromatography and pmr spectra of the products showed that 38 was not formed. Glpc analysis showed that after 41 hours, 43% of 39 and 9% of 41 was formed. The above reaction was also carried out using 35 prepared from nickel dichloride of 99.999% nickel purity (diene:Ni mole ratio = 1:1). During 45 hours, 56.4% of 5a reacted with 55.6% of this amount converted to 26, 21.3% to 42 and 21% to 43. Analysis also showed that 68.8% of 35 had reacted with 19.2% of the amount reacted converted to 38.



5a



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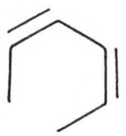


43

High temperatures were necessary to initiate the reaction. Solutions of 35 and 5a in benzene did not afford any observable isomerization of 5a over a 24 hour period at room temperature. The thermolysis of 35 in tetrachloroethylene containing 5a between 60 and 70°C resulted in 56.4% being converted to products during 45 hours. Of the amount reacted, 31% was converted to 26 but 42 and 43 were not detected. Lowering the temperature to between 50 and 55°C produced very little product. During 19 hours, 35% of 5a had reacted but only 1% of 26 and only a trace of 42 and 43 were formed.

The conversion of 5a to products was much lower during the thermolysis of 35 when compared to the catalyst formed from trans-dichlorobis(tri-n-butylphosphine)nickel(II), 24, and DIBAC. Reaction of 35 with DIBAC however resulted in the formation of a catalyst which rapidly isomerized 5a to 26, 42 and 43. Reaction of 35 with triethylaluminum resulted in the destruction of 35 with no rearrangement occurring.

The rearrangement of 5a during the thermolysis reaction compared with the rearrangement of conjugated dienes in HCl saturated solutions.[111] For example, a solution of cis,trans-2,4-hexadiene, 42, in HCl saturated benzene resulted in the formation of 5 to 10% of trans-2-methyl-1,3-pentadiene, 26 and cis, cis-2,4-hexadiene, 43, over a 36 hour period.

*Cis*-1,4-hexadiene, 5a, was therefore heated at 60-70°C in toluene which was saturated with HCl by constantly bubbling it into the solution. No rearrangement occurred although 5a slowly disappeared over a six hour period. A similar experiment with allylbenzene and HCl caused no isomerization of allylbenzene over a 24 hour period.

## D. REARRANGEMENTS INVOLVING NICKEL(0) COMPLEXES

The intermediate formed during the thermolysis of 35 appeared to have properties of both a nickel(0) complex and a nickel hydride. Metal(0) complexes of nickel[38,39,40] are known to insert into C-X bonds (X=Cl or Br). Platinum hydrides are also known to react with tetrafluoroethylene to form complexes containing a Pt-C σ-bond.[129] Metal hydrides are capable of isomerizing alkenes and dienes (introduction).

Ethylenebis(triethylphosphine)nickel(0), 44, was prepared *in situ* by the method of Wilke[130] from nickelacetylacetonate, triethylphosphine, and triethylaluminum in ethylene saturated benzene. The addition of allylbenzene allylbenzene:Ni mole ratio = 10:1) resulted in the isomerization of allylbenzene to *trans*-1-phenyl-1-propene, 41. During 11 hours, 73% of 41 was produced. The presence of ethylene is not necessary since the reaction also occurred in nitrogen saturated benzene containing allylbenzene.

It could not be ascertained that it was 44 alone which caused the isomerization due to the complexity of the side products. Treatment of 3-methyl-1,4-pentadiene with 44 formed *in situ* is known to afford 3-methyl-1-pentene.[116]

Ethylenebis(triphenylphosphine)nickel(0), 45 was prepared and isolated according to the method of Maitlis[131] by Pinke.[111] It is a yellow solid stable under ethylene or nitrogen atmosphere at 0°C. A benzene solution of 45 containing allylbenzene (allylbenzene:Ni mole ratio = 10:1) caused no isomerization over a 3.5 hour period. Addition of 0.2 equivalent of HCl in benzene resulted in the complete isomerization of allylbenzene to 41 within 3.5 hours.

Addition of HCl to a benzene solution containing 45 resulted in the formation of an amber colored solution similar to the one formed when 24 was treated with DIBAC. This reaction was thought to produce a nickel hydride. The Ni-H stretching frequency is generally found between 1900 and 2000 $cm^{-1}$ in the infrared.[74] Attempts to determine the stretching frequency of a nickel hydride formed from 45 and HCl were unsuccessful. This may have been due to the low concentration of nickel hydride in the solution since a 1:1 molar ratio of 45 and HCl resulted in the rapid decomposition of 45. The amount of HCl was therefore held at less than 0.8 equivalents. Because 45 has a high molecular weight (601.3) and is only moderately soluble in benzene, only a dilute solution of the nickel hydride was possible.

Organoaluminum compounds were often used as cocatalysts with transition metal halides to form homogeneous metal catalysts. The aluminum end products derived from these aluminum compounds should be aluminum halides. The effect of aluminum chloride on the catalyst system was studied using 45 and 5a. Addition of aluminum chloride to a flask containing 45 under nitrogen atmosphere resulted in the rapid decomposition of 45. A benzene solution was saturated with aluminum chloride by stirring it overnight under nitrogen atmosphere. The concentration of aluminum chloride was determined by titration of the hydrochloric acid formed on hydrolysis of a portion of the solution. A benzene solution of 45, 5a, and aluminum chloride (diene:Ni:Al mole ratio = 10:1:1) did not result in any rearrangement of 5a within a 30 minute period. Addition of 0.8 equivalents of HCl in benzene resulted in very little rearrangement. Approximately 4% of 5a was converted to products within 30 seconds and very little reacted after this time. Only 2.4% of 26 and 1% each of 42 and 43 were produced during three hours.

A nickel(0) species ethylenebis(tri-o-tolylphosphite)-nickel(0), 46, was prepared without the use of aluminum compounds by Stauffer.[132] A solution of 46, 12, and HCl in toluene (diene:Ni:HCl mole ratio = 10.5:1:0.5) was stirred for 4 hours at room temperature. A rapid rearrangement of 12 ensued which slowly decreased. No reaction occurred after 30 minutes. Only 20.2% of 2-methyl-1,4-pentadiene, 12 was isomerized with 8.7% of the amount isomerized converted to 2,3-dimethyl-1,3-butadiene and 11.4% to *trans*-2-methyl-1,3-pentadiene.

## E. THE REARRANGEMENT OF 1,4-PENTADIENE

Treatment of 1,4-pentadiene with the nickel catalyst formed from DIBAC and *trans*-dichlorobis(tri-n-butylphosphine)-nickel(II), 24, resulted in the formation of isoprene and 1,3-pentadienes. It was found that minor amounts of 4-methyl-1,4-hexadiene and 3-methyl-1,4-hexadiene were also formed.[116]

The reaction was repeated to verify the information obtained from 1,4-pentadiene and gas chromatographic constsnts for 1,4-pentadiene and the products were determined in order to obtain accurate yield data.

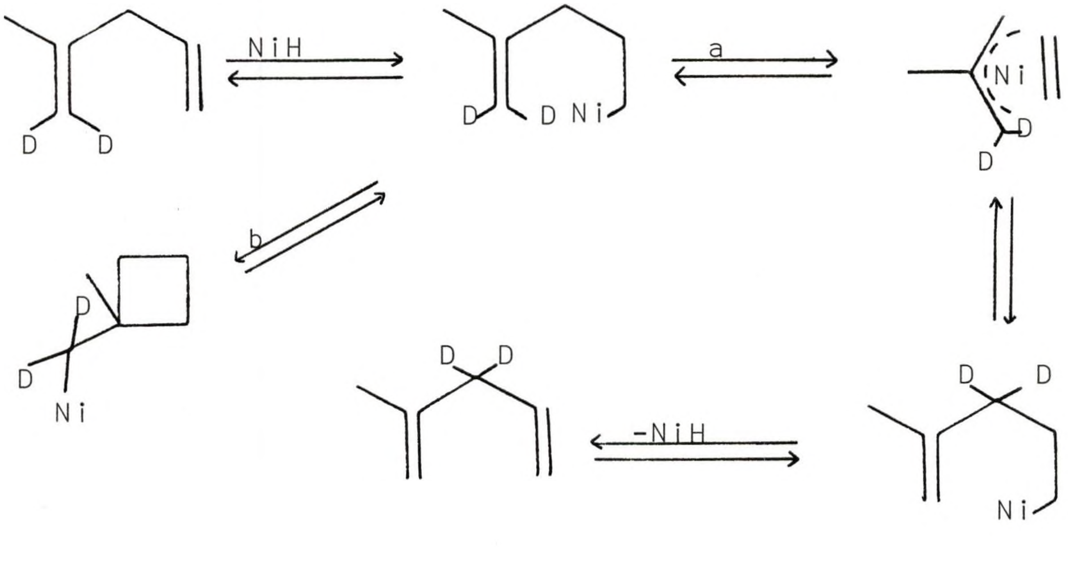
Treatment of 1,4-pentadiene with the nickel catalyst was carried out for four hours at room temperature. Glpc analysis showed that 71% of 1,4-pentadiene had reacted with 24.35% of the amount reacted converted to isoprene, 21.2% to *cis*-1,3-pentadiene, 4.02% to *trans*-1,3-pentadiene, 8.89% to 3-methyl-1,4-hexadiene, and 3.5% to 4-methyl-1,4-hexadiene.

# PART III. DISCUSSION.

Several factors are important in the type II rearrangement of 1,4-dienes. These are the nature of the diene, the catalyst, cocatalyst, and the solvent.

## A. THE SKELETAL REARRANGEMENT OF THE 1,4-DIENES

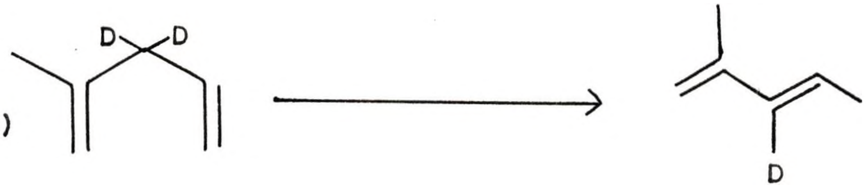
The type II rearrangement of 1,1-dideutero-2-methyl-1,4-pentadiene, 12a, should produce 3,3-dideutero-2-methyl-1,4-pentadiene, 12b, by pathway a (fragmentation route) but would only reform 12a by pathway b (cyclobutylcarbinyl route).[64] Pmr evidence indicated that 12a recovered from the reaction does contain 12b. The results indicated that the type II rearrangement must follow pathway a in the case of 12a (Figures 1, 2, and 3).



Scheme 5. --Possible pathways for the type II rearrangement of 1,1-dideutero-2-methyl-1,4-pentadiene.

2,3-Dimethyl-1,3-butadiene-1-$D_2$, *25a* formed by the type I rearrangement provided additional evidence that the type I rearrangement occurred via the cyclopropylcarbinyl route.[63] Both *12a* and *12b* would produce *25a* by this route and this has been observed. Pmr analysis showed that the methyl:vinyl proton ratio was 98.3% of the theoretical value of 3:1. *Trans*-2-methyl-1,3-pentadiene-1-$D_2$, *26*, should contain substantial amounts of hydrogen at C-1 if the type II rearrangement occurred via pathway *a*. Pmr analysis indicated that there was a substantial amount of hydrogen at C-1 (11.5%) in the reaction carried out in chlorobenzene (Figures 4 and 5). The amount of $D_1$ should also increase (equation 18). Mass spectral analysis indicated that *26a* contained 9.1% $D_1$. This compared with 2.1% $D_1$ in pure *12a* and 3.1% in the mixture of *12a* and *12b*, and 3.9% $D_1$ in *25a*.

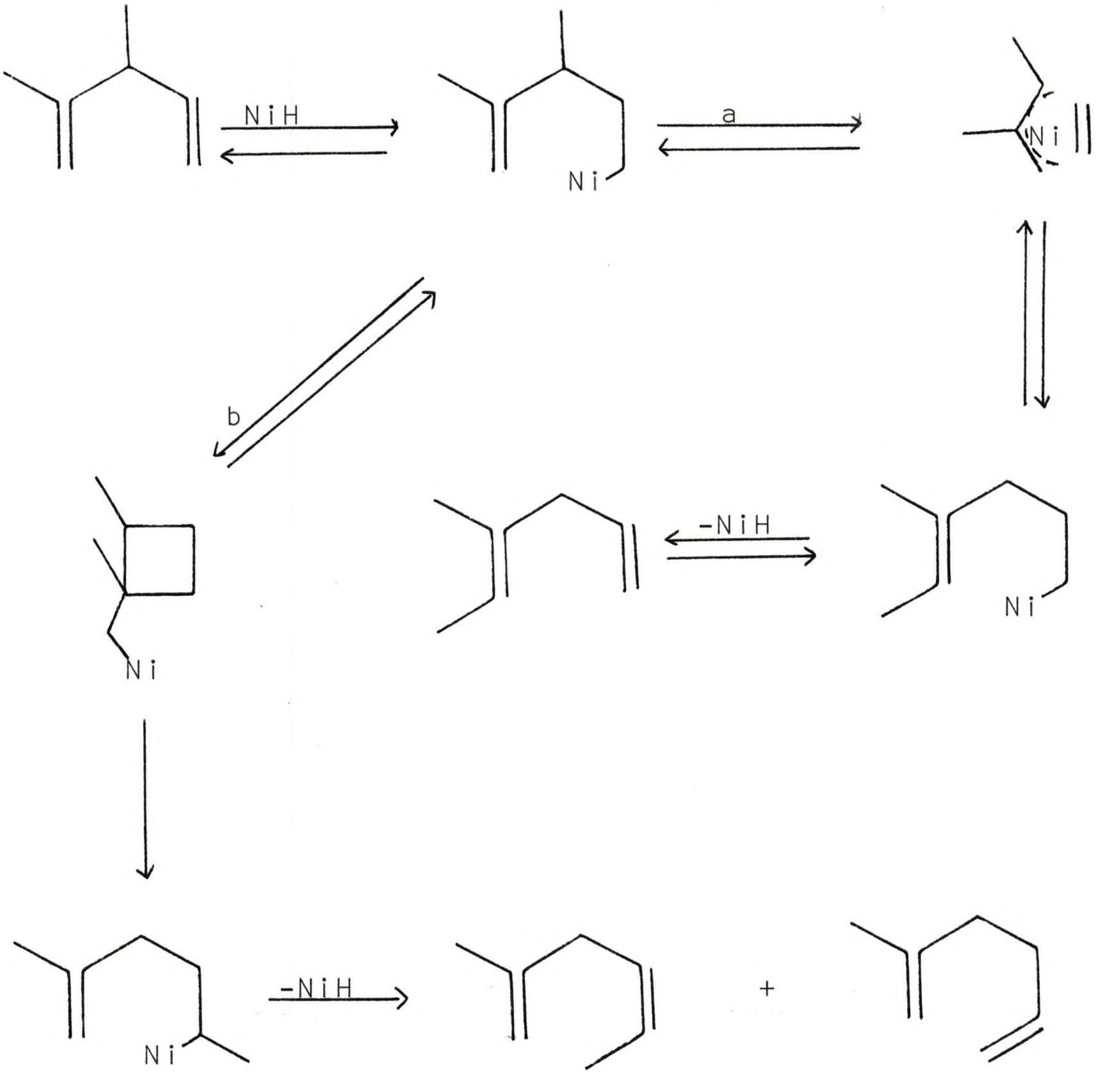
(18)



The transfer of deuterium from C-1 in *12a* to C-3 appeared to be quantitative. Pmr analysis showed that the loss of deuterium in one position was usually offset by deuterium gained in the other position.

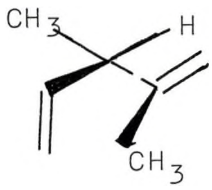
The type II rearrangement of 2,3-dimethyl-1,4-pentadiene *13*, should also form different products by pathway *a* (4-methyl-

1,4-hexadiene, 14) or pathway b (2-methyl-1,4-hexadiene or 2-methyl-1,5-hexadiene). Only one product, (4E)-4-methyl-1,4-hexadiene, 14a, was formed. These results provided further evidence that the type II rearrangement occurred via the fragmentation route (Figures 6 and 7).



