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## Cyclodimerization of 1,3-Pentadiene with Homogeneous Nickel Catalyst

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*University of Central Florida*

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CYCLODIMERIZATION OF 1,3-PENTADIENE  
WITH HOMOGENEOUS NICKEL CATALYST

BY

MORTEZA SOLTANI  
B.S., University of Esfahan, 1971

RESEARCH REPORT

Submitted in partial fulfillment of the requirements  
for the degree of Master of Science: Industrial Chemistry  
in the Graduate Studies Program of the College of Natural Science  
at the University of Central Florida; Orlando, Florida

Winter Quarter  
1980



## ABSTRACT

Piperylene concentrate is a complex mixture of 5-carbon unsaturated hydrocarbons obtained as by-products when naphtha or gas oils are cracked. The major component in this mixture is 1,3-pentadiene.

The cyclodimerization of 1,3-pentadiene in piperylene concentrate by using a nickel catalyst was studied. Various types of ligands were used in the preparation of the nickel catalyst. The effect of each ligand on activity of the catalyst in dimerization of diene, on conversion, and on yield of reaction were investigated. The effect of reaction conditions, such as temperature, pressure, and reaction time, on conversion of monomer, yield of dimer, and selectivity of catalyst were determined.

The activity of catalyst on dimerization of pure 1,3-pentadiene and isoprene also were studied.

Production of various by-products during cyclodimerization of 1,3-pentadiene in piperylene concentrate mixture was a major problem in separation of dimer from these by-products.



## ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. Guy Mattson for his personal guidance and patience during the course of this project; and to Dr. Chris A. Clausen, Dr. Graeme L. Baker, and Dr. John T. Gupton for their suggestions and encouragement leading to the completion of this work.



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## INTRODUCTION

Tremendous amounts of ethylene and propylene are produced each year by thermal cracking of condensate from natural gas<sup>1</sup>. However, due to decreasing production of natural gas, there is a trend towards the use of heavier naphthas and gas oils as cracking stock.

Due to the large amounts of ethane in the lighter gases, relatively small amounts of by-products are formed on the thermal cracking. When the heavier naphthas and gas oils are cracked, large amounts of by-products are produced. The objective of this project was to investigate potential uses for a by-product stream consisting of a mixture of 5-carbon unsaturated hydrocarbons. 1,3-Pentadiene is the major component of this mixture which is known as piperylene concentrate. A typical composite of piperylene concentrate is shown in Table I.

The composition of piperylene concentrate is not constant, and depends on the conditions of cracking employed. The more severe the cracking conditions are, the greater the diene content.

The total production of piperylene concentrate from cracking of naphthas and oil gases has been estimated to be approximately five million tons per year<sup>2</sup>.

Despite the large volume piperylene concentrate produced each year, few commercial uses have been developed. A large amount of piperylene concentrate is being used as fuel for furnaces. A few types of plastisizers and softening agents for resins have



TABLE I

## Typical Composition of Piperylene Concentrate

<u>Component</u>	<u>Weight Percent</u>
2-methyl-1-butene	1.3
2-methyl-2-butene	10.1
cyclopentane	1.8
isoprene	0.57
cyclopentene	27.5
trans-1,3-pentadiene	34.0
cis-1,3-pentadiene	20.0
cyclopentadiene	1.0
Remainders*	3.8

\* consists mainly of C<sub>4</sub> to C<sub>6</sub> unsaturated hydrocarbons, benzene, dicyclopentadiene, and other heavy materials.



been obtained by processes using piperylene concentrate as starting material, but the impurities in piperylene concentrate impair the quality of various products that may be obtained.

It has been the specific objective of this project to cyclo-dimerize the conjugated 1,3-dienes which are present in piperylene concentrate, including trans- and cis-1,3-pentadiene (major) and isoprene (minor). The boiling points of isoprene and 1,3-pentadiene are 37 and 42°C respectively, whereas the boiling points of dimer and trimer are 176 and 260°C respectively. Therefore, the dimer and trimer could be separated from the remainder (unreacted components) by a simple distillation.

#### Uses of Various Components in the Piperylene Concentrate

A number of uses of potential commercial importance have been reported for the various components in piperylene concentrate. A practical means of separating these components would therefore markedly increase the value of this by-product stream.

#### 1,3-Pentadiene

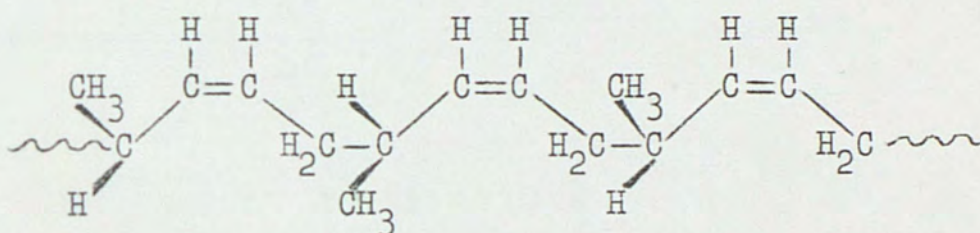
1,3-Pentadiene has been of recent interest because of its use in the preparation of novel polymer structures<sup>3,4</sup>.

A comprehensive review of 1,3-pentadiene polymers by Petrov and Genusov discusses preparation, physical and chemical properties through 1955<sup>5</sup>.

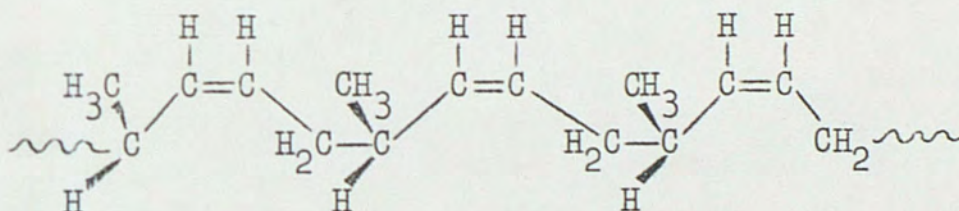
In the polymerization of 1,3-pentadiene several pure polymeric structures are possible because there are two sites in the monomer that may give rise to stereoisomers, i.e., the polymers are



ditactic<sup>6,7</sup>. The conjugated double bond system may give rise to 1,4; 3,4; or 1,2 addition, and the asymmetric carbon atom bearing the side methyl group be either isotactic or syndiotactic. Thus, there are four possible 1,4 addition stereoisomeric polypentadienes: the isotactic and syndiotactic cis-1,4-(a) and (b), and a similar trans-1,4 pair.



(a) Syndiotactic cis-1,4-poly-1,3-pentadiene



(b) Isotactic cis-1,4-poly-1,3-pentadiene

Physical properties of these polymers are shown in Table II.

TABLE II

Physical Properties of 1,3-Pentadiene Polymers

	<u>m.p.</u>
trans-1,4-isotactic	96
cis-1,4-syndiotactic	37 - 53
cis-1,4-isotactic	44

With the homogeneous catalysts of alkylaluminum chloride and



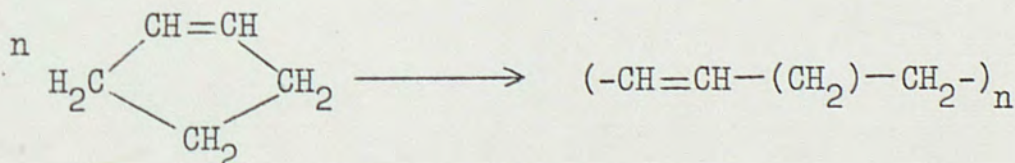
cobalt acetylacetonate only the trans monomer polymerizes and does so to form the syndiotactic cis-1,4-polybutadiene<sup>3,4,8,9</sup>.

Besides its use in the preparation of polymers, a most interesting potential for commercial application for piperylene is the development of catalytic routes to C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub> member ring compounds<sup>10</sup>, (Figure 1). These materials offer a new series of fundamental starting materials for organic synthesis. They may be converted to dicarboxylic acids or lactams known to be valuable starting materials for plastics, polyamides, and polyesters.

Although the dimer and trimer of 1,3-butadiene, 1,5-cyclooctadiene (COD) and 1,5,9-cyclododecatriene (CDT) are commercially available, only the trimer of 1,3-pentadiene 1,5,9-trimethyl-cyclododeca-1,5,9-triene is a commercial product.

### Cyclopentene

Cyclopentene is one of the major components in piperylene concentrate. The primary mechanism for the polymerization of cyclopentene is by ring openings. The opening of a cycloolefin gives an unsaturated structural unit, which may have a cis or trans configuration<sup>3,11,12</sup>.



Physical properties and catalyst systems for polymerization of cyclopentene are shown in Table III.



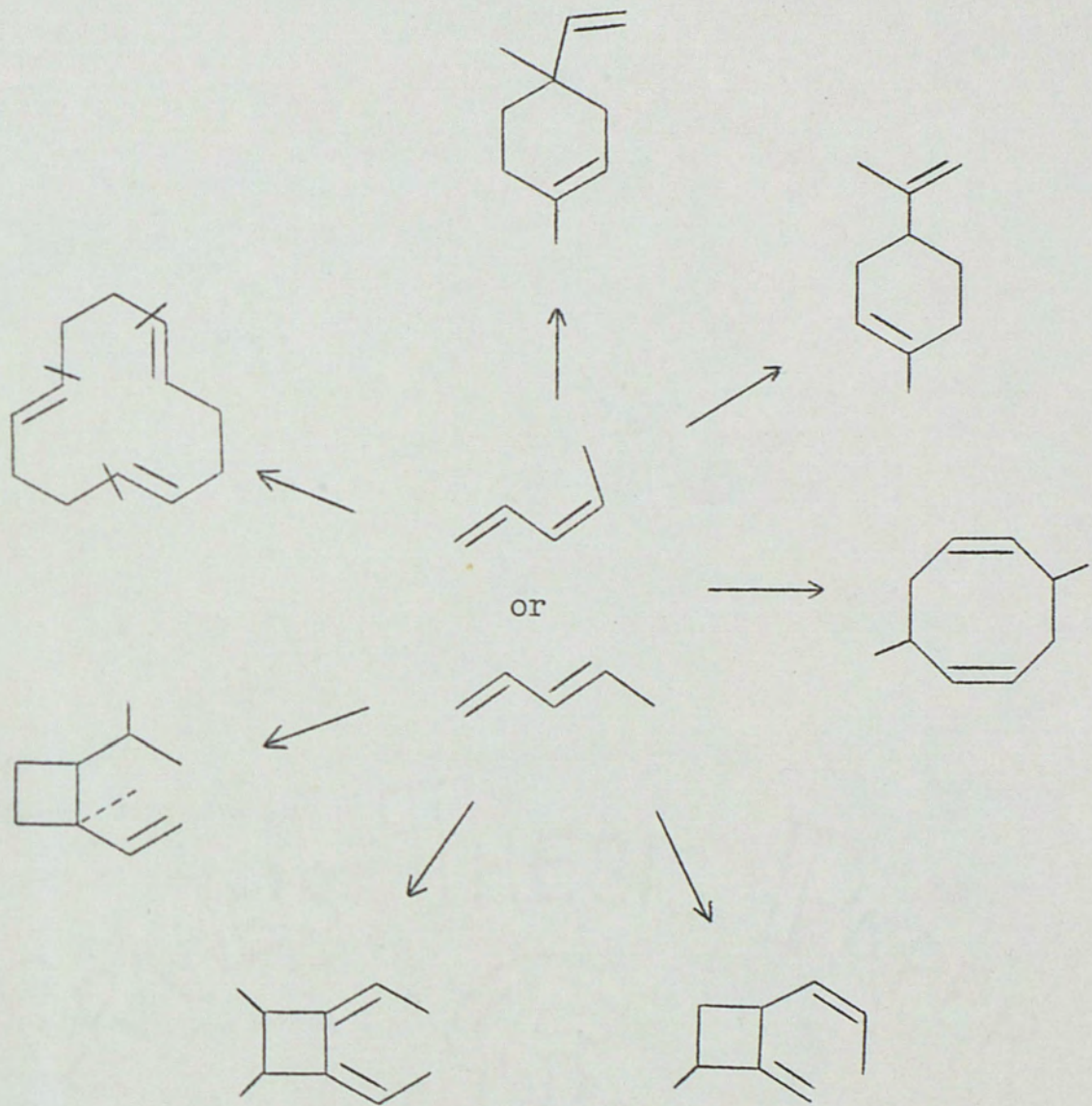
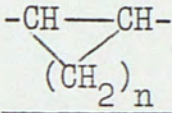


Figure 1. Various synthetic routes from piperylene.



TABLE III

Catalyst Systems for Polymerization of Cyclopentene<sup>13,14</sup>

Catalyst System	Temp. of Polymer	[-CH=CH-(CH <sub>2</sub> ) <sub>n</sub> -]			Structure
		Trans	Cis		
TiCl <sub>4</sub> -Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-30	97	3	0	crystal-line
WCl <sub>6</sub> -Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-30	90	10	0	crystal-line
MoCl <sub>5</sub> -Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-30		99	0	crystal-line

Isoprene

Various catalyst systems have been used for polymerization of isoprene. The structure of polyisoprene is dependent upon the ratio of catalyst components, the reaction temperature, and solvent.

