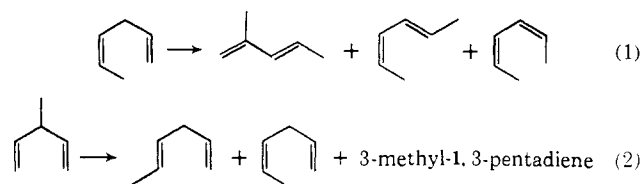


Nickel-Catalyzed Skeletal Rearrangements of 1,4-Dienes<sup>1,2a</sup>Roy G. Miller,\* Paul A. Pinke, Richard D. Stauffer, Harry J. Golden,<sup>2b</sup> and Dennis J. Baker<sup>2c</sup>*Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201. Received October 15, 1973*

**Abstract:** Catalysts derived from dihalobis(trialkylphosphine)nickel(II) complexes and diisobutylaluminum chloride accomplish two types of skeletal isomerization of 1,4-dienes in toluene at 25°. The type I rearrangement generates the isoprenoid carbon skeleton and is exemplified by the conversion of 1,4-pentadiene to 2-methyl-1,3-butadiene. The type II rearrangement is exemplified by the 3-methyl-1,4-pentadiene to 1,4-hexadiene isomerization. A competing reaction, in each case, is the positional isomerization of the terminal double bond in the 1,4-diene reactant to afford conjugated diene products of the same carbon skeleton. Catalysts derived from the reaction of ethylenebis(tri-*o*-tolyl phosphite)nickel(0) and ethylenebis(triphenylphosphine)nickel(0) with hydrogen chloride are also effective in accomplishing the type I rearrangement. A number of methyl-substituted 1,4-dienes have been isomerized by these catalysts and the structures of the rearrangement products have been determined.

Transition metal complexes have been utilized in the homogeneous catalysis of hydrocarbon reactions for 2 decades. The early studies, devoted mainly to catalyst systems capable of affording high molecular weight polymers from alkene precursors, have been extended to include investigations of a wide variety of olefin oligomerization and isomerization reactions.<sup>3</sup> The catalyses of all possible fundamental transformations of chemical bonds in hydrocarbon substrates have now been observed. These include C-H bond formation and cleavage, C-C  $\pi$ - and  $\sigma$ -bond formation, and C-C  $\pi$ - and  $\sigma$ -bond cleavage. The first five of these transformations have been known for years. The sixth phenomenon, metal catalysis of C-C  $\sigma$ -bond fission, is of very recent vintage. The first reports relating to hydrocarbon isomerizations did not appear in the literature until 1967.<sup>4</sup> During a 1-year period, six examples of metal-catalyzed C-C  $\sigma$ -bond cleavage in two types of hydrocarbon substrate—alkenes and strained small ring hydrocarbons—were described.<sup>1a,b,7-11</sup> Other examples of olefin metathesis catalysis<sup>12,13</sup> and of metal-induced isomerizations of

small ring hydrocarbons<sup>14-22</sup> have subsequently appeared in the literature, and a variety of mechanistic interpretations have been presented. This series of papers<sup>23</sup> deals with detailed studies of two metal-



catalyzed transformations<sup>1a</sup> which are described in eq 1 and 2. It will be seen that these diene rearrangements are not only related mechanistically to certain alkene oligomerization reactions, but that they share mechanis-

(1) Some of these results were reported in preliminary communications: (a) R. G. Miller *J. Amer. Chem. Soc.*, **89**, 2785 (1967); (b) R. G. Miller and P. A. Pinke, *ibid.*, **90**, 4500 (1968); (c) R. G. Miller, P. A. Pinke, and D. J. Baker, *ibid.*, **92**, 4490 (1970); (d) R. G. Miller, H. J. Golden, D. J. Baker, and R. D. Stauffer, *ibid.*, **93**, 6308 (1971); (e) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organometal. Chem.*, **29**, C42 (1971).

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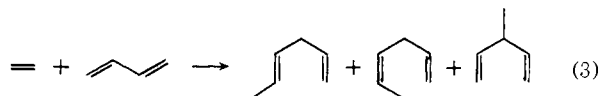
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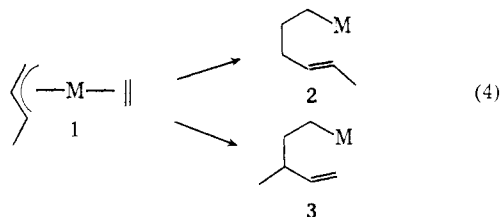
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tic features with some small ring hydrocarbon rearrangements.

The possible close relationship of the diene rearrangements to olefin oligomerization reactions was emphasized by an earlier study. The  $(R_3P)_2NiCl_2/R_2AlCl$  catalyst system was found to add alkenes to 1,3-dienes to afford 1,4-diene products.<sup>24</sup> Thus, ethylene and 1,3-butadiene were readily converted to *trans*- and *cis*-1,4-hexadiene and 3-methyl-1,4-pentadiene in hydrocarbon solvents (eq 3). The products formed in



this transformation and in related reactions of substituted precursors<sup>24</sup> were strikingly similar to those afforded by action of a rhodium catalyst<sup>25</sup> on the same substrates, suggesting mechanistic parallels in the two catalytic processes. The data accumulated in studies of the nickel-catalyzed codimerization<sup>24</sup> along with results from Cramer's excellent mechanistic study of the analogous rhodium-catalyzed reaction<sup>26</sup> suggested that the transformation involved the intervention of at least two types of key organometallic intermediates: (1) a  $\pi$ -allylnickel derivative, **1**, derived from addition of the elements of nickel hydride to the 1,3-diene and coordination of ethylene to the metal, and (2) alkenyl-nickel species, such as **2** and **3**, generated by C-Ni addition to coordinated alkene in **1** (eq 4). The M repre-



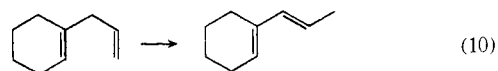
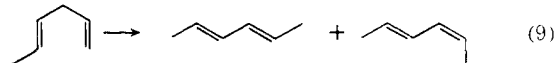
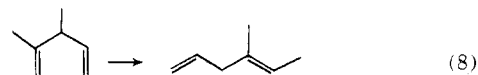
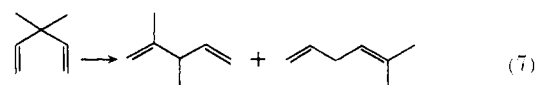
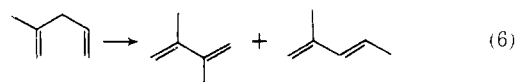
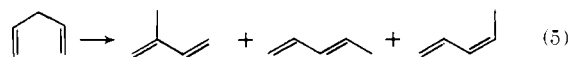
sents the nickel atom with its auxiliary ligands, at least one of which is a trialkylphosphine. Further support for this general scheme was subsequently provided in studies of the same reaction using other nickel catalysts.<sup>27,28</sup>

The experiments which led to the discovery of the 1,4-diene skeletal rearrangements were induced by our interest in the chemistry of the hypothetical alkenyl-nickel species **2** and **3**, complexes characterized by both a localized C-Ni  $\sigma$  bond and side chain unsaturation capable, in principle, of a bonding interaction with the metal. It was anticipated that the synthesis of such compounds in the absence of large amounts of 1,3-dienes or ethylene might allow the observation of new reactions not directly related to the codimerization process. In particular, the absence of large amounts of alkene, capable of competing with the side chain vinyl group for a coordination site on the metal, would be expected to allow intramolecular coordination and the generation of products afforded in intramolecular re-

actions. With this in mind, 1,4-dienes were treated with the catalyst in the expectation that the transfer of nickel hydride to the terminal double bond would generate compounds such as **2** and **3**.

## Results

**Rearrangements Catalyzed by the  $(R_3P)_2NiCl_2/R_2AlCl$  System.** Treatment of a series of 1,4-dienes with *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) (**4**) and diisobutylaluminum chloride in toluene solution at 24–26° led to their catalytic skeletal isomerization and/or double bond migration. The primary isomeric products derived from each diene reactant employed are presented in eq 1, 2, and 5–10. Two types of skeletal



isomerization are evident upon examination of the product structures. Type I is exemplified by the 1,4-pentadiene to isoprene conversion, eq 5, and analogs of this transformation are described in the rearrangements of *cis*-1,4-hexadiene, 2-methyl-1,4-pentadiene, and 3,3-dimethyl-1,4-pentadiene to *trans*-2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and 2,3-dimethyl-1,4-pentadiene, respectively (eq 1, 6, and 7). The simplest example of the type II rearrangement is the 3-methyl-1,4-pentadiene to 1,4-hexadiene conversion (eq 2). Other type II transformations are found in the isomerization of 3,3-dimethyl-1,4-pentadiene and 2,3-dimethyl-1,4-pentadiene to 5-methyl-1,4-hexadiene and 4-methyl-1,4-hexadiene, respectively (eq 7 and 8). 3,3-Dimethyl-1,4-pentadiene was the only diene reactant that was transformed into both type I and type II products. All of the type I products possessed the isoprenoid carbon skeleton and, with the exception of 2,3-dimethyl-1,4-pentadiene, were 1,3-dienes. All of the type II rearrangement products were less branched than the diene reactant, and were 1,4-dienes. In most of the cases, the formation of the skeletal isomerization products was accompanied by the production of conjugated isomers of the 1,4-diene reactant, formally derived from double bond positional isomerization. *trans*-1,4-Hexadiene afforded only *trans,trans*- and *trans,cis*-2,4-hexadiene as isomeric products, eq 9, no skeletal isomerization products being detected. 1-Allylcyclohexene was converted to 1-(1'-*trans*-propenyl)cyclohexene (eq 10) after ethylene was introduced to the reaction mixture in pentane solution.

