Codimerization of α-Olefins and Conjugated Dienes by a Nickel-Based Coordination Catalyst

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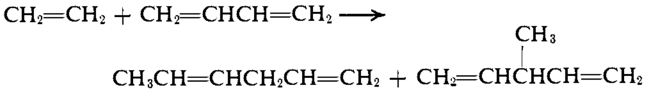
Abstract: The addition of α-olefins to conjugated dienes is accomplished by a catalyst derived from the interaction of bis(tri-*n*-butylphosphine)nickel(II) chloride with diisobutylaluminum chloride. The primary products are linear 1,4-dienes. The catalyst affords *trans*- and *cis*-1,4-hexadiene and 3-methyl-1,4-pentadiene from ethylene and butadiene. The specificity in the formation of 1,4-diene position isomers in the reactions of substituted precursors has provided some insight into the nature of the addition process.

The participation of nickel compounds in the catalysis of olefin–olefin addition reactions has mostly involved cyclooligomerization processes such as the cyclodimerization and -trimerization of butadiene by nickel(0) species[1–5] and the cyclooligomerization of allene.[6] However, the linear oligomerization of conjugated dienes with nickel catalysts also has been observed.[5] Ziegler and co-workers reported[7,8] the dimerization of ethylene by trialkylaluminum catalysts in the presence of nickel compounds. The dimerization of olefins using alkylaluminum chlorides in combination with various nickel compounds has been reported.[9,10]

The recent report by Wilke[3] of the reaction of butadiene with ethylene to give the 2:1 adducts, *trans,cis*-1,5-cyclodecadiene and 1,4,9-decatriene, was the first description of the coreaction of a monoolefin and a conjugated diene over a nickel-based coordination catalyst. A few other examples of the codimerization of monoolefins and conjugate dienes by transition metal catalysts in homogeneous solutions have appeared in the literature: the synthesis of predominantly *trans*-1,4-dienes with a rhodium trichloride catalyst,[11] the stereospecific synthesis of *cis*-1,4-dienes with catalysts derived from the reaction of ferric tris(acetylacetonate) and triethylaluminum[12a] or ferric halides, bisphosphines, and alkylaluminum compounds,[12b] and the preparation of 1,3-dienes using a cobalt acetylacetonate–triethylaluminum catalyst.[13] In this paper we describe the codimerization of α-olefins and conjugated dienes with a nickel-based catalyst to afford linear 1,4-dienes.[14]

Results

Admixture of bis(tri-*n*-butylphosphine)nickel(II) chloride and diisobutylaluminum chloride (Al:Ni = 6) in the presence of butadiene and ethylene in nonpolar solvents at *ca.* 20–70° and low pressures (<10 atm) leads to the formation of 1,4-hexadiene (*trans:cis* = 2.5–2.8) in 60–70% yield and to lesser amounts of 3-methyl-1,4-pentadiene and 2,4-hexadiene. The ratios of 1,4-hexadiene:3-methyl-1,4-pentadiene in reactions carried to only 10–20% conversions were (8–9):1. The best yields of the nonconjugated 1:1 adducts are obtained at moderate butadiene conversions (<50%). When the reaction is allowed to proceed to high butadiene conversion, an appreciable amount of 2,4-hexadiene is formed,[15] together with C_8 dienes formed from 2,4-hexadiene and ethylene.



$$CH_2{=}CH_2 + CH_2{=}CHCH{=}CH_2 \longrightarrow CH_3CH{=}CHCH_2CH{=}CH_2 + CH_2{=}CH\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2$$

The type of nickel compound employed is not critical provided that a phosphine or phosphite grouping is present. Thus, both Ni(II) complexes, such as $(R_3P)_2NiI_2$ and $(R_3P)_2Ni(NO_3)_2$, and Ni(0) complexes, such as $((C_6H_5)_3P)_2Ni(CO)_2$ and $((C_6H_5O)_3P)_2Ni(CO)_2$, can be used. The temperature may be varied depending on the particular combination of olefin, solvent, and catalyst chosen. For example, $(Bu_3P)_2Ni(NO_3)_2$ with i-Bu_2AlCl is active for the synthesis of 1,4-hexadiene in toluene below 0°.

The general utility of the reaction was demonstrated by the synthesis, from substituted precursors, of a number of 1,4-dienes, some of which have not been previously reported. Table I lists the major nonconjugated products formed and the yields obtained.

2-Methyl-1,3-butadiene was allowed to react with ethylene to give 4-methyl-1,4-hexadiene and 2,3-dimethyl-1,4-pentadiene in *ca.* 2.2:1 ratio. The former product was obtained as a mixture of the two geometric isomers which could not be completely separated by vpc. No evidence for the presence of 5-methyl-1,4-hexadiene[17] was found. Thus, with the nickel cata-

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[1] R. E. Foster, U. S. Patent 2,504,016 (1950).

[2] H. W. B. Reed, *J. Chem. Soc.*, 1931 (1954).

[3] G. Wilke, *Angew. Chem.*, **75**, 10 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963), and references cited therein.

[4] N. V. Kutepow, H. Seibt, and F. Meier, German Patent B59415 (1960).

[5] H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem.*, **77**, 318 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 327 (1965).

[6] R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 4247 (1959).

[7] K. Ziegler, *Angew. Chem.*, **67**, 541 (1955).

[8] K. Ziegler, H.-G. Gellert, E. Holzkamp, G. Wilke, E. Duck, and W.-R. Kroll, *Ann.*, **629**, 172 (1960).

[9] G. Nowlin and G. Burnie, U. S. Patent 2,969,408 (1961).

