Olefin-to-Olefin Addition Reactions

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A new synthesis of 1,4-diolefins has been found in the rhodium chloride catalyzed addition of ethylene and propylene to such dienes as butadiene, isoprene, and 1,3-pentadiene. For example, addition of ethylene to butadiene at 50° gives high yields of 1,4-hexadiene and its isomerization product, 2,4-hexadiene. Rhodium and ruthenium derivatives also catalyze the dimerization of ethylene to butenes, butadiene to 2,4,6-octatriene, and methyl acrylate to dimethyl 2-hexenedioate. The exclusively straight-chain structures of the latter two dimers are in marked contrast to the cyclic- and branched-chain dimeric products obtained by many other techniques.

Introduction

In the course of an investigation of the catalytic behavior of certain group VIII metal halides, we found some new condensation reactions of compounds containing a terminal vinyl group. These reactions include dimerizations, as exemplified by the conversion of ethylene to butenes, butadiene to 2,4,6-octatriene, and methyl acrylate to dimethyl 2-hexenedioate, as well as combinations of two different reactants. Of particular interest in the latter category are the reactions of olefins with 1,3-dienes to give 1,4-dienes, e.g., 1,4-hexadiene from ethylene and butadiene. These transformations are effected at temperatures of 30–150° under moderate pressures in alcoholic media containing low concentrations (0.2%) of soluble chlorides of rhodium and ruthenium. The reaction differs from known acid-catalyzed and Friedel–Crafts reactions in that low acidity is employed and ethylene shows high reactivity compared with higher olefins. The reactions differ sharply from those employing coordination catalyst systems, such as those containing triethylaluminum,[1] in that hydroxylic media are employed.

Dimerization of Ethylene. When ethylene is pressured into an alcoholic solution of rhodium trichloride, it is converted to a mixture of 1- and 2-butene to the complete exclusion of higher molecular weight products. The conversion as well as the composition of the butene mixture is dependent on the temperature, the reaction time, and the quantity of catalyst. For example, the product obtained when a 3% solution of rhodium chloride[2] in methanol was pressured to 1000 atm. with ethylene at 45° was shown by gas chromatography to be composed of 2% 1-butene, 78% *trans*-2-butene, and 20% *cis*-2-butene. The product obtained at 150° contained approximately 5% 1-butene. This increase in the concentration of 1-butene in the product prepared at an elevated temperature parallels

the known change in composition of the equilibrium mixture of butenes with temperature.[3] However, dimerization at 30° gave a product containing 38% 1-butene, whereas the equilibrium mixture of straight-chain butenes at 30° contains only approximately 3% of this isomer. When this mixture rich in 1-butene was treated with rhodium chloride for 16 hr. at 30°, the 1-butene content decreased to less than 5%. The high concentration of 1-butene in the product obtained at low temperatures and short reaction times indicates that the terminal olefin is the primary product of the reaction. For a given temperature and reaction time, the conversion of ethylene parallels the concentration of catalyst.

Ethanol or methanol was generally employed as solvent, although good results were also obtained by simply pressuring ethylene into a vessel containing solid rhodium chloride. Ethylene pressures in excess of 100 atm. were employed in most of the work; however, pressures as low as 1 atm. could be used.

Ruthenium chloride[4] as catalyst at 50° also gave a mixture of butenes. At 150°, however, the product consisted of approximately 70% butenes and 30% higher olefins, chiefly hexenes and octenes. Ruthenium tribromide and platinic chloride are also catalysts for the dimerization of ethylene but are not so effective as rhodium chloride. The dimerization of ethylene to butenes with a palladium chloride–ethylene complex in nonhydroxylic solvents has been reported.[5]

Additions with Propylene. Dimerization of propylene with rhodium chloride at 50° or ruthenium chloride at 207° gave low conversions to straight- and branched-chain C_6-olefins which were not completely characterized.

Ethylene and propylene reacted in the presence of rhodium chloride at 60° to give approximately equal amounts of C_4-, C_5-, and C_6-olefins. The C_4- and C_6-olefins were similar to those obtained from ethylene and propylene, respectively. Hydrogenation of the C_5-olefins gave approximately equal amounts of *n*-pentane and 2-methylbutane, thus establishing the carbon skeletons of the product, although the location of the double bonds was not determined. The equal distribution of products among C_4-, C_5-, and C_6-olefins indicates that there is no strong selectivity in the reaction of ethylene with propylene.