Scheme 6. --Possible pathways for the type II rearrangement of 2,3-dimethyl-1,4-pentadiene.

The observation that 2,3-dimethyl-1,3-pentadiene was not formed (type I rearrangement or double bond migration) indicated that the rearrangement proceeded via 1,2-nickel hydride addition as the preliminary step. The exclusive 1,2-nickel hydride addition was probably due to steric hindrance by the methyl groups which shield position four from attack. Addition of nickel will therefore occur at position five of 13.



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Both fragments of the diene have been isolated. Ethylene was trapped in the rearrangement of 1,4-pentadiene to isoprene and 1,3-pentadiene.[116] Minor products 14 and 3-methyl-1,4-hexadiene were presumably formed by the reaction of ethylene with isoprene and 1,3-pentadiene respectively. In the rearrangement of 3-methyl-1,4-pentadiene under propene atmosphere, 2-methyl-1,4-hexadiene was formed by propene presumably capturing the butadiene fragment.[62] The most probable route for the type II rearrangement must be the fragmentation route since products consistent with pathway b have not been found (13 going to 2-methyl-1,4-hexadiene or 2-methyl-1,5-hexadiene).

The fragmentation route is the reverse of the postulated growth step in the codimerization of a conjugated diene and ethylene.[53] This implied that the type II rearrangement was reversible and that the diene products were in equilibrium with the reactants.

Support for the fragmentation route also came from the observation that only in the case of 5a did the loss of starting material approximate the amount of products isolated.[111] In experiments utilizing other 1,4-dienes such as 12 or 1,4-pentadiene there was usually a 20-30% difference in the amount of starting material reacted and the amount of products isolated. The most reactive diene via the type I rearrangement was *cis*-1,4-hexadiene, 5a. It did not form detectable products consistent with the type II rearrangement. Some ethylene was lost during the type II rearrangement of 1,4-dienes as was seen with 1,4-pentadiene. This could also be occurring with the other 1,4-dienes which were capable of isomerizing by both types of rearrangements. It should be noted that 2,3-dimethyl-1,4-pentadiene, 13 which was thought to undergo only the type II rearrangement also showed approximately 40% loss of starting material which was unaccounted for.

## B. THE NICKEL CATALYST

The catalyst is thought to be formed by alkylation of *trans*-dichlorobis(tri-n-butylphosphine)nickel(II), 24 with diisobutylaluminum chloride (DIBAC). Elimination of isobutene could result in the formation of hydridochlorobis(tri-n-butylphosphine)nickel(II), 47 (equation 19).

(19) $$\underset{\underline{24}}{\mathrm{Ni[P(n\text{-}C_4H_9)_3]_2Cl}} + \mathrm{AlCl(i\text{-}C_4H_9)_2} \longrightarrow \mathrm{Cl_2Al(i\text{-}C_4H_9)} +$$

$$\mathrm{Cl[P(n\text{-}C_4H_9)_3]_2Ni\text{-}CH_2\text{-}CH(CH_3)_2} \longrightarrow \mathrm{CH_2{=}C(CH_3)_2} +$$

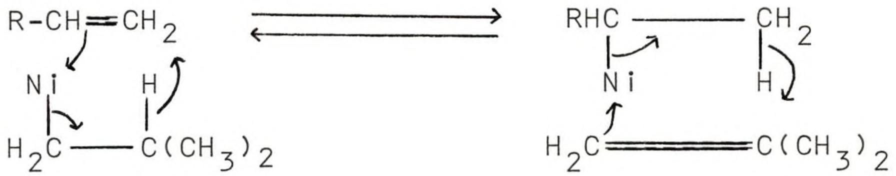
$$\underset{\underline{47}}{\mathrm{HNi[P(n\text{-}C_4H_9)_3]_2Cl}}$$

Alkyl compounds of nickel that contain localized Ni-C σ-bonds are generally unstable and decompose to form alkenes.[74] The β-elimination of metal hydrides from alkylmetal compounds to form alkenes has been discussed (introduction).

The formation of the nickel catalyst may not be the same as that described in equation two. Stable nickel hydrides [74,75,77] have been isolated but these were not active catalysts.[111,132] Dimethylaluminum chloride and 24 afforded an active catalyst.[132] The production of the catalyst from dimethylaluminum chloride evidently did not follow equation two. Several experiments demonstrated that the catalyst must be a nickel hydride or its chemical equivalent. It has been observed[111] that a solution of cis-1,4-hexadiene, 5a, trans-dichlorobis(tri-n-butylphosphine)nickel(II), 24, and

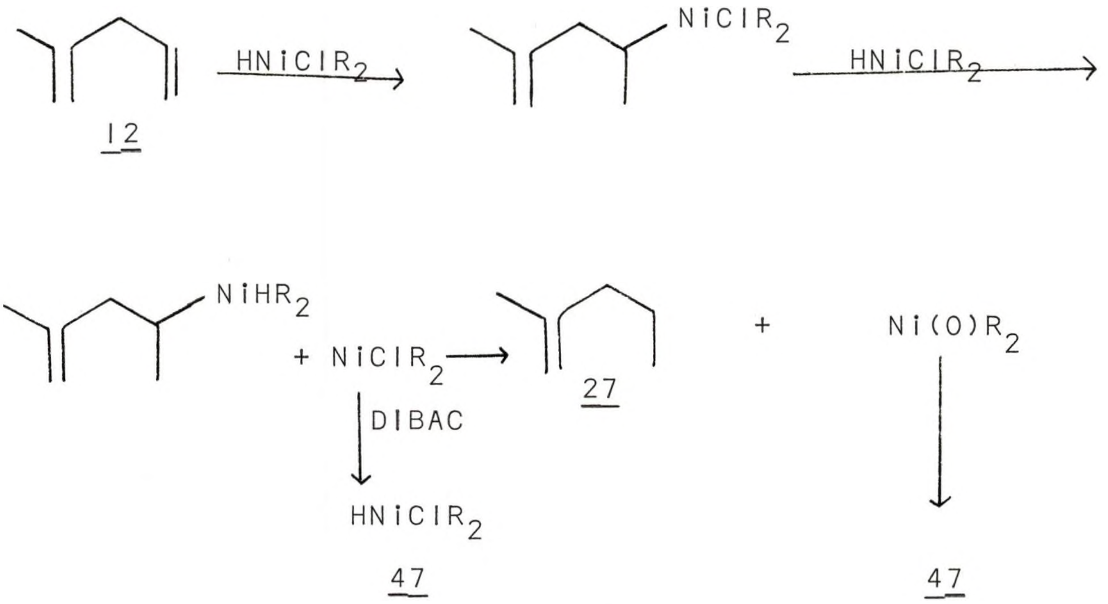
DIBAC at -22°C was catalytically inactive. Addition of ethylene however, resulted in rapid rearrangement to form cis,trans-2,4-hexadiene, 42, and cis,cis-2,4-hexadiene, 43, as major products. Trans-2-methyl-1,3-pentadiene, 26 was formed in low yield. At room temperature, 26 was the major product and 42 and 43 were minor products. Ethylene was not required at room temperature to initiate the reaction. Ethylene may be greatly enhancing the rate of transfer of metal hydride via a route suggested by Marko and his co-workers in the study of the nickel catalyzed insertion of ethylene into an arylmagnesium bond and similar catalyzed alkyl grignard exchange reaction with olefins.[133-135]

(20)



Hydrolysis of DIBAC reagent afforded isobutane and very little isobutene.[136] Both isobutane and isobutene were formed in the rearrangement of dienes with the nickel catalyst formed from Dibac and 24. These were collected and identified. Isobutane was formed by destruction of unreacted DIBAC with alcohol and isobutene presumably from alkylation of nickel.

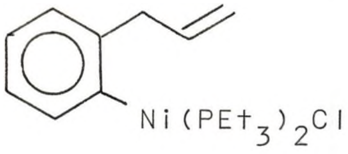
During the rearrangement of 12 at high temperatures, isobutene was the predominant $C_4$ product. The major product from the rearrangement of 2-methyl-1,4-pentadiene, 12, was 2-methyl-1-pentene, 27. The reduction of 12 with a nickel hydride such as 47 would result in the formation of 27. The reaction must be catalytic since 78% of 12 reacted to form products. At a diene:Ni mole ratio of 12:1, this was equivalent to 9.35 moles of 12. The preparation of 27 must also be catalytic since of the 9.35 moles of 12 that reacted, 2.3 moles (35%) were converted to 27. Therefore, only about 4.2% of 27 should be produced unless 47 was regenerated. The implications were that 47 was regenerated as it was used up. Thus, each time an aliquot of reaction mixture was treated with alcohol, the amount of isobutane diminished since the amount of DIBAC had decreased and there was a corresponding increase in isobutene. (Scheme 7: R = $P(C_4H_9)_3$).



Scheme 7. --Hydrogenation of 2-methyl-1,4-pentadiene with trans-hydridochlorobis(tri-n-butylphosphine)Ni(II).

The catalyst has also been used to generate trans-2-hexene from trans-1,4-hexadiene.[116] Cobalt and iron catalysts used in the codimerization of 1,3-dienes and ethylene were also capable of selectively hydrogenating conjugated dienes to monoolefins.[137] The proposed scheme (7) for the hydrogenation of 12 was similar to the one proposed by Orchin and Rupilius[69] for the hydrogenation of butadiene to butenes using $HCo(I)(CO)_4$.

It was also possible to generate an active nickel catalyst by alternate methods. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II), 35, in tetrachloroethylene resulted in the formation of indene, 39, and trans-chloro(trichlorovinyl)bis(triethylphosphine)Ni(II), 37, as major products. Minor products were dichlorobis(triethylphosphine)Ni(II), 36, trans-chloro(2-propenylphenyl)bis(triethylphosphine)Ni(II), 38, allylbenzene, 40, and 1-phenyl-1-propene, 41.[40] The preliminary step in the thermolysis appeared to be formation of indene and hydridochlorobis(triethylphosphine)Ni(II), 48.[128] Dissociation of 48 could form

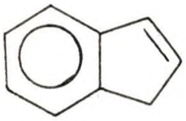


35

$C_2Cl_3Ni(PEt_3)_2Cl$

37

38



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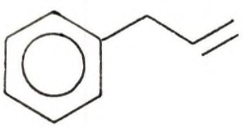

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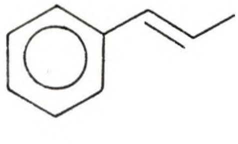


41

HCl and bis(triethylphosphine)Ni(0), 49 (equation 21) which was immediately trapped by solvent to form 37. Some of the hydride, 48, however may isomerize 35 to 38. Protonation of 35 and 38 could afford 36, 40, and 41.[128] Alternatively, reaction of 35 and 38 with hydride, 48 via hydrogenation of the Ni-C bond could occur similar to the route suggested in scheme seven.

$$(21) \qquad \underset{48}{HNi(PEt_3)_2Cl} \rightleftharpoons \underset{49}{HCl + Ni(PEt_3)_2}$$

When thermolysis of 35 was carried out in benzene, 38 was the predominant product. The same intermediate was probably formed in both solvents. The addition of a small amount of tetrachloroethylene to the benzene solution of 35 resulted in a 75% yield of 37. This also indicated that the equilibrium in equation 21 was probably occurring.

The isomerization of 35 to 38 was probably not intramolecular as had been postulated[128] since allylbenzene was catalytically isomerized to 1-phenyl-1-propene, 41. Addition of 5a resulted in it being slowly rearranged to 26, 42, and 43 in the same relative product ratios formed when 5a was treated with the more active catalyst formed from 24 and DIBAC. The isomerization of 5a also supported the hypothesis that the formation of 38 in benzene was not intramolecular since very little 38 was formed even though the thermolysis was carried out for 40-45 hours. The more reactive *cis*-1,4-

hexadiene, 5a appeared to trap the catalyst as it was formed. The thermolysis of 35 in benzene containing allylbenzene did not retard the formation of 38. Cis-1,4-hexadiene may form a less sterically hindered adduct with 48 than would 35. The adduct formed from allylbenzene and 48 would be similar to the adduct formed from 35 and 48. Thus cis-1,4-hexadiene would be able to compete preferentially for the hydride 48. Also 35 and allylbenzene would complete equally for the catalyst and similar amounts of 38 and 41 should be formed. The stability of 3-enylnickel complexes such as the one formed from 5a are known and impart great stability through π-bonding (introduction).

Hydrogenation of the allylic double bond of 35 did not occur as was expected. The hydrogenation of 35 or 38 may not occur unless the catalyst is present in excess. It was observed during the thermolysis of trans-chloro(o-styryl)-bis(triethylphosphine)Ni(II), 2, that ethyl benzene was not formed unless DIBAC was added to the reaction mixture.[138]

An active catalyst should also be formed from HCl and a nickel(0) compound (equation 21). Active dimerization and codimerization catalysts have been formed from HCl and rhodium(I) compounds.[51-52] Ethylenebis(triphenylphosphine)-Ni(0), 45, containing 1% aluminum impurity did not isomerize allylbenzene without the addition of HCl. The catalyst was also capable of rearranging 5a to 26, 42, and 43.[111] Recently, tertiary phosphine and phosphite metal(0) complexes of Ni, Pd, and Os when treated with HCl, sodium borohydride, or hydrogen formed active catalysts capable of rearranging 5a.[139]

## C. THE ALUMINUM COCATALYST

The catalysts formed during the thermolysis of 35 or from HCl and 45 were not as active as the catalyst formed from DIBAC and *trans*-dichlorobis(tri-n-butylphosphine)Ni(II).

Stauffer[132] prepared ethylenebis(tri-o-tolylphosphite)-Ni(0), 46, without the use of organoaluminum compounds. He observed that solutions of HCl and 46 formed a catalyst as active initially as the one formed from DIBAC and 24. It rapidly decreased in activity however over a 30 minute period. Furthermore, the catalyst formed from HCl and 46 did not rearrange 13. It reacted with 12a to form 25a and 26a but not 12b. Treatment of 3,3-dimethyl-1,4-pentadiene with HCl and 46 afforded only 13 which was the type I product. 5-Methyl-1,4-hexadiene which was the type II product was not detected. It thus appeared that the role of the aluminum cocatalyst was not only to form the metal hydride.

A similar situation existed in the catalysts used in the codimerization of 1,3-dienes and ethylene. It was observed that dialkylaluminum halides were more effective cocatalysts than trialkylaluminum compounds during the codimerization with the nickel catalyst formed from 24.[53] Hydridobis[(diphenylphosphino)ethane]Co(I), 10, did not produce an active codimerization catalyst[57] without the use of an organoaluminum compound. The stronger Lewis acid diethylaluminum chloride[140] was a more effective cocatalyst than triethylaluminum. The situation was reversed with dichlorobis[(diphenylphosphino)ethane]Co(II), 9. It was also observed that only Al:Co mole ratios greater than 2:1 resulted in an active catalyst.[89]

Hata and Miyake[86] found that bis(diphenylphosphino)-ethane Fe(0) which catalyzed the codimerization reaction at high temperatures was greatly accelerated at low temperatures by an organoaluminum compound. Furthermore, the most effective catalyst was formed at Al:Fe mole ratios greater than 3:1 and chlorinated organoaluminum compounds were more effective.

The function of the organoaluminum compound besides acting as a reducing agent was also thought to be the removal of a coordinated diphenylphosphinoethane ligand to leave a coordination site for butadiene. The codimerization was thought to occur via a $\pi$-allylmetal ethylene complex which required more coordination sites than are available in 9, 10, or bis-(diphenylphosphino)Fe(0) without ligand dissociation.

Tolman[28,29] had also shown that tetrakis(triethylphosphine)Ni(0) in the presence of sulfuric acid would dissociate to form a hydridotris(triethylphosphite)Ni(II) cation which in the presence of a conjugated diene would form a π-allylnickel(II) complex. This complex was in equilibrium with a π-allyltris(triethylphosphite)nickel(II) species (red) and a π-allylbis(triethylphosphite)nickel(II) species (yellow).