[10] G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

[11] T. Alderson, U. S. Patent 3,013,066 (1961); T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

[12] (a) G. Hata, *ibid.*, **86**, 3903 (1964); (b) M. Iwamoto and S. Yaguchi, *J. Org. Chem.*, **31**, 4290 (1966).

[13] D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); *Angew. Chem. Intern. Ed. Engl.*, **3**, 153 (1964).

[14] The synthesis of 1,4-dienes from acetylene and monoolefins by a thermal process was recently reported by N. F. Cywinski, *J. Org. Chem.*, **30**, 361 (1965).

[15] The conjugated products are derived from the 1,4-dienes. The behavior of the 1,4-dienes in the presence of the catalyst is described elsewhere.[16]

[16] R. G. Miller, submitted for publication.

[17] Obtained through the courtesy of L. Plummer. The compound was prepared from the vinyl Grignard and isoprene hydrochloride. The nmr spectrum of 5-methyl-1,4-hexadiene was expectedly different from that of the 4-methyl isomer and in agreement with that reported in the subsequent literature.[14]

Table I. α-Olefin-Conjugated Diene Codimerization Reactions[a]

Olefin	Pressure, psig[b]	Conjugated diene	Wt, g	Temp, °C	Solvent	Vol., ml	Time, min	Major 1:1 adduct	% convn[c]	% yield[d]
Ethylene	80	Butadiene	180	18–20	Toluene	1200	60	1,4-Hexadiene	33	65
Ethylene	101	1,3-Pentadiene	81	71–75	Perchloroethylene	1100	59	3-Methyl-1,4-hexadiene	30	79
Ethylene	110	2-Methyl-1,3-butadiene	100	69–76	Perchloroethylene	400	42	4-Methyl-1,4-hexadiene	31	33
Ethylene	104	2-Chloro-1,3-butadiene	200	55–60	*n*-Hexane	400	40	4-Chloro-1,4-hexadiene	37	75
Ethylene	79	Cyclo-1,3-hexadiene	25	63–76	Decalin	400	28	3-Vinylcyclohexene	70	83
Ethylene	84	Cyclo-1,3-octadiene	105	65–70	*n*-Hexane	400	12	3-Vinylcyclooctene	19	45
Propylene	102	Butadiene	99	75–90	Perchloroethylene	1100	94	2-Methyl-1,4-hexadiene	31	25

[a] The catalyst was formed by mixing 6 mmoles of diisobutylaluminum chloride and 1 mmole of bis(tri-*n*-butylphosphine)nickel(II) chloride [(Al:Ni = 6)] in the presence of the monomers. [b] Initial total pressure in the system. [c] Based on moles of conjugated diene introduced. [d] Based on moles of conjugated diene reacted.

lysts the products obtained from isoprene resulted by attachment of the ethylene carbon skeleton at positions 1 and 3, in contrast to the iron catalyst,[12a] where attachment occurred at positions 1 and 4.

1,3-Pentadiene and ethylene gave a single 1:1 product, 3-methyl-1,4-hexadiene, consisting mainly of the *trans* isomer. It is noteworthy that, throughout this series of methyl-substituted butadienes, the nickel catalyst yields codimerization products similar to those previously reported for the $RhCl_3$ catalyst[11] but which differ from those found by Hata[12a] using $Fe(AA)_3$–R_3Al catalyst. Thus, with the latter system, ethylene and 1,3-pentadiene yield *cis*-3-methyl-1,4-hexadiene and *cis*-1,4-heptadiene. Formally, it appears that with the nickel catalyst ethylene bonds exclusively at position 4 of the 1,4-pentadiene. However, under Discussion we will advance an alternative hypothesis.

Ethylene and 2-chloro-1,3-butadiene reacted readily to give the 4-chloro-1,4-hexadienes, bp 114–115°, as major products. The mixture consisted of *trans* and *cis* isomers (9:1), which were identified after isolation by preparative vpc. The structure proofs, which eliminated the possibility of the chlorine residing at the 5 position, were based on data given in Tables II and III. Table II contains pertinent observed chemical shifts and coupling constants of the *trans*- and *cis*-chlorodienes along side those of the *trans*- and *cis*-2-chloro-2-butenes, and Table III gives a similar comparison of infrared data.[18] The only other 1:1 nonconjugated adduct present in >1% yield was 2-chloro-3-methyl-1,4-pentadiene, formed in 7% yield. The structure of this product was established unequivocally by examination of its infrared and nmr spectra, as described in the Experimental Section.

Table II. Comparison of the Methyl Proton Resonance Spectra of *cis*- and *trans*-4-Chloro-1,4-hexadiene with Those of *cis*- and *trans*-2-Chloro-2-butene

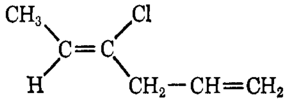
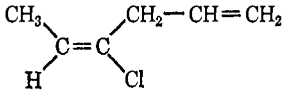
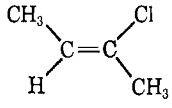
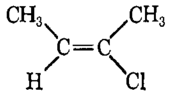
	
$\delta = 1.69$ ppm $J_{5,6} = 6.8$ cps	$\delta = 1.63$ ppm $J_{5,6} = 7.1$ cps
	
$\delta(CH_3(4)) = 1.70$ ppm $J_{1,3} = 1.2$ cps $J_{3,4} = 6.7$ cps	$\delta(CH_3(4)) = 1.65$ ppm $\delta(CH_3(1)) = 2.02$ ppm $J_{1,3} = 1.3$ cps $J_{3,4} = 7.2$ cps

Table III. Infrared Vibrational Frequencies Associated with the Chloro-Substituted Olefinic Bond of *cis*- and *trans*-4-Chloro-1,4-hexadiene and of the 2-Chloro-2-butenes and 4-Chloro-4-octenes

Vibrational mode		Frequency, cm⁻¹: 4-Cl-1,4-HD	C_4H_7Cl	$C_8H_{15}Cl$
=CH out-of-plane	*trans*	802	798	811
deformation	*cis*	823	823	826
C=C stretch	*trans*	1675	1674	1662
(fundamental)	*cis*	1665	1665	1653

1,3-Cyclohexadiene and 1,3-cyclooctadiene reacted rapidly with ethylene to give 3-vinylcyclohexene and 3-vinylcyclooctene, respectively. However, cyclopentadiene failed to react with ethylene under the conditions we examined.