Polymerization of isoprene with Ziegler Natta catalysts, AlR<sub>3</sub> + TiCl<sub>3</sub> (or TiCl<sub>4</sub>, VCl<sub>3</sub>, VCl<sub>4</sub>, etc.) gives cis-1,4- and cis-3,4-polyisoprene depending what catalyst is used<sup>6</sup>.

Cyclopentadiene

The polymerization of cyclopentadiene with triisobutylaluminum titanium tetrachloride catalyst system is reported to yield polycyclopentadiene with 1,4-structure<sup>15</sup>. The versatile reactivity of an active methylene group and double bond conjugation.

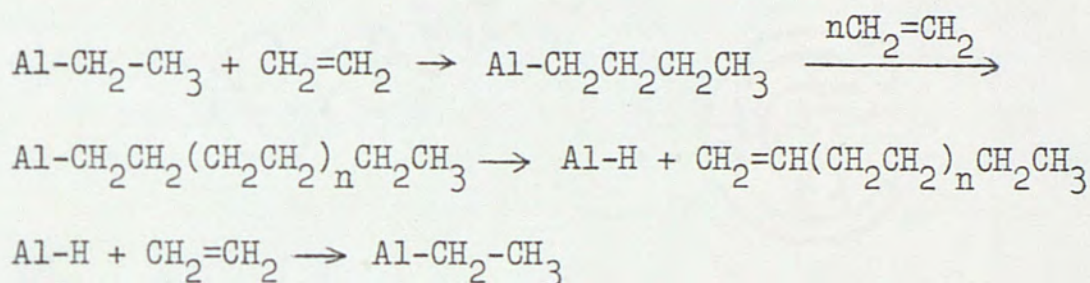
Oligomerization and Co-Digomerization of 1,3-Dienes

The discovery in 1952 by K. Ziegler and his co-workers that ethylene reacts with triethyl aluminum in the presence of nickel to

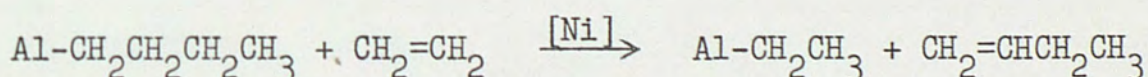


produce 1-butene has had great importance<sup>16-22</sup>.

In 1949 it had been discovered that long-chain aluminum-alkyls could be produced by the repeated insertion of ethylene molecules into the Al-C bond. This growth reaction terminated, however, after the statistical insertion of approximately 100 molecules.



At the end of a long series of experiments a new and initially unwelcomed effect suddenly made its appearance: termination occurred after one insertion step and 1-butene was produced practically quantitatively<sup>23</sup>. A search for the origin of this phenomenon showed that it was associated with traces of nickel salts present in the autoclave, which was made of chrom-nickel steel and, in contrast to normal practice, had been cleaned with nitric acid. This effect became known as the "nickel effect."



As it was suspected that metallic co-catalysts may have caused premature chain termination in the original insertion reactions, a systematic study of the effect of other transition metals was undertaken and resulted, in the Fall of 1953, in the discovery of the Ziegler catalysts and the low-pressure polymerization of ethylene.



The remarkable ability of certain complexes derived from nickel carbonyl to oligomerize acetylenic compounds to cyclooctatetraene was first discovered by Reppe and Schweckendick<sup>24</sup>. This eight membered ring synthesis, and also the preparation of cyclic products from strained olefins (e.g., bicycloheptatriene) and acrylonitrile, have been adequately reviewed elsewhere<sup>25</sup>.

As early as 1954, Reed<sup>26,27</sup> had shown that butadiene reacts in the presence of nickel containing catalysts to produce cis,cis-1,5-cyclooctadiene. The catalyst employed was the so-called "Reppe-type Catalyst,"  $(\text{Lig})_2\text{Ni}(\text{CO})_2$ ; where ligand = phosphine or phosphite, which was previously activated with acetylene. Among others, Reppe himself had shown that this catalyst system was able to convert substituted olefins to six membered ring compounds.

A thorough investigation of the catalytic properties of nickel in its lower valency states could only be undertaken after a research group at Mülheim in West Germany had succeeded in isolating carbonyl-free nickel catalysts containing a stoichiometric ratio of metal to ligand. The extremely active catalyst containing zero-valent nickel may be prepared very easily using the method discovered by Wilke et al.<sup>28</sup>, whereby nickel acetylacetonate is reduced with an organoaluminum compound (e.g., diethyl aluminum ethoxide or triethylaluminum) in the presence of a suitable ligand - phosphite, phosphines and oligo-olefins (e.g., 1,5-cyclooctadiene and 1,5,9-cyclododecatriene) have been shown particularly effective. In the absence, or with a deficiency, of such stabilizing ligands the reduction of



nickel-acetylacetonate leads to the precipitation of metallic nickel. Phosphites and phosphines serve as the electron donating ligands.

As yet no oligomerization or co-oligomerization products of butadiene have been commercially produced by processes using nickel-containing catalysts: 1,5,9-cyclodecatriene is synthesized using titanium-based catalysts and 1,5-cyclooctadiene is not manufactured on a large scale. The situation in the latter case, and in the case of dimethyl-1,5-cyclooctadiene, however, may change with the development of new synthesis of polymers based on the metathesis of cycloolefins<sup>29</sup>.

#### Cyclodimerization of 1,3-Butadiene

As a result of investigations on the thermal oligomerization of butadiene, a number of cyclic hydrocarbons which are difficult to obtain by other methods, such as 1-vinyl-3-cyclohexene and 1,5-cyclooctadiene can now be easily prepared. These products are accompanied, according to Reed<sup>26</sup>, by small quantities of 1,3,7-octatriene, formed by open-chain linkage of two butadiene molecules. Although the cyclic hydrocarbons are formed from butadiene in a remarkably simple manner, the reaction conditions and the yield make the thermal oligomerization of butadiene unsuitable for large scale synthesis<sup>30</sup>.

The dimerization of butadiene to cyclooctadiene in the presence of nickel catalyst was first described briefly by Foster<sup>31</sup>. Shortly afterwards, Reed dimerized butadiene with the catalyst



used by Reppe et al. for the cyclization of acetylene. 1,5-Cyclooctadiene was obtained in 30%-40% yield when nickel carbonyl phosphines and nickel carbonyl phosphites were used.

Wilke<sup>32</sup>, finally succeeded in showing that nickel catalysts containing no carbonyl groups are indeed the most active catalyst, and the catalysts are poisoned by carbon monoxide. He used complexes of nickel(0), which were obtained by reduction of nickel salts with metal alkyls in the presence of electron donor ligands.

The reduction of nickel(II) in the presence of butadiene as the only available ligand (i.e., naked nickel - a nickel complex from which all the bonded ligands are easily displaced by butadiene) produces a catalyst which is able to trimerize butadiene to a mixture of 1,5,9-cyclododecatriene isomers<sup>38</sup>.

The cyclotrimerization reaction described above can be converted into a cyclodimerization reaction by blocking one of the vacant coordination positions around the nickel atom<sup>26,30,32</sup>. Phosphines and phosphites in the ligand-to-nickel ratio of 1:1 have been found to be particularly effective.

The main products of the complete conversion of butadiene (e.g., at 80°C and atmospheric pressure) are cyclooctadiene (COD) and VCH (vinyl cyclohexene). The ratio of COD to VCH is dependent on the ligand attached to the nickel atom (Table IV).

#### Cyclotrimerization of Butadiene

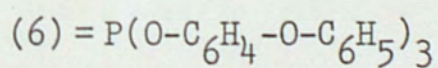
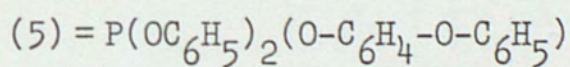
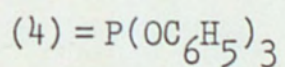
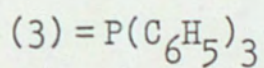
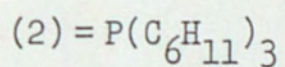
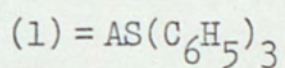
In 1956, Wilke discovered that certain Ziegler Natta catalysts containing titanium bring about the ready cyclotrimerization of



TABLE IV

Cyclodimerization of Butadiene With Nickel-Ligand Catalysts<sup>34</sup>

<u>% of Product</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>	<u>(6)</u>
VCH%	5.8	39.6	26.8	7.4	5.8	3.1
COD	17.3	41.1	64.3	81.1	88.4	96.5
CDT	60.4	14.4	6.0	9.2	4.4	0.2
> C <sub>12</sub>	14.1	4.8	2.8	2.3	2.4	0.2
Gm. butadiene/gm Ni/hr	20	35	180	100	190	780





butadiene to give high yield of trans,trans,cis-1,5,9-cyclododecatriene. The titanium catalyst is very selective and extremely active.

Ligand-free zero valent nickel can also cyclotrimerize butadiene to 1,5,9-cyclododecatriene (CDT). A "ligand-free" zero valent nickel catalyst is defined as a system in which the only ligands associated with the metal are organic groups readily displaced by the reactant.

#### Cyclic Oligomerization of Substituted 1,3-Dienes

Extension of the study of cyclization reactions to substituted butadiene was restricted to methyl substituted species for the following reasons<sup>35</sup>:

- (a) the starting materials (isoprene, cis- and trans-piperylene) are available in large amounts;
- (b) the stereochemistry of the reaction products would provide insight on the reaction mechanism; and
- (c) the configuration of products could be relatively easily determined by gas chromatography, and the usual physical and chemical methods.

The method used by Heimbach et al.<sup>34</sup> to identify the various isomers formed, warrants a short digression. Several groups<sup>36,37,38</sup> have made use of the fact that by using a deficiency of methylene groups (generated by irradiation of diazomethane), insertion occurs, to give the corresponding methyl compound, to an extent which reflects quite accurately the number and ratio of the different types

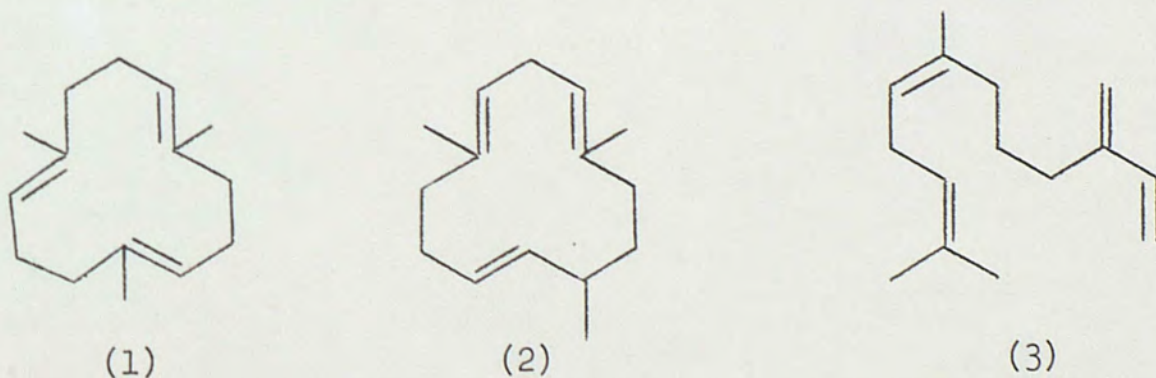


of C-H groups present in the molecule. The products are therefore, relatively easy to identify by gas chromatography. Furthermore, the number of products from the dimerization of methyl-substituted butadiene is restricted. General reactions for cyclic dimerization and codimerization of substituted 1,3-butadiene are shown in Figure 2.

#### Cyclotrimerization of Substituted 1,3-Dienes

The cyclotrimerization of 1,3-dienes other than butadiene has received relatively little attention. The study of cyclotrimerization of substituted 1,3-dienes alone has apparently been limited to isoprene and piperylene<sup>29</sup>.

Isoprene is not cyclotrimerized by the "ligand-free" zero valent catalysts. However, use of the "nickel-ligand" catalyst results in both cyclic dimerization and trimerization. The trimeric product has been shown to consist mainly of 1,5,9-trimethyl-CDT (4); 1,5,10-trimethyl-CDT (2); and the linear famesene (3).



The distribution of the products is controlled by the ligand attached to the nickel.