Both the per cent conversion of 1,4-diene to products

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and the per cent yields of isomeric products based upon the total amount of diene reacted varied with the nature of the 1,4-diene reactant. Yield and conversion data are tabulated in Table I. *cis*-1,4-Hexadiene was consistently transformed into isomeric C-6 products in >60% yields at 75–80% conversions. Relatively high yields were also obtained in experiments employing 2,3-dimethyl-1,4-pentadiene as the reactant. On its treatment with the catalyst precursors in chlorobenzene, 50–60% yields of 4-methyl-1,4-hexadiene could be achieved over a wide conversion range and a yield of 91% at 36% conversion was achieved in one instance. The yields of primary isomeric products afforded by other 1,4-dienes were, in some cases, substantially lower. Some mediocre yields could be attributed to reactions of the primary C-6 products with the catalyst to afford secondary isomerization products. This was found to be a major yield-limiting factor in reactions of 3-methyl-1,4-pentadiene and 3,3-dimethyl-1,4-pentadiene, and an important but less serious consequence in the reaction of 2,3-dimethyl-1,4-pentadiene. In these three cases, the primary hydrocarbon products were 1,4-dienes which were found, in independent experiments, to isomerize in the presence of the catalyst (Table I).

The conjugated primary hydrocarbon products were not isomerized by the  $(n\text{-Bu}_3\text{P})_2\text{NiCl}_2/i\text{-Bu}_2\text{AlCl}$  catalyst system. In a series of experiments, isoprene, *trans*- and *cis*-1,3-pentadiene, *cis*-2-methyl-1,3-pentadiene, and *trans*,*cis*- and *cis*,*cis*-2,4-hexadiene were treated with the catalyst in toluene solution at 24–26°. In each case, no isomeric hydrocarbon products were detected in the product mixtures. It could also be concluded that *trans*,*trans*-2,4-hexadiene was not skeletally isomerized since no rearrangement products were detected in product mixtures derived from treatment of *trans*-1,4-hexadiene with the catalyst (Table I). Evidence that *trans*-2-methyl-1,3-pentadiene was not isomerized by the catalyst to *cis*-1,4-hexadiene or to *trans*,*cis*- or *cis*,*cis*-2,4-hexadiene was provided by the analysis of the product mixtures from the *cis*-1,4-hexadiene rearrangement. It was found that the *trans*-2-methyl-1,3-pentadiene:2,4-hexadiene product ratio did not decrease with time during a given experiment (Table II). Although the conjugated C-6 dienes were not isomerized by the catalyst, their presence appeared to inhibit the catalysis of the 1,4-diene rearrangements. The primary conjugated products seemed to exert a form of "feed-back" inhibition which decreased the catalyst activity with increasing conjugated diene concentrations. It is also noteworthy that the catalyst did not cause geometric isomerization of 1,4-diene substrates. Thus, *cis*-1,4-hexadiene was not converted to *trans*-1,4-hexadiene nor was the latter isomer transformed into the former.

The 2-methyl-1,3-pentadiene:2,4-hexadiene product ratios varied in a series of experiments in which the initial *cis*-1,4-hexadiene concentration was varied but the initial 1,4-diene:Ni molar ratios were the same. The data in Table II indicate that the 2-methyl-1,3-pentadiene:2,4-hexadiene product ratio increased with decreasing initial *cis*-1,4-hexadiene concentration. Evidence that this variation of the product ratio is associated with the initial terminal double bond concentration is also presented in Table II. Two experiments were conducted in which mixtures of 1-hexene and *cis*-1,4-hexadiene were employed. The total initial alkene

concentration was maintained at 0.16 *M*. The 2-methyl-1,3-pentadiene:2,4-hexadiene product ratios obtained in these experiments closely paralleled one another, and were the same, within the experimental error, as those obtained in the experiment with an initial 0.16 *M* concentration of *cis*-1,4-hexadiene. The half-lives for the conversion of *cis*-1,4-hexadiene to products in the experiments employing 1-hexene were *ca.* 1 min whereas the half-life for the conversion of 1-hexene to products (predominantly 2-hexenes) was 60 min for the 1:1 *cis*-1,4-hexadiene–1-hexene mixture. The presence of 1-hexene caused the ultimate conversion of a higher percentage of the *cis*-1,4-hexadiene to products than was experienced in its absence.

The nature of the phosphine ligand was also found to influence the 2-MePD:2,4-HD product ratio. Treatment of toluene solutions of *cis*-1,4-hexadiene and *trans*-dichlorobis(trialkylphosphine)nickel(II) with diisobutylaluminum chloride (1,4-diene:Al:Ni = 12:4:1, [1,4-diene] = 0.12 *M*) afforded 2-MePD:2,4-HD product ratios of 0.8, 1.5, and 2.7 at *ca.* 50% conversions when trimethyl-, triethyl-, and tri-*n*-butylphosphine, respectively, were employed as ligands. The spread in product ratios over a wide range of % conversions was found to be narrow in each case and was comparable to the minor variations reported in Table II. Triallylphosphine and tricyclohexylphosphine could also be employed as ligands in the  $(\text{R}_3\text{P})_2\text{NiCl}_2$  catalyst precursor. However, the catalysts derived from these two compounds showed a relatively low activity for the *cis*-1,4-hexadiene rearrangement. Dichlorobis(triphenylphosphine)nickel(II), on treatment with diisobutylaluminum chloride, afforded a diene isomerization catalyst only after ethylene was introduced to the reaction mixture.

Control experiments demonstrated that the diene rearrangement catalysts were generated *via* the reaction of the alkylaluminum compound with the nickel complex. Treatment of 3-methyl-1,4-pentadiene and *cis*-1,4-hexadiene, in separate experiments, with *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) in toluene solution at 24° afforded no skeletal isomerization or loss of diene substrate. Similar experiments in which the dienes were treated with diisobutylaluminum chloride afforded no rearrangement products. To examine the possible effect on catalyst activity of trace metal impurities in the nickel catalyst component, *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) was prepared from a sample of nickel dichloride which was attributed to have a 99.999% purity. Treatment of a toluene solution of this sample in the presence of *cis*-1,4-hexadiene led to the formation of the usual products (Table II) in product ratios that were comparable to those afforded by a catalyst derived from reagent grade nickel dichloride. The course of this reaction with time was representative of results from experiments in which nickel compounds derived from other sources were employed. The conduct of experiments under a nitrogen atmosphere was shown to have no adverse effect on catalyst activity by comparison with results obtained when an argon atmosphere was employed.

**Rearrangements Catalyzed by the  $(\text{R}_3\text{P})_2\text{NiC}_2\text{H}_4/\text{HX}$  System.** Ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (5) and ethylenebis(triphenylphosphine)nickel(0) (6), on treatment with hydrogen halides, afforded effective