Yields of nonconjugated 1:1 adducts were drastically reduced as alkyl substitution on the olefin monomer was increased. Although ethylene and butadiene reacted readily over a wide temperature range, temperatures of 85–90° were required to produce only mediocre yields of C_7 dienes from propylene and butadiene. The yield of the major nonconjugated product, 2-methyl-1,4-hexadiene, was only 25%. 1-Hexene and butadiene, in the same temperature range, gave only a 4% yield of a product presumed to be 2-butyl-1,4-hexadiene, and isobutylene failed to give a codimer product. Codimer formation in the propylene reaction was accompanied by the production of higher molecular weight oligomers (65% conversion of butadiene, assuming that the product is derived from butadiene alone), bp >39° (1.3 mm), which appear to be polybutadienes terminated by units derived from propylene. The lowest molecular weight material possessed vinylidene unsaturation, as evi-

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(18) R. C. Ferguson, *J. Polymer Sci.*, A2, 4735 (1964).

denced by strong absorption near 11.2 μ in the infrared. The absorption was reduced, but still of medium intensity in higher molecular weight fractions. The conversion of butadiene to oligomers in the 1-hexene reaction approached 47% on the same basis as used above. This product also showed absorption (medium) near 11.2 μ. Of the butadiene introduced in the isobutylene reaction, 83% was converted to predominantly *trans*-1,4-polybutadiene of low molecular weight. It is noteworthy that infrared absorption due to vinylidene unsaturation was absent in this polymer. Admixture of the catalyst with butadiene in the absence of a monoolefin for 60 min at 78–84° afforded a 58% conversion to low molecular weight polybutadiene (viscous oil) which possessed units derived from 1,4 and 1,2 addition, but contained no vinylidene unsaturation.

The active species catalyzes a number of side reactions, all of which are suppressed by high concentrations of conjugated diene. In the absence of a conjugated diene capable of reaction with an olefin over the catalyst, ethylene is rapidly dimerized to 1-butene which is in turn isomerized to *trans*- and *cis*-2-butene. The formation of butenes is almost eliminated in ethylene–butadiene codimerizations carried to only *ca.* 50% butadiene conversion. The isomerization of 1,4-hexadiene to 2,4-hexadiene is similarly dependent upon the butadiene conversion. In the reactions of ethylene with substituted butadienes (*cf.* Table I) higher boiling products were formed; these appear mainly to be conjugated isomers of the primary 1:1 adducts and compounds formed from further reaction of these conjugated diene products with ethylene.[19] Similar results were noted with $RhCl_3$.[11]

Attempts to isolate the catalyst species or nickel compounds derived therefrom have been unsuccessful. However, a number of observations do shed light on its nature. The codimerization has not been accomplished in the absence of a trivalent phosphorous moiety, presumably bonded to nickel. Interestingly, the presence of a phosphine or phosphite is not a requirement for the dimerization of ethylene and propylene nor for the polymerization of butadiene. Mixtures of β-diketone enolate complexes of nickel(II) and diisobutylaluminum chloride form very active olefin dimerization catalysts when a conjugated diene is not present. On introduction of butadiene, the olefin dimerization does not occur and polybutadiene is formed. Bis(2,2,6,6-tetramethyl-3,5-heptanedione)nickel(II), on combination with diisobutylaluminum chloride (Al:Ni = 6) in the presence of ethylene and butadiene, afforded a 54% conversion to predominantly *trans*-1,4-polybutadiene. When these catalyst precursors were allowed to react under the same conditions, in the presence of triphenylphosphine (P:Ni = 2), ethylene and butadiene reacted to give the C_6 dienes and the polymerization of butadiene did not occur. The activity of the catalyst formed in this manner was essentially the same as that derived from reaction of preformed bis(phosphine)nickel(II) dihalides with dialkylaluminum halides.

The alkylaluminum compounds are not of equivalent activity. Trialkylaluminum compounds in general give less active catalysts than aluminum alkyls containing one or more halide atoms per aluminum. These results are in accord with proposals[20–22] that certain olefin polymerization catalysts consist of complexes in which the transition metal is associated, *via* halogen bridging, with other metal compounds.