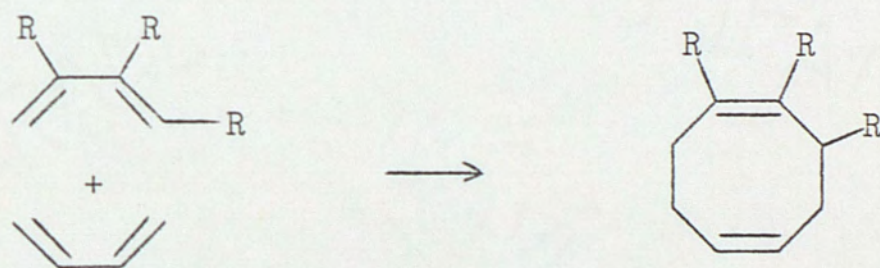
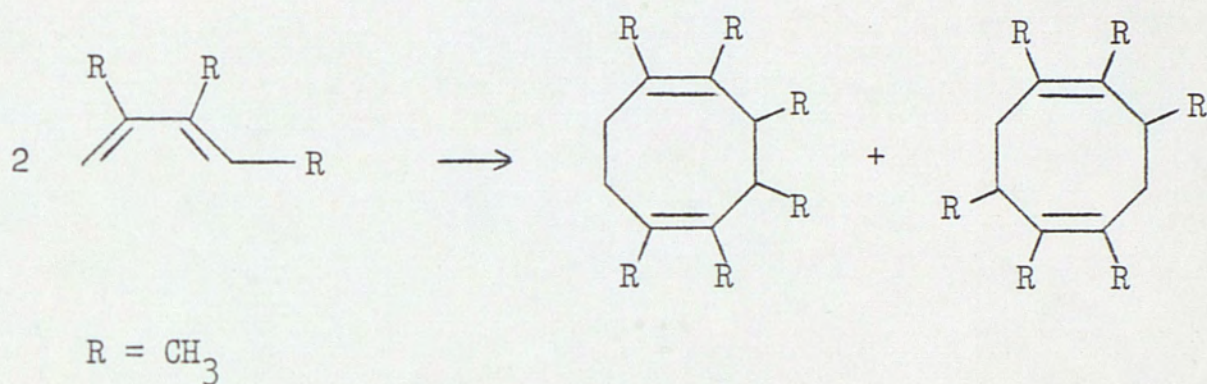


Figure 2. General reactions for dimerization and codimerization.



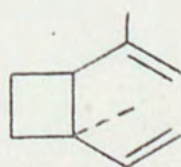
Cyclic trimerization of 1,3-pentadiene has been reported<sup>39</sup>, using a titanium tetra-n-butoxide  $Ti(n-OC_4H_9)_4$  and diethyl-aluminum chloride  $Al(C_2H_5)_2Cl$  in benzene under nitrogen atmosphere. The main product of this process is 1,5,9-trimethyl-1,5,9-cyclododecatriene that is commercially available in 98% mixture of isomers.

#### Cyclodimerization of Substituted 1,3-Dienes

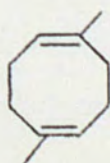
The cyclodimerization reaction has been extended to include cis- and trans-piperylene, isoprene, 2,3-dimethyl-butadiene, 1,3-hexadiene, 1,3,5-hexatriene, and chloroprene. The codimerization of butadiene with a substituted 1,3-diene (e.g., piperylene) or two differently substituted 1,3-dienes has also been studied<sup>29</sup>.

Most of the serious investigations have been carried out with a  $Ni-P(OC_6H_4\text{-ortho-}C_6H_5)_3$  catalyst that is conveniently prepared by adding one equivalent of the phosphite to bis-(cyclooctadiene)-nickel. In general, the substituted 1,3-dienes react far less readily than butadiene itself. This is illustrated in Table V for the methyl substituted 1,3-dienes.

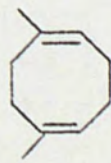
The products from the cyclodimerization reaction usually consists of a mixture of substituted divinylcyclobutane (DVCB), COD, VCH derivatives, e.g., 4-8, derived from isoprene.



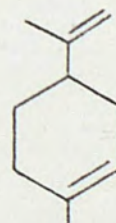
4



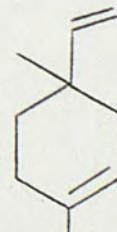
5



6



7



8



TABLE V

The Cyclodimerization of Methyl-Substituted 1,3-Dienes<sup>a</sup>

<u>1,3-Diene</u>	<u>Rate</u> <u>gm dim/gm Ni/hr</u>	<u>C<sub>6</sub> Ring</u> <u>%</u>	<u>C<sub>8</sub> Ring</u> <u>%</u>
Butadiene	220	2.3	97.2
Piperylene	31	5.3	90.9
Isoprene	14	34.8	55.1
2,3-Dimethylbutadiene	0.6	86.3	6.1
2,4-Hexadiene	0	-	-

a - From Refs. 27, 29



The distribution of the products, as well as their structure, depends on both the reaction conditions and the nature of the substituents.

From the cyclodimerization of cis-piperylene all four possible isomers of dimethylcyclooctadiene, 9-12, may be isolated. The trans isomer, however, gives principally 10 and 11<sup>40</sup>.



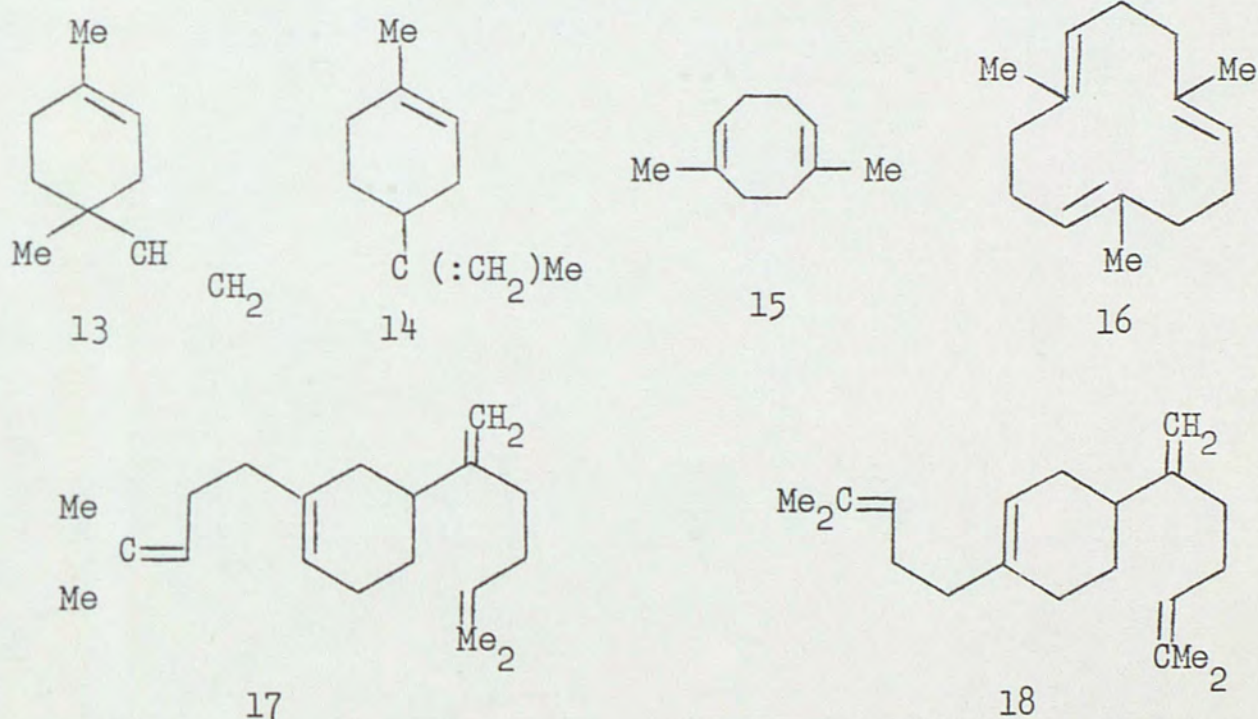
Zvesh, et al.<sup>41,42</sup>, have patented a process for cyclodimerization of 1,3-butadiene, isoprene, piperylene with a catalyst system consisting essentially of the reduction product obtained by mixing (a) a nickel compound selected from the group consisting of nickel bromide, nickel acetate and nickel acetylacetonate; (b) a triaryl phosphite selected from the group consisting of triphenylphosphite, tri-p-tolyl-phosphite, tri-o-tolyl-phosphite containing from 5-10% by weight of diaryl phosphite selected from the group consisting of diphenyl phosphite, and phenyl-p-tolyl phosphite; (c) a reducing agent selected from the group consisting of alkali metal hydrides, sodium hydride, lithium hydride and sodium borohydride; and (d) a catalyst forming diluent selected from THF, diglyme, and dioxane. The cyclodimerization reaction was carried out at 150°C and 250 psi for two hours.

Dzhemilene et al.<sup>43</sup>, used  $\text{Ni}(\text{acac})_2 - (\text{PhO})_3\text{P} - \text{Et}_2\text{NAlEt}_2$  in PhMe for catalytic cyclodimerization of piperylene. This process gave



mixtures of 6 and 8 membered cyclic compounds. The optimum yield of cis-3,4, and cis- and trans-3,7-dimethyl-1,5-cyclooctadiene (15:85 ratio) was 77% and obtained after four hours at 120°C.

Dzhemilene et al.<sup>44</sup>, used  $\text{Ni}(\text{acac})_2$ ,  $\text{Et}_2\text{Al}$  and  $(\text{PhO})_3\text{P}$  in  $\text{Ph}_2\text{O}$  or THF for cyclodimerization of isoprene. The products were 13-18.



The major product in this process was dimethyl-1,5-cyclooctadiene (18).

1,3-Dienes are cyclodimerized at 0-200°C over catalysts obtained by a reaction at 100-400°C of a divalent Ni compound,  $\text{PR}_3$ ,  $\text{P}(\text{OR})_3$ ,  $\text{P}(\text{NR}_2)_3$  (R = alkyl or aryl group) and an alkali or alkali earth metal amide in the presence of the diene<sup>45</sup>.

Tolstikov et al.<sup>46</sup>, prepared 1,5-dimethyl-1,5-cyclooctadiene



by cyclic dimerization of piperylene in the presence of a homogeneous catalyst containing  $\text{Ni}(\text{acac})_2$ , a  $\text{P}(\text{OR})_3$  modifier, and  $\text{AlR}_3$  ( $\text{R} = 3\text{-methyl heptadienyl, cyclohexenylethyl}$ ; and  $\text{AlR}_3 = \text{perhydroalumo phenolene}$  in  $\text{Ph}_2\text{O}$  at  $80\text{-}150^\circ\text{C}$ .

Misono et al.<sup>48</sup>, cyclodimerized isoprene to 1,5- and 2,5-dimethyl-1,5-cyclooctadiene with a  $\text{Co}(\text{III})$  or  $\text{Fe}(\text{III})$  acetylacetonate and a bidentate electron donor and  $\text{Et}_2\text{Al}$ . No reaction was observed when  $\text{Ph}_3\text{P}$  was used as electron donor.  $\text{P}(\text{OPh})_3$ , tri-*o*-tolylphosphite, gave only polymer. The most selective catalyst was found to be  $\text{Fe}(\text{III})$  or  $\text{Co}(\text{III}) (\text{acac})_3$  and 2,2'-dipyridyl. In addition to dimethyl-COD they identified other isomers:

- (a) 1-methyl-4-isopropenyl-1-cyclohexene,
- (b) 2-methyl-4-isopropenyl-1-cyclohexene,
- (c) 1,4-dimethyl-4-vinyl-1-cyclohexene (dimethyl VCH) and
- (d) 2,4-dimethyl-4-vinyl-1-cyclohexene (dimethyl VCH).

Paushkin et al.<sup>47</sup> studied the cyclodimerization of butadiene, isoprene, and piperylene. The cyclodimerization of butadiene was carried out in a furnace reactor at  $420\text{-}480^\circ\text{C}$  and volume space velocity 33-100/hour. The products were analyzed by gas chromatograph. Vinyl-cyclohexene (VCH) was the major product with 47% yield. From cyclodimerization of isoprene, the following were identified:

- (a) 1-methyl-4-isopropylcyclohex-6-ene (major product)
- (b) 1,3-dimethyl-4-vinyl-cyclohex-6-ene
- (c) 1-methyl-3-isopropylcyclohex-6-ene
- (d) 1,3-dimethyl-3-vinylcyclohex-6-ene



- (e) 2,5-dimethyl-1,5-cyclooctadiene
- (f) 2,6-dimethyl-1,5-cyclooctadiene (major product)

The reaction carried out in a quartz tube at 530-550° and volume space 150-200/hour with a maximum yield of 40%. For dimerization of 1,3-pentadiene they used a mixture of 34% cis and 66% trans. The reaction was carried out at 150-260° for 1-4 hours. The maximum yield, 73%, based on feed, was obtained from runs made at 260° for 1.5 hours. The following products were identified:

- (a) 1,3-dimethyl-2-vinylcyclohex-5-ene
- (b) 1,2-dimethyl-3-vinylcyclohex-5-ene
- (c) 1-methyl-2-propenylcyclohex-5-ene
- (d) 1-methyl-3-propenylcyclohex-5-ene
- (e) 3,4-dimethyl-1,5-cyclooctadiene
- (f) 3,6-dimethyl-1,5-cyclooctadiene

Shimaev et al.<sup>49</sup>, studied the catalytic cyclodimerization of piperylene. They found that conversion of 1,3-pentadiene and selectivity of product formation depends on which isomer of 1,3-pentadiene was in the starting material. If cis was present, 3,4- and 3,7-dimethyl-1,5-cyclooctadiene with substituents in the axial position were formed. From trans-1,3-pentadiene, dimers with the substituents in the equatorial position were obtained. The catalyst system has been reported to consist of  $\text{Ni}(\text{acac})_2$  and  $\text{P}(\text{OC}_6\text{H}_4\text{-Ph-ortho})_3$  and  $\text{Bu}_3\text{Al}$  at 100°C.