Table I. 1,4-Diene Isomerization Reactions<sup>a</sup>

Diene reactant (mmol)	Solvent <sup>b</sup> (ml)	Ni compd (mmol)	Cocatalyst (mmol)	Time, min	Conversion, %	Isomeric products <sup>c</sup> (% individual yields)		Isomeric products (total % yield)
						2-Me-1,3-BD	1,3-PD	
1,4-PD (44)	(251)	A (3.67)	<i>i</i> -Bu <sub>2</sub> AlCl (13.8)	90	33	63	13	76
1,4-PD (2.1)	(35)	A (0.35)	<i>i</i> -Bu <sub>2</sub> AlCl (1.2)	210	64	30	2	32
				30	29	56	5	61
1,4-PD (2.7)	(14.5)	B (0.22)	HCl (0.16)	180	69	30	6	36
				0.5	25	67	28	95
				1.0	45	64	26	90
						2-Me-1,3-PD	2,4-HD	
<i>cis</i> -1,4-HD (4.25)	(36)	A (0.24)	<i>i</i> -Bu <sub>2</sub> AlCl (0.90)	5	50	62	16	78
<i>cis</i> -1,4-HD (2.31)	(18)	A <sup>d</sup> (0.19)	<i>i</i> -Bu <sub>2</sub> AlCl (0.78)	2	51	51	23	70
				30	74	53	22	75
<i>cis</i> -1,4-HD (1.80)	(15)	A <sup>e</sup> (0.15)	<i>i</i> -Bu <sub>2</sub> AlCl (0.60)	2	35	62	22	84
				30	73	56	19	75
<i>cis</i> -1,4-HD (1.50)	(13)	B (0.13)	HCl (0.09)	3	51	34	46	80
				10	80	34	46	80
<i>cis</i> -1,4-HD (2.26)	(15.5)	B (0.19)	HCl (0.12)	0.5	38	66	28	94
				2.5	80	66	28	94
<i>cis</i> -1,4-HD (2.07) <sup>p</sup>	(15)	B (0.16)	HCl (0.13)	1	21	30	28	58
				6	44	25	40	65
<i>cis</i> -1,4-HD (2.26)	(15.5)	B (0.19)	HBr (0.17)	30	59	9	78	87
				120	81	4	85	89
<i>cis</i> -1,4-HD (3.60)	(20)	C (0.49)	HCl (0.49)	0.5	72	45	50	95
				10	31	64	22	86
				30	35	56	22	78
<i>cis</i> -1,4-HD (2.00)	(15)	A (0.15)	Me <sub>2</sub> AlCl (0.68)	240	49	54	26	80
				2	18	40	37	77
				80	76	33	30	63
						2,3-Me <sub>2</sub> -1,4-PD	5-Me-1,4-HD	
3,3-Me <sub>2</sub> -1,4-PD (18.9)	(105)	A (1.58)	<i>i</i> -Bu <sub>2</sub> AlCl (6.20)	20	51	11	31	42
				40	58	15	47	62
3,3-Me <sub>2</sub> -1,4-PD (3.20)	CH <sub>2</sub> Cl <sub>2</sub> (20)	A (0.27)	<i>i</i> -Bu <sub>2</sub> AlCl (1.10)	60	76	7	22	29
				100	87	6	18	24
3,3-Me <sub>2</sub> -1,4-PD (1.56) <sup>r</sup>		B (0.13)	HCl (0.10)	12	44	17	26	43
						4-Me-1,4-HD		
2,3-Me <sub>2</sub> -1,4-PD (2.26)	(20.5)	A (0.19)	<i>i</i> -Bu <sub>2</sub> AlCl (0.67)	15	21	26	26	26
				30	30	34	34	34
2,3-Me <sub>2</sub> -1,4-PD (4.23)	C <sub>6</sub> H <sub>5</sub> Cl (41)	A (0.35)	<i>i</i> -Bu <sub>2</sub> AlCl (1.24)	60	40	42	42	42
				180	50	56	56	56
2,3-Me <sub>2</sub> -1,4-PD (6.15)	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> (61)	A (0.52)	<i>i</i> -Bu <sub>2</sub> AlCl (1.81)	15	21	60	60	60
				30	36	91	91	91
2,3-Me <sub>2</sub> -1,4-PD (1.78)		B (0.17)	HCl (0.13)	120	56	54	54	54
				5	11	55	55	55
				15	25	57	57	57
				30	37	44	44	44
				60	43	48	48	48
				0.5	8	0	0	0
				3	1	0	0	0
				390	1	0	0	0
						2,3-Me <sub>2</sub> -1,3-BD	2-Me-1,3-PD	
2-Me-1,4-PD (8.52)	(72)	A (0.71)	<i>i</i> -Bu <sub>2</sub> AlCl (2.50)	120	54	26	24	50
2-Me-1,4-PD (4.26)	(36)	A (0.36)	<i>i</i> -Bu <sub>2</sub> AlCl (1.24)	10	15	1.6	1.3	3
				30	19	2.2	2.0	4
2-Me-1,4-PD (5.85)	C <sub>6</sub> H <sub>5</sub> Cl (40)	A (0.40)	<i>i</i> -Bu <sub>2</sub> AlCl <sup>h</sup> (1.61)	120	28	4	4	8
				15	44	3.4	9.5	13
				30	47	4.7	13.9	19
				60	56	6.3	16.9	23
				240	68	10.3	23.1	33
				390	74	10.7	24.2	35
2-Me-1,4-PD (4.26)	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> (40)	A (0.40)	<i>i</i> -Bu <sub>2</sub> AlCl <sup>h</sup> (1.24)	15	32	4.6	53	58
				30	41	4.5	54	59
				60	49	3.8	53	57
				120	62	4.0	49	53

Table I (Continued)

2-Me-1,4-PD (2.53)	(20.5)	B (0.24)	HCl (0.24)	0.5 30 60	6 20 20	45 43 45	55 56 55	100 99 100
<i>trans</i> -1,4-HD (12)	(100)	A (1.00)	<i>i</i> -Bu <sub>2</sub> AlCl (4.00)	120	34	t,t-2,4-HD 64	t,c-2,4-HD 24	88
<i>trans</i> -1,4-HD (2.28)	(14.5)	B (0.23)	HCl (0.12)	0.5 3	32 82	27 27	71 71	98 98
<i>trans</i> -1,4-HD (1.02)	(5.7)	C (0.14)	HCl (0.09)	0.5 60	20 29	47 41	39 44	86 85

<sup>a</sup> All experiments were conducted in the 24–26° range unless noted otherwise. Yield and conversion data for more than one time period are presented for most of the experiments. The abbreviations employed are the following: hexadiene, HD; pentadiene, PD; butadiene, BD; methyl, Me; isobutyl, *i*-Bu; *t*, *trans*; *c*, *cis*. Nickel compounds: transdichlorobis(tri-*n*-butylphosphine)nickel(II), A; ethylenebis(tri-*o*-tolyl phosphite)nickel(0), B; ethylenebis(triphenylphosphine)nickel(0), C. <sup>b</sup> Toluene was employed as solvent unless indicated otherwise. <sup>c</sup> The products listed were the primary hydrocarbon products. Any isomeric products derived from further isomerization of the primary products are not included. <sup>d</sup> The nickel complex, A, was prepared from 99.999% NiCl<sub>2</sub>. <sup>e</sup> Conducted under an argon atmosphere. <sup>f</sup> Conducted at 0°. <sup>g</sup> Conducted at –22°. <sup>h</sup> In 1 ml of toluene.

Table II. Diene Product Ratios from *cis*-1,4-Hexadiene Isomerizations<sup>a</sup>

Initial alkene concn, <i>M</i>	Time, min	Conversion, %	Isomer yield, %	Product ratio <sup>b</sup> : 2-MePD:2,4-HD	t,c-:c,c-2,4-HD <sup>b</sup>
0.04	0.5	10	56	3.4	1.9
0.04	1.0	30	71	3.6	2.9
0.04	30	59	77	3.7	3.3
0.04	240	78	63	3.7	3.4
0.08	0.5	20	46	2.9	2.2
0.08	1.0	32	47	3.3	3.3
0.08	2.0	48	55	3.2	2.7
0.08	30	73	62	3.1	3.2
0.13 <sup>c</sup>	0.5	15	72	2.6	2.8
0.13 <sup>c</sup>	1.0	37	59	2.7	3.2
0.13 <sup>c</sup>	2.0	51	70	2.7	3.0
0.13 <sup>c</sup>	30	74	72	2.7	3.3
0.16	0.5	24	45	2.3	3.3
0.16	1.0	43	49	2.4	3.4
0.16	3.0	64	69	2.4	3.2
0.16	30	77	65	2.3	3.3
0.20	0.5	19	69	2.2	4.4
0.20	1.0	34	76	2.4	3.6
0.20	2.0	53	70	2.2	3.3
0.20	30	81	70	2.2	3.5
0.40	0.5	31	48	1.7	3.4
0.40	2.5	63	74	2.1	3.5
0.40	10	67	75	2.0	3.5
0.40	80	87	71	1.9	3.6
0.16 <sup>d</sup>	0.7	40	78	2.1	3.5
0.16 <sup>d</sup>	1.0	53	84	2.1	3.3
0.16 <sup>d</sup>	2.0	73	79	2.2	3.5
0.16 <sup>d</sup>	10	83	80	2.3	4.0
0.16 <sup>d</sup>	30	92	76	2.5	4.7
0.16 <sup>e</sup>	1.5	56	74	2.1	3.1
0.16 <sup>e</sup>	2.0	66	71	2.2	3.5
0.16 <sup>e</sup>	10	84	73	2.4	3.4
0.16 <sup>e</sup>	30	86	72	2.5	3.9

<sup>a</sup> All reactions were conducted under a nitrogen atmosphere in dry deoxygenated toluene solutions at 25°. In each case, the initial alkene:Al:Ni molar ratio was 12:4.1:1.0. 2-MePD and 2,4-HD refer to *trans*-2-methyl-1,3-pentadiene and 2,4-hexadiene, respectively. t,c- and c,c- refer to *trans,cis*- and *cis,cis*-. <sup>b</sup> The product ratios determined from analyses of aliquots removed after reaction periods of 1 min and longer were estimated to be accurate to ±0.1. The measurements after only 0.5 min in the experiments employing the lower initial alkene concentrations were less accurate due to the smaller amounts of products present. <sup>c</sup> The NiCl<sub>2</sub> employed in the preparation of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) used in this experiment was attributed to have 99.999% purity. <sup>d</sup> The total alkene concentration was 0.16 *M*: 0.08 *M* in *cis*-1,4-hexadiene and 0.08 *M* in 1-hexene. <sup>e</sup> The total alkene concentration was 0.16 *M*: 0.107 *M* in *cis*-1,4-hexadiene and 0.053 *M* in 1-hexene.