The resulting amber solution was similar to the one formed in toluene containing a diene when 24 was treated with DIBAC.

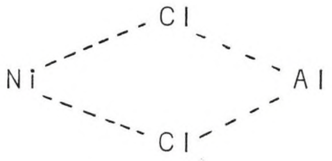
DIBAC may also function similarly in the catalyst formed from it and 24. Hydridochlorobis(tri-n-butylphosphine)Ni(II), 47, normally has five potential coordination sites. These are adequate for the type I rearrangement which require only five coordination sites to form the 3-enylnickel chelate. The type II rearrangement would require an extra coordination site in the formation of the π-allylnickel(II)ethylene complex from 47. The extra coordination site may be gained by utilizing an empty 4d orbital or by dissociation of one of the tri-n-butylphosphine ligands (equation 22; R = butyl).

(22)

$PR_3 \cdot DIBAC$

## D. THE SOLVENT

Various ionic nickel-aluminum complexes have been proposed as intermediates in the nickel-aluminum catalyst systems.[53,141] Most of these possible intermediates incorporated a complex containing bridged halogen bonds. Such an intermediate should decrease the electron density around the nickel atom through elongation of the Ni-Cl bond.

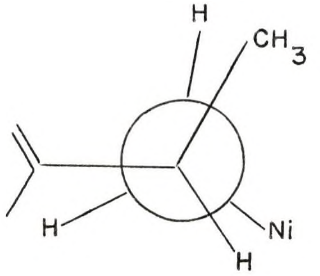


If such an intermediate was improtant, it should be affected by increasing the polarity of the solvent and a change in the reaction should be observed. The rearrangement of 12 was carried out in toluene, chlorobenzene, and 1,2-dichlorobenzene (dielectric constant = 2.38, 5.62, and 9.93 respectively at 25°C). The most noticeable effect caused by increasing the polarity of the solvent was on the formation of 2,3-dimethyl-1,3-butadiene, 25 and *trans*-2-methyl-1,3-pentadiene, 26. The ratio of 26/25 formed in toluene was slightly less than 1.0. The ratio increased to 2.0 in chlorobenzene. A new product, *cis*-2-methyl-1,3-pentadiene, 28, was also formed. Thus, the overall ratio of 2-methyl-1,3-pentadienes/2,3-dimethyl-1,3-butadiene was 2.6. A much more pronounced effect was noted in 1,2-dichlorobenzene. The amount of 25 was less than 28 and the ratio of 2-methyl-1,3-pentadienes/2,3-dimethyl-1,3-butadiene increased to 12.

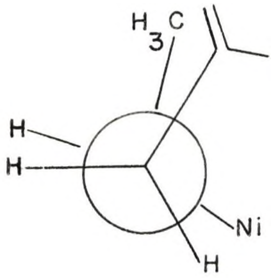
The results indicated that 25 was formed via the type I rearrangement but 26 and 28 were formed via double bond migration. The common intermediate appeared to be the 2,1-metal hydride adduct of 2-methyl-1,4-pentadiene, 12.

The solvent did not appear to affect the type I rearrangement of 12 since the same relative amounts of 25 were formed in chlorobenzene as in toluene. The increase in the reaction of 12 in chlorobenzene was due to the much greater rate of conversion of 12 to products and the increase in the rate of formation of 26. The decrease in the rate of formation of 25 in 1,2-dichlorobenzene as compared to toluene or chlorobenzene may be due to the inability of the type I rearrangement to compete effectively for the 1,2-nickel hydride adduct of 12.

The high *trans*/*cis* ratio of 2-methyl-1,3-pentadienes was also expected. Cramer had shown in the isomerization of 1-butene with a rhodium hydride catalyst that the major product was *trans*-2-butene.[48] The isomerization of 12 to 25 and 26 could also be rationalized in a similar manner. *Cis*-Addition and *cis*-elimination of nickel hydride would require the nickel atom to be in close proximity of hydrogen on the adjacent carbon. Steric properties dictate that the nickel hydride adduct a of 12 should be more stable than the adduct b as a result, 26 should be the predominant product rather than 28.



a

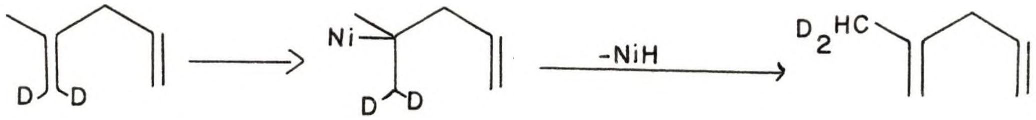


b

The type II rearrangement was also faster in the more polar solvents. In chlorobenzene, 19.2% of 12b was formed within two hours from 12a. This implied that 38.4% of the molecules were undergoing fragmentation. This compared with 16% of 12b formed in 6.5 hours in toluene. Similar results were also obtained from the rearrangement of 13 to 14a. After 30 minutes in toluene, 49.3% of 14a (24.3% conversion of 13) was formed. This compared with 91% of 14a (36.4% conversion of 13) after 30 minutes in chlorobenzene.

The results of the rearrangement of 13 in 1,2-dichlorobenzene could not be easily interpreted since double bond migration in initially formed 14a occurred almost immediately. Metal hydride addition to the substituted double bond appeared to be occurring in 1,1-dideutero-2-methyl-1,4-pentadiene, 12a when the rearrangement was carried out in 1,2-dichlorobenzene. Pmr analysis indicated that 17% $D_2$

was lost at C-1 but only 11.5% $D_2$ gained at C-3. Mass spectral analysis showed that the 12a and 12b mixture contained 2.1% $D_0$, 8.17% $D_1$ and 89.7% $D_2$. The large amount of $D_1$ indicated that some metal hydride addition metal deuteride elimination may be occurring. Some deuterium may also be incorporated in the C-2 methyl group (equation 23).

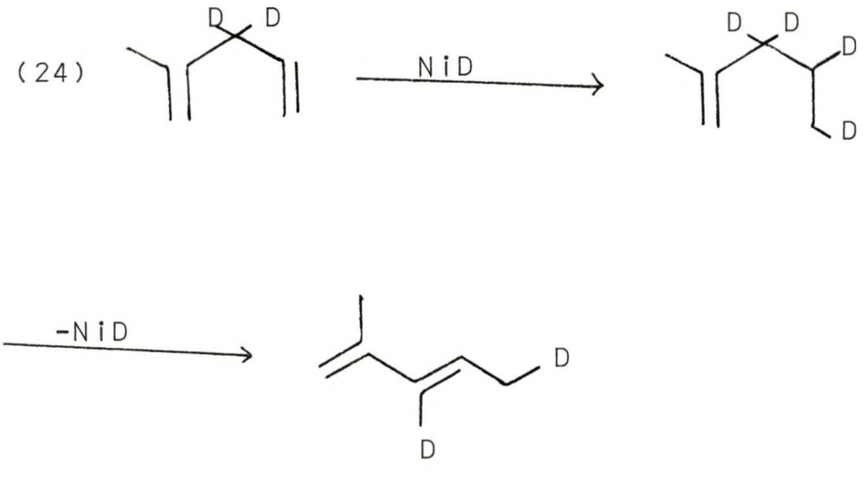
(23) 

Very little, if any, metal hydride addition occurred at the substituted double bond during the rearrangement of 12a in chlorobenzene or toluene. There was only a minimal increase in $D_1$ in recovered 12a from the rearrangement of 12a in toluene or chlorobenzene. Detailed mass spectral analysis of the C-2 methyl group in pure 12a indicated the possibility of a small amount of deuterium in the methyl group. This small amount of deuterium actually showed a decrease of deuterium in the methyl group of starting material recovered from the rearrangement of 1,1-dideutero-2-methyl-1,4-pentadiene, 12a which would not be the case if nickel hydride addition was occurring at the substituted double bond.

Because of the rapid isomerization of 12a via double bond migration in the more polar solvents, the correct amount of 12b initially formed could not be accurately determined. The amount of 12b converted to deutero-2-methyl-1,3-pentadiene, 26b, could be estimated from the excess $D_1$ found in 26a compared with the amount of $D_1$ found in recovered 12a. In the rearrangement of 12a in chlorobenzene, recovered 12a contained 3.93% $D_1$ which compared with 9.1% $D_1$ in 26a. This implied that an additional 5.2% of 12b was formed. Thus, at least 48.8% of the molecules had undergone fragmentation.

A 2,1-nickel deuteride addition and metal deuteride elimination would result in some molecules of 26a being determined as $D_2$ instead of $D_1$ (equation 24). The methyl groups of 25a should also contain deuterium if this was occurring to any appreciable extent. The very close agreement between the methyl and vinyl protons (98.3%) indicated that very little of this was occurring.

(24)



## E. THE TYPE II REARRANGEMENT

Several observations could now be drawn regarding the type II rearrangement: (1) the most probable catalyst was a nickel hydride; (2) the preliminary step in the reaction was the 1,2-nickel hydride addition to the terminal unsubstituted double bond of the 1,4-diene; (3) the rearrangement was reversible; (4) the aluminum cocatalyst was necessary; (5) the rearrangement followed the fragmentation route; and (6) the polarity of the solvent affected the rate of formation of products.

The above observations could also be used to illustrate several similarities and differences between the type I and type II rearrangements. The nickel hydride catalyzed both rearrangements and addition of catalyst to the unsubstituted terminal double bond of the 1,4-diene also appeared to be the preliminary step in both rearrangements.

The position of the addition of the catalyst to the terminal double bond was different in the type I (2,1-nickel hydride addition) and type II (1,2-nickel hydride addition) rearrangements. The reaction pathways also were different. These observations have been demonstrated by the reaction of 2,3-dimethyl-1,4-pentadiene which only underwent the type II rearrangement; 1,1-dideutero-2-methyl-1,4-pentadiene which underwent both rearrangements; and _cis_-1,4-hexadiene which only underwent the type I rearrangement.

The aluminum cocatalyst necessary for the type II rearrangement was not needed initially for the type I rearrangement since the catalyst formed in the absence of aluminum compounds did not react with 2,3-dimethyl-1,4-pentadiene via the type I rearrangement.

# PART IV. EXPERIMENTAL

## A. EQUIPMENT AND MATERIALS

1. Equipment. --Infrared spectra were recorded on the Beckman IR 12 and the Perkin Elmer Infracord 137 recording spectrophotometers. Infrared absorptions were reported in reciprocal centimeters ($cm^{-1}$). The proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer using neat samples or solutions in either carbon tetrachloride or deuterated benzene. Chemical shifts were reported as $\tau$ values in units of parts per million (ppm) downfield from tetramethylsilane. Mass spectra were recorded by Morgan Shaffer Inc. and on the Dupont 21-491 mass spectrometer.

Product yields from the diene rearrangement reactions were determined by gas liquid phase chromatography (glpc). The diene products were analyzed on the 20 ft. x 3/8 in. 20% β,β'-oxydipropionitrile on firebrick 60/80 column (β,β'). The alkenes were analyzed on the 15 ft.x 1/4 in. 20% silicon rubber (Se-30) on Chromsorb P 60/80 column. The aromatic hydrocarbons were analyzed on a 20 ft. x 3/8 in. 20% 1,2,3-tris(2-cyanoethoxy)-2-propane on 60/80 Chromsorb P (TCEP) column

2. Materials. --Anhydrous diethylether was obtained from freshly opened cans or distilled from sodium wire. Tetrahydrofuran was dried by distillation from lithium aluminum hydride and stored over molecular sieves type 4a (Linde Air Products). Pentane (Fischer Pesticide Grade) was used without

further purification. Hexane (reagent grade) was washed with 5% potassium permanganate, dried over anhydrous calcium chloride, and distilled from sodium wire. It was stored over silica gel. Tetrachloroethylene was stored over molecular sieves and filtered through alumina prior to being used. Toluene (ACS certified spectroanalyzed) was distilled from sodium wire and stored over molecular sieves. Commercial absolute ethanol was refluxed over magnesium ethoxide and distilled directly into the reaction flask prior to carrying out reactions. Allyl bromide was dried over anhydrous magnesium sulfate, distilled, and stored over molecular sieves. Allyl chloride was dried over anhydrous calcium chloride, distilled, and stored over molecular sieves. Acetyl chloride was dried over molecular sieves, distilled, and stored over molecular sieves in a tightly closed bottle. Diethylmethyl malonate (Aldrich Chemical Co.) was dried over anhydrous magnesium sulfate and distilled prior to use. Aluminum oxide, acid washed, purchased from J. T. Baker Chemical Co., was heated at 110°C for an hour before being used. Bis(2,4-pentanedianato)nickel(II) (Research Organic/Inorganic Chemical Co.), tri-n-butylphosphine (Aldrich Chemical Co.), triethylphosphine (Orgmet, Inc.), triethylaluminum (neat), diisobutylaluminum chloride (25% in toluene), and diisobutylaluminum hydride (neat) (Texas Alkyls Inc.), lithium aluminum deuteride: minimum 99% deuterium (Merck Sharpe and

Dohme of Canada Ltd.), vinylmagnesium chloride; 1 molar in tetrahydrofuran (Alfa Inorganics, Inc.), nickel dichloride; 99.999% purity (Alfa Inorganics, Inc.), and 1-butanol (ACS Fischer Certified Grade) were all used as obtained. 2-Methyl-1,4-pentadiene, trans-2-methyl-1,3-pentadiene, 2-methyl-1-pentene, allylbenzene, 2-chloro-1-benzoic acid, and triphenylphosphine were all obtained from Aldrich Chemical Co. cis-1,4-Hexadiene and ethylenebis(triphenylphosphine)-Ni(0) were obtained from P. Pinke. Ethylenebis(tri-o-tolylphosphite)-Ni(0) was obtained from R. Stauffer. Dichlorobis-(tri-n-butylphosphine)Ni(II) and dichlorobis(triethylphosphine)Ni-(II) were prepared according to the method of Jensen and Nygard.[142] 1-Allyl-2-chlorobenzene was prepared from allyl chloride and the Grignard derived from 1-chloro-2-iodobenzene.

## B. THE SYNTHESIS OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE

1. Preparation of diethyl-1-pentene-4,4-dicarboxylate.--Sodium metal (24.9 g, 1.08 moles) was added in small pieces to 750 ml of absolute ethanol over a one hour period under nitrogen atmosphere. Redistilled diethylmethyl malonate (188.6 g, 1.08 moles) was added to the flask. Freshly distilled allyl chloride (114 g, 1.49 moles) was added to the flask over a one hour period. The solution was then refluxed for twenty hours. The ethanol was then removed on a steam bath.

An aquesous solution of 15% sodium chloride was added to the cooled solution and the lower layer discarded. The diethyl-1-pentene-4,4-dicarboxylate, 19, was dried over anhydrous magnesium sulfate, filtered, and vacuum distilled at 101-106°C (13 mm) to afford 183.1 g (79%). The pmr spectrum showed a multiplet at $\tau$3.95 to 4.63 for the C-4 vinylic proton, a perturbed doublet centered at $\tau$4.98 and 3.47 for the two C-5 protons; a quartet at $\tau$5.92 (J=7 Hz) for the $CH_2$ group of the ester ethoxy group, a doublet at $\tau$7.47 (J=7 Hz) for the two C-3 protons, a triplet at $\tau$8.8 (J=8 Hz) for the C-2 methyl group (strong singlet) and the methyl of the ester ethoxy group. The infrared spectrum showed bands at 3097, 930 and 1030 cm$^{-1}$ (monosubstituted vinylic), 1650 cm$^{-1}$ (C=C), and 1740 cm$^{-1}$ (C=O).