In this project, a catalyst system consisting of  $\text{Ni}(\text{acac})_2$ , triphenyl phosphite, and diphenylphosphite and a reducing agent,



sodium borohydride, was used to cyclodimerize 1,3-pentadiene. The maximum conversion of 1,3-pentadiene using this catalyst system at 350° and 500 psi was 97% with ~68% yield based on 1,3-pentadiene charged. The effect of different ligands on selectivity of dimethyl-COD also was studied.

#### Thermodynamics

There are no thermochemical data available for the dimers and trimers of 1,3-pentadiene and isoprene except  $H_F^{\circ}$  298 for two derivatives of VCH. However, the thermochemical data for various components of piperylene concentrate are given in Table VI.

The various physical properties of dimers of isoprene and piperylene that have been reported in literature is not complete. Some data for boiling points and refractive indices are shown in Table VII.



TABLE VI

Thermochemical Data For 5-Carbon Unsaturated Compounds<sup>a</sup>

<u>Formula</u>	<u>Name</u>	<u>State</u>	<u>Molecular Weight</u>	$\Delta H_f^{\circ}$ <sub>298</sub>	$\Delta G_f^{\circ}$ <sub>298</sub>	<u>log K<sub>p</sub></u>
C <sub>5</sub> H <sub>8</sub>	cyclopentene	G	68.114	7.87	26.48	-19.410
C <sub>5</sub> H <sub>8</sub>	1,3-trans-pentadiene	G	68.114	18.60	35.07	-25.708
C <sub>5</sub> H <sub>8</sub>	1,3-cis-pentadiene	G	68.114	18.70	34.84	-25.54
C <sub>5</sub> H <sub>8</sub>	isoprene	G	68.114	18.10	34.86	-25.55
C <sub>5</sub> H <sub>6</sub>	cyclopentadiene	G	66.098	32.00	42.86	-31.41
C <sub>5</sub> H <sub>10</sub>	cyclopentane	G	70.130	-18.46	9.23	-6.763
C <sub>5</sub> H <sub>10</sub>	2-methyl-1-butene	G	70.130	-8.68	15.68	-11.495
C <sub>5</sub> H <sub>10</sub>	2-methyl-2-butene	G	70.130	-10.17	14.26	-10.453
C <sub>10</sub> H <sub>16</sub>	1,5-dimethyl-3-vinyl cyclohexene	L	136.228	-28.6	--	--
C <sub>10</sub> H <sub>16</sub>	1-isopropyl-4-methyl-1,3-cyclohexadiene	L	136.228	-13.5	--	--

a - ref. 50



TABLE VII

## Physical Properties of Dimers

Name of Dimer	Monomer	B.P. (°C)	$n_D^{20}$	Reference
1,4-dimethyl-4-VCH-1	isoprene	163-167	--	51
1,4-dimethyl-4-VCH-2	isoprene	173-174	--	51
2,4-dimethyl-4-VCH-1	isoprene	42-44/10 <sub>47mm</sub>	1.4630	51
1-methyl-4-isopropyl-VCH-6	isoprene	173	1.4750	51
1,3-dimethyl-3-VCH-6	isoprene	-	--	-
-methyl-3-isopropenyl-VCH-6	isoprene	-	--	-
1,3-dimethyl-3-VCH-6	isoprene	159	1.4670	48
2,5-dimethyl-1,5-COD	isoprene	-	--	-
2,6-dimethyl-1,5-COD	isoprene	-	--	-
1,2-dimethyl-2-VCH-5	1,3-pentadiene	158/77 <sub>47mm</sub>	1.4655	48
1,2-dimethyl-3-VCH-5	1,3-pentadiene	160/80 <sub>47mm</sub>	1.4650	48
1-methyl-2-propenyl-VCH-5	1,3-pentadiene	167/83.5 <sub>47mm</sub>	1.4696	48
1-methyl-3-propenyl-VCH-5	1,3-pentadiene	170/86 <sub>47mm</sub>	1.4739	48
3,4-dimethyl-1,5-COD	1,3-pentadiene	172	1.4819	48
3,6-dimethyl-1,5-COD	1,3-pentadiene	176	1.4855	48
2-methyl-4-isopropenyl-VCH-1	1,3-pentadiene	-	--	-



## EXPERIMENTAL

A number of runs, utilizing liquid phase reaction at elevated pressure and temperature were performed to investigate the cyclo-oligomerization of piperylene and isoprene.

The piperylene concentrate, isoprene 99+% and piperylene 99% (mixture of cis and trans) have been used as starting materials for this project. A typical composition of piperylene concentrate is presented in Table I. The specification of reagents and instruments used for synthesis and analysis are shown in Table VIII.

The components of the starting materials and products were analyzed on a Perkin-Elmer Sigma I Gas Chromatographic System equipped with flame ionization (F.I.D.) and thermal conductivity (T.C.D.) detectors. This system integrates the area under each peak, compares each peak area to the total peak area, and calculates the weight percent of each component using a programmed response factor.

The column for analysis of the piperylene concentrate consisted of a ten foot section of one-eighth inch thin wall stainless steel tubing packed with 20 weight percent sebaconitrile on 80-90 mesh acid washed (AW) Anakrom C22 followed by a 20 foot section of one-eighth inch thin wall stainless steel tubing, packed with 15 weight percent bis-(2-methoxyethyl) adipate on 60-80 mesh chromosorb white non-acid washed (NAW).

The starting materials and unreacted starting materials (after separation from high boiling point fraction by distillation) were



TABLE VIIISpecification of Reagents and Instruments For  
Synthesis and AnalysisReagents:

- Anhydrous Ethyl Ether - Mallinckrodt, 0.01% H<sub>2</sub>O, ACS reagent grade
- Benzene - Fisher Scientific Company, ACS reagent grade
- Nitrogen - Airco, Inc.
- Sodium Hydride - 50% dispersion in mineral oil, Aldrich Chemical Co.
- Sodium Borohydride - 98+%, Aldrich Chemical Co.
- Triphenyl phosphite - 97%, Aldrich Chemical Co.
- Diphenyl phosphite - Aldrich Chemical Co.
- Nickel acetylacetonate - 99%, Aldrich Chemical Co.
- Acetyl acetonate (ACAC) - Strem Chemical, Inc.
- Phenol - Laboratory grade, Fisher Scientific Co.
- Tetrahydrofuran (THF) - Stabilized, Mallinckrodt Co.
- ortho-phenylphenol - practical grade, Eastman
- para-phenylphenol - practical grade, Eastman
- Phosphorous trichloride - Baker reagent
- Pyridine - Analysed reagents, ACS reagent grade, McB
- Isoprene - 99+%, Gold Label, Aldrich Chemical Co.
- Molecular Sieve 3Å - Linde 3Å, 1/16" pellets, Alfa Products
- 1,5,9-Trimethyl-cyclododeca-1,5,9-triene - 98% mixture of isomers, Aldrich Chemical Co.
- Isopropyl alcohol - Spectro ACS, Eastman
- 1,3-Pentadiene 99% - mixture of cis and trans, Dow Chemical Co.
- Piperylene Concentrate - Dow Chemical Co.
- Cyclopentene - Baker reagent grade
- Cyclopentane - J.T. Baker Chemical Co.
- 2-methyl-1-butene - practical, Eastman
- 2-methyl-2-butene - practical, Eastman



TABLE VIII (cont.)Specification of Reagents and Instruments For  
Synthesis and AnalysisInstruments:

- Adiabatic Annular Teflon Spinning Band Distillation Column, Nester/Fauster Manufacturing Corp.
- Pressure Reaction Apparatus, Series 4500, Parr Instrument Co.
- Infrared Spectrometer - Perkin Elmer 457, Grating Infrared Spectrophotometer
- Melting Point Apparatus - Thomas Hoover Capillary Melting Point Apparatus
- NMR - Varian T-60, NMR Spectrometer System
- Sigma I Gas Chromatographic System, Perkin Elmer
- Refractometer - Bausch and Lomb refractometer with bath and circulator



analyzed isothermally at 60°C with a helium flow rate of 25 ml per minute. The injection temperature was set at 75°C and the flame ionization detector zones 1 and 2, at 250° and 150°C respectively. These conditions were held until all major peaks eluted, usually after 26 minutes.

The response factors employed were from literature values<sup>52</sup>. These values were all approximately 1.0. The retention times of various components of piperylene concentrate on this column are given in Table IX.

TABLE IX

Approximate Retention Times for Components In  
Piperylene Concentrate On Steel Column

<u>Component</u>	<u>Retention Time, minutes</u>
2-Methyl-1-Butene	9.66
2-Methyl-2-Butene	11.11
Cyclopentane	12.56
Isoprene	14.76
Cyclopentene	15.85
trans-1,3-Pentadiene	17.84
cis-1,3-Pentadiene	19.33
Cyclopentadiene	22.48

The column used for analysis of low boiling point materials (i.e. piperylene, isoprene, etc.) tended to load up with heavy



molecules after prolonged use. Therefore, the column was purged with high flow rate of carrier gas (helium) usually 50-60 ml per minute at 90-100°C. The maximum temperature for the column is between 100-110°C.

It was necessary to check the retention times of components on the column periodically. For this purpose, a standard sample of trans-1,3-pentadiene 99% was used without distillation. The samples of cyclopentane, cyclopentene, 2-methyl-1-butene and 2-methyl-2-butene were used after distillation.

For analysis and identification of dimers and trimers of piperylene and isoprene, it was necessary to find a column having enough resolution for various unreacted piperylene concentrate components and oligomers. Four glass columns were examined for this purpose. The specifications of these columns are given in Table X.

Glass column OV-1 was found to have the best resolution for isomers of dimer and trimer, but not for components of piperylene concentrate. The retention times of these low boiling point components were between 0.60 to 0.80 minute with only two overlapped peaks for all eight components in piperylene concentrate.

The reaction products containing dimers, trimers, unreacted components and by-products were analyzed with OV-1 column using a programmed temperature. Initial oven temperature was set on 50°C for two minutes and increased with a rate of 5° per minute to a final temperature of 160°C. The total time of program was 34 minutes. Injection temperature was set on 260° and temperature of detector



TABLE X

Specification of Glass Columns Used For Analysis of Oligomers

<u>Length (ft)</u>	<u>% Liquid Phase</u>	<u>Solid Support</u>	<u>Mesh Size</u>	<u>Liquid Phase</u>	<u>Commercial Name</u>	<u>Maximum Temp (°C)</u>
6	3	Chromasorb W-HP	100-120	Dimethyl silicon	OV-1	350
6	10	Chromasorb Q	100-120	Silicon Rubber Gum	SE-30	350
6	3	Chromasorb Q	80-100	Silicon Rubber Gum	SE-30	350
12	10	Chromasorb Q	100-120	Silicon Rubber Gum	SE-30	350



zones (F.I.D.) 1 and 2, on 250° and 150°C respectively. Flow rate of helium (carrier gas) was 15 ml per minute.

Since no isomers of the dimer were commercially available, some runs were made to synthesize these isomers. The isomers synthesized were separated by an adiabatic annular teflon spinning band distillation column. The refractive indices of different fractions were measured by refractometer at 20°C and used along with data of infra-red spectra for identification of fractions collected at different temperatures.

The only oligomer commercially available is a trimer of 1,3-pentadiene 1,5,9-trimethyl-1,5,9-cyclododecatriene that is a 98% mixture of isomers. The response factors of dimers and trimers were measured, but because the isomers were not pure, the results were confusing. Therefore, response factor 1.00 was used for all components. The approximate retention times for oligomers are shown in Table XI.

Synthesis of Tris-ortho-biphenylphosphite<sup>53-56</sup> (O-C<sub>6</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>-O)<sub>3</sub>P

Into a one liter three-necked flask equipped with mechanical stirrer, Friedrich condenser and additional funnel, was placed 55.105 grams (0.5 mol) ortho-phenylphenol dissolved in 50 ml anhydrous diethyl ether and 39.55 grams (0.5 mol) dry pyridine. 22.88 grams (1/6 mol) phosphorous trichloride was dissolved in 50 ml anhydrous diethyl ether and cooled in ice and water mixture and then transferred to the additional funnel.

The three-necked flask was placed in an ice water bath. While



TABLE XI

Retention Times of Oligomers on OV-1 Glass Columns

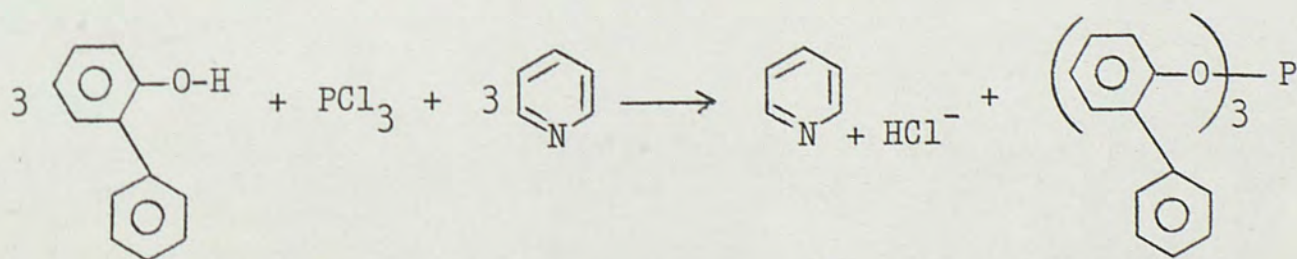
<u>Component</u>	<u>Retention Time (minutes)</u>
Dimethyl-1,5-COD	7.30
Dimethyl-1,5-COD	7.80
Dimethyl-VCH	8.00
Dimethyl-VCH	8.50
Methyl-2-propenylcyclohexene	9.13
Methyl-1-propenylcyclohexene	9.40
1,5,9-Trimethyl-1,5,9-CDT	21.16
	20.10
	25.61



stirring the mixture in the flask, the phosphorous trichloride solution was added dropwise. All of the phosphorous trichloride solution was added to the flask in 30 minutes. The mixture was stirred for two more hours to complete the reaction, and then the white pyridine hydrochloride salt was separated by filtration.