catalysts for the accomplishment of the type I rearrangement. In a typical experiment conducted at 25° under argon, addition of hydrogen chloride to a toluene solution of ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (**5**) and *cis*-1,4-hexadiene (diene:nickel:HCl ratio = 12:1.0:0.63) caused a rapid conversion of the 1,4-diene to *trans*-2-methyl-1,3-pentadiene, and *trans,cis*- and *cis,cis*-2,4-hexadiene. When an initial diene concentration of 0.15 *M* was employed, the 2-MePD:2,4-HD product ratio over a wide range of conversion was *ca.* 2.3:1.0. The product ratio of *trans,cis*-: *cis,cis*-2,4-hexadiene was 0.5:1.0. A decrease in both the rate of conversion of 1,4-diene to products and in the 2-MePD:2,4-HD product ratio resulted when the reaction temperature was lowered. Table I presents data from these experiments. Addition of a moderate excess of hydrogen chloride did not substantially alter the catalyst activity. When a diene:nickel:HCl ratio of 11:1:3 was employed at 25°, the same isomeric C-6 products were formed (2-MePD:2,4-HD ratio = 2.4, *trans,cis*-: *cis,cis*-2,4-HD ratio = 0.61). During 30 sec, 38% of the *cis*-1,4-hexadiene was converted to the C-6 isomers in 98% yield. After 3 min (79% conversion), the C-6 isomer yield was 88%. The catalyst derived from HBr and **5** was particularly effective, 72% of the *cis*-1,4-hexadiene being converted to C-6 isomers in high yield during 30 sec, Table I. Trifluoroacetic acid was much less effective as a cocatalyst. During 1 min at 25° only 15% of *cis*-1,4-hexadiene was converted to the C-6 isomers in 60% yield (diene:Ni:CF<sub>3</sub>CO<sub>2</sub>H = 12:1:0.6, [diene] = 0.13 *M*). The reaction ceased at this point. The 2-MePD:2,4-HD product ratio was 3.0:1.0.

Treatment of **6** with less than 1 equiv of HCl afforded a very active but short-lived catalyst for the *cis*-1,4-hexadiene isomerization (Table I). Addition of an excess of HCl to this nickel(0) complex in the presence of *cis*-1,4-hexadiene led to the rapid decomposition of the catalyst. Acetic acid was not effective in forming a diene rearrangement catalyst when mixed with **6** in the presence of *cis*-1,4-hexadiene.

A number of other 1,4-dienes were treated with the catalyst derived from HCl and ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (Table I). In each case, the same type I rearrangement product as that afforded by the (*n*-Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>/*i*-Bu<sub>2</sub>AlCl system was formed. No type II rearrangement products were detected in the product mixtures. In most cases, the catalyst was short lived,

giving low conversions to isomeric products, although some of the yields were quite high. In particular, 1,4-pentadiene was converted to isoprene and 1,3-pentadiene in >90% yield.

*trans*-1,4-Hexadiene was converted to *trans,trans*- and *trans,cis*-2,4-hexadienes in high yields at relatively high conversions (Table I). As was observed when the  $(n\text{-Bu}_3\text{P})_2\text{NiCl}_2/i\text{-Bu}_2\text{AlCl}$  catalyst was employed, no skeletal rearrangement products were detected in the product mixture. The *trans,cis* : *trans,trans*-2,4-hexadiene product ratio was 2.6:1.0. The catalyst derived from **5** and HCl consistently afforded diene double bond migration product mixtures in which isomers with the *cisoid* configuration predominated.

Type II rearrangement products could be generated on addition of isobutylaluminum dichloride to reaction mixtures derived from treatment of **5** with HCl in the presence of a 1,4-diene. The alkylaluminum compound was added to a reaction mixture in toluene derived from 3,3-dimethyl-1,4-pentadiene, **5**, and HCl (diene:Ni:HCl:Al ratio = 12:1.0:0.8:3.0) 15 min after activating the nickel with HCl. Five minutes after the addition of the isobutylaluminum dichloride, 22% of the diene reactant had been converted in 36% yield to 2,3-dimethyl-1,4-pentadiene and 5-methyl-1,4-hexadiene (43:57 ratio). As the reaction proceeded, the amount of 5-methyl-1,4-hexadiene increased to 63% of the isomeric product mixture. During 30 min, 36% of the 3,3-dimethyl-1,4-pentadiene was converted to these two products.

More than 30 control experiments were conducted in order to demonstrate that the diene rearrangement catalyst was derived from the nickel(0) compounds and HCl and that these compounds did not, independently, cause the isomerization of the 1,4-diene reactant or of the isomeric diene products. Neither **5** nor **6** caused the isomerization of *cis*- or *trans*-1,4-hexadiene under conditions which, in the presence of HCl or HBr, afforded an active catalyst. During 4 hr at 25°, neither saturated solutions of HCl in toluene nor solutions with HCl concentrations comparable to those used in the catalysis caused the detectable isomerization of *cis*- and *trans*-1,4-hexadiene, of *trans,cis*- or *cis,cis*-2,4-hexadienes, or of *trans*-2-methyl-1,3-pentadiene. In each case, <2% loss of diene starting material was experienced and no isomeric products could be detected. Experiments in which each 2,4-hexadiene geometric isomer was treated with **6** and HCl (*ca.* 1:1) demonstrated that the skeletal rearrangement product, *trans*-2-methyl-1,3-pentadiene, afforded by the nickel(0)/HCl system was not derived from the 2,4-hexadienes. In each of these experiments, less than 2% loss of starting material was experienced and no rearrangement products were detected during a 4-hr period at 25°.

A number of attempts were made to detect, spectroscopically, the species formed when hydrogen chloride reacted with **5**. The visible spectrum of **5** in benzene solution shows an absorption band at 350 nm and a shoulder with an inflection at 382 nm.<sup>29</sup> A new transient absorption band could be observed when a  $2.5 \times 10^{-3}$  M solution of **5** was treated with an equal molar quantity of hydrogen chloride. This new band appeared as a shoulder on the more intense bands of **5**

(29) W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970).

with an inflection at 427 nm ( $\epsilon$  *ca.* 300). As repetitive scans of this region were made, the new band slowly disappeared. Addition of more than an equal molar amount of hydrogen chloride produced rapid decomposition of the compound, accompanied by the deposition of solid material and loss of the orange color of the solution. Addition of an equal molar amount of hydrogen chloride to a solution of **5** containing an excess of *cis*-1,4-hexadiene resulted in the generation of the 427-nm band, but the band did not disappear as rapidly as when the diene was absent. An excessive amount of hydrogen chloride, as before, resulted in the rapid decomposition of the species responsible for the colored solution. The 427-nm band was *not* observed when only **5** and *cis*-1,4-hexadiene were mixed in benzene.

Infrared spectra of equal molar amounts of **5** and hydrogen chloride in toluene or benzene failed to exhibit a band in the 1800–1900-cm<sup>-1</sup> region attributable to a Ni–H stretching frequency,<sup>30</sup> immediately after the compounds were mixed. As was the case with other relatively concentrated solutions, extensive precipitation of solid material occurred as the toluene or benzene solutions of hydrogen chloride were being added to well-stirred solutions of **5**. Solutions of **6** and hydrogen chloride behaved similarly and no 1900-cm<sup>-1</sup> band was observed.

Elemental analysis of **6**, prepared by the general procedure of Maitlis,<sup>31</sup> indicated the presence of *ca.* 1 mol % of an aluminum impurity in the sample. Since it was desirable to prepare compounds of this class in the absence of aluminum, an alternate route was developed. The properties of **5** and **6** were first reported by Wilke<sup>32</sup> but the detailed experimental conditions for their syntheses were not described. Gosser and Tolman<sup>33</sup> had subsequently observed, spectroscopically, that one of the phosphite ligands of tris(*tri-o*-tolyl phosphite)nickel(0) could be replaced by ethylene. However, the experimental details for isolating **5** by this route were not reported. We succeeded in preparing **5** free of aluminum impurities *via* this method. The more convenient method for preparation of **5** in higher yields using the triethylaluminum reduction procedure<sup>29</sup> was employed after it was demonstrated that the trace aluminum impurities did not influence the course of the diene isomerizations.

## Discussion

Our remarks will be restricted to a discussion regarding the identification of the diene transformations and of the catalyst species responsible for their accomplishment. Interpretation of results in terms of detailed mechanisms for the diene rearrangements will be deferred to the accompanying papers<sup>2,3</sup> where other more mechanistically pertinent results are presented.

The results demonstrate that the observed rearrangements are due to reactions of 1,4-dienes and that the conjugated by-products do not undergo skeletal transformations at 24–26°. They indicate that the forma-

(30) (a) K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **8**, 519 (1969); (b) K. Jonas and G. Wilke, *ibid.*, **9**, 312 (1970); (c) M. L. H. Green, T. Saito, and P. J. Tanfield, *J. Chem. Soc. A*, 152 (1971); (d) *ibid.*, 469 (1971); (e) R. A. Schunn, *Inorg. Chem.*, **9**, 394 (1970).

(31) P. M. Maitlis, D. Pollock, M. L. Games, and J. W. Pryde, *Can. J. Chem.*, **43**, 470 (1965).

(32) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **3**, 105 (1963).