Discussion

It is clear that carbons 3–6 in the 1,4-hexadiene skeleton are derived from the conjugated diene and that carbons 1 and 2 come from the α-olefin when one considers the positions of substitution in the products listed in Table I. The product structures seem best explained by a reaction path that would involve, initially, the addition of a nickel hydride complex to the conjugated diene to afford a substituted allylnickel species. The participation of transition metal hydrides in the homogeneous catalysis of the hydrogenation of olefins has been proposed by a number of workers.[23–24] The generation of such a species in the present case could arise *via* one of the routes suggested by Sloan and co-workers,[25] involving a nickel hydride β elimination from an alkylnickel precursor. It is interesting that these workers found a catalyst derived from triisobutylaluminum and bis(tri-*n*-butylphosphine)nickel(II) chloride to be an effective olefin hydrogenation catalyst. We have found that, in the absence of hydrogen, the same system catalyzes the codimerization of ethylene and butadiene. Heck[26] has suggested the participation of a halonickel dicarbonyl hydride in the nickel-catalyzed olefin carboxylation reaction and in the acrylate synthesis.[27] The role of transition metal hydride complexes in the double bond positional isomerization of olefins has recently been discussed.[28]

The products formed in these reactions can be explained by methylallylnickel intermediates possessing either classical or nonclassical electronic structures. The "insertion" of ethylene into positions a or b of π-methylallylnickel complex I[29] would give alkylnickel complexes which on Ni–H elimination afford the isomeric 1,4-dienes observed. The involvement of the corresponding σ-methylallylnickel derivatives as the components of a rapidly equilibrating mixture analogous to the allylmagnesium system[31] could explain the product structures equally well. π Complexes of nickel not involving the transfer of hydrogen have been reported as active species in the cyclooligomerization of butadiene.[3]

Precedent exists for the formation of both π-1-methylallyl and σ-1-methylallyl transition metal compounds

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[19] 2,4-Hexadiene was found to react readily with ethylene to give a mixture of C_8 diene products. See Experimental Section.

[20] W. L. Carrick, *J. Am. Chem. Soc.*, **80**, 6455 (1958).

[21] W. P. Long and D. S. Breslow, *ibid.*, **82**, 1953 (1960).

[22] P. Cossee, *J. Catalysis*, **3**, 80 (1964).

[23] R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

[24] S. J. Lapporte and W. R. Scheutt, *J. Org. Chem.*, **28**, 1947 (1963).

[25] M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963).

[26] R. F. Heck, *ibid.*, **85**, 2013 (1963).

[27] (a) W. Reppe and H. Kröper, *Ann.*, **582**, 38 (1953); (b) W. Reppe, *ibid.*, **582**, 1 (1953).

[28] R. Cramer, *J. Am. Chem. Soc.*, **88**, 2272 (1966).

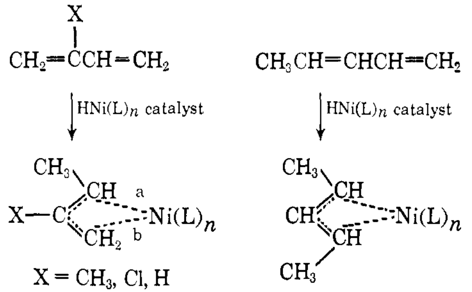
[29] Numerous π-allyl and π-methylallylnickel complexes are known.[30]

[30] (a) G. Wilke and B. Bogdanovic, *Angew. Chem.*, **73**, 756 (1961); (b) R. F. Heck, J. C. W. Chien, and D. S. Breslow, *Chem. Ind.* (London), 986 (1961); (c) E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **16b**, 77 (1961); (d) E. O. Fischer and G. Bürger, *Chem. Ber.*, **94**, 2409 (1961); (e) E. O. Fischer and H. Werner, *Z. Chem.* (Leipzig), **2**, 174 (1962).

[31] J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

through the addition of transition metal hydride complexes to butadiene.[32]

All of the products isolated and characterized in our work can be pictured as being formed *via* an initial 2,1 addition of Ni–H to the least substituted[33] double bond of the conjugated precursor. This mode of addition can lead *directly* to I or, alternatively, to a mixture of the corresponding σ-methylallyl complexes. It is to be especially noted that 1,3-pentadiene would afford a symmetrical nickel π complex (II) according to this scheme, and therefore a single 1:1 product, as was observed.



I

II

Although the high specificity in the formation of 1,4-diene position isomers does not rule out the possibility of 4,1 addition of Ni–H to the substituted conjugated diene, it certainly renders this mode of addition highly unlikely as a major path to methylallylnickel intermediates since one would expect to find products derived from a 1,4 addition also. It is significant that niether 1,4-heptadiene nor 3-ethyl-1,4-pentadiene could be found in the product mixture from 1,3-pentadiene. Analogously, chloroprene and isoprene gave only the 4-substituted 1,4-hexadienes and 2-chloro-3-methyl-1,4-pentadiene and 2,3-dimethyl-1,4-pentadiene, respectively, all of which could arise through I or the corresponding σ structures. Products pictured as being derived from the 1,4 addition of Ni–H to the conjugated dienes were not detected. In contrast, the ferric tris(acetylacetonate)–triethylaluminum catalyzed codimerization of ethylene and conjugated dienes gives both *cis*-1,4 and *cis*-4,1 adducts as the only major products.[12a]

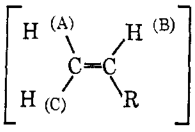
Experimental Section[34]

Equipment and Materials. The codimerization reactions were carried out in a 1.9-l. stainless-steel autoclave. The vessel was fitted with a mechanical stirrer activated by an air-driven motor, two gas inlet tubes, a port for the introduction of solids, two catalyst injection tubes, a rupture disk, a thermocouple well, and an outlet leading to a back-pressure regulator. The back-pressure regulator was set to vent at pressures *ca.* 20 psig above the operating pressure. The polymerization grade ethylene and propylene were passed through separate molecular sieve columns prior to entry into the reactor. The butadiene (Matheson instrument grade) was passed through a molecular sieve column and distilled from a tared cylinder into the reactor. The experiments were conducted in an atmosphere free from oxygen and moisture.

Vapor Phase Chromatography of Products. All yields are based on weights of distilled products or were determined by vpc analysis of known weights of mixtures of isomeric products, isolated by distillation. Standard mixtures of isomeric products were analyzed in order to determine the relationship between mole ratio and relative signal intensity. In general, no corrections were needed. The product ratios from ethylene–chloroprene reaction were based on signal intensity alone.