2. Preparation of 2-methyl-4-pentenoic acid.[118]--Hydrolysis of 19 (183 g, 0.86 mole) was carried out using one gram of potassium hydroxide and one ml of water for each gram of the ester. A double surface condenser is necessary to control the spontaneous reaction. After the spontaneous reaction terminated, the solution was then refluxed gently for an additional 45 minutes. To this solution was then added 175 ml of water and the ethanol was removed by distillation. The solution was cooled in an ice bath and made distinctly acidic with hydrochloric acid. The 1-pentene-4,4-dicarboxylic acid, 20, was collected by liquid-liquid extraction with diethylether. The diacid 20 was then decarboxylated by

by heating in an oil bath at 160-170°C (10-20 mm). 2-Methyl-4-pentenoic acid, 16, was removed by distillation (93-100°C) as it formed. The yield of 16 was 66.7 g (68.4%). The pmr spectrum of 16 showed a singlet at $\tau$1.38 for the $CO_2$-H, a multiplet at $\tau$3.73 to 4.53 for the C-4 proton, a perturbed doublet at $\tau$4.85 and $\tau$5.06 for the two protons at C-5, a multiplet at $\tau$7.17 to 8.23 for the C-2 proton and the two C-3 protons, and a doublet at $\tau$8.83 (J=7 Hz) for the C-2 methyl group. The infrared spectrum showed bands at 3090 $cm^{-1}$, 920 $cm^{-1}$, 995 $cm^{-1}$ (monosubstituted vinylic), 1648 $cm^{-1}$ (C=C), and 1718 $cm^{-1}$ (C=O).

3. Preparation of ethyl-2-methyl-4-pentenoate.--The acid 16 (35 g, 0.31 mole) was added to a flask containing 40 ml of absolute ethanol, 75 ml of dry benzene, and three ml of sulfuric acid. The solution was refluxed for 11 hours under nitrogen atmosphere at 94-97°C. The water was removed as it was formed using a Dean-Stark trap. The solution was cooled and shaken with an aqueous solution of 15% sodium chloride and the lower layer was discarded. The upper layer was washed with an aqueous solution of 10% sodium chloride-10% sodium carbonate and dried over anhydrous magnesium sulfate. The benzene was removed by distillation under reduced pressure. The ethyl-2-methyl-4-pentenoate, 21, was distilled at 80-82°C (71 mm) to afford 32.4 g (75%).

The pmr spectrum of 21 showed a multiplet at $\tau$3.87 to 4.53 for the C-4 vinylic proton, a perturbed doublet centered at $\tau$4.88 and 5.10 for the two C-5 vinylic protons, a quartet at $\tau$5.82 (J=7 Hz) for the methylene of the ester ethoxy group, a multiplet at $\tau$7.33 to 8.28 for the C-2 proton and the two C-3 protons, a multiplet from $\tau$8.68 to 8.92 for the C-2 methyl group and the methyl of the ester ethoxy group. The infrared spectrum showed bands at 3090, 920, 1,000 $cm^{-1}$ (monosubstituted vinylic), 1650 $cm^{-1}$ (C=C), and 1740 $cm^{-1}$ (C=O).

4. *Preparation of 1,1-dideutero-2-methyl-4-penten-1-ol*.--Lithium aluminum deuteride, *22a*, (3 g, 0.07 mole) was placed in the reaction flask under nitrogen atmosphere *via* a glove bag. Anhydrous diethylether (50 ml) was added to the flask and the solution stirred for five minutes. A solution of *21* (191. g, 0.135 mole) in 60 ml of anhydrous ether was placed in an equi-pressure dropping funnel and added to the flask at such a rate as to produce gentle refluxing of the ether. An additional 100 ml of ether was then added and the solution stirred for one hour. The excess *22a* was carefully destroyed with water. The solution was added to 200 ml of 12.5% sulfuric acid and ice. The ether layer was removed and the water layer was extracted three times with 50 ml aliquots of ether. The combined ether extracts were washed twice with an aqueous solution of 10% sodium chloride-10% sodium carbonate and dried over anhydrous magnesium sulfate. The solution was filtered and the ether removed under vacuum. Distillation under vacuum at 114-116°C (146 mm) afforded 13.7 g (100%) of

1,1-dideutero-2-methyl-1-penten-1-ol, 23a.

The reaction had previously been carried out several times with lithium aluminum hydride to obtain 87-90% of 2-methyl-4-penten-1-ol, 23.

The pmr spectrum of 23 possessed a multiplet at $\tau$3.85 to 4.52 for the C-4 vinylic proton, a perturbed doublet centered at $\tau$ 5.0 and 5.17 for the two C-5 protons and the O-H proton, a multiplet at $\tau$ 7.63 to 8.82 for the two C-3 protons and the C-2 proton, a doublet at $\tau$ 6.6 (J=6 Hz) for the two C-1 protons, and a doublet at $\tau$ 9.08 (J=6 Hz) for the C-2 methyl group. The pmr spectrum of 23a was the same as 23 except for the expected disappearance of the doublet at $\tau$ 6.6 and the O-H proton shifted to $\tau$5.5.

The infrared spectrum of 23a was not run for fear of loss of sample. The infrared spectrum of 23, however, showed bands at 3080, 915, 99c $cm^{-1}$ (monosubstituted vinylic) and 1645 $cm^{-1}$ (C=C) indicating that double bond isomerization does not occur during the reaction.

5. Preparation of 1,1-dideutero-2-methyl-4-pentenylacetate.--The alcohol 23a (13.7 g, 0.134 mole) was added to a flask containing 100 ml of anhydrous ether and 12 g of pyridine. The solution was cooled to 0°C and acetyl chloride (13.2 g, 0.168 mole) was added to the flask under nitrogen atmosphere over a twenty minute period. The solution was allowed to warm to room temperature and stirred under nitrogen for three

hours. It was then refluxed for an additional two hours. To the flask were then added 50 ml of cold water and the lower layer was discarded. The ether layer was washed successively with 100 ml of 10% hydrochloric acid, 100 ml of water, 100 ml of an aqueous solution of 10% sodium chloride-10% sodium carbonate, and 100 ml of water. The ether layer was then dried over anhydrous magnesium sulfate, filtered, and the ether removed under vacuum. Distillation at 99-102$^{\circ}$C (111 mm) afforded 19.3 g (80%) of 1,1-dideutero-2-methyl-4-pentenylacetate, 15a.

The reaction had previously been carried out several times with 23 to obtain similar yields of 15.

The pmr spectrum of 15 possessed a multiplet at $\tau$ 3.95 to 4.5 for the C-4 proton, a perturbed doublet centered at $\tau$ 4.88 and 5.10 for the two C-5 vinylic protons, a multiplet at $\tau$ 7.77 to 8.32 for the two C-3 protons, the C-2 proton, and a strong singlet at $\tau$ 8.03 for the acetyl methyl group. It also possessed a doublet at $\tau$ 6.58 (J= 7 Hz) for the C-2 methyl group.

The pmr spectrum of 15a was essentially the same except for the expected disappearance of the doublet at $\tau$ 6.09.

The infrared spectrum of 15a was not run for fear of loss of sample. The infrared spectrum of 15 however possessed bands at 3090, 920, 1,000 cm$^{-1}$ (monosubstituted vinylic), 1649 cm$^{-1}$ (C=C), and 1750 cm$^{-1}$ (C=O) which indicated that no double bond isomerization was occurring.

6. Preparation of 1,1-dideutero-2-methyl-1,4-pentadiene.--The acetate 15a (8.3 g, 0.098 mole) was pyrolized by passing it slowly through a ten inch column of glass ringlets heated to 600°C with a nitrogen atmosphere of about five liters per hour. The product was collected at the end of the column with two traps immersed in dry ice-acetone baths. The product was separated from the acetic acid by distillation at 50-70°C. The residue was passed through the column and the product was collected as before. Preparative gas liquid phase chromatographic (glpc) on the 20 ft. $\beta,\beta'$ column at 30°C afforded 1.4 g of 1,1-dideutero-2-methyl-1,4-pentadiene, 12a (17%).

The pyrolysis was carried out several times previously with 15 to afford 2-methyl-1,4-pentadiene, 12 in similar yields.

The pmr spectrum of 12 has been characterized[122] and shows the following: a multiplet at $\tau$3.96 to 4.57 for the C-4 proton; a perturbed doublet of 8-line singlets at $\tau$4.89 and 5.13 for the two C-5 protons; a singlet at $\tau$5.32 for the two C-1 protons; a doublet at $\tau$7.29 (J=6 Hz) for the two C-3 protons; and a singlet at $\tau$8.31 for the C-2 methyl group.

The pmr spectrum of 12a was essentially the same except that the singlet at $\tau$5.32 for the two C-1 protons had disappeared as expected.

The C-2 methyl group was used as an internal standard to determine the integral ratios of the protons in 12a.

TABLE 3

INTEGRAL RATIOS FOR PURE

1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE

| Protons | Position (τ) | Relative Ratios |
|---|---|---|
| C-1; two | 5.32 | 0.0432 |
| C-2 Methyl; three | 8.31 | 3.0 |
| C-3; two | 7.29 | 1.99 |
| C-4; one | 3.96 to 4.57 | 1.11 |
| C-5; two | 4.89, 5.13 | 2.07 |

The ratio of 0.0432 at C-1 indicated that there was 97.8% $D_2$ at that position. The mass spectral analysis of 12a indicated that it contained 1.2% $D_o$, 2.78% $D_1$, 96% $D_2$, and 0.02% $D_3$.

## C. THE GENERAL PROCEDURE FOR THE REARRANGEMENT REACTION OF 1,4-DIENES

The reactions were normally carried out in a 100 ml single neck side arm flask fitted with a three-way stopcock and a magnetic stirring bar. The side arm (used for aliquot removal) was capped with a rubber septum.

To the flask was added trans-dichlorobis(tri-n-butylphosphine)Ni(II), 24 (0.378 g, 0.71 mmole) and the flask was purged with nitrogen. To the flask was then added 70 ml of nitrogen purged solvent and 9.52 mmoles of diene. The red solution was then treated with two ml of 25% diisobutylaluminum chloride in toluene (2.5 mmoles). Diisobutylaluminum chloride will be referred to as DIBAC. The resulting amber solution was stirred at room temperature under nitrogen atmosphere (diene:Ni:Al mole ratio = 12:1:3.5). The reaction was monitored by periodic removal of standard sized aliquots which were quenched with a fixed quantity of 2-propanol and then analyzed by glpc analysis on the 20 ft. β,β' column at 60°C with a helium flow rate of 170 ml/minute. The reaction was terminated at the desired conversion with 1-butanol and the resulting solution distilled to give a diene rich fraction. The diene products were then collected via glpc and identified by infrared and pmr spectra.

## D. THE REARRANGEMENT REACTION OF 2-METHYL-1,4-PENTADIENES

1. The rearrangement reaction of 2-methyl-1,4-pentadiene in toluene.--The reaction was carried out according to the general procedure except that 0.191 g of 24 (0.358 mmole), 35 ml of toluene, 0.35 g of 12 (4.26 mmoles), and one ml of

the 25% DIBAC solution (1.24 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.4). Periodically 0.15 ml aliquots of solution were removed and shaken in a stoppered test tube containing 0.07 ml of 2-propanol for glpc analysis. Analysis by glpc indicated the formation of two new products. The reaction was terminated after 6.5 hours with one ml of 1-butanol. The resulting solution was distilled (50-100°C) to give about two ml of distillate. Preparative glpc analysis on the 20 ft. β,β' column at 60°C and a helium flow rate of 170 ml/minute resulted in the isolation of 2,3-dimethyl-1,3-butadiene, 25, as the lower retention time product. This was identified by comparative pmr spectra.[116,122] The higher retention time product was collected in the same manner and was also identified by comparative pmr to be *trans*-2-methyl-1,3-pentadiene, 26.[111,116] The lowest retention peak was unreacted 12.

2. *The rearrangement reaction of 2-methyl-1,4-pentadiene in chlorobenzene*. --The general procedure for the rearrangement of dienes was followed except that 0.21 g of 24 (0.4 mmole), 40 ml of chlorobenzene, 5.85 mmoles of 12, and 1.3 ml of 25% DIBAC in toluene (1.6 mmoles) were used (diene:Ni:Al mole ratio = 15:1:4). The reaction was terminated after 6.5 hours with two ml of 1-butanol. The products were separated from the solvent by distillation and collected by preparative glpc on the 20 ft. β,β' column. A new product

eluted before 26 was identified by comparative pmr spectra to be cis-2-methyl-1,3-pentadiene, 28.[111]

### TABLE 4

### YIELD DATA FOR THE REARRANGEMENT OF 2-METHYL-1,4-PENTADIENE IN TOLUENE

| Time (minutes) | % Conversion | % Yield of 25 | % Yield of 26 |
|---|---|---|---|
| 10 | 15.4 | 1.6 | 1.3 |
| 30 | 19.4 | 2.2 | 2.0 |
| 60 | 23.1 | 3.0 | 3.0 |
| 120 | 28.2 | 4.2 | 3.9 |
| 390 | 35.0 | 7.8 | 6.8 |

3. The rearrangement reaction of 2-methyl-1,4-pentadiene in 1,2-dichlorobenzene. --The general procedure for the rearrangement of dienes was followed except that 0.192 g of 24 (0.36 mmole), 40 ml of 1,2-dichlorobenzene, 4.26 mmoles of 12, and one ml of 25% DIBAC in toluene (1.24 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.8). The reaction was terminated after two hours with two ml of 1-butanol. The products were separated from the solvent by distillation and collected by preparative glpc on the 20 ft. β,β' column.

## TABLE 5

## YIELD DATA FOR THE REARRANGEMENT REACTION OF 2-METHYL-1,4-PENTADIENE IN CHLOROBENZENE

| Time (Minutes) | % Conversion | % Yield of 25 | % Yield of 26 | % Yield of 28 |
|---|---|---|---|---|
| 15 | 44 | 3.4 | 7.1 | 2.43 |
| 30 | 47.2 | 4.7 | 11.3 | 2.6 |
| 60 | 55.8 | 6.3 | 13.5 | 3.1 |
| 240 | 67.8 | 10.3 | 19.9 | 3.2 |
| 390 | 74.05 | 10.7 | 21.3 | 2.9 |

## TABLE 6

## YIELD DATA FOR THE REARRANGEMENT REACTION OF 2-METHYL-1,4 PENTADIENE IN 1,2-DICHLOROBENZENE

| Time (Minutes) | % Conversion | % Yield of 25 | % Yield of 26 | % Yield of 28 |
|---|---|---|---|---|
| 15 | 31.9 | 4.6 | 47.14 | 6.2 |
| 30 | 41.2 | 4.5 | 47.14 | 7.15 |
| 60 | 49.2 | 3.8 | 46.15 | 6.8 |
| 120 | 61.8 | 4.0 | 43.26 | 5.6 |

4. The rearrangement reaction of 1,1-dideutero-2-methyl-1,4-pentadiene in toluene. --The general procedure for the rearrangement or dienes was followed except that 0.083 g of 24 (0.15 mmole), 14 ml of toluene, 1.7 mmoles of 12a, 0.4 ml of 25% DIBAC in toluene (0.5 mmole) were used (diene:Ni:Al mole ratio = 11:1:3.2). The reaction was terminated after 6.5 hours with two ml of 1-butanol. The products were separated from the solvent by distillation and collected by preparative glpc on the 20 ft. β,β' column.

TABLE 7

YIELD DATA FOR THE REARRANGEMENT REACTION OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE IN TOLUENE

| Time (Minutes) | % Conversion | % Yield of 25a | % Yield of 26a |
|---|---|---|---|
| 5 | 13.5 | 2.2 | 1.7 |
| 15 | 19.4 | 3.18 | 3.18 |
| 30 | 20.5 | 3.6 | 3.18 |
| 60 | 26.2 | 4.4 | 4.14 |
| 240 | 43.15 | 9.1 | 7.32 |
| 390 | 42.3 | 11.5 | 10.2 |

The pmr spectrum of recovered 12a was analyzed using the C-2 methyl group as an internal standard. Comparison with the pmr spectrum of pure 12a showed a gain of 15% $D_2$ at C-3 and a loss of 16.8% $D_2$ at C-1. This indicated that an average of 15.9% 3,3-dideutero-2-methyl-1,4-pentadiene, <u>12b</u> was formed. Mass spectral analysis of recovered <u>12a</u> showed 2.9% $D_1$ 99.5% $D_2$, and 1.6% $D_3$ as compared with 2.2% $D_1$ and 97.8% $D_2$ in pure <u>12a</u>.