The precipitate was washed with diethyl ether. The ether solution was transferred to a 500 ml flask and was connected to a rotary vacuum evaporator. The diethyl ether and unreacted pyridine was evaporated at 25 mm Hg and 50-60°C. The residue in the flask, after evaporation of solvent, was a pale-yellow high viscous liquid. For crystallization of triester, several solvents were examined. The viscous liquid was finally dissolved in 25 ml boiling isopropyl alcohol and allowed to stand for two days for crystallization.

The white crystals were collected and dried in a vacuum dessicator. The melting point of the crystals was 75°C. For recrystallization, the crystals were dissolved in 25 ml hot isopropyl alcohol and after two days the crystals were collected and dried in the same manner. The melting point of crystals was 83-85°C. The melting point and boiling point of tris-ortho-biphenyl phosphite has been reported as 95° and 340°C, respectively<sup>56,57</sup>. The reaction sequence for triester synthesis is shown below.





Infrared spectra of tris-ortho-biphenyl phosphate, pyridine and ortho-phenyl phenol were used to determine the purity of triester and its structure. The I.R. spectra of trialkyl and triaryl phosphite exhibits a moderately broad band near  $1030\text{ cm}^{-1}$  which has been associated with P-O-C linkage. Although there is a general agreement that a band near  $1000\text{ cm}^{-1}$  is characteristic of the P-O-C structure, there is some divergence of opinion on the point<sup>58,59</sup>.

The I.R. spectra of ortho-phenyl phenol showed an absorption in  $3590\text{ cm}^{-1}$  for O-H stretch in phenol. The I.R. spectra of tris-ortho-biphenyl phosphite did not show any absorption above the  $3100\text{ cm}^{-1}$  C-H stretch band.

#### Preparation of Catalyst

##### (A) Triphenyl phosphite System:

A mixture of 5.14 grams (0.02 mol) nickel acetylacetonate, 24.8 grams (0.08 mol) of triphenyl phosphite containing 8 weight percent diphenylphosphite and 5 weight percent phenol, and 50 ml of THF (dried over  $3\text{\AA}$  molecular sieve), were placed in a 250 ml flask equipped with a magnetic stirrer and a reflux condenser. Finally, 1.52 grams sodium borohydride was added. The flask was heated by a heating mantle and stirring started. The reflux of the mixture continued for 4-5 hours at  $65-68^\circ\text{C}$  under a stream of nitrogen to prevent oxidation. The dark brown-black slurry material was cooled and the flask was purged with nitrogen and stoppered.

##### (B) Tris-ortho-biphenyl phosphite System

A mixture of 5.14 grams (0.02 mol) nickel acetylacetonate,



10.6 tris-o-biphenyl phosphite (0.02 mol), 2.0 gram NaH (0.04 mol), and 35 ml THF were mixed and refluxed with the same process described above, and the brown-green colored mixture was sealed under nitrogen and stoppered.

(C) Triphenyl phosphine System

A mixture of 5.14 grams (0.02 mol) nickel acetylacetonate, 4.6 gram (0.02 mol) triphenyl phosphine, 2 gram (0.04 mol) NaH and 35 ml THF were mixed and refluxed with the same procedure described above, and the dark brown-black mixture was sealed under nitrogen and stoppered.

(D) Tris-o-biphenyl phosphite System

A suspension mixture of 5.14 gram (0.02 mol) nickel acetylacetonate, 10 gram (0.02 mol) tris-o-biphenyl phosphite, and 3 gram (0.08 mol) sodium amide,  $\text{NaNH}_2$  50%, in benzene was prepared. The suspension was kept in a stoppered bottle under nitrogen.

Cyclodimerization of 1,3-Pentadiene

The pressure reactor used for all dimerization reactions was a model 4500 Parr pressure reaction apparatus. The body of the reactor is made of type-316 stainless steel, a molybdenum stabilized, austenitic chromium-nickel steel which is resistant to corrosive chemicals. The reactor is equipped with a 2000 psi gauge, 3 needle valves, and a safety pressure relief. To facilitate the charge and discharge of material in the reactor, a special Pyrex glass liner was used which is resistant to high temperature and pressure. The reactor is also equipped with an internal thermocouple connected to



an automatic temperature controller.

Two grams (2 millimole Ni) of catalyst mixture was placed in the reactor along with 72 grams of cold piperylene concentrate ( $-50^{\circ}\text{C}$ ). The reactor was purged with nitrogen for two minutes. The temperature controller was set on  $150^{\circ}\text{C}$ . The thermocouple on the reactor was calibrated with a  $0.1^{\circ}\text{C}$  thermometer using boiling water as a reference. The stirring started and after 30 minutes the pressure in the reactor reached 220 psi (at  $150^{\circ}\text{C}$ ). Because of the exothermic nature of the reaction, the temperature and pressure of the reactor exceeded the set point and reached  $175^{\circ}\text{C}$  and 350-400 psi.

After two hours, the reactor was cooled to  $0^{\circ}\text{C}$  using an ice and water bath. The pressure in the reactor was released by opening the outlet needle valve. The reactor head was removed and the materials, including liquid and catalyst residue were transferred to a pre-weighed cylinder. The possible loss of material was determined by calculating the difference in weight of materials charged and discharged. A portion of this liquid was used for analysis and identification of products by gas chromatography after filtration through 44-Whatman filter paper.

#### Separation of Unreacted Starting Materials From Products

Twenty ml of filtered liquid was placed in a 50 ml pot of the distillation apparatus. The low boiling point components were separated at pot temperature  $70^{\circ}\text{C}$  and head  $38-50^{\circ}\text{C}$ . The volume of distillate was determined and used for calculation of conversions along with its analysis on gas chromatography.



### Separation of Isomers of Dimer

Because the boiling points of the isomers of the dimer are very close - differing by only 3°C - the adiabatic annular spinning band column was used as the distillation apparatus.

The adiabatic annular spinning band distillation system is one of the most effective distillation apparatus. It consists of a rotary spiral band (Teflon), which acts as the packing. The rotary spiral offers the advantages of low hold-up, low pressure drop, high efficiency, high through-put and a low tendency to flood. A stirrer on the bottom of the band helps increase boil-up so that less heat is required in the pot, lessening the chance of thermal decomposition. The still is vacuum jacketed and silvered making it adiabatic.

After stripping off unreacted materials, the high boiling point fraction was placed in a pot of spinning band distillation apparatus. The pot temperature control was set on midrange, band rotation on 100% (7200 rpm), and reflux ratio on total reflux. The system was operated at total reflux for two hours to reach equilibrium. The pot and head thermocouples were previously calibrated with an external thermocouple. The reflux ratio was changed to 20:1 when the temperature of the head reached 150°C. The heat input to the pot was adjusted to achieve a rate of 16-20 drops/minute from blue tip in the bottom of the condenser. Under these conditions, fractions were collected at 159°, 162°, 167°, 170°, 172°, 174°, and 176°C.

The refractive index of each fraction was determined at 20°C and compared with data from literature. In most fractions, the data



were consistent, and differences for some fractions were assigned to the impurities in them. I.R. spectra of fractions were used to study the structure of the fractions.

Using the technique described above, fractions were collected at 25-47 mm Hg vacuum, and at head temperatures from 75° to 94°C.



## RESULTS AND DISCUSSION

If the 1,3-pentadiene in piperylene concentrate could be selectively cyclodimerized to high boiling point dimers, it could be separated from the other components in the piperylene concentrate by distillation. The main objective of this project was to evaluate nickel catalyst systems to cyclodimerize 1,3-pentadiene, while having a minimum catalytic affect on the other components of piperylene concentrate.

The catalyst systems used in this project were based on nickel (0) with various phosphites and phosphines as ligands in various Ni:ligand molar ratios.

Piperylene concentrate, pure 99+% isoprene and pure 1,3-pentadiene 99% (mixture of 66% trans and 34% cis isomers) were used as starting materials.

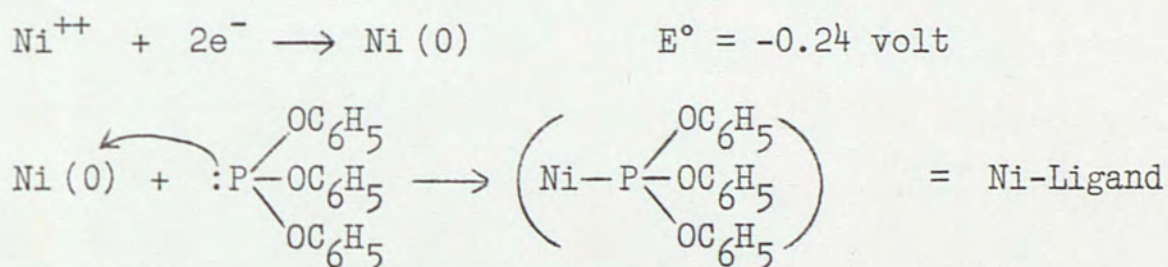
### Mechanism of Catalyst Formation

The nickel (+2) compound, nickel acetylacetonate, was reduced by a reducing agent (sodium borohydride or sodium hydride) generating nickel (0), which then reacts with electron donor ligands to give a donor-acceptor Ni-ligand complex that has been used as a catalyst for cyclodimerization reactions<sup>60</sup>.

Trialkyl and triaryl phosphites and phosphines are all good donors toward d-group transition metals. A characteristic feature of d-group transition metals is their ability to form complexes of neutral CO and basic molecules such as phosphines and phosphites<sup>61</sup>.



In many of these complexes, the metal atoms are in low-positive or zero formal oxidation states. It is a characteristic of these ligands that they can stabilize low oxidation states. The stabilization could be the result of Lewis acid-Lewis base interaction in which the nickel (0) is regarded as a Lewis base. This property is associated with the fact that these ligands have lone electron pairs. The configuration of nickel in the outer shell is  $3d^8, 4s^2$ , and for phosphorous is  $3s^2, 3p^3$ . Therefore, two lone electron pairs can transfer to a nickel atom.



The electron donating character of phosphites and phosphines depends on an inductive and steric effect (steric hindrance) of aryl and phenyl substituted aryl groups.

During the preparation of the catalyst it was evident that the order of addition of catalyst components is very important and will determine the activity of the catalyst. The reducing agent should be added last, when the nickel (+2) compound and ligand are available as a homogeneous mixture in the solvent (THF). The addition of a reducing agent in the absence of ligand results in the formation of metallic nickel as a precipitate which has no catalytic activity for cyclodimerization of 1,3-pentadiene. The activity of



these catalysts also depends on the purity of the reagents used and the procedure of weighing and refluxing the mixture. Preparation of the catalysts in a glove box (dry box) under argon or nitrogen pressure is recommended. Extreme cleanliness is also required because of the sensitivity of phosphites and reducing agents to oxygen, moisture, carbon monoxide, and other unknown poisons.

The data in this report are best understood with the following definitions:

1) conversion - the difference in weights of component charged to reactor and discharged from reactor, divided by the former, all multiplied by 100;

2) yield of dimer based on monomer charged - weight of dimer in the discharge divided by the weight of monomer in the charge, all multiplied by 100;

3) yield of dimer based on monomer converted - weight of dimer in the discharge divided by the weight of monomer converted, all multiplied by 100.

#### Cyclodimerization by Ni-Lig With Triphenyl phosphine as Ligand

The result of cyclodimerization in piperylene concentrate with a catalyst system consisted of Ni-Lig = 1:1 with triphenyl phosphine  $(C_6H_5)_3P$  as ligand, is shown in Table XII. The reaction of cyclodimerization was carried out at 150°C and 220 psi under nitrogen atmosphere. Two millimole nickel was used per 100 gram 1,3-pentadiene as catalyst.



TABLE XII

The Data For Cyclodimerization With Ni-Lig=1:1

<u>Component</u>	<u>Conversion (%)</u>
2-methyl-1-butene	18.6
2-methyl-2-butene	20.7
cyclopentane	33.7
isoprene	31.5
cyclopentene	20.62
trans-1,3-pentadiene	27.07
cis-1,3-pentadiene	28.1
cyclopentadiene	78.81

The results show that the catalyst system consisting of triphenyl phosphine as ligand is not selective for cis- and trans-1,3-pentadiene. The undesired conversion of 2-methyl-2-butene, etc., are high. The conversion of cyclopentadiene is even greater than conversion of 1,3-pentadiene. The products of these side reactions are unknown. The yield of dimer based on 1,3-pentadiene charged was 17% and the yield of dimer based on converted 1,3-pentadiene was 60.12%. This means that nearly 40% of converted 1,3-pentadiene has converted to by-products. This is evident in the gas chromatogram of the final product.