The C_6 chlorodienes were analyzed on a 12 ft × 0.25 in. 25% tricresyl phosphate on Chromosorb column, operated isothermally at 115°, with a helium flow rate of 60 cc/min. The other diene products were analyzed on a 15 ft × 0.25 in. 20% β,β'-oxydipropionitrile on firebrick column, programmed from 40 to 70° at 5°/min, flow rate 60 cc/min, and on a 8 ft × 0.75 in. 20% 1,2,3-tris(2-cyanoethoxypropane) on Chromosorb column, operated isothermally at 47°, flow rate 127 cc/min. The C_4 products were analyzed on a 6 ft×0.25 in. column of 20% Esteramide on firebrick, operated at 0°, flow rate 40 cc/min.

Nmr Spectra of the 1,4-Dienes. In each of the nmr spectra described below, the "array" of peaks attributed to the olefinic protons consisted of the ABC spectrum of the terminal vinyl protons superimposed on the resonances of the protons associated with the internal double bond when present. The spectra of the 1,4-hexadienes were quite complex due to spin coupling of the vinyl protons with allylic methylene protons. The spectra of the 3-methyl-1,4-pentadienes were simpler. The resonance of proton B in these cases consisted of a distinct octet, the expected multiplicity if one allylic proton were present. All spectra exhibited resonances with chemical shifts characteristic of doubly allylic methylene protons.



Codimerization of Ethylene and Butadiene. Bis(tri-*n*-butylphosphine)nickel(II) chloride, 0.534 g (1.00 mmole), was dissolved in 1.1 l. of dry deoxygenated perchloroethylene. The deep red solution was cooled to 0° and 200 g (3.7 moles) of butadiene was distilled into the reactor. The solution was then warmed to 65° and ethylene was charged until the total pressure in the system reached 106 psig. Diisobutylaluminum chloride, 1.2 ml (6.0 mmoles), dissolved in 4 ml of perchloroethylene, was then added to the stirred mixture. The solution immediately became orange-amber in color. The pressure dropped as the monomers were consumed, and on reaching 100 psig ethylene was allowed to pass into the reactor on demand. After 60 min at 65–70° the reaction was terminated by the addition of 3 ml of 2-propanol. The mixture was then cooled to 20° and the system was vented through two traps, cooled to −78°. The traps were then connected to the exit of a distillation column and the product mixture was refluxed until the remaining butenes and unreacted butadiene had distilled into the cold traps. Distillation afforded 130 g of C_6 fraction, bp 49–83°, containing 15% 3-methyl-1,4-pentadiene, 53% *trans*-1,4-hexadiene, 21% *cis*-1,4-hexadiene, and 9% of the 2,4-hexadienes. The remaining 2% of the mixture consisted of 3-methyl-1,3-pentadiene and three other minor products.

The C_4 fraction that was recovered, 77 g, consisted of 85% butadiene, 8% 1-butene, 4% *trans*-2-butene, and 3% *cis*-2-butene.

Identification of the C_6 Dienes. A product mixture obtained in the manner described above was extracted with water and then dried over anhydrous magnesium sulfate. Fractionation afforded a sample of 3-methyl-1,4-pentadiene, bp 48.0–50.0° (lit.[35] bp 55°). The infrared spectrum possessed peaks at 3.28 (m), 3.4 (s), 3.5 (w), 6.11 (s), 6.84 (m), 7.06 (m), 7.28 (m), 10.05 (m), and 10.95 (s) μ. The nmr spectrum showed an array of peaks from 6.07 to 4.80 ppm (olefinic protons), a multiplet centered at 2.82 ppm (doubly allylic tertiary proton), and a doublet centered at 1.07 ppm (methyl), the ratio of the areas being 5.9:1.0:3.1.

A central cut of the 1,4-hexadiene fraction, bp 64.2–64.5° (lit.[36] bp 63–64.8°), was shown to consist of two components that pos-

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[32] (a) W. W. Prichard, U. S. Patent 2,600,671 (1952); (b) H. B. Jonassen, R. I. Stearns, J. Kenttamaa, D. W. Moore, and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958); (c) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961); (d) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

[33] By least substituted is meant the number *or size* of substituents.

[34] The nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 instrument using neat samples or solutions in carbon tetrachloride. All chemical shifts are reported in parts per million downfield from tetramethylsilane. The infrared spectra were obtained with a Perkin-Elmer Model 221 recording spectrophotometer. All boiling points and melting points are uncorrected.

[35] R. R. Dreisbach, "Physical Properties of Chemical Compounds. II," Advances in Chemistry Series, No. 22, American Chemical Society, Washington, D. C., 1959.

[36] B. H. Shoemaker and C. E. Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931).

sessed vpc retention times identical with those of *trans*- and *cis*-1,4-hexadiene. Comparison of the infrared [bands at 6.10 ($C{=}C$), 10.05 and 10.96 (vinyl), 10.33 (*trans*-$CH{=}CH$–), and 14.2 μ (*cis* –$CH{=}CH$–)] and nmr (array from 6.14 to 4.78 ppm and complex multiplets centered at 2.74 and 1.62 ppm, 5.0:2.0:3.0) spectra with authentic samples[11,12] of the *trans* and *cis* isomers served as a conclusive identification. A central fraction of the 2,4-hexadiene distillate, bp 80.0–80.5° (lit.[37] bp 80–82°), contained by vpc analysis three major components, totaling 99% of the mixture. The components possessed retention times identical with those of the *trans,-trans*, *trans,cis*, and *cis,cis* isomers[9] and composed 57, 37, and 5% of the mixture, respectively. Two minor components were present, one having a retention time identical with that of *cis*-3-methyl-1,3-pentadiene. The retention time of the other geometric isomer of 3-methyl-1,3-pentadiene was found to be the same as that of the *trans,trans*-2,4-hexadiene. The nmr spectrum of the 2,4-hexadiene mixture showed an array of peaks from 6.58 to 5.08 ppm and a doublet centered at 1.65 ppm, the ratio of the areas as determined from the integrated peak intensities being 3.92:6.06. The infrared spectrum showed peaks at 6.0 (w), 6.1 (w), 10.14 (s), 10.57 (m), 10.77 (m), 12.22 (m), 13.34 (w), 14.23 (m) and 14.7 (w) μ. The spectra indicated that the 3-methyl-1,3-pentadiene present was less than 5% of the mixture.