TABLE 8

PMR DATA FOR THE REARRANGEMENT OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE IN TOLUENE

| Number of Protons | Position ($\tau$) | Integral Ratio |
|---|---|---|
| C-4; one | 3.96-4.57 | 1.06 |
| C-5; two | 4.98,5.13 | 2.06 |
| C-3; two | 7.29 | 1.70 |
| C-2 Methyl; three | 8.31 | 3.00 |
| C-1; two | 5.32 | 0.378 |

5. <u>The rearrangement reaction of 1,1-dideutero-2-methyl-1,4-pentadiene in chlorobenzene</u>. --The procedure was the same as the general procedure for the rearrangement of 1,4-dienes except that 0.425 g of <u>12a</u> (5.06 mmoles), 43 ml of chlorobenzene, 0.242 g (0.453 mmole) of <u>24</u>, and 1.2 ml of 25% DIBAC in toluene (1.49 mmoles) were used (diene:Ni:Al mole ratio = 11:1:3.2). The reaction was terminated after two hours with

two ml of 1-butanol. The products were separated from the solvent by distillation and collected *via* preparative glpc on the β,β' column.

## TABLE 9

## YIELD DATA FOR THE REARRANGEMENT REACTION OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE IN CHLOROBENZENE

| Time (Minutes) | % Conversion | % Yield of 25a | % Yield of 26a | % Yield of 28a |
|---|---|---|---|---|
| 15 | 33.1 | 9.0 | 16.7 | 1.8 |
| 30 | 38.5 | 16.45 | 38.4 | 5.9 |
| 60 | 52.2 | 15.8 | 35.1 | 4.4 |
| 120 | 56.3 | 22.3 | 34.5 | 3.8 |

## TABLE 10

## PMR DATA FOR THE REARRANGEMENT OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE IN CHLOROBENZENE

| Number of Protons | Position ($\tau$) | Integral Ratios |
|---|---|---|
| C-1; two | 5.32 | 0.427 |
| C-2 Methyl; three | 8.31 | 3.00 |
| C-3; two | 7.29 | 1.622 |
| C-4; one | 3.96-4.57 | 1.07 |
| C-5; two | 4.89,5.13 | 2.02 |

The C-2 methyl group was used as an internal standard to analyze the pmr spectrum of recovered 12a. Comparison of the pmr spectrum of recovered 12a with that of pure 12a showed a gain of 18.5% $D_2$ at C-3 and a loss of 19.9% $D_2$ at C-1. This indicated that an average of 19.2% 3,3-dideutero-2-methyl-1,4-pentadiene, 12b was formed.

The products of the type I rearrangement (25a and 26a) were also analyzed by mass spectrometry and pmr spectroscopy.

The pmr spectrum of 1,1-dideutero-*trans*-2-methyl-1,3-pentadiene, 26a showed the following: a perturbed doublet at $\tau$3.39 (J=15 Hz) for the vinylic proton at C-3; an overlapping multiplet at $\tau$4.0-4.66 for the vinylic proton at C-4; a perturbed singlet at $\tau$5.0 for the two protons at C-1; a singlet superimposed upon a slightly perturbed doublet at $\tau$8.20 (J=5 Hz) for the C-2 methyl group and the three C-5 protons. The pmr spectrum of 26a showed only a small singlet at $\tau$5.20 (due to the reaction of 3,3-dideutero-2-methyl-1,4-pentadiene formed during the rearrangement of 1,1-dideutero-2-methyl-1,4-pentadiene). The integral ratios using the six methyl protons as a standard showed 0.24 at C-1 (12% $H_2$); 1.00 at C-3; 1.13 at C-4; and 6.00 for the C-2 methyl group and the three protons at C-5. The mass spectral analysis showed 0.5% $D_0$, 9.07% $D_1$, 89.5% $D_2$, and 0.86% $D_3$.

The pmr spectrum of 25 showed a doublet at $\tau$5.03 (J=5 Hz) for the four protons at C-1 and C-4; and a single $\tau$ at $\tau$8.10 for the six protons on the C-2 and C-3 methyl groups. The pmr spectrum of 25a was the same except that the intensity of the doublet at τ5.03 was reduced. The integral ratios using the six methyl protons as an internal standard showed a ratio of 2.95 (98.33% of the expected 3:1 ratio).

The mass spectral analysis of 25a showed the following: 1.83% $D_0$, 3.93% $D_1$, 92.8% $D_2$, and 1.42% $D_3$.

6. The rearrangement reaction of 1,1-dideutero-2-methyl-1,4-pentadiene in 1,2-dichlorobenzene. --The general procedure for the rearrangement of dienes was followed except that 55 ml of 1,2-dichlorobenzene, 6.75 mmoles of 25a, 0.3 g (0.56 mmole) of 24, and 1.6 ml of 25% DIBAC in toluene (1.98 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.5). The reaction was terminated after 1.5 hours with two ml of 1-butanol. The products were separated by distillation and collected by preparative glpc on the 20 ft. β,β' column.

TABLE II

THE YIELD DATA FOR THE REARRANGEMENT OF 1,1-DIDEUTERO-2-METHYL-1,4-PENTADIENE IN 1,2-DICHLOROBENZENE

| Time (Minutes) | % Conv. version | % Yield of 26a | % Yield of 25a | % Yield of 28a |
|---|---|---|---|---|
| 1 | 23.41 | 10.89 | 1.90 | 1.71 |
| 5 | 27.42 | 25.78 | 4.06 | 3.25 |
| 30 | 37.9 | 39.08 | 3.5 | 6.5 |
| 60 | 48.0 | 39.81 | 4.6 | 5.4 |
| 90 | 56.4 | 38.71 | 4.6 | 4.8 |

The pmr spectrum indicated that the singlet at τ5.32 for the two protons at C-1 had increased in intensity by 0.342 (17.2% $H_2$) and the doublet at τ7.29 (J=6.4 Hz) for the two protons at C-3 had decreased in intensity from 1.99 to 1.77 (11.5% $D_2$) in recovered 12a. There was a minimum of 11.5% 3,3-dideutero-2-methyl-1,4-pentadiene, 12b, in recovered 12a. The other products were 25a, 26a, and 28a.

Mass spectral analysis of recovered 1,1-dideutero-2-methyl-1,4-pentadiene, 12a showed 2.12% $D_0$, 8.17% $D_1$, and 89.71% $D_2$. Recovered 26a contained 1.54% $D_0$, 11.2% $D_1$, 85.78% $D_2$, 1.02% $D_3$, and 0.44% $D_4$. The pmr spectrum of 26a was analyzed using the C-2 proton as an internal standard. The relative peak intensities were 0.876 (12.4% D) for the vinylic proton at C-4; 0.283 (14.1% $H_2$) for the two C-1 protons; and 4.23 (30% D) for the six methyl protons.

7. The rearrangement reaction of 2-methyl-1,4-pentadiene in toluene at 50-55°C. --The apparatus used in the general procedure for the rearrangement of dienes was modified by inserting a condenser between the side arm flask and the threeway stopcock. To the flask were added 0.116 g (0.21 mmole) of 24, 40 ml of nitrogen purged toluene, and 2.53 mmoles of 2-methyl-1,4-pentadiene, 12. The flask was then immersed in an oil bath at 50-55°C and 0.15 ml of solution removed and shakened with 0.07 ml of 2-propanol in a stoppered test tube. To the flask was then added 0.6 ml of 25% DIBAC in toluene (0.74 mmole) (diene:Ni:Al mole ratio =

12:1:3.4). The reaction was monitored periodically by removing 0.15 ml aliquots and treating as before for glpc analysis. The reaction was terminated after 6.5 hours with two ml of 1-butanol. The products were separated from the solvent by distillation and collected by preparative glpc on the 20 ft. β,β' column.

Glpc analysis indicated that the major product was one eluted before 12. Comparative pmr spectra with an authentic sample purchased from Aldrich Chemical Company confirmed that this product was 2-methyl-1-pentene, 27.[123] The products from the normal rearrangement of 12 in toluene 25 and 26, were formed in low yields.

TABLE 12

YIELD DATA FOR THE REARRANGEMENT REACTION OF 2-METHYL-1,4-PENTADIENE IN TOLUENE AT 50-55°C

| Time (Minutes) | % Conversion | % Yield of 27 | % Yield of 25 | % Yield of 26 |
|---|---|---|---|---|
| 15 | 12 | - | 0.93 | 0.68 |
| 60 | 25.4 | - | 1.55 | 1.6 |
| 180 | 50 | 6.9 | 2.1 | 2.4 |
| 240 | 68 | 21.7 | 1.64 | 4.1 |
| 300 | 75.2 | 25.2 | 1.26 | 4.3 |

8. <u>The rearrangement reaction of 2-methyl-1,4-pentadiene using ethylenebis(tri-o-tolylphosphite)Ni(0) and HCl</u>.--Ethylenebis(tri-o-tolylphosphite)Ni(0) (0.19 g, 0.24 mmole) was placed in a small round bottom flask topped with a medium porosity filtering tube. It was dissolved in four ml of nitrogen purged toluene and filtered into a 50 ml side arm flask under nitrogen atmosphere. A small magnetic stirring bar was placed in the flask and it was topped with a three-way stopcock. The solution was diluted to 20 ml with toluene and 2.53 mmoles of <u>12</u> were added to the flask. Aliquots were removed periodically and subjected to glpc analysis on the β,β' column. HCl in toluene (0.5 ml, 0.121 mmole) was added to the solution (diene:Ni:HCl mole ratio = 10.5:1:0.5) and stirred for four hours. Periodically 0.1 ml aliquots were removed and shaken in air to destroy the catalyst. These were subjected to glpc analysis. The reaction was terminated after four hours by shaking the solution in air. The products were removed by distillation and collected by preparative glpc. Glpc analysis indicated that the reaction had ceased after 30 minutes. Pmr spectra of the products showed that these were <u>25</u> and <u>26</u>.

TABLE 13

YIELD DATA FOR THE REARRANGEMENT REACTION OF 2-METHYL-1,4-PENTADIENE WITH ETHYLENEBIS(TRI-o-TOLYLPHOSPHITE)Ni(0)

| Time (Minutes) | % Conversion | % Yield of 25 | % Yield of 26 |
|---|---|---|---|
| 0.5 | 6.2 | 45.3 | 54.7 |
| 30 | 20.2 | 43.2 | 56.3 |
| 60 | 20.1 | 45.5 | 55 |
| 240 | 19.6 | 45.7 | 56 |

## E. THE SYNTHESIS OF 2,3-DIMETHYL-1,4-PENTADIENE AND CIS, TRANS-4-METHYL-1,4-HEXADIENE

A 500 ml three neck round bottom flask was equipped with a magnetic stirring bar, an extension joint capped with a rubber septum (for aliquot removal), a bubbler tube (for saturating the system with ethylene), and a reflux condenser topped with a three-way stopcock for ethylene atmosphere. To the flask were added 200 ml of anhydrous chlorobenzene and 1.093 g of 24 (2.05 mmoles) and the mixture was purged with nitrogen. Ethylene was then bubbled vigorously into the solution for 15 minutes. Isoprene (20 g, 300 mmoles) was added through the septum to the solution and ethylene was bubbled into the solution for an additional fifteen minutes. An aliquot (0.15 ml) was removed and shaken in a stoppered test tube containing 0.07 ml of 2-propanol. To the solution was quickly added 6 ml of 25% DIBAC in toluene (7.45 mmoles) and the solution stirred for 30 minutes at 23-25°C under ethylene atmosphere by bubbling ethylene vigorously into the solution. Another aliquot was removed and treated as before. The reaction was then terminated with 5 ml of 1-butanol. The isomeric butenes were removed by stirring the solution at room temperature for one hour. The unreacted isoprene was removed by distillation.

A fraction boiling at 70-96°C was collected and further separated by distillation from a spinning column. The fraction from the spinning band column boiling at 77-82°C contained mostly 2,3-dimethyl-1,4-pentadiene, 13 and the fraction collected at 90-95°C contained mostly *cis*,*trans*-4-methyl-1,4-hexadiene, 14. These were further purified by preparative glpc on the 20 ft. β,β' column at 40°C and a He flow rate of 170 ml/minute.

The aliquots were used to calculate the yields of products by glpc analysis using the method described in the general procedure for the rearrangement of dienes.

The chromatograms contained three peaks. The first was unreacted isoprene (63% conversion to products), the second was 13 (11.97% yield), and the third was a doublet for a mixture of *cis*,*trans*-14 (53.9% yield).

The pmr spectrum of <u>13</u> possessed the following: a complex array from τ3.94 to 5.33; a multiplet of five distinct peaks centered at τ7.22 (J=7 Hz); a singlet at τ8.33; and a doublet at τ8.90 (J=7 Hz). The ratio of the respective peaks intensities were 5.0:1:3.0.

The pmr spectrum of <u>14</u> possessed the following: a complex array of peaks between τ3.88 and τ5.20; a doublet at τ7.30 (J=7 Hz); and a multiplet centered near τ8.38. The relative peak intensities were 3.94:2.0:5.9.

## F. THE REARRANGEMENT REACTION OF 2,3-DIMETHYL-1,4-PENTADIENE AND *CIS*, *TRANS*-4-METHYL-1,4-HEXADIENE

1. *The rearrangement reaction of 2,3-dimethyl-1,4-pentadiene in toluene*.--The general procedure for the rearrangement of dienes was followed except that 0.1 g of <u>24</u> (0.19 mmole), 20 ml of toluene, 0.22 g of <u>13</u> (2.26 mmoles), and 0.54 ml of 25% DIBAC in toluene (0.76 mmole) were used (diene: Ni:Al mole ratio = 12:1:4). The reaction was terminated after five hours with two ml of 1-butanol. The products were removed by distillation and collected by preparative glpc on the 20 ft. β,β' column. The only isomeric hydrocarbon formed was 4-methyl-1,4-hexadiene.

### TABLE 14

### YIELD DATA FOR THE REARRANGEMENT REACTION OF 2,3-DIMETHYL-1,4-PENTADIENE IN TOLUENE

| Time (Minutes) | % Conversion | % Yield of 4-Methyl 1,4-hexadiene |
|---|---|---|
| 15 | 22 | 25.7 |
| 30 | 29.9 | 34.4 |
| 60 | 39.6 | 41.5 |
| 120 | 45.25 | 47.8 |
| 180 | 49.6 | 55.6 |
| 300 | 56.2 | 47.8 |

2. The rearrangement reaction of 2,3-dimethyl-1,4-pentadiene in chlorobenzene.--The general procedure for the rearrangement of dienes was followed except that 0.191 g of 24 (0.35 mmole), 40 ml of chlorobenzene, 0.408 g of 13 (4.23 mmoles), and 1.0 ml of the 25% DIBAC in toluene (1.24 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.5). The reaction was terminated after two hours with two ml of 1-butanol. The only isomeric hydrocarbon product formed was 4-methyl-1,4-hexadiene.

## TABLE 15

## YIELD DATA FOR THE REARRANGEMENT REACTION OF 2,3-DIMETHYL-1,4-PENTADIENE IN CHLOROBENZENE

| Time (Minutes) | Percent Conversion | % Yield of 4-Methyl-1,4-hexadiene |
|---|---|---|
| 15 | 20.8 | 60.1 |
| 30 | 36.4 | 90.8 |
| 60 | 47.2 | 55.1 |
| 120 | 55.8 | 53.6 |

3. <u>The rearrangement reaction of 2,3-dimethyl-1,4-pentadiene in 1,2-dichlorobenzene</u>.--The general procedure for the rearrangement of dienes was followed except that 60 ml of 1,2-dichlorobenzene, 0.59 g of <u>13</u> (6.15 mmoles), 0.277 g of <u>trans</u>-dichlorobis(tri-n-butylphosphine)Ni(II), <u>24</u> (0.52 mmole), and 1.46 ml of 25% DIBAC in toluene (1.81 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.5). The reaction was terminated after three hours with two ml of 1-butanol. The products were separated from the solvent by distillation and the products were collected by preparative glpc on the 20 ft. β,β' column. Only one isomeric product (4-methyl-1,4-hexadiene) was formed. It, however, rearranged to two minor products as it formed.