Dimerization of Butadiene. Attempts to dimerize butadiene at 50° with rhodium chloride catalyst under the best conditions found for the dimerization of ethylene gave very low conversions to products chiefly of higher molecular weight than the dimer. However,

(1) (a) K. Ziegler, *et al., Ann.*, **629**, 172 (1960); (b) K. Ziegler, *et al., Angew. Chem.*, **67**, 541 (1955); (c) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964); (d) G. Hata, *Chem. Ind.* (London), 223 (1965).

(2) The rhodium chloride used in these investigations was commercial RhCl₃·3H₂O.

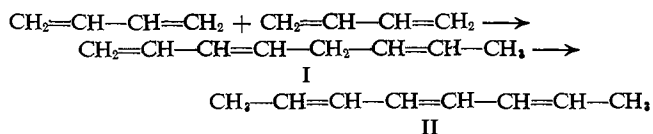(3) J. E. Kilpatrick, *et al., J. Res. Natl. Bur. Std.*, **36**, 559 (1946).

(4) The ruthenium chloride used was the commercial product which was a hydrated mixture of ruthenium tri- and tetrachlorides.

(5) J. T. van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

use of a combination of rhodium chloride with potassium acetate at 100° gave a 54% conversion to a mixture containing approximately 70% dimers and 30% higher molecular weight products. Fractional distillation separated the dimers into approximately equal amounts of higher and lower boiling components. The higher boiling component was identified as 2,4,6-octatriene by hydrogenation to *n*-octane (3 moles of hydrogen required), by the correspondence of its boiling point and refractive index with reported values,[6] and by ultraviolet and infrared spectral analyses, which showed it to be a conjugated triene free of terminal unsaturation. Treatment of the triene with a trace of iodine at room temperature converted it to the known[6a] all-*trans* 2,4,6-octatriene, m.p. 52–54°.

The lower boiling dimer fraction comprised a mixture of dienes and trienes as indicated by quantitative hydrogenation. When a portion of this material was heated with alcoholic potassium hydroxide and distilled, vinylcyclohexene and additional 2,4,6-octatriene were obtained. These results indicate that the lower boiling dimer fraction consisted of a mixture of vinylcyclohexene and incompletely conjugated linear dimers of butadiene. The latter were converted to the conjugated trienes by the alkali.

By analogy with the dimerization of ethylene, it is proposed that the dimerization of butadiene yields an incompletely conjugated triene, such as I, as the primary adduct and that this is subsequently isomerized to the more stable 2,4,6-octatriene, II. Presumably, the

$$CH_2=CH-CH=CH_2 + CH_2=CH-CH=CH_2 \longrightarrow$$
$$CH_2=CH-CH=CH-CH_2-CH=CH-CH_3 \longrightarrow$$
$$\text{I}$$
$$CH_3-CH=CH-CH=CH-CH=CH-CH_3$$
$$\text{II}$$

vinylcyclohexene is formed simultaneously and independently by a noncatalyzed thermal reaction. The conversion of butadiene to noncyclic dimers has been effected[7] with combinations of triethylaluminum with several cobalt compounds. The products are chiefly 3-methylheptatrienes. Similar products were obtained using "cobalt–diene complexes."[8] Combinations of nickel compounds and reducing agents have also given noncyclic dimers from butadiene.[9]

Dimerization of Methyl Acrylate. The linear dimerization of an acrylic compound has also been accomplished for the first time by the use of rhodium and ruthenium chlorides. Thus, a high yield of dimethyl 2-hexenedioate was obtained by heating a solution of methyl acrylate in methanol to 140° in the presence of rhodium chloride. Essentially no higher molecular weight products were formed. The dimer was char-

$$CH_2=CHCOOCH_3 \xrightarrow[\text{MeOH}]{RhCl_3 \cdot 3H_2O}$$
$$CH_3OOCCH=CHCH_2CH_2COOCH_3$$
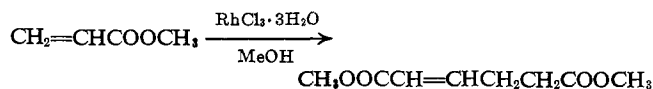
(6) (a) Urion, *Kolloid-Z.*, 63, 86 (1933); (b) R. Kuhn and C. Grundmann, *Ber.*, 71, 442 (1938).
(7) S. Otsuka, T. Kikuchi, and T. Taketomi, *J. Am. Chem. Soc.*, 85, 3709 (1963); S. Tanaka, K. Mabuchi, and N. Shimazaki, *J. Org. Chem.*, 29, 1626 (1964).
(8) D. Wittenberg, *Angew. Chem.*, 75, 1106 (1963).
(9) L. B. Luttinger, *J. Org. Chem.*, 27, 1591 (1962).

acterized through its physical constants, infrared and ultraviolet spectra, and by hydrogenation to dimethyl adipate. The dimerization was also accomplished in 48% yield with ruthenium chloride at 210°. Surprisingly, addition of a small amount of ethylene to the latter system permitted use of a much lower temperature, *i.e.*, 150°, and gave a 56% yield of dimer and a low conversion to the ethylene–methyl acrylate adduct, methyl 3-pentenoate (*vide infra*). The marked promoting activity of ethylene in this reaction is of interest in respect to the mechanism of the catalysis.