Isolation and Identification of Products from Substituted Precursors. The experiments were conducted using the same general procedure as that described for the codimerization of ethylene and butadiene.

Reaction of Ethylene with 1,3-Pentadiene. Of the products boiling below 109°, 99% was 3-methyl-1,4-hexadiene by vpc analysis. The product, bp 83.0–84.0° (lit.[11] bp 84°), $n^{25}\text{D}$ 1.4135, showed peaks in the infrared at 6.17, 10.1, 10.36 (*trans* –$CH{=}CH$–), 10.98, and a weak band at 13.7 μ (*cis* –$CH{=}CH$–). The nmr exhibited a complex array of peaks from 6.09 to 4.74 ppm, a singlet at 2.75 ppm, and doublets centered at 1.63 and 1.05 ppm, the ratio of areas being 5:1:3:3.

Reaction of Ethylene with 2-Methyl-1,3-butadiene The product mixture contained two C_7 nonconjugated position isomers, 2,3-dimethyl-1,4-pentadiene and 4-methyl-1,4-hexadiene. The former product, bp 79.0–79.9°, $n^{25}\text{D}$ 1.4134, could be isolated by column distillation. The infrared spectrum exhibited bands at 6.04 (sh), 6.06, 10.03 and 10.94 (vinyl), and 11.21 μ ($CH_2{=}CR_2$). The nmr showed an array from 6.06 to 4.67 ppm, a multiplet of five discernible peaks centered at 2.78 ppm, an apparent triplet centered at 1.67 ppm, and a doublet at 1.10 ppm. The ratio of the respective peak intensities was 4.9:1.1:3.1:3.1.

Anal. Calcd for C_7H_{12}: C, 87.4; H, 12.5. Found: C, 87.2; H, 12.4.

4-Methyl-1,4-hexadiene was isolated as a mixture of the geometric isomers. The material, bp 91–93° (lit.[11] bp 91–92°), $n^{25}\text{D}$ 1.4232, exhibited bands at 6.17 ($C{=}C$), 10.10 and 10.99 (vinyl), and 12.13 μ ($R_2C{=}CHR$) in the infrared. The nmr spectrum of the mixture possessed an array of peaks between 6.12 and 4.80 ppm, a doublet at 2.70 ppm, and a multiplet centered near 1.62 ppm, in a 3.96: 1.99:6.04 ratio. Vapor phase chromatography of the sample indicated the presence of two components (2:1). Although the major component possessed a retention time identical with that of 5-methyl-1,4-hexadiene, the nmr spectrum of the major component, after isolation by preparative vpc, indicated it to be a geometric isomer of 4-methyl-1,4-hexadiene.

Reaction of Ethylene with 2-Chloro-1,3-butadiene. Fractionation of the product mixture afforded 2-chloro-3-methyl-1,4-pentadiene, bp 51.5–52.1° (132 mm), $n^{25}\text{D}$ 1.4392. The infrared spectrum exhibited significant peaks at 6.2 ($C{=}C$), 10.1 and 10.88 (vinyl), and 11.3 μ ($CH_2{=}CClR$), and the nmr spectrum showed an array from 6.17 to 4.92 ppm, a multiplet (five discernible peaks) centered at 3.10 ppm, and a doublet centered at 1.22 ppm, in a 4.8:1.0:3.2 ratio.

Anal. Calcd for C_6H_9Cl: Cl, 30.4. Found: Cl, 30.2.

The major fraction, the 4-chloro-1,4-hexadienes, bp 114–115°, proved to be a mixture of the *trans* and *cis* isomers. A central cut, bp 114.2–114.6°, was analyzed.

Anal. Calcd for C_6H_9Cl: C, 61.8; H, 7.8; Cl, 30.4. Found: C, 62.1; H, 7.8; Cl, 30.7.

The ultraviolet spectrum showed only end absorption with $\lambda_{\max}$ below 210 mμ (ϵ_{230} 122). The geometric isomers were isolated by preparative vpc. The structure proofs of *trans*-4-chloro-1,4-hexadiene, $n^{25}\text{D}$ 1.4482, and *cis*-4-chloro-1,4-hexadiene, $n^{25}\text{D}$ 1.4500, were based on the infrared and nmr spectra which are discussed under Results. The nmr spectrum of the *trans* isomer exhibited an array from 6.20 to 4.90 ppm, a pair of multiplets centered at 3.02 ppm, and a pair of triplets centered at 1.69 ppm. The *cis* isomer showed an array of peaks from 6.17 to 4.94 ppm and doublets at 3.08 and 1.63 ppm. The ratio of the respective peak areas was 4:2:3 in both cases. The secondary coupling, J_{36}, in the *cis* isomer was weaker than in the *trans* compound; thus the fine structure was not resolved.