### TABLE 16

### YIELD DATA FOR THE REARRANGEMENT REACTION OF 2,3-DIMETHYL-1,4-PENTADIENE IN 1,2-DICHLOROBENZENE

| Time (Minutes) | Percent Conversion | % Yield of 4-Methyl-1,4-hexadiene |
|---|---|---|
| 5 | 10.49 | 55.4 |
| 15 | 24.6 | 57.2 |
| 30 | 37.4 | 43.7 |
| 60 | 43.4 | 47.7 |
| 180 | 57.5 | 32.8 |

4. Reduction of 4-methyl-1,4-hexadiene with diisobutylaluminum hydride.--4-Methyl-1,4-hexadiene (2.9 g, 0.03 mole) was placed in a glass tube and purged with nitrogen at liquid nitrogen temperatures. It was allowed to warm to room temperature under nitrogen atmosphere. Diisobutylaluminum hydride (5.6 ml, 0.053 mole) was added to the tube along with a small magnetic stirring bar. The tube was sealed and heated at 70°C for 16 hours with constant stirring. It was then cooled to room temperature and placed in an ice bath. The tube was broken open and quickly placed under nitrogen atmosphere. Water was carefully added to the tube until the vigorous reaction ceased. It was then completely hydrolyzed by carefully adding 12.5% sulfuric acid. The mixture was placed in a small separatory funnel and the lower layer discarded.

The hydrocarbon layer was washed with water and dried over molecular sieves.

The 4-methyl-1,4-hexadiene, 14, consisted of two isomers with the isomer of longest retention time on the 20 ft. β,β' column the major component. Glpc analysis indicated that 50% reaction of 14 had occurred. The 3-methyl-2-hexenes were separated from 14 on the β,β' column and separated into two products on the 15 ft. Se-30 column at 45°C with a He flow rate of 60 ml/minute (Figure 8).

The smallest product was analyzed by decoupling the methyl protons in the pmr spectrum (Figure 9). The methyl peak furthest downfield was split into a sharp doublet at $\tau$8.35. The major product was also analyzed by decoupling the methyl protons in the pmr spectrum (Figure 10). These showed up as a very intense singlet at $\tau$8.43. The major product was therefore (2E)-3-methyl-2-hexene or *trans*-3 methyl-2-hexene. The minor product was (2Z)-3-methyl-3-hexene or *cis*-3-methyl-2-hexene. The literature values are $\tau$8.40 and 8.33 respectively for the *trans* and *cis*-3-methyl-2-hexenes.[85] The major product in the rearrangement of 13 was therefore (4E)-4-methyl-1,4-hexadiene, 14a.

5. *The rearrangement of 4-methyl-1,4-hexadienes.*--The general procedure for the rearrangement of dienes was followed except that 70 ml of chlorobenzene, 0.82 g of 14 (8.5 mmoles), 0.479 g of 24 (0.71 mmole), and two ml of 25% DIBAC in toluene (2.5 mmoles) were used (diene:Ni:Al mole ratio = 12:1:3.5). The reaction was terminated after three hours with

two ml of 1-butanol. The products were separated from the solvent by distillation and collected by preparative glpc on the 20 ft. β,β' column.

Glpc analysis indicated the presence of a small product before 14 was eluted, two minor products, and one major product after 14 was eluted. The pmr spectrum of the first product showed it to be 2,3-dimethyl-1,4-pentadiene. The pmr spectrum of the first product eluted after unreacted 14 possessed the following: a doublet at $\tau$4.23 (J=12 Hz); a multiplet from $\tau$4.45 to 4.85; and an apparent triplet centered at $\tau$8.3. The relative peak intensities were 1:2:8.9. This product was attributed to (2E, 4E)-3-methyl-2,4-hexadiene, 32. The pmr spectrum of the second product eluted after unreacted 14 possessed the following: a doublet at $\tau$3.6 (J=16 Hz); a multiplet from $\tau$4.28 to 4.88; and an apparent triplet centered at $\tau$8.27. The relative peak intensities were 1:2:8.7. The second product after 14 was eluted was attributed to (2Z, 4E)-3-methyl-2,4-hexadiene, 33, because of the coupling constant of the protons at C-4 and C-5 (*trans*) and the third peak after 14 was eluted. The third product eluted after 14 was the major one and the pmr spectrum of this product possessed a doublet at $\tau$3.92 (J=16 Hz), a multiplet from $\tau$4.2 to $\tau$4.8; and an apparent doublet at $\tau$8.34. The relative peak intensities were 1:2:8.6. The infrared spectrum exhibited bands at 960, 1310 (weak), and 1656 $cm^{-1}$ which can be attributed to a disubstituted trans alkene linkage. A band at 840 $cm^{-1}$ attributed to (2E, 4E)-3-methyl-2,4-hexadiene, 31.

TABLE 17

YIELD DATA FOR THE REARRANGEMENT REACTION OF 4-METHYL-1,4-HEXADIENES

| Time (Minutes) | % Conversion | % Yield of 13 | % Yield of 31 | % Yield of 32 | % Yield of 33 |
|---|---|---|---|---|---|
| 60 | 45.5 | 2.18 | 62.7 | 9.3 | 11.0 |
| 120 | 51.61 | 2.1 | 59.1 | 8.5 | 9.8 |
| 180 | 54.46 | 2.1 | 55.2 | 7.7 | 9.5 |

## G. THE SYNTHESIS OF TRANS-CHLORO(2-ALLYLPHENYL)-BIS(TRIETHYLPHOSPHINE)NICKEL(II)

1. The synthesis of 2-chloro-1-iodobenzene.--Sulfuric acid (36 g, 0.5 mole) was poured into 150 ml of water contained in a liter beaker and cooled to room temperature. 2-Chloro-1-aniline (31.85 g, 0.25 mole) was slowly added to the acid with stirring. The amine salt precipitated as finely divided crystals. The solution was then cooled to -10°C in an ice-salt bath. Potassium nitrite (42.5 g, 0.5 mole) was dissolved in 60 ml of water and added drop wise to the solution with the temperature maintained below -5°C. Sodium iodide (90 g,

0.6 mole) was dissolved in 60 ml of water and cooled to 0°C. It was then cautiously added to the reaction mixture. The solution was then allowed to warm to 50°C over a two hour period.

The crude 2-chloro-1-iodobenzene was extracted with three 75 ml aliquots of carbon tetrachloride. The aliquots were then washed with 20% sodium thiosulfate until the purple color of iodine had disappeared. The carbon tetrachloride solution was then washed with 20% hydrochloric acid, water, and dried over anhydrous calcium chloride. Vacuum distillation at 100-180°C afforded 108 g (90.6%) of 2-chloro-1-iodobenzene.

2. The synthesis of 2-chloro-1-allylbenzene.-- Magnesium turnings (2.43 g, 0.1 mole) were placed in a 250 ml three neck flask equipped with a magnetic stirring bar, equi-pressure dropping funnes, a three-way stopcock, and a reflux condenser topped with a three-way stopcock for nitrogen atmosphere. With nitrogen passing through the apparatus, water vapor was removed by warming the apparatus for fifteen minutes with a bunsen burner. The apparatus was allowed to cool and 100 ml of anhydrous ether was added to the reaction flask via the dropping funnel. 2-Chloro-1-iodobenzene (23.9 g, 0.1 mole) dissolved in 30 ml of ether was added to the dropping funnel and about five ml of the solution added to the reaction flask. Heat was used to initiate the reaction and the rest of the solution was added at such a rate as to generate a gentle refluxing of the ether.

Freshly distilled allyl bromide (12.1 g, 0.1 mole) dissolved in 30 ml of ether was placed in the funnel and allowed to slowly drop into the flask overnight. The solution was then refluxed for an hour. Unreacted Grignard was carefully destroyed with 25% hydrochloric acid. The solution was diluted with 100 ml of water and placed in a separatory funnel. The lower layer was discarded. The product was washed with 20% sodium thiosulfate, dried over anhydrous calcium chloride, and the ether removed under vacuum. Distillation at 43-45°C (1.1 mm) resulted in 18.3 g (39%) of 2-chloro-1-allylbenzene. It was stored over molecular sieves.

3. The synthesis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II).-- The apparatus described in the synthesis of 2-chloro-1-allylbenzene was set up containing 0.54 g of magnesium (.022 mole). To the flask were added 30 ml of anhydrous tetrahydrofuran. 2-Chloro-1-allylbenzene (3.35 g, 0.022 mole) freshly distilled and dissolved in 30 ml of tetrahydrofuran was placed in the dropping funnel. Ten drops of solution were added to the flask and it was heated to vigorous reflux. Three drops of methyl iodide were added to initiate the reaction. The solution was then cooled to a gentle reflux and the rest of the solution added to the flask over a two hour period. The solution was allowed to reflux for a total of 48 hours.

In a 500 ml round bottom flask were placed 4.75 g of trans-dichlorobis(triethylphosphine)Ni(II), 36 (0.013 mole), 100 ml of tetrahydrofuran, and a magnetic stirring bar. The solution was then purged with nitrogen. The Grignard solution was placed in the equi-pressure dropping funnel and slowly added to the rapidly stirred red solution until the foam produced by the stirring bar turned yellow permanently. The solvent was then removed under vacuum. To the flask was added 300 ml of pentane. Ten ml of ethanol was also added to destroy any unreacted Grignard. The solution was removed with a large syringe and filtered through a medium porosity glass filter under nitrogen pressure. The solvent was then removed under vacuum.

The crude product was dissolved in 20 ml of benzene and chromatographed on a specially prepared alumina column. The column of acid washed alumina (400 ml) was purged with 500 ml of nitrogen purged hexane and left under nitrogen atmosphere overnight. The product was eluted under nitrogen atmosphere with nitrogen purged hexane and ether. The unreacted dichloro-bis(triethylphosphine)Ni(II) was destroyed when the solvent concentration reached 30% (v/v) ether/hexane.

The solvent containing the yellow product was removed under vacuum. It was then recrystallized from a solution of benzene and methanol. The yield of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II), 35, was 3.5 g (61%) and had a melting point of 64-65°C. It was stored in a refrigerator under nitrogen atmosphere.

## H. THE THERMOLYSIS REACTIONS OF TRANS-CHLORO(2-ALLYLPHENYLBIS(TRIETHYLPHOSPHINE)NICKEL(II)

1. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in benzene.--To a 50 ml side arm round bottom flask was added 0.895 g of 35 (2.0 mmoles). A small magnetic stirring bar was placed in the flask and a reflux condenser attached to the flask. The condenser was topped with a three-way stopcock for nitrogen atmosphere. The system was purged with nitrogen and 10 ml of nitrogen purged benzene was added. The flask was immersed in an oil bath maintained between 60 and 70°C. The solution turned red and a brown sand-like material began to precipitate after one hour. A small amount of green precipitate also formed and adhered to the sides of the flask.

The reaction was stopped after sixteen hours, cooled, and the solution chromatographed on a specially prepared nitrogen purged alumina column (see preparation of 35). The product was eluted with hexane and ether. The amount of ether was increased by 10% (v/v) each time an additional 100 ml of solvent was used. Aliquots before the yellow products were eluted, were concentrated under vacuum to about 15 ml. The aliquots containing products (80 ml each) were placed in tared flasks and the solvent removed under vacuum. The pmr spectrum of each aliquot sample was run using deuterated benzene as a solvent. The analysis indicated that 56.5% of

35 had reacted with 39% of the amount that reacted converted to trans-chloro(2-propenylphenyl)bis(triethylphosphine)Ni(II), 38.

Analysis of the hydrocarbon products was carried out by preparing a glpc standard of indene, 39, allylbenzene, 40, 1-phenyl-1-propene, 40, and 1,2-dibromobenzene (internal standard). The ratios of 39, 40, and 41 to the internal standard (peak areas) were carefully recorded. To the concentrated aliquot was added 0.1 g of 1,2-dibromobenzene and the glpc analysis carried out. The column used for this work was the 20 ft. TCEP column at 160°C and a He flow rate of 60 ml/minute. The analysis showed that of the amount of 35 that had reacted, 1.36% of this amount was converted to 40, 1.6% to 41, and 10.9% to 39.

2. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in tetrachloroethylene.--The conditions for the rearrangement of 35 in benzene were followed except that 0.85 g of 35 (1.9 mmoles) and 10 ml of tetrachloroethylene were used. The temperature was maintained at 80-85°C for 2.5 hours. The product solution was chromatographed on the specially prepared alumina column as before. Maintaining the concentration of ether at less than 30% resulted in the rapid elution of trans-chloro(trichlorovinyl)bis(triethylphosphine)Ni(II), 37, but not 35 or 38. These were then eluted by increasing the concentration of ether in the hexane/ether solutions.

Analysis indicated that 95.9% of 35 was converted to products. Of this amount 53.5% was converted to 39, 5.11% to 40, 2% to 41, 6.42% to 38, and 48.07% to 37.

3. *The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in benzene containing tetrachloroethylene.*--The conditions for the thermolysis of 35 in benzene were followed except that 1.19 g of 35 (2.7 mmoles, 10 ml of benzene, and 0.155 g of tetrachloroethylene (0.93 mmole) were used. The temperature was maintained between 60 and 70°C for 24 hours.

Analysis indicated that 96.4% of 35 was converted to products. Of this amount, 28.4% was converted to 39, 24.3% to 38, 1.05% to 40, and 8.05% to 41. The amount of 37 formed was 75% of the theoretical amount.

4. *The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in benzene containing allylbenzene.*--The conditions for the thermolysis of 35 in benzene were followed except that 0.908 g of 35 (2.03 mmoles), 10 ml of benzene, and 0.522 g of allylbenzene (4.42 mmoles) were used (allylbenzene;Ni mole ratio ≃ 2:1). The temperature was maintained between 60 and 70°C for 26 hours.

Analysis indicated that 78.7% of 35 had reacted with 53.5% of this amount converted to 38 and 22% to 39. The amount of allylbenzene reacted was 97.4% with 63.7% of this amount converted to 41.

5. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in toluene containing cis-1,4-hexadiene.--The general conditions for the thermolysis of 35 in benzene were followed except that 0.986 g of 35 (2.2 mmoles), 14 ml of toluene, and 5.4 mmoles of cis-1,4-hexadiene, 5a, were used (diene:Ni mole ratio = 2.45:1). The temperature was maintained between 60 and 70°C for 41 hours. No observable reaction of 5a occurred within the first six hours. The rearrangement of 5a was followed by glpc on the 20 ft. $\beta,\beta'$ column. Aromatic hydrocarbons were analyzed as before on the TCEP column.

Analysis showed that 56.3% of 35 had reacted with 9% of the amount reacted converted to 40 and 41, and 43% to 39. Column chromatographic analysis and pmr spectrum of unreacted 35 showed that 38 had not been produced. The diene products from a previous reaction were identified by comparative pmr spectra[111] to be trans-2-methyl-1,3-pentadiene, 26, cis, trans-2,4-hexadiene, 42, and cis, cis-2,4-hexadiene, 43. After 41 hours, 25.5% of 5a was converted to products with 58.7% of the amount reacted converted to 26, 21.1% to 42, and 20.7% to 43.

The above reaction was also carried out at room temperature. No rearrangement of 5a occurred over a 24 hour period. The solution was divided in half. One part was placed in a nitrogen purged side arm flask. Addition of triethylaluminum in hexane (Al:Ni mole ratio = 1:1) resulted in a rapid reaction but none of the expected 1,3-dienes were formed. To the other part of the solution was added 25% DIBAC in toluene (Al:Ni mole ratio = 1:1). A rapid reaction to form trans-2-methyl-1,3-pentadiene, 26, cis, cis2,4-hexadiene, 43 and cis, trans-2,4-hexadiene, 42 occurred.

6. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) prepared from very pure nickel dichloride in benzene containing cis-1,4-hexadiene.--The nickel dichloride used to prepare 35 contained nickel of 99.999% purity. The general conditions for the thermolysis of 35 in benzene were followed except that 1.06 g of the very pure 35 (2.4 mmoles), 10 ml of benzene, and 2.0 mmoles of 5a were used (diene:Ni mole ratio = 0.85:1). The reaction was run between 60 and 70°C for 45 hours.