(33) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

tion of the 1,3-diene products in the type I rearrangement is an irreversible process. The results from one experiment conducted at  $-22^\circ$  in which *cis*-1,4-hexadiene was treated with ethylenebis(tri-*o*-tolyl phosphite)-nickel(0) and hydrogen chloride (Table I) may indicate that conjugated dienes were interconverted in this instance since the 2-methyl-1,3-pentadiene:2,4-hexadiene product ratio changed with time. However, this was not a generally observed phenomenon and the interconversion was not demonstrated to occur in this case. Prior work has demonstrated that the catalyst derived from **4** and diisobutylaluminum chloride causes the oligomerization of 1,3-dienes and accomplishes the addition of 1,3-dienes to alkenes.<sup>24</sup> The intervention of  $\pi$ -allylnickel derivatives in these transformations has been proposed<sup>24,27,28</sup> and  $\pi$ -allylnickel formation may be the cause of the conjugated diene inhibition of the 1,4-diene rearrangements.

It is particularly interesting that the Ni(0)-HCl system catalyzes the type I rearrangement but is incapable of affording the type II change. The significance of this finding is emphasized by the observation that a nickel species derived from **4** and diisobutylaluminum chloride exhibits catalytic properties identical with those of the  $(R_3P)_2NiC_2H_4-HCl$  system. The similarities in behavior included the conversions of every 1,4-diene reactant in eq 1, 2, and 10-14 to the same type I rearrangement product and/or double bond migration isomers. These isomeric hydrocarbon products were the same in every respect in terms of carbon skeleton and double bond geometry irregardless of the catalyst precursors employed. This similarity of action extended to the rearrangements of vinylcyclopropane derivatives.<sup>1b,23b</sup>

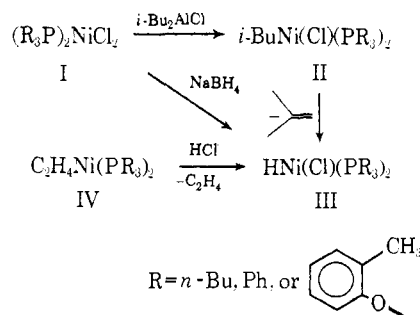
The fact that **4** and diisobutylaluminum chloride also generate a catalyst for the type II skeletal rearrangement indicates that the latter combination affords two distinct catalyst species and that the roles of the Lewis acid component in catalyst generation are not identical. The nature of the type II catalyst and the more extensive role of the aluminum component in its generation become apparent when the mechanistic differences in the type I and type II rearrangements are examined.<sup>23c</sup> The rates of conversion of 1,4-dienes to isomeric products were generally quite different in the type I and type II transformations. Whereas high conversions of diene reactants to products could be accomplished in minutes in many of the type I rearrangements, comparable conversions of some 1,4-dienes to type II products required hours (Table I).

The probable role of the alkylaluminum compound in the generation of the type I catalyst is described in Scheme I. Catalysts for the type I rearrangement have now been prepared by three distinct routes and, in each case, precedent exists in group VIII chemistry for the generation of a metal hydride complex from the catalyst precursors. The pertinent chemistry<sup>34</sup> is described in Scheme I. Treatment of I with diisobutylaluminum chloride should give II and isobutylaluminum dichloride. This type of reaction has been documented and alkylnickel compounds derived from reactions of organoaluminum compounds with nickel(II) complexes have been synthesized.<sup>35</sup> The reaction involving II

(34) For a recent review of the chemistry of  $\sigma$ -bonded hydride and carbon derivatives of nickel, see D. R. Fahey, *Organometal. Chem. Rev.*, **7**, 245 (1972).

(35) (a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida,

Scheme I



and III has been demonstrated to occur in analogous platinum complexes<sup>36</sup> and has been considered as a possible step in a variety of nickel-catalyzed alkene and alkyne reactions,<sup>16,19,37</sup> the first instance being the suggestion that steps such as this were involved in the nickel-catalyzed hydrogenation of alkenes.<sup>38</sup> The oxidation of IV by HCl to form III finds precedent in a number of recent syntheses of hydridonickel complexes based upon this general reaction.<sup>29a,39</sup> This Ni(0)-Ni(II) interconversion is reminiscent of the analogous Rh(I)-Rh(III) interconversion involving the addition of HCl to  $C_2H_4Rh(I)$  complexes.<sup>3b</sup> The importance of this process in rhodium-catalyzed ethylene dimerization<sup>40</sup> and butene isomerization<sup>41</sup> has been demonstrated by Cramer. The combination of **4** with sodium borohydride has recently been shown to generate a catalyst for the rearrangement of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene and *trans,cis*- and *cis,cis*-2,4-hexadienes.<sup>42</sup> The sodium borohydride reaction has also been used to synthesize hydridonickel complexes<sup>30a,34,43</sup> providing precedent for the formation of III by this route in Scheme I.

## Experimental Section

All experiments involving organometallic compounds were conducted in a nitrogen or argon atmosphere in deoxygenated solvents. Transfers of air-sensitive solids were carried out in a dry-box or glove bag, and liquids were transferred with hypodermic syringes through three-way stopcocks or rubber serum caps. Filtrations were carried out through Schlenk-type sintered glass filters of medium porosity.

Boiling points and melting points were uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Swartzkopf Microanalytical Laboratory, Woodside, N. Y.

Proton magnetic resonance (pmr) spectra were recorded on a Varian Associates Model A-60 spectrometer using tetramethyl-

and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965); (b) G. Wilke and G. Herrmann, *Angew. Chem., Int. Ed., Engl.*, **5**, 581 (1966); (c) P. W. Jolly, K. Jonas, C. Kruger, and Y. H. Tsay, *J. Organometal. Chem.*, **33**, 109 (1971); (d) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3350 (1971).

(36) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962); (b) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968).

(37) For examples, see (a) R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966); (b) M. Uchino, Y. Chauvin, and G. Lefebvre, *C. R. Acad. Sci., Ser. C*, **2**, 103 (1967); (c) J. J. Eisch and M. W. Foxton, *J. Organometal. Chem.*, **12**, 33 (1968); (d) L. Faraday, L. Bencze, and L. Markó, *ibid.*, **17**, 107 (1969); (e) C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 2994 (1972); (f) K. Tamayo Y. Kiso, K. Sumitani, and M. Kumada, *ibid.*, **94**, 9268 (1972).

(38) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963).

(39) W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *Inorg. Chem.*, **9**, 392 (1970).

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

(41) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966).

(42) L. W. Gosser and G. W. Parshall, *Tetrahedron Lett.*, 2555 (1971).

(43) M. L. H. Green and T. Saito, *Chem. Commun.*, 208 (1969).



silane as an internal standard. Infrared spectra were recorded on a Beckman IR-12 or a Perkin-Elmer Model 137 spectrometer. Ultraviolet and visible spectra were obtained on a Cary 14 instrument. Gas chromatographic separations of dienes were accomplished by using Varian Aerograph 90-P3 instruments and the following columns: (1) 20 ft  $\times$   $\frac{3}{8}$  in. and (2) 15 ft  $\times$   $\frac{3}{8}$  in. 20%  $\beta,\beta'$ -oxydipropionitrile on Firebrick 60-80 columns, (3) a 20 ft  $\times$   $\frac{3}{8}$  in. 20% 1,2,3-tris(2-cyanoethoxy)propane on 60-80 Chromosorb P column.

**Materials.** Hydrocarbon solvents were freshly distilled and were stored over type 4A molecular sieves (Linde Air Products) or silica gel. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride and was stored over molecular sieves. Anhydrous diethyl ether was obtained from freshly opened 1-lb containers and used directly or was distilled from phosphorus pentoxide. Acetonitrile was distilled from calcium hydride and methanol was distilled from magnesium methoxide before use.

Triethylaluminum (TEA), diisobutylaluminum chloride (DIBAC), diisobutylaluminum hydride (DIBAH), isobutylaluminum dichloride (MONOBAC), and dimethylaluminum chloride, neat or 25% wt/wt solutions in toluene, were purchased from Texas Alkyls Inc. Ethylene, hydrogen chloride and 1,3-butadiene (C. P. Grade) were purchased from Matheson Gas Products. Hydrogen bromide and *o*-cresol were purchased from J. T. Baker Co., and 3,3-dimethylglutaric acid was purchased from Aldrich Chemical Co. The tricyclohexyl-, triethyl-, tri-*n*-butyl-, and triallylphosphines were purchased from Orgmet, Inc. Bis(1,2-diphenylphosphino)ethane and nickel dichloride (99.999%) were obtained from Research Organic/Inorganic Chemical Corp. Trimethylphosphine was obtained from the thermolysis of its silver iodide complex<sup>44</sup> according to the procedure of Thomas and Eriks.<sup>45</sup> 1,4-Pentadiene and 2-methyl-1,4-pentadiene were purchased from Columbia Organic Chemicals Co., Inc., and Aldrich Chemical Co., respectively.