The remaining C_6 chlorodienes, bp 69–70° (84 mm), $n^{25}\text{D}$ 1.4793, $\lambda_{\max}$ 230 (ϵ 17,200), appeared to be a mixture of the 3-chloro-2,4-hexadienes. The infrared spectrum showed peaks at 6.10 (w), 6.22 (m), 10.5 (s), 10.76 (sh), 12.13 (m), and 12.91 (m) μ. The nmr spectrum was quite complex, exhibiting an array of peaks from 6.34 to 5.43 ppm and a multiplet centered near 1.77 ppm, in a 2.9:6.1 ratio.

Reaction of Ethylene with 1,3-Cyclohexadiene. The product, 3-vinylcyclohexene, bp 58–59° (76 mm) (lit.[14] bp 128°), $n^{25}\text{D}$ 1.4647, exhibited peaks at 6.08, 10.07, 10.99, 11.25 (sh), 13.81, and 14.2 (sh) μ. The nmr spectrum possessed an array of peaks from 6.09 to 4.25 ppm, a broad peak at 2.75 ppm, and two multiplets centered near 1.92 and 1.67 ppm, the ratio being 5.1:1.0:5.9.

Anal. Calcd for C_8H_{12}: C, 87.19; H, 12.81. Found: C, 87.25; H, 12.95.

Reaction of Ethylene with 1,4-Cyclooctadiene. 3-Vinylcyclooctene, bp 59.0–60.3° (12–13 mm), $n^{25}\text{D}$ 1.4801, possessed an infrared spectrum with peaks at 6.11, 10.08, 10.37 (w), 10.95, 13.21, and 14.0 μ. The nmr spectrum showed an array from 5.83 to 4.56 ppm, a multiplet centered near 3.02 ppm, and two broad peaks at 2.00 and 1.50 ppm, in a 4.8:0.9:10.3 ratio.

Reaction of Propylene with Butadiene. The major product fraction, 2-methyl-1,4-hexadiene, bp 91.0–92.0° (lit.[11] bp 90–91°), $n^{25}\text{D}$ 1.4203, exhibited strong bands in the infrared at 10.36 (*trans* –$CH{=}CH$–) and 11.25 μ ($R_2C{=}CH_2$) and a broad weak band at 14.5 μ (*cis* –$CH{=}CH$–). Analysis by vpc indicated a *trans*:*cis* ratio of 4. The nmr spectrum exhibited two multiplets centered at 5.47 and 4.73 ppm and multiplets at 2.74 and 1.72 ppm, the ratio of the peak intensities being 2:2:2:6. The characteristic ABC pattern associated with –$HC{=}CH_2$ was absent. However, the presence of a minor component (same retention time as *trans*-2-methyl-1,4-hexadiene) was indicated by a weak shoulder at 10.9 μ and a weak resonance at 2.08 ppm.

Reaction of 1-Hexene with Butadiene. The product, believed to be 2-butyl-1,4-hexadiene, bp 58–61° (18 mm), $n^{25}\text{D}$ 1.4392, possessed an infrared spectrum similar to that of 2-methyl-1,4-hexadiene with characteristic peaks at 10.34 and 11.23 μ.

Ethylene and 2,4-Hexadiene. The reaction afforded a mixture of 1:1 adducts, bp 108–109.4°, $n^{25}\text{D}$ 1.4213–1.4220, believed to be 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene (lit.[11] bp 109–110°). The infrared spectrum showed peaks at 6.1, 10.1, 10.35, and 10.98 μ. The mr spectrum was complex but contained the general features of all of the spectra of 1,4-dienes with terminal vinyl unsaturation. The ratio of aliphatic to olefinic protons was 9.0:5.0 as determined from the integrated peak intensities.

Dimerization of Ethylene. A solution of bis(tri-*n*-butylphosphine)nickel(II) chloride, 0.534 g (1.00 mmole), in 550 ml of dry deoxygenated toluene was warmed to 58° and ethylene was charged to 61 psig. Diisobutylaluminum chloride, 1.20 ml (6.0 mmoles), was then added to the stirred mixture. A vigorously exothermic reaction ensued, accompanied by a pronounced pressure drop even though ethylene was allowed to feed into the reactor on demand. The temperature reached 69° within 1 min, whereupon the mixture was cooled to 65°. The reaction was terminated after a total of 4 min by the addition of 3 ml of 2-propanol. The C_4 fraction, 55 ml, was collected as described above and was analyzed by vpc. The chromatogram indicated the presence of 1-butene (6%), *trans*-2-butene (60%), and *cis*-2-butene (31%).

Oligomerization of Butadiene. Butdaiene, 98 g (1.81 moles), was distilled into the pressure reactor which contained a solution of 0.534 g (1 mmole) of bis(tri-*n*-butylphosphine)nickel(II) chloride in 400 ml of dry deoxygenated *n*-hexane. The mixture was then warmed to 78° and diisobutylaluminum chloride, 1.20 ml (6.0 mmoles), was charged. The stirred mixture was maintained at 78–84° for 1 hr, after which the reaction was terminated by the addition of 3 ml of 2-propanol. Thirty grams of unreacted butadiene was recovered. The *n*-hexane was removed by distillation, affording a residue which consisted of 56.5 g of butadiene oligomers (a viscous pourable oil). No volatile components (up to 100° (1.5 mm)) were present. The infrared spectrum of the polymer, peaks at 6.12 (m), 10.1 (sh), 10.35 (s), 10.98 (m), and 13.8 (m) μ (broad, extending beyond 14 μ), indicated that *trans*-1,4, *cis*-1,4,

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[37] J. Reif, *Ber.*, **41**, 2739 (1908).

and 1,2 addition had all occurred to an appreciable extent. No evidence for the presence of vinylidene unsaturation was found.

Bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II)–Diisobutylaluminum Chloride Catalyzed Polymerization of Butadiene. Butadiene, 202 g (3.74 moles), was distilled into the reactor which contained a solution of 0.425 g (1.00 mmole) of bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II) in 1100 ml of dry deoxygenated perchloroethylene. The red-violet solution was then warmed to 75°, and ethylene was charged until the total pressure was 130 psig. Diisobutylaluminum chloride, 1.2 ml (6.0 mmoles), was then charged. The resulting mixture, orange in color, was then stirred for 30 min with no temperature rise or ethylene pressure drop noticeable. The temperature was then raised to 84° and maintained there for another 30 min before the reaction was terminated in the usual manner.

Distillation afforded 121 g of unreacted butadiene. No C$_6$ dienes were present in the product mixture. A major portion of the solvent was then removed *in vacuo* and the residual solution was treated with 1 l. of methanol, causing a polymer fraction to separate. The polymer was isolated and dried *in vacuo*, affording 68 g of a syrupy mass. The infrared spectrum of the material indicated that it was predominantly *trans*-1,4-polybutadiene.

Codimerization of Ethylene and Butadiene with a Catalyst Derived from Bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II), Triphenylphosphine, and Diisobutylaluminum Chloride. Butadiene, 97 g (1.80 moles), was distilled into the reactor, which contained a solution of 0.524 g (2.0 mmoles) of triphenylphosphine and 0.425 g (1.0 mmole) of bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II) in 1100 ml of dry deoxygenated perchloroethylene. The stirred mixture was then warmed to 63° and ethylene was charged until the total pressure was 97 psig. Diisobutylaluminum chloride, 1.2 ml (6.0 mmoles), was then added and the mixture was stirred at 63–68° for 1 hr before the reaction was terminated in the usual manner.

Distillation of the product mixture afforded 36 g of C$_4$ olefins consisting of butadiene (80%), 1-butene (17%), *trans*-2-butene (2%), and *cis*-2-butene (1%), as determined by vpc analysis.

The C$_6$ fraction consisted of a 72-g mixture of 3-methyl-1,4-pentadiene (12%), 1,4-hexadiene (71%, *trans*:*cis* = 3.7), and 2,4-hexadienes (17%).

Preparation of Bis(tri-*n*-butylphosphine)nickel(II) Chloride. The compound, prepared by the method of Jensen[38] in 80.5% yield from nickel chloride hexahydrate and tributylphosphine, exhibited mp 46–47° (lit.[38] mp 48–49°).

Preparation of Bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II). The compound was prepared by the method of Cotton and Fackler[39] by hydrolysis of the analogous copper(II) chelate and reaction of the thus purified dipivaloylmethane with nickel acetate. The yield of material, mp 219.5–222.6° (lit.[39] mp 217–221°, no yield given), was 15% based on the copper chelate.

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[38] K. A. Jensen, *Z. Anorg. Chem.*, **229**, 265 (1936).

[39] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

The Conformational Rivalry between the Nonbonding Electron Pair and the Proton on Nitrogen

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Abstract: Nuclear magnetic resonance and infrared evidence indicate that piperidine exists predominantly, but not completely, in the isomeric form with the lone pair equatorial. The nmr results are independent of any special effects of concentration or solvent.

The question of the steric requirements of a nonbonding electron pair relative to the requirements of a proton was perhaps considered first by Barton and Cookson[3] and subsequently in detail by numerous authors.[4] Although originally there was some controversy concerning the relative sizes of the lone pair and the methyl group,[5] little doubt remains that the latter is considerably larger.[6,7] A general consensus has developed in support of the contention that the proton is qualitatively larger than the lone pair.[7,8] By means of dipole-moment and thermodynamic calculations on piperidine, piperazine, and N-methylpiperazine, Allinger, *et al.*,[7] obtained an energy difference of 0.46 kcal/mole between the lone pair and the proton on nitrogen, with the proton being the larger. Since almost all previous work[8] has involved either highly substituted derivatives or polycyclic analogs of piperi-

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[2] National Science Foundation Undergraduate Research Participant, 1965–1967.

[3] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 44 (1956).

[4] For a review of the literature of this subject, see F. G. Riddell, *ibid.*, in press.

[5] M. Aroney and R. J. W. Le Fèvre, *J. Chem. Soc.*, 3002 (1958); M. J. Aroney, C.-Y. Chen, R. J. W. Le Fèvre, and J. D. Saxby, *ibid.*, 4269 (1964).

[6] The "larger" of two groups involved in a conformational rivalry by dent of attachment to a common atom in an otherwise unsubstituted, saturated six-membered ring is operationally defined as that group which preferentially assumes the equatorial position. Such an orientation may not directly reflect the relative sizes of the groups as measured, for example, by van der Waals radii. See E. L. Eliel, *Angew. Chem. Intern. Ed., Engl.*, **4**, 761 (1965), for a discussion of this point.

[7] N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *Tetrahedron Letters*, 3345 (1964); *J. Am. Chem. Soc.*, **87**, 1232 (1965).

[8] T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc.*, 218 (1961); *J. Chem. Soc.*, 2637 (1962); A. R. Katritzky, *Record Chem. Progr.*, **23**, 223 (1962); R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc.*, 257 (1964); N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963); M. J. Aroney, C.-Y. Chen, R. J. W. Le Fèvre, and A. N. Singh, *J. Chem. Soc., Phys. Org.*, 98 (1966); P. J. Brignell, A. R. Katritzky, and P. L. Russell, *Chem. Commun.*, 723 (1966); E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.*, **88**, 5347 (1966).