Addition of Ethylene to Butadiene. The addition of ethylene to butadiene with rhodium chloride catalyst occurs with great facility and to the almost complete exclusion of the dimerization of either component. The reaction occurs rapidly at 50° in high conversions to give over 90% yields of a mixture of 1,4- and 2,4-hexadiene. In the presence of excess ethylene and at somewhat higher temperatures (*e.g.*, 100°), further reaction occurs to give chiefly C_8-diolefins formed by the addition of ethylene to the hexadienes. The addition of ethylene to butadiene, 1,3-pentadiene and isoprene to give 1,4-dienes has been accomplished[1c,8] using a combination of iron acetylacetonate and triethylaluminum. This process is stereospecific and gives exclusively the *cis* isomers but is not structurally specific and gives a mixture of isomeric products from 1,3-pentadiene and from isoprene.

The 1,4-hexadienes (b.p. 65°), 2,4-hexadienes (b.p. *ca.* 83°), and C_8-1,4-dienes (b.p. 110°) were easily separated by distillation. Gas chromatography was employed to separate the *cis–trans* isomers of the different hexadienes. By this technique, 1-*trans*-4-hexadiene and 1-*cis*-4-hexadiene were isolated for infrared characterization as were the *trans,trans*, *cis,trans* and *cis,cis* forms of 2,4-hexadiene. Gas chromatography was also effective for separating the structurally isomeric C_8-diolefins, *viz.*, 3-ethyl-1,4-hexadiene and 3-methyl-1,4-heptadiene. Among the hexadienes studied, the *trans* isomers were the lower boiling and had lower refractive indices and shorter elution times on a chromatographic column than did the *cis* isomers.

Use of mild reaction conditions gave low conversions to products that were almost exclusively 1,4-hexadiene. As more vigorous conditions were employed, the 2,4-hexadiene content rose and some C_8-diolefins were formed. This suggests that 1,4-hexadiene is the primary product of the addition and that 2,4-hexadiene is formed by a subsequent isomerization. This reaction sequence is parallel to that proposed for the dimerization of ethylene.
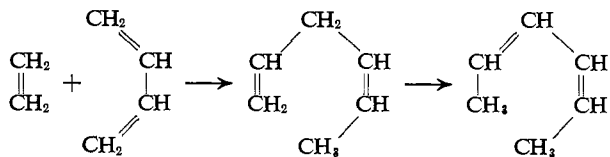
The formation of C_8-dienes in this system is believed to involve the addition of ethylene to *conjugated* C_6-dienes. Thus, 1,4-hexadiene may isomerize to the two possible conjugated C_6-dienes, 1,3- and 2,4-hexadiene. Reaction of these dienes with ethylene would give two isomeric nonconjugated C_8-diolefins.

$$CH_2=CH-CH_2-CH=CH-CH_3$$

$$CH_2=CH-CH=CH-CH_2CH_3 \quad CH_3-CH=CH-CH=CH-CH_3$$

$$\downarrow C_2H_4 \qquad\qquad \downarrow C_2H_4$$

$$CH_3-CH=CH-CH-CH_2CH_3 \quad CH_3CH_2-CH=CH-CH-CH_3$$

| |
CH
‖
CH$_2$
3-ethyl-1,4-hexadiene

| |
CH
‖
CH$_2$
3-methyl-1,4-heptadiene

Examination of the product indicated that these unconjugated C$_8$-diolefins were produced exclusively. Thus, the C$_8$-diolefins were separated by gas chromatography and hydrogenated to give 3-ethylhexane and 3-methylheptane. In this proposed mode of addition, the ethylene becomes attached to the substituted terminal carbon atom of the diene system. This is in accord with the observed orientation in the addition of ethylene to 1,3-pentadiene (*vide infra*).

The formation of 3-ethyl-1,4-hexadiene would require the intermediate formation of 1,3-hexadiene. Numerous reaction mixtures have been carefully examined for this diene, but it has never been found in more than trace quantities. Accordingly, it is assumed that 1,3-hexadiene is so reactive toward ethylene that it is consumed as soon as it is formed. This assumption is supported by the fact that the analogous terminally substituted butadiene, 1,3-pentadiene, is by far the most reactive diene that has been examined in the reaction with ethylene.