*trans*-1,4-Hexadiene and 3-methyl-1,4-pentadiene were prepared by the method of Alderson, Jenner, and Lindsey.<sup>26</sup> *cis*-1,4-Hexadiene was prepared by the procedure of Hata.<sup>46</sup> Samples of *trans*-2-methyl-1,3-pentadiene and *trans,trans*-, *trans,cis*-, and *cis*-, *cis*-2,4-hexadienes were purchased from Chemical Samples Co., Columbus, Ohio. The dichlorobis(trialkylphosphine)nickel(II) complexes, where alkyl = ethyl, *n*-butyl, methyl, allyl, and cyclohexyl, were prepared by the general procedure of Jensen and Nygaard.<sup>47</sup> Dichlorobis(triphenylphosphine)nickel(II) was prepared by the method of Venanzi.<sup>48</sup>

**Determination of Product Yields in Diene Rearrangement Reactions.** The percentage conversions of dienes to products were based upon the amount of starting material lost as determined from the decrease in the glpc peak areas relative to their magnitudes before addition of the DIBAC or HX cocatalyst. Dilution accompanying the addition of cocatalysts solutions was accounted for in the yield calculations. All isomer yields were based upon the percentage of *reacted* starting material converted to isomeric products. Glpc peak areas were measured with a Lasico planimeter. Samples from reaction aliquots were injected into the gas chromatograph after quenching with 2-propanol. The 20 ft  $\times$   $\frac{3}{8}$  in.  $\beta,\beta'$ -oxydipropionitrile column at 60° with a helium flow rate of 170 ml/min effectively separated most isomeric diene products.

The relationships between recorder signal areas and sample quantities were determined by analysis of standard mixtures and these relationships were used to calculate the yields. For example, the retention times and the ratios of recorded peak areas for a standard mixture containing equimolar amounts of dienes were: *trans*-1,4-hexadiene, 8.8 min, 0.96; *cis*-1,4-hexadiene, 9.4 min, 1.00; *cis*-2-methyl-1,3-pentadiene, 12.0 min, 0.99; *trans*-2-methyl-1,3-pentadiene, 13.2 min, 1.01; *trans,trans*-2,4-hexadiene, 15.6 min, 0.94; *trans,cis*-2,4-hexadiene, 17.9 min, 1.00; *cis,cis*-2,4-hexadiene, 19.5 min, 1.03. This essentially 1:1 correspondence of peak areas of equimolar mixtures was found to be true for other diene product mixtures described in this paper.

**Reactions of Dienes with the (R<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>/R'<sub>2</sub>AlCl Catalyst System. General Procedure.** A dry, deoxygenated toluene solution of the dichlorobis(trialkylphosphine)nickel(II) compound and the 1,4-diene reactant was treated with a toluene solution of DIBAC (Al:Ni molar ratio = 3.5-4.0:1.0) at 24-26°. The resulting amber

solution was stirred under nitrogen and the progress of the reaction was followed by the periodic removal of aliquots which were quenched with 2-propanol or 1-butanol and then analyzed by glpc. The reaction was terminated at the desired conversion of 1,4-diene to products by addition of the alcohol quencher and the resulting red toluene solution was washed with water and then dried over calcium chloride. The product mixture was then fractionally distilled to afford diene-rich toluene solutions. The diene products were then separated and collected by preparative glpc and were identified by their pmr and infrared spectra. Glpc analyses of quenched product mixtures showed the presence of two peaks immediately following the air peak with retention times identical with those of isobutane and isobutene. The compounds were isolated and identified by mass spectrometry in an experiment employing 2-methyl-1,4-pentadiene as the reactant. The isobutene was also isolated from a product mixture derived from *trans*-1,4-hexadiene and was identified by its gas phase infrared spectrum.

The applications of this general procedure to some specific reactions are exemplified by the following experiments.

**Isomerization of *cis*-1,4-Hexadiene.** A solution of *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) (**4**), 0.127 g (0.24 mmol), and *cis*-1,4-hexadiene, 0.35 g (4.25 mmol), in 35 ml of toluene was treated with diisobutylaluminum chloride (0.75 ml of a 25% wt/wt solution, 0.90 mmol). The resulting solution was stirred for 2 hr at 25° after which the reaction was terminated by the addition of 2-propanol. Glpc analysis of the product mixture indicated that the conversion of *cis*-1,4-hexadiene to products during 2 hr was 78% with a C-6 isomer yield of 78%. The isomeric product mixture consisted of *trans*-2-methyl-1,3-pentadiene, 79%, *trans,cis*-2,4-hexadiene, 16%, and *cis,cis*-2,4-hexadiene, 5%. The half-life for the conversion of *cis*-1,4-hexadiene to products under the above conditions was *ca.* 5 min.

**Isomerization of 3-Methyl-1,4-pentadiene.** A sample of 3-methyl-1,4-pentadiene, 98.2% pure and containing 1.8% *trans*-1,4-hexadiene by glpc analysis, 1.0 g (12 mmol), and **4**, 0.534 g (1.0 mmol), were dissolved in 100 ml of toluene. A 1.0-ml aliquot was then removed for glpc analysis. Diisobutylaluminum chloride, 0.80 ml (4.0 mmol), was then added and the resulting solution was stirred at 24° for 3 hr and 1.0-ml aliquots were removed periodically, treated with 0.04 ml of methanol, and analyzed by glpc. After 3 hr, the whole reaction mixture was treated with methanol to terminate the reaction.

Glpc analysis of the 90-min aliquot indicated that 53% of the 3-methyl-1,4-pentadiene had been converted to products. The C-6 product mixture consisted of components with retention times identical with those of the 1,4-hexadienes (*trans*:*cis* = 11), 35% yield, *trans*-2-methyl-1,3-pentadiene, 4%, *cis*-3-methyl-1,3-pentadiene, 8%, *trans,trans*-2,4-hexadiene and *trans*-3-methyl-1,3-pentadiene, 15%, *trans,cis*-2,4-hexadiene, 3%, and two unidentified components present in *ca.* 7 and 9% yields.

**Treatment of Conjugated Dienes with the Catalyst.** In a typical experiment, a toluene solution of **4** and the diene (0.12 M) was treated with a 25% wt/wt solution of DIBAC in toluene (diene Al: Ni ratio = 12:4:1). The resulting amber solution was stirred under nitrogen at 24-26° for 12 hr. Small aliquots were removed periodically, were quenched with 2-propanol, and then analyzed by glpc.

When *trans,cis*-2,4-hexadiene was employed as the reactant, 9% was consumed during a 10-hr period and 1% of a product with a retention time identical with that of *trans,trans*-2,4-hexadiene was detected as the only C-6 isomeric product. During 12 hr, 20% of *cis,cis*-2,4-hexadiene was converted to products with only a small amount (2% yield) of a C-6 isomer, *trans,trans*-2,4-hexadiene, being formed. *trans*-2-Methyl-1,3-pentadiene was not detected in either of the above product mixtures.

When a mixture of *trans*- and *cis*-1,3-pentadiene was treated with the catalyst in the above manner, no skeletally isomeric products were detected in the reaction mixture during a 19-hr period. During the first hr, *ca.* one-half of the *trans*-1,3-pentadiene had reacted while the *cis*-1,3-pentadiene remained. After 19 hr, all of the *trans* isomer had disappeared and most of the *cis* isomer had reacted. No change in the isoprene concentration was noted during a 7-hr period after this diene was treated with the catalyst in the manner described above.

In a similar experiment, **4**, 0.130 g (0.24 mmol), and *cis*-2-methyl-1,3-pentadiene, 0.23 g (2.82 mmol), in 35 ml of toluene were treated with 0.77 ml of a 25% wt/wt solution of DIBAC in toluene (0.93 mmol) and the resulting solution was stirred for 2 hr at 25°. Glpc analysis of the quenched 2-hr aliquot indicated that no detectable

(44) Supplied to us by Dr. Francis Randall.

(45) R. Thomas and K. Eriks, *Inorg. Syn.*, **9**, 60 (1967).

(46) G. Hata, *J. Amer. Chem. Soc.*, **86**, 3903 (1964).

(47) K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

(48) L. M. Venanzi, *J. Chem. Soc.*, 722 (1958).



amounts of C-6 isomers were present. Ten per cent of the reactant diene was consumed during the 2-hr period.

**Isomerization of *cis*-1,4-Hexadiene using a Catalyst Prepared from 99,999% NiCl<sub>2</sub>.** In the usual manner, **4**, 0.103 g (0.19 mmol), prepared from 99,999% NiCl<sub>2</sub>, and *cis*-1,4-hexadiene, 0.193 g (2.3 mmol), in 17.4 ml of toluene were treated with DIBAC (0.78 mmol). The resulting solution was stirred at 25° under nitrogen. The half-life for the conversion of diene reactant to products was *ca.* 2 min with a *trans*-2-methyl-1,3-pentadiene:2,4-hexadiene product ratio of 2.7:1.0 in the 2-min aliquot. The per cent conversions to products during 30 sec and 30 min were found to be 16 and 73%, respectively.