Cyclodimerization With Ni-Lig Catalyst (Lig. = Triphenyl Phosphite)

The cyclodimerization of piperylene concentrate and pure



isoprene were studied using a catalyst system which consisted of Ni-Lig=1:1, with Lig = triphenyl phosphite. The data for cyclodimerization of piperylene concentrate and pure isoprene are shown in Table XIII.

The conversion of 1,3-pentadiene (cis and trans) at 80°C and 150 psi (#23), is less than at 150°C and 220 psi. The table shows that the conversion of diene and yield of dimer increases as time of reaction increases from two hours to 10 hours. The yield of dimer based on converted diene also increases at the same time. The cyclodimerization of isoprene 99+% shows a high conversion but the yield of dimer is poor. The reason is that most of the isoprene has been converted to a polymer. Polymer usually is a major by-product of cyclodimerization of pure isoprene.

The conversions of other components of piperylene concentrate in these reactions also increases with increasing temperature of reaction and reaction time. These undesired side reactions reduce the yield of dimer. The effect of temperature of reaction on conversion and time of reaction on conversion and yield using triphenyl phosphite as ligand are shown in Figures 3 and 4.

#### Cyclodimerization with Ni-Lig (Lig = Tri- and Diphenyl phosphite)

The cyclodimerization of pure isoprene, pure 1,3-pentadiene, and piperylene concentrate was studied with a catalyst system which consisted of Ni-Lig=2:1 with triphenyl phosphite and diphenyl phosphite as ligand. The amount of diphenyl phosphite was 5 weight



TABLE XIII

Data of Cyclodimerization of Diene With Ni-Lig = 1:1 Catalyst  
(Ligand = Triphenyl Phosphate)

Run #	I.D. Starting Material	Conversion %		% Yield Based On: Charged	Reaction Conditions Temp. (°C)	Pressure (psi)	Time (hr)	Atmosphere		mmole Ni/ 100 g diene
		Trans	Cis					N <sub>2</sub>	Ar	
27	pipery- lene	40	34.3	66.6	150	220	10	+		2.0
23	pipery- lene	7.45	12.74	--	150	150	2	+		2.5
19*	pipery- lene	16.8	6.5	5.51	150	220	2		+	2.0
20	pipery- lene	9.69	5.45	7.2	150	220	2		+	2.0
12	isoprene 99%	--	69	32	150	220	2		+	2.5
24	pipery- lene	23	34.1	10.48	150	220	2		+	2.5

\*The change of materials (piperylene concentrate and catalyst) was performed in a dry box.



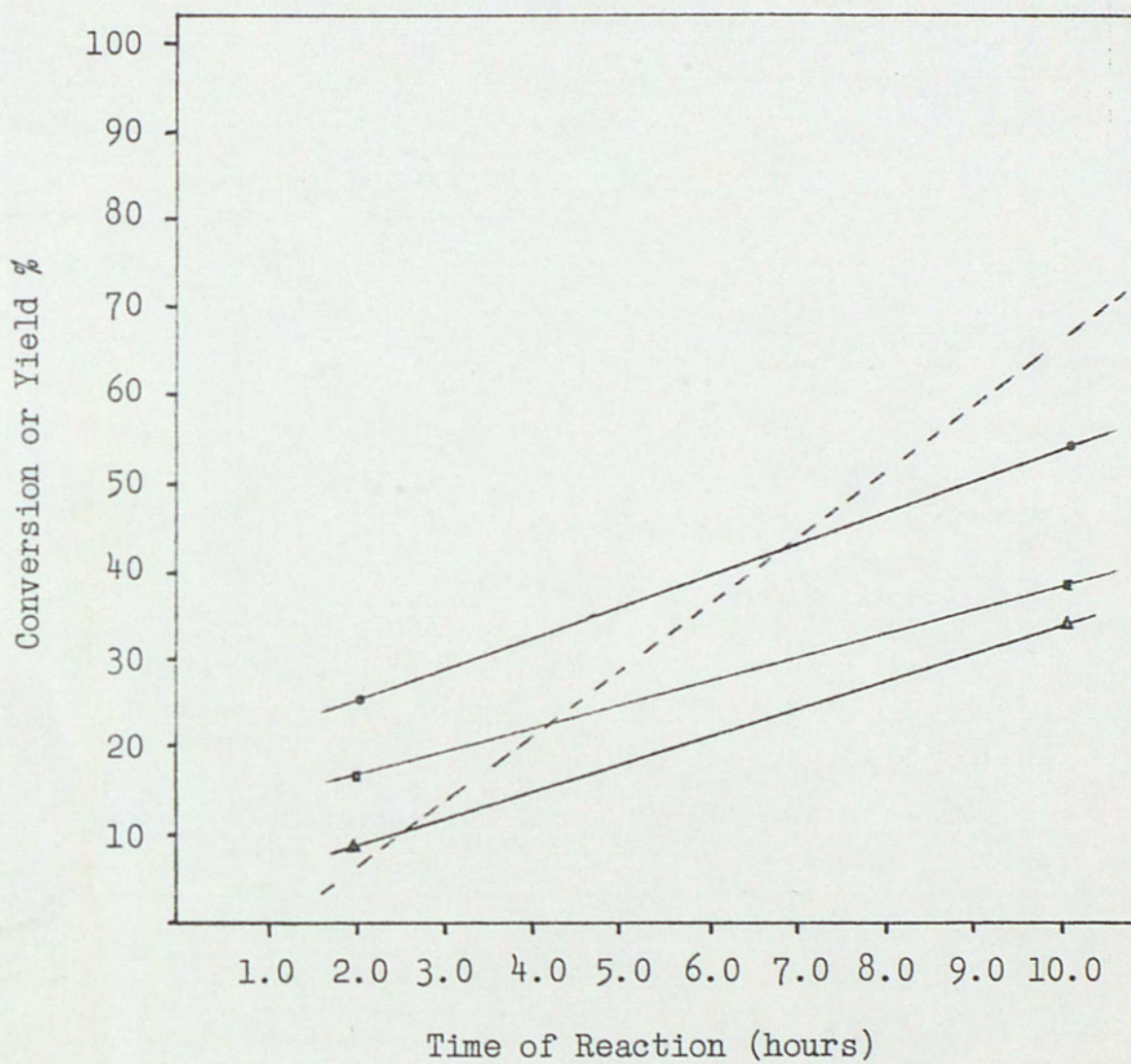


Figure 3. Effect of reaction time on yield and conversion (Ligand =  $(C_6H_5O)_3P$ ).

- isoprene
- trans-1,3-pentadiene
- ▲ cis-1,3-pentadiene
- - + - - yield



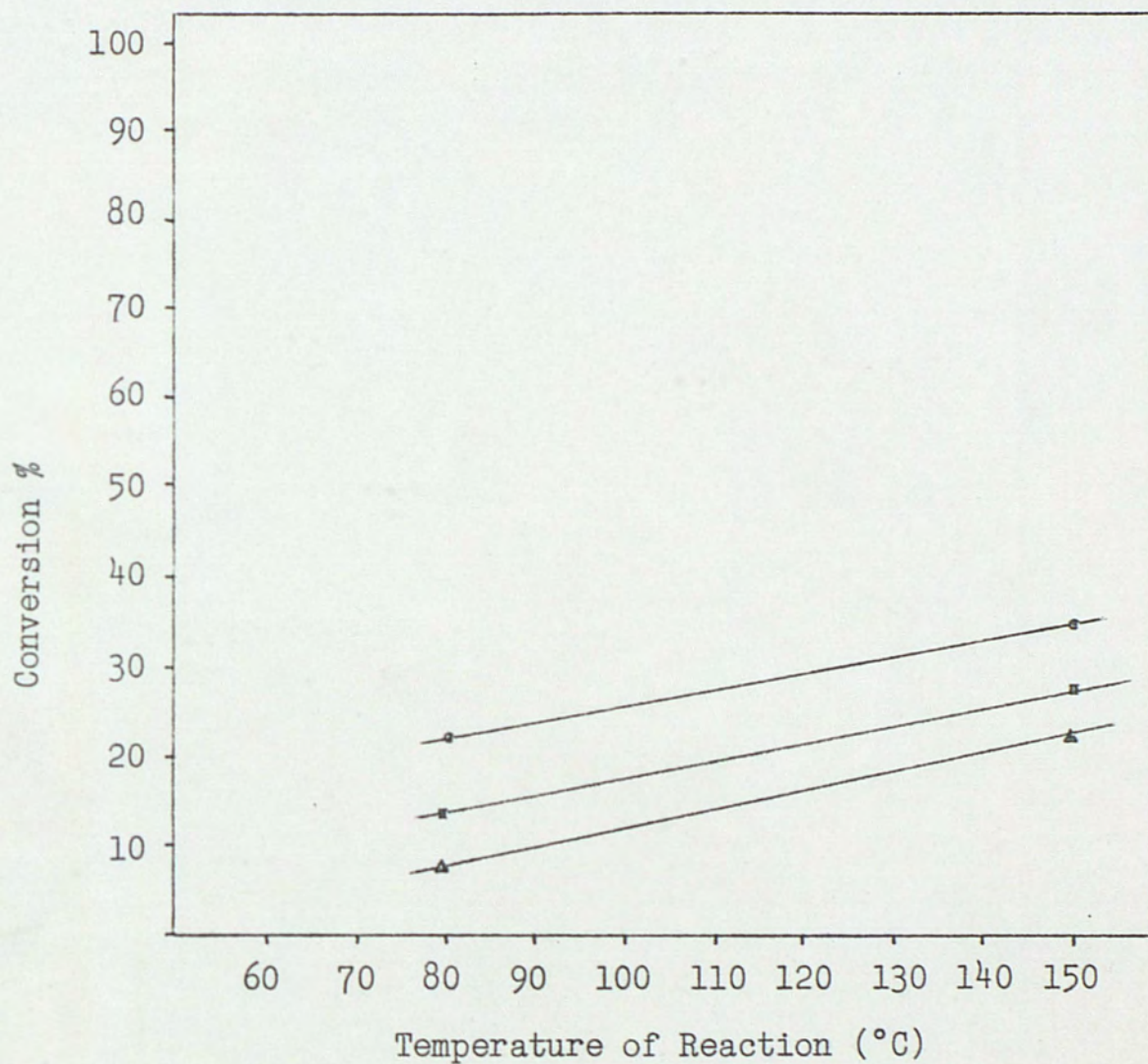


Figure 4. Effect of temperature of reaction on conversion (Ligand =  $(C_6H_5O)_3P$ ).

- Legend:
- isoprene conversion
  - trans-1,3-pentadiene conversion
  - ▲ cis-1,3-pentadiene conversion



percent of diphenyl and triphenyl phosphite mixture, and 5 weight percent of phenol was also added. Diphenyl phosphite and phenol seems to activate the ligand and stabilize the Ni-Lig bond. The results for this study are shown in Tables XIV and XV.

In most cases, the conversion of trans-1,3-pentadiene is higher than conversion of the cis isomer. Both conversion and yield in these reactions are highly dependent on the temperature and pressure of the reaction. The time of reaction is also an important factor in the cyclodimerization process.

The maximum conversion of cis- and trans-1,3-pentadiene was in 350°C and 500 psi (run #32). The yield of dimer at these conditions was maximum - 66%, but the yield of dimer based on the 1,3-pentadiene converted was 68% in this case. The time required to approach this conversion and yield was 50 minutes. One of the reasons that the yield of dimer based on 1,3-pentadiene converted is only 68%, is that the side reactions at this temperature and pressure decreases the yield by formation of a series of by-products. This is confirmed by studying the G.C. chromatogram for this run, which shows alot of by-products with different boiling points. Table XV shows the conversion of components of piperylene concentrate other than dienes. The conversion of these side reactions was over 40% in the case of cyclopentene and cyclopentane. The conversion of isoprene (run #36) was 70% and the yield of dimer was only 25%, with a formation of polymer. The effect of reaction time on conversion of cis- and trans-1,3-pentadiene and isoprene, and on



TABLE XIV

Cyclodimerization of Piperylene Concentrate and Isoprene With Ni-Lig  
(Ligand = Di- and Triphenyl Phosphite)

Run #	I.D. Starting Material	Conversion %		% Yield Based On Charged	Reaction Conditions		mmole Ni/ 100 g Diene		
		Trans	Cis		Time (hr)	Temp. Pressure (C) (psi)			
29	piperylene	50.6	40	41	78	20	150	220	2.0
30	pure isoprene	--	--	25.2	32.4	2	150	220	2.0
32	piperylene	97	96.5	66.4	68.8	0.8	350	500	3.0
33	piperylene	21.3	18.2	12.7	63.5	0.8	150	240	2.5
37	piperylene	56	81	42	81	20	150	220	3.0
39	piperylene	37.5	33	14.3	40	1.5	200	300	2.5



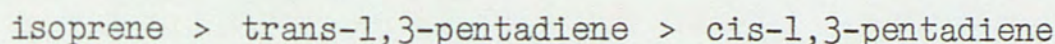
TABLE XV

Cyclodimerization of Piperylene Concentrate and  
Conversion of Other Components

Run #	I.D. Starting Material	Conversion %					Reaction Conditions		
		2-methyl-1-butene	2-methyl-2-butene	cyclo-pentane	cyclo-pentene	cyclo-pentadiene	Time (hr)	Temp. (°C)	Pressure (psi)
29	piperylene	4.3	7.98	9.2	9.97	100	20	150	220
32	piperylene	3.18	33.6	4.3	41.26	87	0.8	350	500
33	piperylene	0.1	11.3	4.92	10.56	75	0.8	150	240
37	piperylene	19.76	18.88	31.13	20.63	100	20	150	220
39	piperylene	16.1	13	24	12.8	83	1.5	200	300



yield of dimer is shown in Figure 5. It is evident that the yield of dimer and conversion of dienes are dependent on the reaction time. The conversion of isomers of 1,3-pentadiene and isoprene as shown in Figure 5 are in the order:



The effect of temperature on conversion and yield is shown in Figure 6. The conversion of 2-methyl-2-butene, cyclopentane, and cyclopentene show these components are more sensitive to reaction temperature than cyclopentadiene and 2-methyl-1-butene.