Whereas the addition of ethylene to butadiene was normally carried out in dilute solutions of the catalyst in ethanol or methanol, it was found, surprisingly, that if only one or two parts of alcohol per part of catalyst was employed, the reaction proceeded substantially as well as in the presence of a gross quantity of solvent. If, however, all solvent was excluded from the reaction system, the conversions obtained were approximately one-third those obtained with alcohol present. Other solvents that appear to promote the reaction include *t*-butyl alcohol and acetone. In contrast, gross quantities of diethyl ether or chloroform can be tolerated in the reaction system but do not appear to have a promoting effect.

In addition to influencing the conversion, the amount of alcohol used appeared to influence strongly the ratio of *cis*- to *trans*-hexadienes obtained. With little or no alcohol present, the ratio of *trans* to *cis* isomer is around 2.6. In the presence of gross quantities of alcohol, the *trans/cis* ratio rises to 10 or 20 (Table I).

Table I. Effect of Ethanol on the Rhodium Chloride Catalyzed Addition of Ethylene to Butadiene[a]

Ethanol, ml.	Conversion, %	Fraction isomerized[b]	*trans/cis* ratio[c]
0	26	0.11	2.7
0.5	46	...	2.5
1.0	76	0.33	2.8
10	86	...	3.4
200	85	...	19

[a] Reaction conditions: 0.5 g. of RhCl$_3$·3H$_2$O; 1:1 molar ratio ethylene/butadiene; 50°; 16 hr. [b] This is the fraction of the hexadiene that has been isomerized to the conjugated isomer, *i.e.*, 2,4-hexadiene/total hexadienes. [c] This is the ratio of 1-*trans*-4-hexadiene to 1-*cis*-4-hexadiene.

The effect of water as solvent was also examined since, as noticed earlier, modest conversions were obtained by contacting the reactants with the hydrated catalyst. When small quantities of extra water were added to the catalyst (*e.g.*, 0.5 part of water per part of catalyst), the conversion to adduct increased severalfold. If, however, a large quantity of water was added, the reaction was almost completely inhibited. Samples of commercial hydrated rhodium chloride which were subsequently dehydrated either thermally or by treatment with thionyl chloride were substantially inactive in the ethylene–butadiene reaction unless water was added to the system.

The total conversion and the product distribution are both strongly dependent on the ethylene–butadiene ratio. Thus, at 50°, maximum conversions were obtained at an ethylene–butadiene ratio of 1:1, and the major products were 1:1 adducts (Table II). The production of C$_8$-diolefins and the dimerization of ethylene were both favored by employing more ethylene. (Other experiments employing a large excess of ethylene at temperatures of 70–100° gave almost exclusively C$_8$-diolefins.)

Table II. Effect of the Ethylene–Butadiene Ratio in the Rhodium Chloride Catalyzed Addition[a]

Mole fraction of C$_2$H$_4$	Conversion, %	C$_4$	C$_6$	C$_8$	Nonvolatile residue	Fraction of C$_6$ dienes isomerized
0.00	2	...	...	...	100	...
0.19	32	1	78	3	18	0.09
0.45	54	2	91	3	4	0.20
0.59	39	5	88	5	2	0.16
1.00	23	100	...	...	0	...

[a] Ethylene and butadiene were charged in the indicated ratios (expressed as mole fraction of ethylene in the total hydrocarbons charged) with 0.2 g. of RhCl$_3$·3H$_2$O and 1 ml. of ethanol, and the mixtures were heated for 16 hr. at 50°.

The use of 0.45 mole fraction of ethylene gave a product comprising 2% butenes and 94% C$_6$- and C$_8$-dienes. The dienes arose from the addition of ethylene to butadiene, whereas the butenes arose from dimerization of ethylene. Thus, under these conditions the reaction between the unlike components occurred at a rate approximately 50 times that of the dimerization of ethylene. The nonvolatile portion of the product is highest in reaction mixtures rich in butadiene. This suggests that some condensation reaction of butadiene is responsible for the nonvolatile portion of the product.

The extent of the isomerization of the initially formed 1,4-hexadiene to 2,4-hexadiene parallels the over-all conversion (see Tables I and II). Thus, vigorous reaction conditions give high conversions and high ratios of conjugated to unconjugated products.