**Isomerization of *cis*-1,4-Hexadiene using (*n*-Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> (**4**) and DIBAC under an Argon Atmosphere.** A solution of **4**, 0.080 g (0.15 mmol), prepared from reagent grade NiCl<sub>2</sub>·6H<sub>2</sub>O, and *cis*-1,4-hexadiene, 0.15 g (1.8 mmol), in 14.5 ml of argon-purged toluene was treated with DIBAC (0.6 mmol, 0.5 ml of a 25% solution in toluene). The resulting solution was stirred under argon at 25° for 60 min. The half-life for the conversion of *cis*-1,4-hexadiene to products was *ca.* 2 min. The per cent conversions during 30 sec and 30 min were 15 and 74%, respectively. The *trans*-2-methyl-1,3-pentadiene:2,4-hexadiene ratio was 2.8:1.0 at 50% conversion.

**Variation of the Trialkylphosphine Ligands on Nickel.** Toluene solutions (14.5 ml) of the (R<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> (R = methyl, ethyl, *n*-butyl, or cyclohexyl), 0.15 mmol, and *cis*-1,4-hexadiene, 0.15 g (1.8 mmol), were treated with DIBAC solutions in toluene (0.50 ml, 0.60 mmol) and the mixtures were stirred at 25° under nitrogen for 60 min. The half-lives for the conversion of *cis*-1,4-hexadiene to products using catalysts employing the linear trialkylphosphine ligands were all *ca.* 2 min, whereas the tricyclohexylphosphine system gave a *t*<sub>1/2</sub> of *ca.* 60 min.

An analogous experiment employing *trans*-dichlorobis(triethylphosphine)nickel(II) provided a *trans*-2-methyl-1,3-pentadiene:2,4-hexadiene product ratio of 1.5:1.0 at low conversions, the ratio slowly decreasing as the reaction proceeded. The *t*<sub>1/2</sub> for this reaction was *ca.* 1.5 hr.

Less than 2% of the *cis*-1,4-hexadiene was converted to products during 5 hr at 26° in an analogous experiment employing dichlorobis(triphenylphosphine)nickel(II) as the nickel component. Ethylene was then rapidly passed through the reaction mixture and 90% of the diene reactant was converted to products during 17 min. The yield of the usual C-6 products, *trans*-2-methyl-1,3-pentadiene and the *trans,cis*- and *cis,cis*-2,4-hexadienes, was *ca.* 20%. Higher molecular weight products with glpc retention times corresponding to C-8 dienes were detected in the product mixture.

**Reactions of Dienes with the (R<sub>3</sub>P)<sub>2</sub>NiC<sub>2</sub>H<sub>4</sub>/HX Catalyst Systems. Isomerization of *cis*-1,4-Hexadiene by Ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (**5**) and HCl.** Ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (**5**), 0.150 g (0.19 mmol), and *cis*-1,4-hexadiene, 0.19 g (2.26 mmol), were dissolved in 15 ml of argon-purged toluene. The resulting yellow solution was stirred at 26° for 48 min and small aliquots were removed for glpc analysis. During this period of time <1.5% of the diene was lost and no isomeric diene products were detected. Addition of HCl, 0.16 mmol (0.5 ml of a *ca.* 0.33 M solution in toluene), to the above mixture produced an amber solution which was stirred for 20 min after which the mixture was treated with a small portion of 2-propanol that had not been deoxygenated. Alternatively, the reactions could be terminated by shaking the product mixture in air. Reaction aliquots were quenched in the same manner. The diene products (Table I) and unreacted starting material were collected by preparative glpc and were identified by their pmr spectra.

Analogous experiments were conducted at 0 and -22°. The results are tabulated in Table I.

**Treatment of *cis*-1,4-Hexadiene with Ethylenebis(triphenylphosphine)nickel(0) (**6**).** A yellow solution of **6**, 0.167 g (0.272 mmol), and *cis*-1,4-hexadiene, 0.30 g (3.6 mmol), in 10 ml of toluene was stirred at 25° under nitrogen for 40 hr. Small aliquots were removed periodically and were quenched by shaking in air. Less than 5% of the diene reactant had been converted to products during the 40-hr period and no isomeric C-6 dienes were detected.

**Isomerization of *cis*-1,4-Hexadiene by **6** and HCl.** A toluene solution of **6**, 0.296 g (0.485 mmol), and *cis*-1,4-hexadiene, 0.30 g (3.6 mmol), was treated with 1.2 ml of a 0.33 M solution of HCl in toluene (0.40 mmol). The solution was then stirred for 4 hr after which the reaction was terminated by shaking the mixture in air. Aliquots which were removed for analysis were quenched in the same manner. The volatile products were removed from the product mixture by flash distillation at 40° (1 mm) and then distilled

on an efficient column. The C-6 isomers were then collected *via* preparative glpc and were identified by their pmr spectra. The addition of ethylene to a solution which contained the diene:Ni:HCl ratio used above did not noticeably alter the rate of conversion of *cis*-1,4-hexadiene to products.

**Treatment of the 2,4-Hexadiene Geometric Isomers with **6** and HCl.** In a manner analogous to that in the above experiment, toluene solutions of **6** and each 2,4-hexadiene isomer were treated with HCl and were stirred at 25° under nitrogen. Glpc analyses of the solutions after 5 hr showed that only 2-3% of the 2,4-hexadiene had been lost and no detectable amounts of C-6 isomeric products had been formed.

**Treatment of 1,4- and 2,4-Hexadienes with HCl.** In separate experiments, toluene solutions of *cis*-1,4-hexadiene, *trans*-1,4-hexadiene, and *trans,trans*-, *trans,cis*-, and *cis,cis*-2,4-hexadienes were treated with HCl for 4 hr at 25° under conditions of concentration (*ca.* 0.12 M in diene) and diene:HCl ratio (12:1) comparable to those employed in the diene rearrangement reactions described above. Glpc analyses of the product mixtures showed that <2% of each diene was lost during this period of time and, in each case, no detectable amounts of isomeric products were formed.

**Treatment of 1,4-Dienes with Other Potential Catalysts. Isomerization of 3,3-Dimethyl-1,4-pentadiene by **5**, HCl, and *i*-BuAlCl<sub>2</sub>.** A toluene solution of **5**, 0.12 g (0.16 mmol), and 3,3-dimethyl-1,4-pentadiene, 0.18 g (1.86 mmol), was treated with a toluene solution of HCl (0.12 mmol) and then, after 15 sec, with isobutylaluminum dichloride, 0.72 g (0.47 mmol). The resulting amber-colored solution was stirred at 25°. An orange solid slowly precipitated during the course of the reaction. During 15 min, 22% of the reactant diene was converted in 36% yield to 5-methyl-1,4-hexadiene and 2,3-dimethyl-1,4-pentadiene, present as 57 and 43% of the isomeric product mixture, respectively.

**Treatment of *cis*-1,4-Hexadiene with Chloro(hydrido)bis(tricyclohexylphosphine)nickel(II).** Chloro(hydrido)bis(tricyclohexylphosphine)nickel(II) was prepared according to the procedure of Green and Saito.<sup>30</sup> The yellow crystalline product displayed a peak at 1920 cm<sup>-1</sup> (KBr) in its infrared spectrum attributed to the Ni-H stretching frequency.<sup>30</sup>

*cis*-1,4-Hexadiene, 0.15 g (1.8 mmol), was added to a solution of the hydridonickel complex, 0.14 g (0.21 mmol), in *ca.* 15 ml of toluene. The mixture was stirred under nitrogen at 25° for 24 hr. Glpc analysis of the 24-hr aliquot showed that none of the *cis*-1,4-hexadiene had reacted. The temperature of the solution was then raised to 50°. During 9 hr at this higher temperature, no conversion of 1,4-diene to products had occurred.

Addition of ethylene to a freshly prepared solution of the above components failed to cause the isomerization of *cis*-1,4-hexadiene during 5 hr at 25°.

Pmr spectra of a 1:1 mixture of *cis*-1,4-hexadiene and chloro(hydrido)bis(tricyclohexylphosphine)nickel(II) in C<sub>6</sub>D<sub>6</sub> showed no change in the vinyl proton spectrum from that of *cis*-1,4-hexadiene in the absence of the nickel compound during a 5-hr period. An infrared spectrum of this solution, recorded 1 hr after the components were mixed, failed to exhibit the 1920-cm<sup>-1</sup> band.

**Treatment of *cis*-1,4-Hexadiene with *trans*-Borohydrido(hydrido)-bis(tricyclohexylphosphine)nickel(II) and *trans*-Dichlorobis(tri-*n*-butylphosphine)nickel(II) (**4**).** *trans*-Borohydrido(hydrido)bis(tricyclohexylphosphine)nickel(II) was prepared according to the procedure of Green, Munakata, and Saito.<sup>49</sup> The resulting yellow solid decomposed under argon at 122-128° (lit.<sup>49</sup> 121-125°).

*trans*-Borohydrido(hydrido)bis(tricyclohexylphosphine)nickel(II), 0.120 g (0.18 mmol), in 7 ml of toluene was treated with a solution of **4**, 0.070 g (0.13 mmol), in 5 ml of toluene at 25°. After 2 min, *cis*-1,4-hexadiene, 0.13 g (1.57 mmol), was added to the ambered solution. During the following 20 min, two products—one with a glpc retention time identical with that of *trans*-2-methyl-1,3-pentadiene, and one with a retention time shorter than that of *cis*-1,4-hexadiene—were afforded in *ca.* 35% yield. The *trans*-2-methyl-1,3-pentadiene composed 47% of the C-6 product mixture. *trans,cis*- and *cis,cis*-2,4-hexadienes were detected in an aliquot analyzed after 6 hr.