Analysis indicated that 37.4% of 35 had reacted with 35% of the amount reacted converted to 38. During 45 hours, 56.4% of 5a had reacted with 55.6% of the amount that reacted converted to 26, 21.3% to 42 and 21% to 43.

7. The thermolysis of trans-chloro(2-allylphenyl)bis(triethylphosphine)Ni(II) in tetrachloroethylene containing cis-1,4-hexadiene.--The general conditions for the thermolysis of 35 in benzene were followed except that 0.51 g of 35 (1.1 mmoles), 7 ml of tetrachloroethylene, and 1.1 mmoles of 5a were used (diene:Ni mole ratio = 1:1). The reaction was

run between 60 and 70°C for 44 hours.

Analysis indicated that 32.5% of 5a had reacted with 63.3% of the amount that reacted converted to 26. Analysis also showed that 100% of 35 was converted to products with 39.5% of 37 formed.

The above reaction was also carried out at 50-55°C. Although 35% of *cis*-1,4-hexadiene, 5a, reacted during 19 hours, only a trace of isomeric hydrocarbon products were formed.

8. The reaction of allylbenzene with HCl.--A 50 ml three neck round bottom flask was equipped with a reflux condenser, magnetic stirring bar, and a bubbler tube. The condenser was topped with a three-way stopcock for nitrogen atmosphere. To the flask was added six ml of nitrogen purged benzene and 15 mmoles of allylbenzene. The solution was saturated with HCl by constantly bubbling it into the solution for 20.5 hours between 60 and 70°C. No rearrangement of allylbenzene occurred.

9. The reaction of cis-1,4-hexadiene with HCl.--The above apparatus was used. *Cis*-1,4-hexadiene (2 mmoles) and six ml of nitrogen purged benzene were placed in the flask and treated as above. The *cis*-1,4-hexadiene slowly reacted during six hours but no isomeric hydrocarbons were formed.

## I. REARRANGEMENTS WITH ETHYLENEBIS(TERTIARY PHOSPHINE)-NICKEL(O) COMPOUNDS

1. The reaction of allylbenzene with ethylenebis(triethylphosphine)Ni(0) formed in situ.--To a fifty ml round bottom flask were added 0.96 g of bis(2,4-pentanedianato)Ni(II), 10 ml of benzene, and a small magnetic stirring bar. A small equi-pressure dropping funnel was placed in the neck of the flask and it was topped with a three-way stopcock for inert gas atmosphere. The solution was purged with nitrogen. It was then purged with ethylene. To the solution was then added one gram of triethylphosphine (8.5 mmoles). The flask was cooled to 0°C in an ice bath and 8.5 mmoles of triethylaluminum in benzene was placed in the dropping funnel. It was slowly and carefully added to the flask. Allylbenzene (5 g, 0.04 mole) was added to the flask (diene:Ni mole ratio = 12:1). The solution was stirred at room temperature for 21 hours. Periodically one ml alliquots were removed and hydrolyzed with two ml of water. GLPC analysis on TCEP column at 160°C and a He flow rate of 60 ml/minute showed that isomerization of allylbenzene to trans-1-phenyl-1-propene was occurring. During three hours, 55.4% of trans-1-phenyl-1-propene was formed. This increased to 75% within 11 hours. Some polymerization occurred since the amount of 41 decreased to 67% after 21 hours.

2. The reaction of allylbenzene with ethylenebis(triphenylphosphine)Ni(0) and HCl.--Ethylenebis(triphenylphosphine)-

Ni(0), 45 (0.14 g, 0.228 mmole) was placed in a tared 50 ml side arm flask (nitrogen purged) while immersed in an ice bath. To the flask were added 5 ml of nitrogen purged benzene and 2.28 mmoles of allylbenzene. The solution was stirred under nitrogen atmosphere at room temperature for 3.5 hours. No rearrangement occurred. To the flask was then added 0.16 ml of 0.29 N HCl in benzene (allylbenzene: Ni:HCl mole ratio = 10:1:0.2). An amber solution formed and the allylbenzene rearranged to 41 within 3.5 hours.

3. *The reaction of cis-1,4-hexadiene with ethylenebis(triphenylphosphine)Ni(0) in benzene containing aluminum chloride*. --Ethylenebis(triphenylphosphine)Ni(0), 45 (0.15 g, 0.25 mole) was weighed as before in a nitrogen purged 50 ml side arm flask. To the flask were added 14 ml of nitrogen purged benzene and 2.1 mmoles of *cis*-1,4-hexadiene, 5a. Aluminum chloride in benzene (0.076 ml, 2.5 mmoles) was then added to the flask and the solution was stirred for 30 minutes at room temperature. Aliquots removed and analyzed on the $\beta, \beta'$ column showed that no isomerization of 5a occurred. HCl (0.6 ml, 2.0 mmoles) in benzene (diene:Ni:Al mole ratio 10:1:1:0.8) was then added to the solution. A small amount of reaction occurred within the first 30 seconds and none thereafter. Only 4% of the *cis*-1,4-hexadiene was converted to products. Of the amount that reacted, 57.5% was converted to 26, 19.2% to 42, and 23.6% to 43.

## J. SUPPORTING REACTIONS

1. <u>The rearrangement of 1,4-pentadiene</u>.--The rearrangement of 1,4-pentadiene with the catalyst formed from DIBAC and <u>24</u> had previously been carried out by Baker.[116] The products formed were 2-methyl-1,3-butadiene, <u>50</u>, <u>cis</u>-1,3-pentadiene, <u>51</u>, <u>trans</u>-1,3-pentadiene, <u>52</u>, and traces of 3-methyl-1,4-hexadiene, <u>53</u>, and 4-methyl-1,4-hexadiene, <u>14</u>.

The rearrangement was carried out again in order to obtain a more accurate determination of the product yields.

3-Methyl-1,4-pentadiene was prepared from 1,3-pentadiene and ethylene under one atmosphere of ethylene with the catalyst formed from DIBAC and <u>24</u> using an adaption of the procedure of Miller, Kealy, and Barney.[53]

A gas chromatographic standard solution was prepared by adding 0.3933 g of 1,4-pentadiene (5.77 mmoles), 0.152 g of 2-methyl-1,3-butadiene (2.23 mmoles), 0.033 g of 3-methyl-1,4-hexadiene (0.34 mmole), 0.393 g of 4-methyl-1,4-hexadiene (0.408 mmole), and 0.0733 g of 1,3-pentadiene (1.06 mmoles) in a 50 ml volumetric flask and diluted to the mark with toluene.

Aliquots of 25, 26 and 27 microliters of the glpc standard solution were then analyzed on the β,β' column at 60°C with a helium flow rate of 170 ml/minute. The following constants (mmole/unit area) were determined: 1,4-pentadiene ($1.158 \times 10^{-4}$); 2-methyl-1,3-butadiene ($1.219 \times 10^{-4}$); 3-methyl-1,4-hexadiene ($1.185 \times 10^{-4}$); 4-methyl-1,4-hexadiene ($0.989 \times 10^{-4}$); and _cis_ and _trans_-1,3-pentadiene ($1.179 \times 10^{-4}$).

TABLE 18

YIELD DATA FOR THE REARRANGEMENT OF 1,4-PENTADIENE

| Time (Min.) | % Conversion | % Yield of _50_ | % Yield of _51_ | % Yield of _52_ | % Yield of _53_ | % Yield of _14_ |
|---|---|---|---|---|---|---|
| 30 | 43.0 | 18.2 | 3.03 | 8.2 | 5.18 | 2.86 |
| 63 | 44.5 | 24.7 | 2.35 | 6.17 | 12.9 | 2.9 |
| 180 | 63.8 | 26.4 | 2.8 | 5.2 | 9.5 | 3.0 |
| 240 | 71.0 | 24.35 | 2.2 | 4.02 | 8.89 | 3.5 |

The rearrangement of 1,4-pentadiene was carried out using the general procedure for the rearrangement of 1,4-dienes except that 0.354 g of _24_ (0.667 mole), 75 ml of nitrogen purged toluene, and 1.9 ml of 25% DIBAC in toluene were used (diene:Ni:Al mole ratio = 12:1:4). The progress of the reaction was followed by glpc analysis of the aliquots on the β,β' column as in the general procedure. The reaction was terminated after four hours with two ml of 1-butanol.

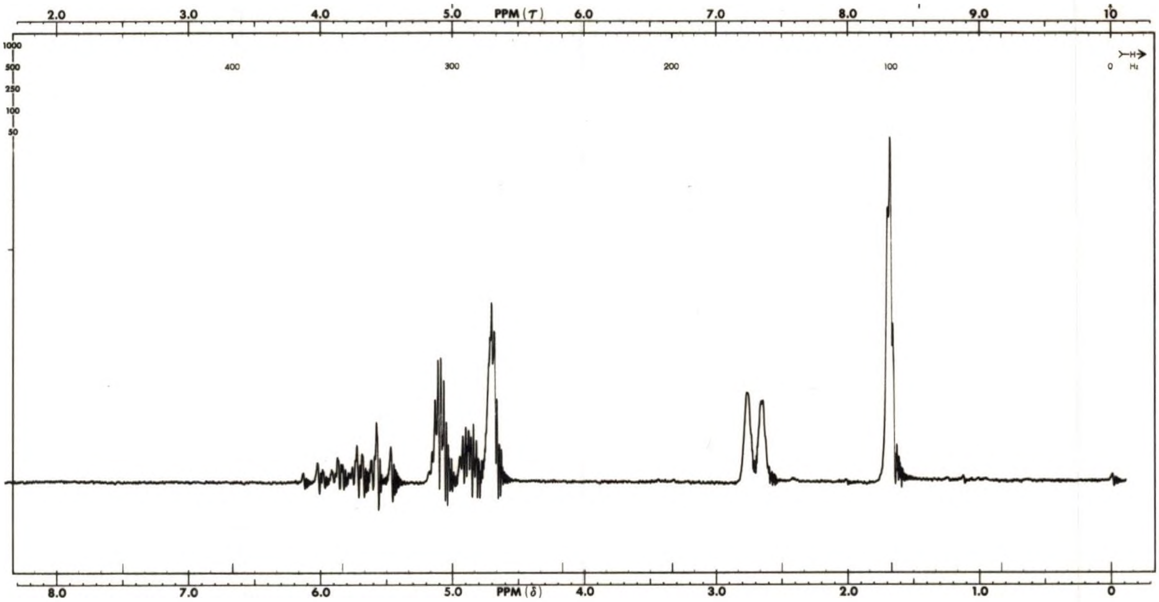


Fig. 1.--Pmr spectrum of 2-methyl-1,4-pentadiene. ($CCl_4$)

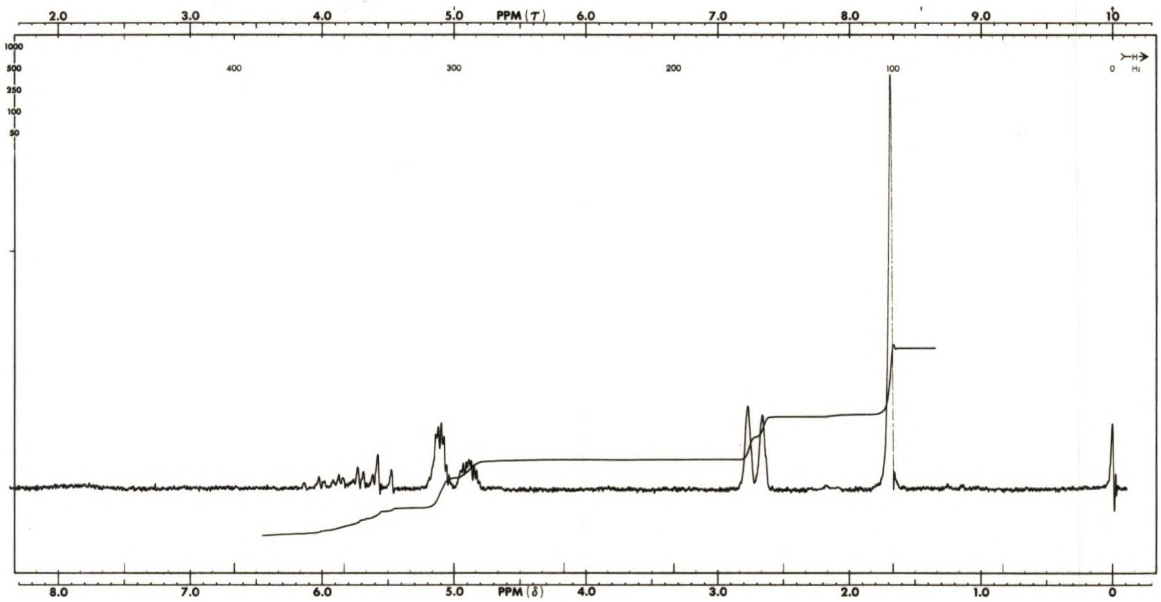


Fig. 2.--Pmr spectrum of 1,1-dideutero-2-methyl-1,4-pentadiene. ($CCl_4$)

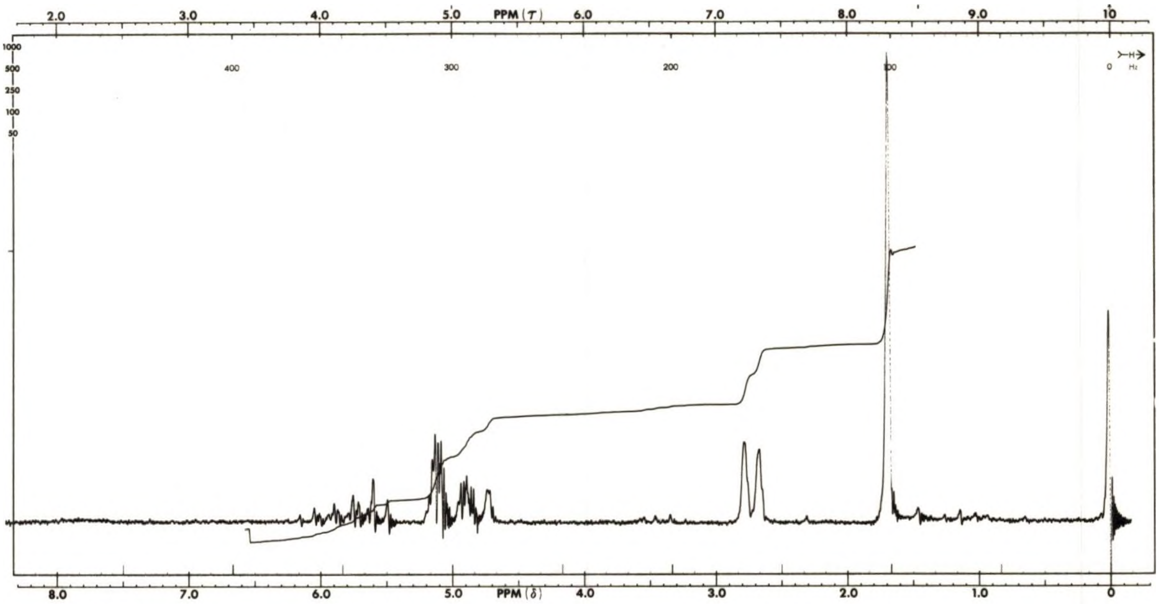


Fig. 3.--Pmr spectrum of 1,1 and 3,3-dideutero-2-methyl-1,4-pentadiene. ($CCl_4$)