Cyclodimerization With Ni-Lig Catalyst Where Ligand =  $(\text{C}_6\text{H}_5\text{-}2\text{-C}_6\text{H}_4\text{O})_3\text{P}$

The results of cyclodimerization of 1,3-pentadiene in piperylene concentrate with a catalyst system consisting of Ni-Lig=1:1 using  $(\text{C}_6\text{H}_5\text{-}2\text{-C}_6\text{H}_4\text{O})_3\text{P}$  as ligand, is shown in Table XVI. The results of these cyclodimerization reactions can be compared with results of cyclodimerization with Ni-triphenyl phosphite and Ni-tri- and diphenyl phosphite system. These data are shown in Table XVII. Comparison of yield of dimer, based on 1,3-pentadiene converted, shows that using tris-ortho-biphenyl phosphite as ligand in Ni-Lig catalyst system increases conversion, yield, and has a higher selectivity toward dimer formation, especially dimethylcyclooctadiene. The reason for this higher selectivity may be the steric effect of the bulky-o-phenyl groups. This will be discussed below in mechanistic considerations.

As in the case of using triphenyl phosphite as ligand, this catalyst system was used to study the effect of reaction time and



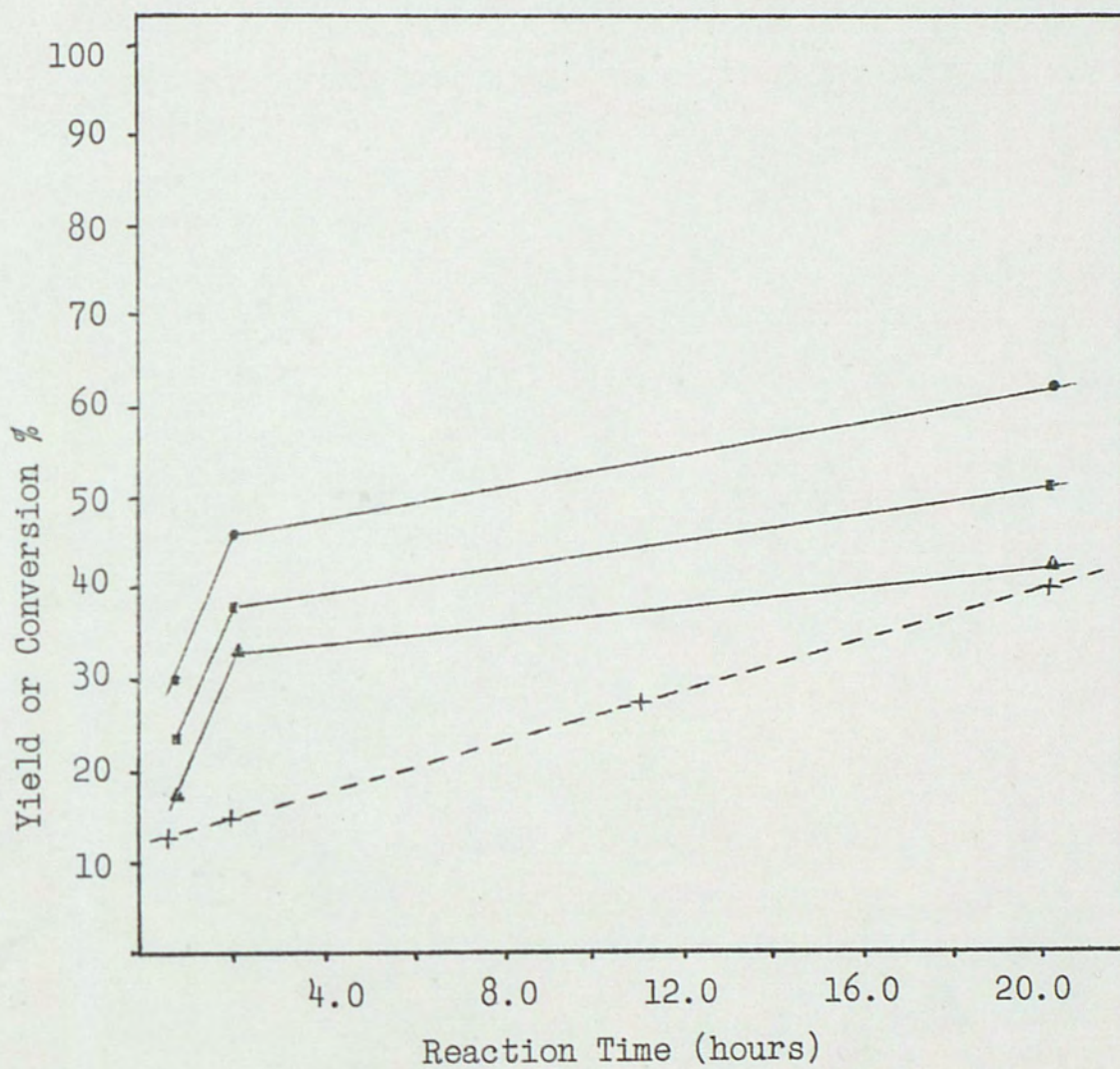


Figure 5. Effect of reaction time on conversion and yield.

Legend:

- isoprene conversion
- trans-1,3-pentadiene conversion
- ▲ cis-1,3-pentadiene conversion
- +-- yield



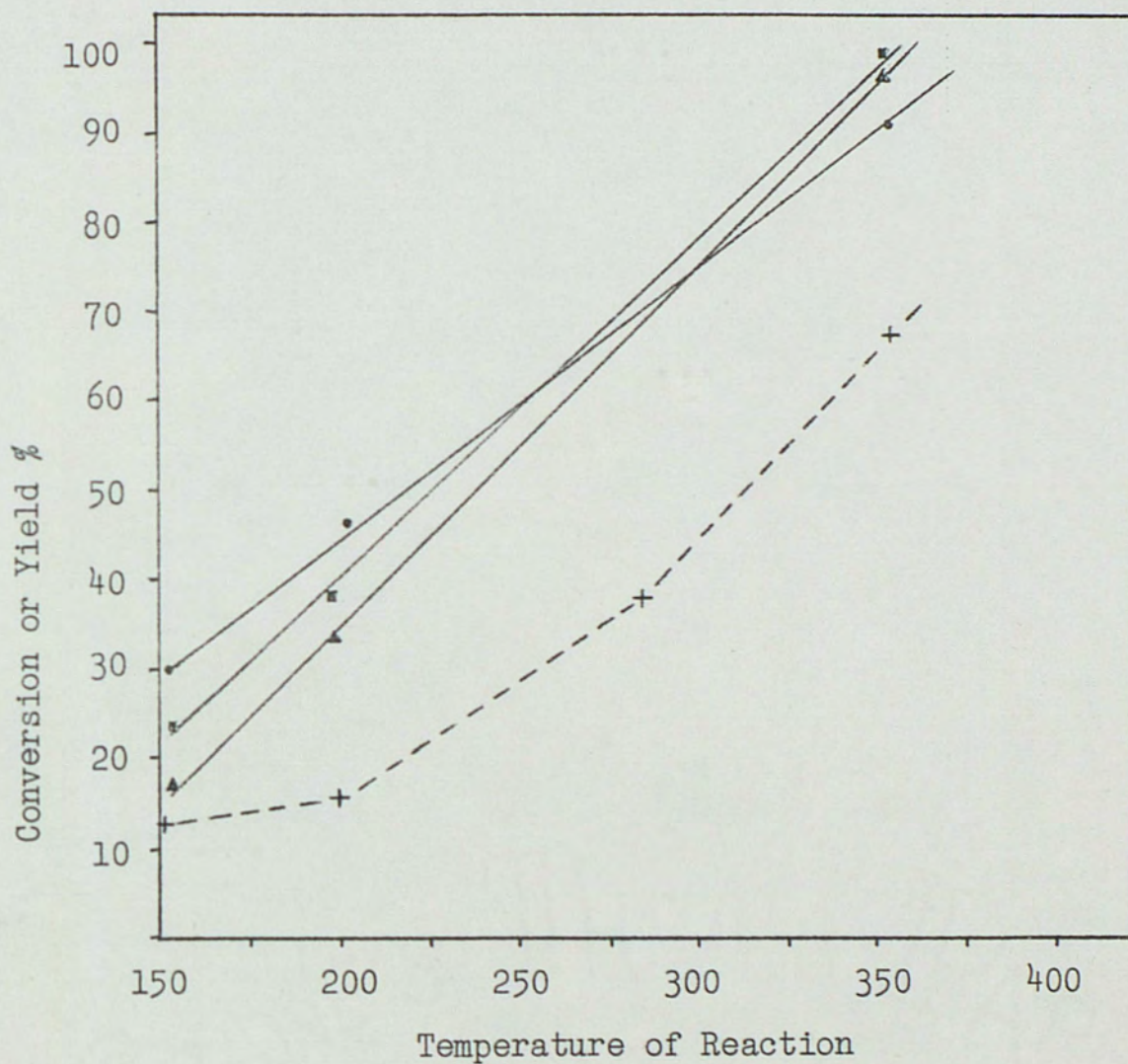


Figure 6. Effect of temperature of reaction on conversion and yield.

Legend:     • isoprene conversion  
              ▪ trans-1,3-pentadiene conversion  
              ▲ cis-1,3-pentadiene conversion  
              -- + -- yield



TABLE XVI

Results of Cyclodimerization With  $(C_6H_5-2-C_6H_5O)_3P$   
As Ligand in Ni-Lig Catalyst

Run #	I.D. Starting Material	Conversion %		Charged	% Yield Based On Converted	Reaction Conditions		mmole Ni/ 100 g Diene		
		Trans	Cis			Time (hr)	Temp. (°C)		Pressure (psi)	
21	piperylene	25	23	32	14	58	2	150	220	2.0
22	piperylene	25	25	35	13	50	2	150	220	2.5
40	piperylene	40	37	65	40	70	2	250	340	2.0
25	piperylene	24.1	19.24	32	35	75	4	150	220	2.5
31	piperylene	35	36.2	40	18.63	24.5	2	150	220	2.5
26	piperylene	15.24	23	51	17	58	2	150	220	2.0



TABLE XVII

Comparison of Various Ligands And Their Effect On Yield

Run #	I.D. Starting Material	Conversion %		% Yield Based On Charged	Reaction Conditions		Catalyst System Ligand	
		Trans	Cis		Time (hr)	Temp. (°C)		Pressure (psi)
19	piperylene	16.8	6.5	5.5	2	150	220	Ni-Triphenyl phosphite = 1:1
26	piperylene	23	15.4	17	2	150	220	Ni-(C <sub>6</sub> H <sub>5</sub> -2-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> P = 1:1
33	piperylene	21.3	18.2	12.7	2	150	220	Ni-Tri, diphenyl phosphate = 2:1



temperature on conversion and yield. The data for this study are depicted in Table XVI. Both conversion and yield of reaction are dependent on time and temperature of reaction.

The effect of Ni-tris-ortho-biphenyl phosphite on components of piperylene concentrate (other than dienes) was studied by using pure components as starting materials. The data for this study is shown in Table XVIII. The nature of products from the conversion of pure components is not known, but the G.C. chromatogram shows that these have high boiling points and different retention times. Comparison of results of these reactions with conversion of the same component in piperylene concentrate shows that the conversion in pure state is much less than conversion in mixture (i.e. piperylene concentrate). Therefore, it is possible to assume that in the presence of nickel catalyst, the components of piperylene concentrate undergo a series of reactions with relatively high boiling point products, but the nature of these reactions and products is not known.

#### Cyclodimerization of 1,3-Pentadiene 99%

In this section, the cyclodimerization of 1,3-pentadiene 99% with a catalyst system consisting of Ni-Lig = 1:1 with triphenyl phosphite and tri-ortho-biphenyl phosphite as ligand was studied. In the case of triphenyl phosphite, diphenyl phosphite (5%) and phenol (5%) were also used as stabilizers for ligand. The results of these reactions are shown in Table XIX.

The results of cyclodimerization of 1,3-pentadiene (pure 99%) shows the relationship between temperature of reaction and conversion



TABLE XVIII

Effect of Ni-(C<sub>6</sub>H<sub>5</sub>-ortho-C<sub>6</sub>H<sub>4</sub>O)<sub>3</sub>P on Piperylene Concentrate

Run #	Starting Material	Conv. %	Reaction Conditions		mmole Ni/ 100 g diene
			Time (hr)	Temp. (°C) Pressure (psi)	
41	pure cyclopentane	0.55	2	150 220	5
42	pure cyclopentene	30.4	2	150 220	5
43	pure 2-methyl-2-butene	2.2	2	150 220	5
44	pure 2-methyl-1-butene	1.1	2	150 220	5

\* All reactions were carried out under nitrogen.