**Synthesis of Starting Materials.** The sources of diene reactants and nickel complexes which were purchased or were prepared by routine procedures are revealed in the Materials section. The experimental procedures for the preparations of compounds, the properties of which are of particular importance or where the literature methods were modified by us, are presented here.

(49) M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc. A*, 469 (1971).

**Ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (5).** The title compound was prepared according to procedures reported by Tolman and coworkers.<sup>29,32</sup>

**Method A.** Sodium borohydride, 3.0 g (75 mmol), was slowly added to a well-stirred solution of nickel nitrate hexahydrate, 2.0 g (7.0 mmol), and tri-*o*-tolyl phosphite, 10.0 g (32 mmol), in 50 ml of acetonitrile. After the sodium borohydride addition was complete, the mixture was stirred for an additional 2 hr. The resulting dark suspension was filtered, and the solvent was removed *in vacuo* leaving a red grease as a residue. The red grease was dissolved in 50 ml of benzene and the resulting mixture was filtered, affording a yellow-orange solution. This solution was slowly syringed into 300 ml of ethylene-saturated methanol. The product, a yellow solid, crystallized when the methanol-benzene solution was cooled to 0°. The yellow solid was then filtered and washed several times with cold ethylene-saturated methanol, after which it was dried *in vacuo*. Recrystallization from ethylene-saturated methanol gave 0.68 g, 12% of the title compound. The yellow crystals were stored under argon at -78°.

The pmr spectrum (C<sub>6</sub>D<sub>6</sub>) exhibited resonances at  $\tau$  8.06 (s, 4 H, coordinated C<sub>2</sub>H<sub>4</sub>), 7.86 (s, 18 H), 3.11 (m, 18 H), and 2.56 (m, 6 H).

**Method B.** Nickel acetylacetonate, 1.15 g (4.5 mmol), and tri-*o*-tolyl phosphite, 3.2 g (9.0 mmol), in 60 ml of ethylene-saturated methanol at -50° were treated with a toluene solution of triethylaluminum (9.9 mmol). After the addition was complete, the mixture was allowed to warm to 30° affording a yellow-orange solution. About 30 ml of toluene was then removed *in vacuo* and *ca.* 150 ml of ethylene-saturated methanol was then added gradually. On cooling the mixture to 0°, yellow crystals separated. They were filtered and dried *in vacuo*. Recrystallization from benzene-methanol gave 2.4 g, 68%, of the product. The pmr spectrum was identical with that of the material prepared by method A and with the spectrum reported by Seidel and Tolman.<sup>29</sup> The visible spectrum of the product in benzene (*ca.* 2.0 × 10<sup>-4</sup> M) exhibited the expected<sup>29</sup>  $\lambda_{\max}$  at 350 nm and shoulder with an inflection at 382 nm.

**Ethylenebis(triphenylphosphine)nickel(0) (6).** The title compound was prepared by the general procedure of Greaves, Lock, and Maitlis.<sup>30</sup> To a suspension of nickel acetylacetonate, 4.0 g (15.6 mmol), and triphenylphosphine, 8.0 g (30.4 mmol), in 60 ml of ethylene-saturated ether under an ethylene atmosphere at 0°, was slowly added a hexane solution of triethylaluminum (32.6 mmol). A yellow solution resulted which was stirred for 24 hr at 0° under an ethylene atmosphere. The yellow crystals which separated were filtered under an ethylene atmosphere, washed six times with cold ethylene-saturated ether, and then dried with a rapid stream of ethylene gas. The crystals were stored under an ethylene atmosphere at 0°: pmr (C<sub>6</sub>D<sub>6</sub>)  $\tau$  2.10-2.55 and 2.56-3.1 (two broad peaks, 30 H) and 7.17 (s, 3.3 H, coordinated C<sub>2</sub>H<sub>4</sub> protons). *Anal.* Calcd for C<sub>40</sub>H<sub>34</sub>P<sub>2</sub>Ni: Ni, 9.60. Found: Ni, 9.74. Analysis indicated the presence of a 1 mol % aluminum impurity (0.045% Al by weight).

Attempted recrystallization of the product from ethylene-saturated diethyl ether afforded a yellow crystalline solid, the pmr spectrum of which (C<sub>6</sub>H<sub>6</sub>) did not exhibit a peak in the  $\tau$  7 region but did possess resonances indicative of the presence of diethyl ether. The ratio of aromatic:alkyl proton peak intensities was consistent with the formula: [(Ph<sub>3</sub>P)<sub>2</sub>Ni]<sub>2</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. *Anal.* Calcd for C<sub>38</sub>H<sub>70</sub>P<sub>4</sub>Ni<sub>2</sub>O: Ni, 9.50; P, 9.96. Found: Ni, 9.59; P, 10.21. The Al content was determined to be <0.01 mol %. This sample did not cause the skeletal rearrangement of *cis*-1,4-hexadiene in the presence of HCl.

(50) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.* **46**, 3879 (1968).

**3,3-Dimethyl-1,4-pentadiene.** The title compound was prepared in five steps, starting with 3,3-dimethylglutaric acid.

**3,3-Dimethyl-1,4-pentanediol.** The acid chloride of 3,3-dimethylglutaric acid was prepared by refluxing the acid, 25 g (0.15 mol), in 100 ml of thionyl chloride containing 3 ml of dimethylformamide for 12 hr. Distillation of the product at 95-96° (11 mm) afforded 28.15 g, 95% yield, of the acid chloride. If DMF was not employed, the formation of the acid chloride was not observed.

The acid chloride, 28.15 g (0.143 mol), in 25 ml of ether was added to 9.48 g (0.25 mol) of lithium aluminum hydride in 300 ml of ether at such a rate that a light reflux could be maintained throughout the reduction. The reaction mixture was stirred for 1 hr after addition was complete. The mixture was then treated carefully with 100 ml of water, then 25 ml of 10% H<sub>2</sub>SO<sub>4</sub> in water, followed by enough water to dissolve the aluminum salts. Continuous liquid-liquid extraction with ether for 3 days gave, upon distillation at 135-136° (1 mm) (lit.<sup>51,52</sup> bp 95-98° (0.25 mm)), 11.65 g, 62% yield of the diol: pmr (CCl<sub>4</sub>)  $\tau$  6.35 (t, 2 H), 7.5 (s, 1 H), 8.46 (t, 2 H), 9.04 (s, 3 H).

**3,3-Dimethyl-1,5-pentanediol *p*-Toluenesulfonate.** 3,3-Dimethyl-1,5-pentanediol, 16.17 g (0.122 mol), in 350 ml of anhydrous pyridine was treated over a 5-hr period with a solution of 51.57 g (0.270 mol) of *p*-toluenesulfonyl chloride in 200 ml of pyridine while the temperature was maintained between 0 and 5°. The mixture was then stirred for *ca.* 12 hr at room temperature. The resulting solution was then poured into ice-water after which the mixture was extracted with four 250-ml portions of ether. The ether phase was then washed with 30% hydrochloric acid, then with 5% NaHCO<sub>3</sub>, followed by saturated NaCl solution. After drying the ether solution over anhydrous calcium chloride, the solvent was removed affording a light yellow oil which crystallized on standing at 0°. Recrystallization from methanol gave 16.55 g, 31% yield, of the ditosylate mp 56-57°: pmr (CCl<sub>4</sub>)  $\tau$  2.50 (4 H), 6.03 (t, 2 H), 7.59 (s, 3 H), 8.49 (t, 2 H), and 9.29 (s, 3 H).

**1,5-Dibromo-3,3-dimethylpentane.** The 3,3-dimethyl-1,5-pentanediol tosylate, 16.55 g (0.030 mol), was treated for 24 hr with 10.77 g (0.124 mol) of lithium bromide in 150 ml of refluxing anhydrous acetone. During this period the lithium tosylate slowly precipitated from solution. The mixture was then cooled to room temperature and 50 ml of water was added. The resulting aqueous solution was extracted with four 50-ml portions of ether; the ether extract was washed with 100 ml of saturated NaCl solution and then dried over anhydrous magnesium sulfate. Distillation gave 8.0 g of the title compound, bp 97-98° (3 mm) (lit.<sup>53</sup> 80-81.5° (1.3 mm)).

**3,3-Dimethyl-1,4-pentadiene.** The compound was prepared by the procedure of Meinwald and Smith<sup>53</sup> as originally developed by Ciola and Burwell.<sup>54</sup> A mixture of 1,5-dibromo-3,3-dimethylpentane, 10.8 g (42 mmol), sodium iodide, 1.5 g (10 mmol), and 2-methylquinoline, 25 g (0.20 mol), was heated for 2 hr at 90°. The temperature of the heating bath was gradually raised until the product distilled at 60-65° through a small column attached to the reaction flask. After drying the distillate over Drierite, the product was redistilled, bp 68-70° (lit.<sup>53</sup> bp 69.5-70°), affording 2.23 g, 55% yield. The pmr spectrum was the same as that reported by Meinwald and Smith.<sup>53</sup>

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