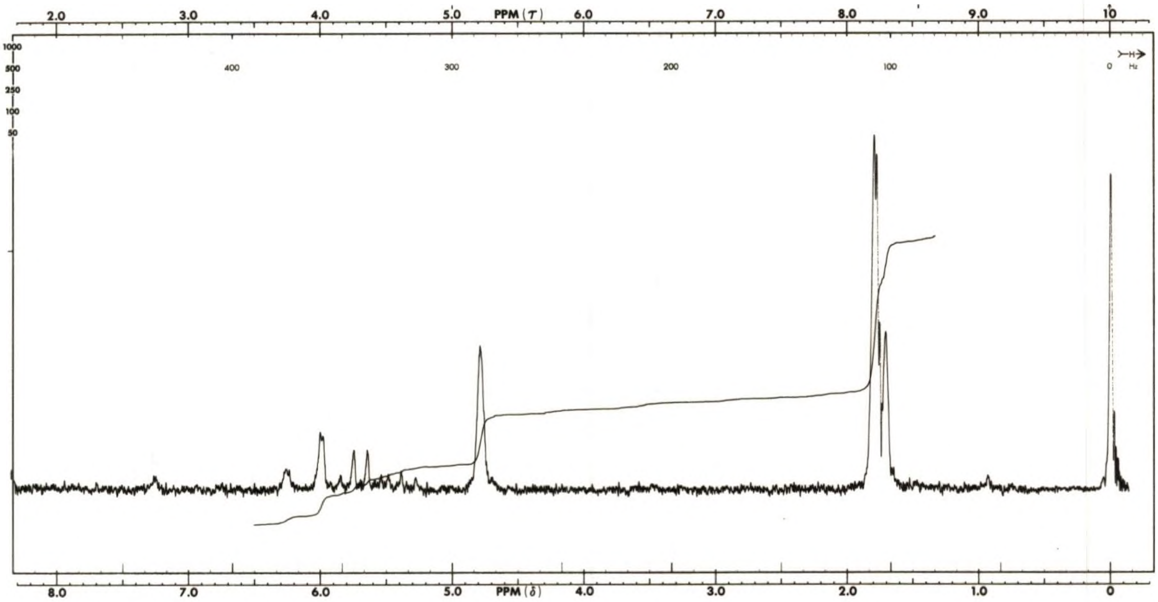


Fig. 4.--Pmr spectrum of trans-2-methyl-1,3-pentadiene. ($CCl_4$)

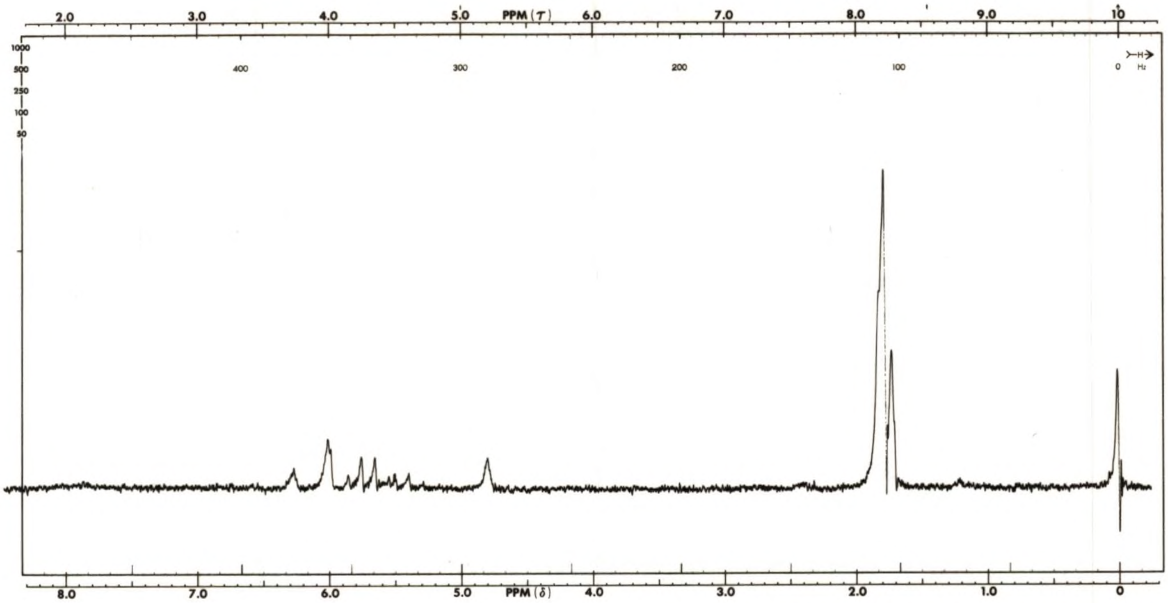


Fig. 5.--Pmr spectrum of 1,1-dideutero-trans-2-methyl-1,3-pentadiene. ($CCl_4$)

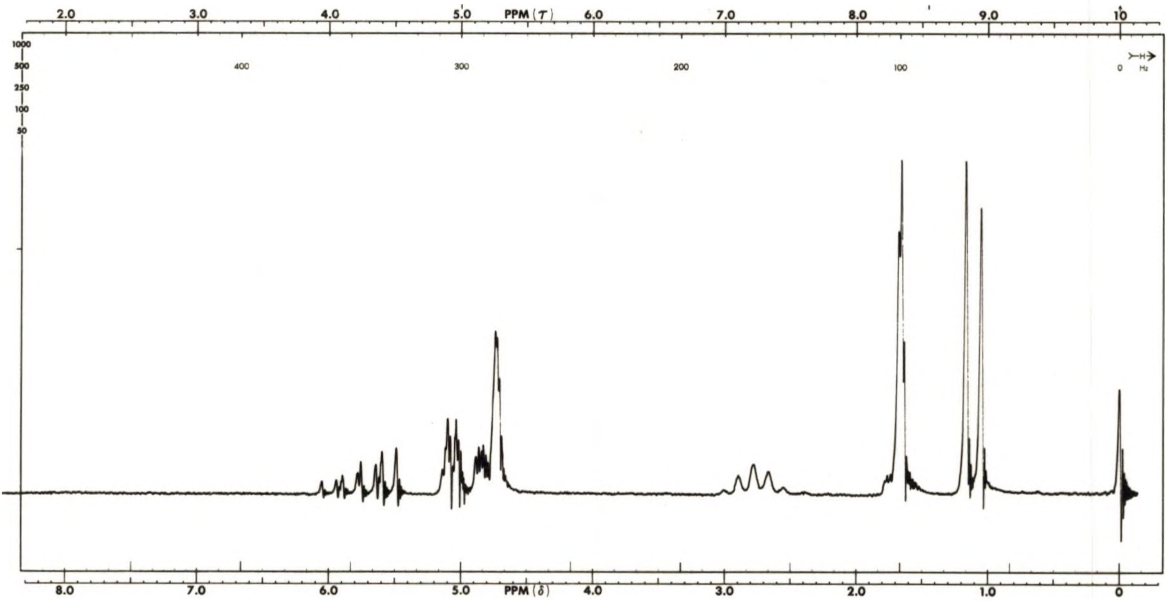


Fig. 6.--Pmr spectrum of 2,3-dimethyl-1,4-pentadiene. ($CCl_4$)

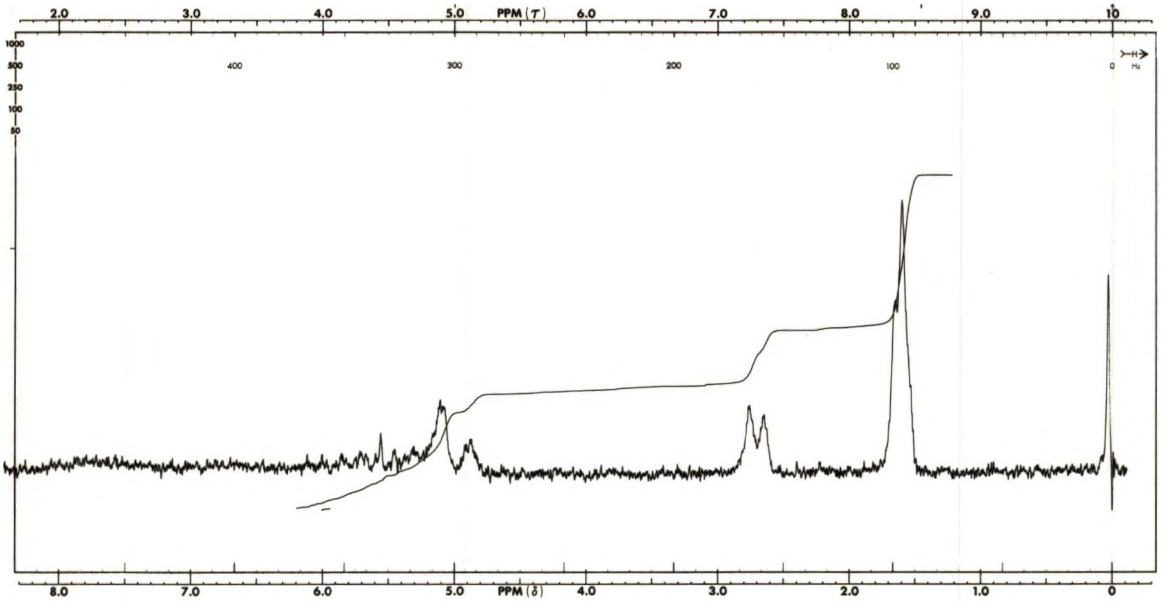


Fig. 7.--Pmr spectrum of 4-methyl-1,4-hexadiene. ($CCl_4$)

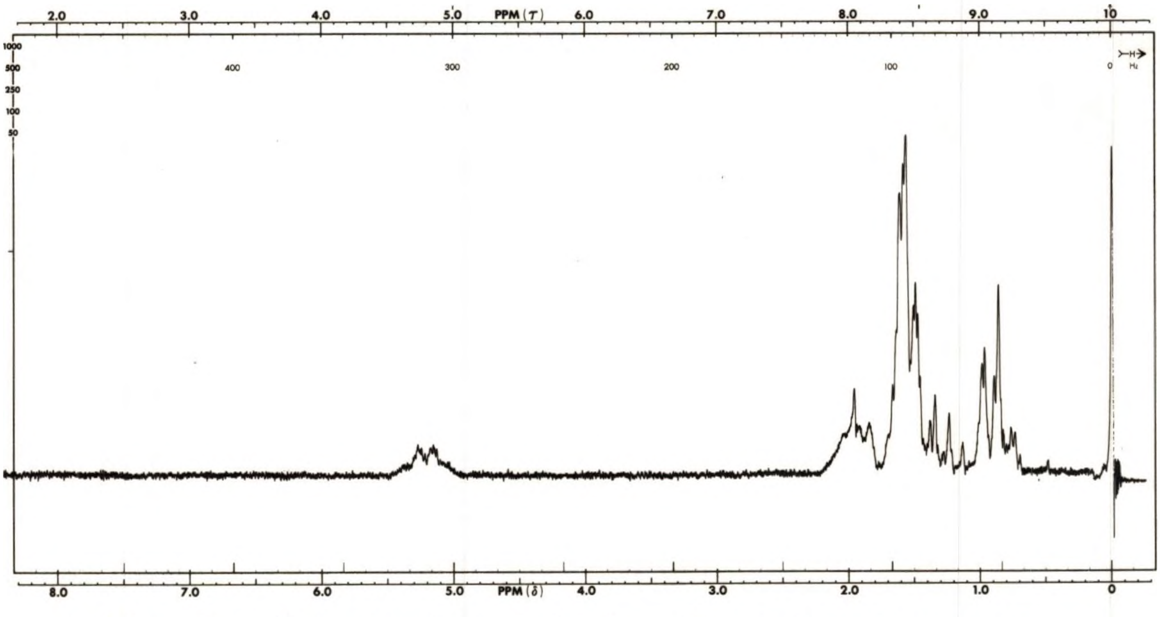


Fig. 8.--Pmr spectrum of <u>cis</u>, <u>trans</u>-3-methyl-2-hexene. ($CCl_4$)

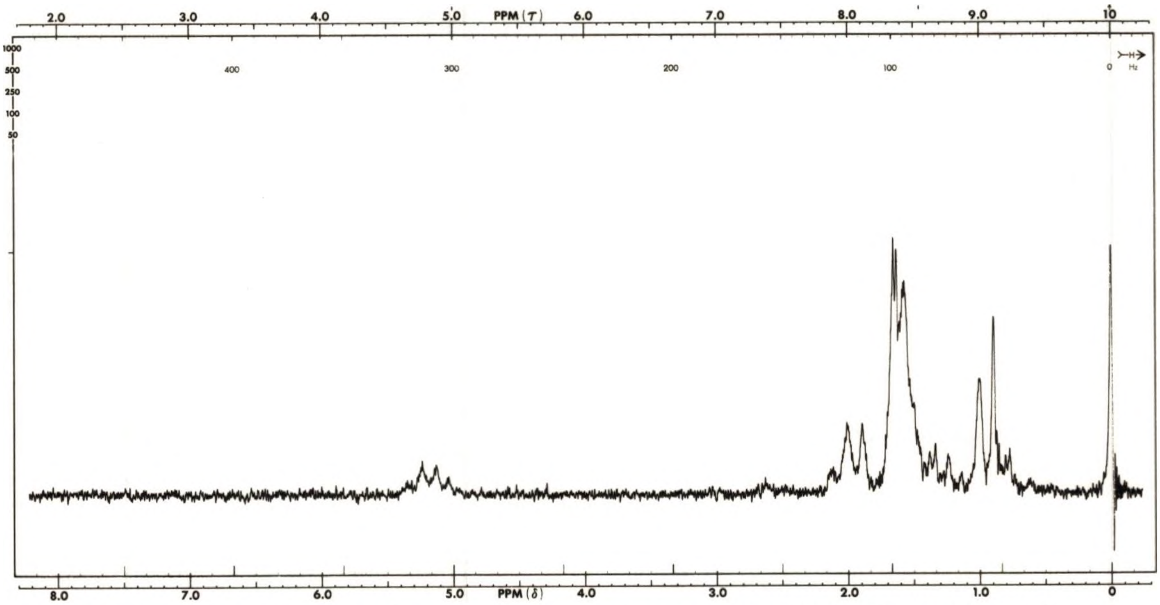


Fig. 9.--Decoupled pmr spectrum of (2Z)-3-methyl-2-hexene. ($CCl_4$)

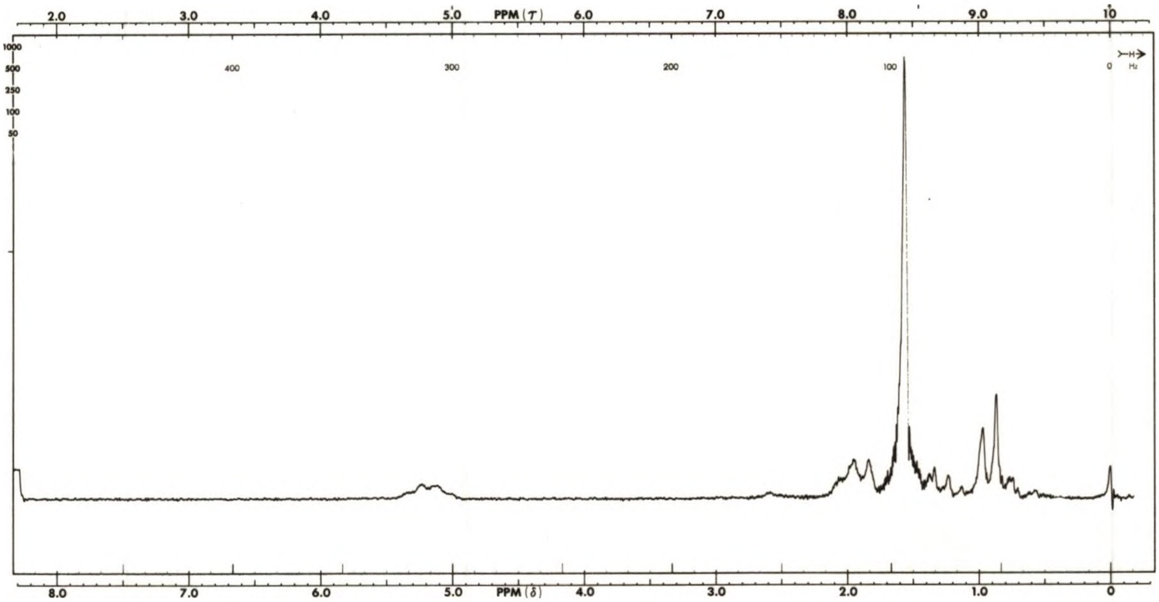


Fig. 10.--Decoupled pmr spectrum of (2E)-3-methyl-2-hexene. ($CCl_4$)

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