TABLE XIX

Cyclodimerization of Pure 1,3-Pentadiene With Ni-Lig = 1:1 Catalyst  
 (Ligand =  $(C_6H_5O)_3P$  or  $(C_6H_5-2-C_6H_4O)_3P$ )

Run #	Conv. %	% Yield		Reaction Conditions		mmole Ni/ 100 g Diene	Type of Catalyst
		Charged	Based On Converted	Time (hr)	Temp. (°C)		
34	9.8	9.26	95	2	150	220	$(C_6H_5O)_3P$
35	54	52	80	2	200	300	$(C_6H_5-2-C_6H_4O)_3P$
37	95	70	81	2	300	450	$(C_6H_5-2-C_6H_4O)_3P$
38	14.5	9	70	2	150	220	$(C_6H_5O)_3P$



of diene and yield of dimer. The conversion of trans isomer is higher than cis isomer. The yield of dimer based on 1,3-pentadiene converted, shows a better conversion of diene to dimer. One reason is that there are not any impurities to react with 1,3-pentadiene to form by-products and decrease the yield.

#### Mechanistic Considerations and Effect of Ligand on Activity and Selectivity of Catalyst

Heimback et al. studied the effect of different ligands in Ni-Lig=1:1 catalyst in the rate and composition of products of butadiene. The data for this study are shown in Table XX. According to the report, maximum rates of conversion are obtained with a nickel-ligand ratio of 1:1. The yield of cyclooctadiene and ratio to vinylcyclohexene is ligand dependent and it can be seen that both electronic and steric effects are involved. Tris-ortho-biphenyl phosphite has the maximum rate of conversion in known phosphites and phosphines. The yields of cyclooctadiene (butadiene as monomer) and dimethylcyclooctadiene (1,3-pentadiene as monomer) also maximize yield using  $(C_6H_5\text{-ortho-}C_6H_4O)_3P$  as the ligand. Replacing the phenyl group in  $P(OC_6H_4\text{-ortho-}C_6H_5)_3$  with a methyl group in the ortho position, decreased the rate of conversion and yield of cyclooctadiene by 400 grams  $C_4H_6/g. Ni hr.$  and 4% respectively. Changing the position of the methyl group on the benzene ring from ortho to meta and para decreases the rate and yield of reaction. This is shown in Table XXI. Steric effects are important to the activity of Ni-Lig catalyst. Therefore, the high steric hindrance of the phenyl group in



TABLE XX

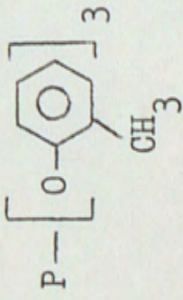
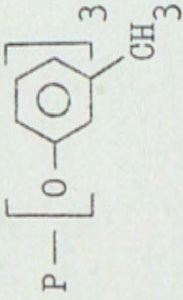
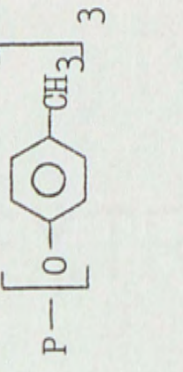
Effect of Ligand in Ni-Lig Catalyst On  
Rate and Yield of Products

Ligand	Rate g C <sub>4</sub> H <sub>6</sub> /g Ni/hr	Products		
		COD	VCH	CDT
1) P(OC <sub>6</sub> H <sub>4</sub> -ortho-C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	780	96	3.1	0.2
2) P(OC <sub>6</sub> H <sub>4</sub> -ortho-CH <sub>3</sub> ) <sub>3</sub>	400	92	3.7	1.4
3) P(OC <sub>6</sub> H <sub>4</sub> -meta-CH <sub>3</sub> ) <sub>3</sub>	110	74	8.1	10.8
4) P(OC <sub>6</sub> H <sub>4</sub> -para-CH <sub>3</sub> ) <sub>3</sub>	70	73	8.8	9.7
5) P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	100	81	7.4	9.2
6) P(C <sub>5</sub> H <sub>6</sub> ) <sub>3</sub>	180	64	21	6
7) P(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	35	41	40	14



TABLE XXI

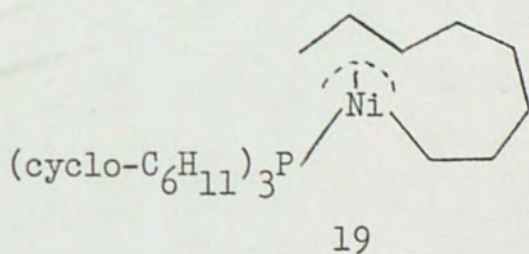
Position of  $\text{CH}_3$ -Group in Phenyl Group of Phosphite and  
Its Relationship With Rate and Conversion

Component	Ortho Position	Meta Position	Para Position
			
Rate - g $\text{C}_4\text{H}_6$ /g Ni/hr	400	110	70
Yield of Cyclo-octadiene	92	74	73

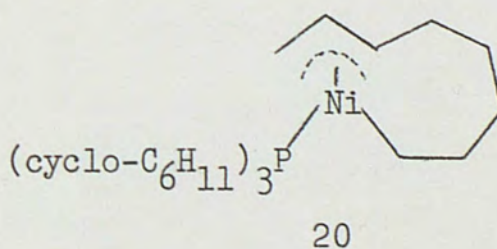


$(\text{C}_6\text{H}_5\text{-ortho-C}_6\text{H}_4\text{O})_3\text{P}$  can account for its greater activity. Methyl and phenyl groups in meta and para positions have only electronic effects in the ligand and their corresponding activity in catalysis is less than for the ortho position.

Both product analysis and the study of model compounds have been used to investigate the mechanism of cyclodimerization of 1,3-pentadiene and isoprene<sup>11</sup>. Valuable information on the detailed course of the reaction has been obtained by determining the stereochemistry of the products<sup>11,16</sup>. Two intermediate complexes have been isolated, derived from isoprene, and cis-piperylene during the cyclodimerization process of related diene by Ni-Lig catalyst (19,20). The structures of these complexes have been confirmed by x-ray studies<sup>34,35</sup>.



Intermediate Derived from Isoprene



Intermediate Derived from  
cis-1,3-Pentadiene

The cyclodimerization of 1,3-pentadiene using a "nickel-ligand" catalyst is believed to occur in a step-wise manner: two pentadiene molecules react at a nickel atom to form a  $\pi$ -allyl- $\text{C}_8$ -nickel-ligand intermediate (eg. 21-23), which reacts further through the corresponding bis- $\sigma$ -allyl form (eg. 24,25) to give the cyclic products.



Dimethyl cyclooctadiene originated from 25, dimethyl vinyl cyclohexene from 26, and divinyl dimethyl cyclobutane from 24. The overall mechanism is shown in Figure 6. The distribution of the products is determined by the concentration and reactivity of these intermediates which, in turn, is influenced by the reaction conditions and the steric effect and electronic properties of the ligand. It has been understood that maximum conversion to dimethyl cyclooctadiene requires the presence of a ligand having low basicity and high steric requirements<sup>11</sup>. However, it has been shown that trans-1,3-pentadiene dimerizes much more readily than its cis isomer<sup>62</sup>.



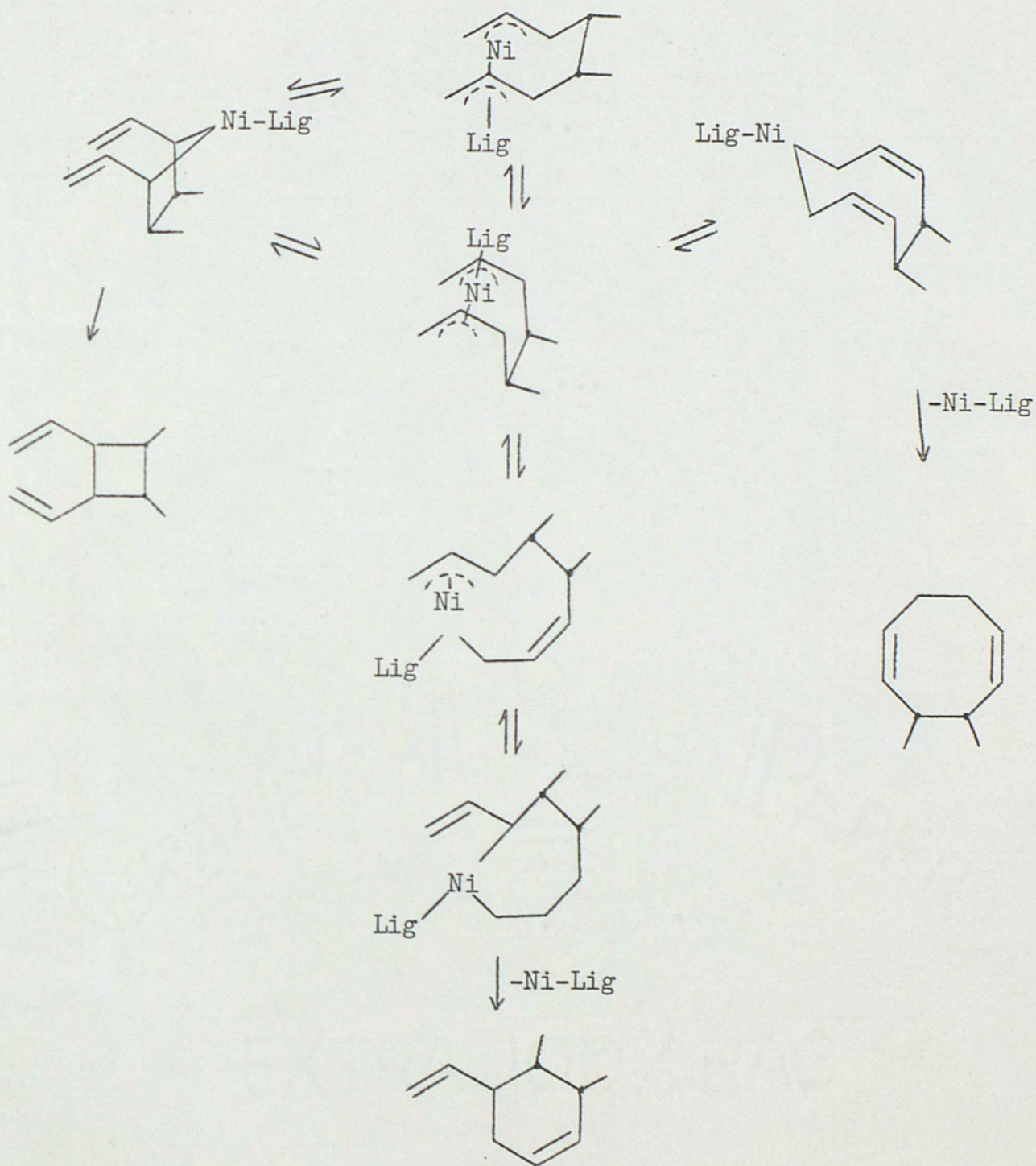


Figure 7. Mechanism of dimer formation.



## CONCLUSIONS

The results obtained in this study lead to the following conclusions:

(1) The isomers of 1,3-pentadiene and isoprene can be separated from the other components in the piperylene concentrate through the conversion of 1,3-pentadiene and isoprene to high boiling point dimers and separation of these dimers by distillation.

(2) In the preparation of catalysts, the order of addition of reagents is very important and reducing agent should be added last.

(3) Since the catalyst is nickel in the zero valent oxidation state, it is oxidized and poisoned readily by oxygen and carbon monoxide in the air. Therefore, the preparation, and the transfer to reactor vessel should be carried out with care.

(4) If this project is continued, it is suggested that the preparation of the catalysts and charging of the reactor be carried out in a dry box to prevent oxidation and poisoning of catalyst.

(5) The optimum amount of catalyst required is found to be 2-2.5 millimole nickel per 100 g diene charged to the reactor.

(6) The ratio of ligand to nickel could be 1:1 to 6:1, but the optimum ratio is 1:1.

(7) Both conversion and yield of reaction are dependent on the time and temperature of reaction. At 80°C the conversion and yield are minimum and increase to maximum at 350°C.



(8) The conversion of trans-1,3-pentadiene is higher than the cis isomer.

(9) The nickel catalyst has no appreciable effect on the components of piperylene concentrate other than 1,3-pentadiene and isoprene when used in pure form and under the same reaction conditions, but in the mixture, they undergo unknown reactions to form a series of by-products. The conversion of these components is dependent on reaction temperature and other reaction conditions.

(10) The conversion of isomers of 1,3-pentadiene and isoprene are in the following order:

isoprene > trans-1,3-pentadiene > cis-1,3-pentadiene

(11) The tris-ortho-biphenyl phosphite ligand has highest selectivity towards dimer formation and increases the rate and yield of reaction under the same reaction conditions.

(12) Mixtures of triphenyl and diphenyl phosphite, when used as a ligand, give better results than pure triphenyl phosphite.

(13) The separation of dimers with various boiling points from 158° to 176°C from the by-products originated from other components of piperylene concentrate requires an efficient fractional distillation system.



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