Addition of Ethylene to 1,4- and 2,4-Hexadiene. Since 1,4- and 2,4-hexadiene are formed by the addition of ethylene to butadiene and appear to be intermediates in the formation of C$_8$-diolefins in the ethylene–butadiene reaction, a study of their alkylation has been made. As shown in Table III, C$_8$-diolefins were obtained when these hexadienes were treated with eth-

Table III. Reactions of 1,4- and 2,4-Hexadiene[a]

Diene employed (1 mole)	Quantity of ethylene, moles	1,4-Hexa-diene, %	2,4-Hexa-diene, %	C$_8$-Di-olefins, %
1,4-Hexadiene	0	73	26	0
1,4-Hexadiene	1.5	14	59	20
2,4-Hexadiene	1.5	0	35	65

[a] In each experiment, 0.2 g. of RhCl$_3$·3H$_2$O and 1 ml. of ethanol were employed with reaction times of 16 hr. at 50°.
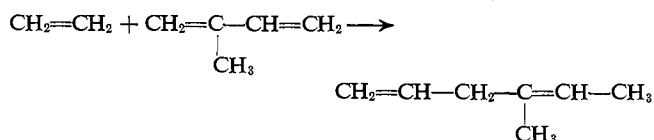
ylene in the presence of rhodium chloride catalyst at 50°. The conjugated diene gave somewhat more than three times the conversion obtained with the nonconjugated isomer. These results suggest that the 1,4-diene isomerized to the 2,4-diene prior to reaction with ethylene. The isomerization appears to proceed to a much greater extent in the presence of ethylene than in the ethylene-free system. This promoting effect of ethylene on the isomerization of the 1,4-diene is analogous to the promoting effect observed in the dimerization of methyl acrylate (*vide supra*).

The C$_8$-diolefins were separated by gas chromatography and identified as 3-ethyl-1,4-hexadiene and 3-methyl-1,4-heptadiene. The carbon skeletons were determined by hydrogenation to the appropriate alkanes. Further characterization was based on boiling point, refractive indices, and infrared spectra. As proposed in the earlier section on the ethylene-butadiene reaction, it is probable that 1,3-hexadiene is an intermediate in the synthesis of 3-ethyl-1,4-hexadiene and, thus, it would follow that interconversion between the two conjugated dienes occurs.

Addition of Ethylene to 1,3-Pentadiene. The reaction of ethylene with 1,3-pentadiene was the most facile addition encountered in this work. Conversions of over 95% were obtained at 50° in the presence of 0.2% rhodium trichloride trihydrate. The adduct was shown to be 3-methyl-1,4-hexadiene. Catalytic hydrogenation gave 3-methylhexane (identified by its infrared spectrum). The infrared spectrum of the diene showed that it contained two nonconjugated double bonds, one in a vinyl group and the other internal (a *cis–trans* mixture). This structure arises from addition of ethylene to the 4-position of the diene.

$$CH_2{=}CH_2 + HC{=}CH{-}CH{=}CH_2 \longrightarrow$$
$$\qquad\qquad\quad \underset{\displaystyle CH_3}{|}$$

$$CH_2{=}CH{-}\underset{\displaystyle \underset{|}{CH_3}}{CH}{-}CH{=}CH{-}CH_3$$
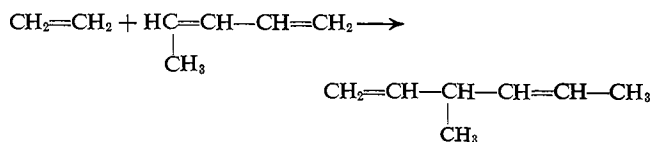
Addition of Ethylene to Isoprene. The reaction of ethylene with isoprene was more sluggish than that of ethylene with butadiene, and, at 50°, only very low conversions were obtained. The 1:1 adduct, a nonconjugated diene, was identified as 4-methyl-1,4-hexadiene by its infrared spectrum, by hydrogenation to 3-

$$CH_2{=}CH_2 + CH_2{=}\underset{\displaystyle \underset{|}{CH_3}}{C}{-}CH{=}CH_2 \longrightarrow$$

$$CH_2{=}CH{-}CH_2{-}\underset{\displaystyle \underset{|}{CH_3}}{C}{=}CH{-}CH_3$$

methylhexane, and by comparison of its physical constants with published values.[10] The structure of the

product corresponds to the attachment of the ethylene residue to the terminal carbon atom of isoprene nearer the methyl group. When more catalyst was employed and the temperature raised to 70°, a high conversion was obtained, but the product was chiefly a 2:1 adduct (of undetermined structure) formed by the addition of a second molecule of ethylene to the primary adduct. Thus, in this system it was not possible to obtain high conversions of a 1:1 adduct.

Addition of Ethylene to 2-Chloro-1,3-butadiene. The addition of ethylene to 2-chloro-1,3-butadiene at 50° with a rhodium chloride catalyst gave a 1:1 adduct in approximately 40% conversion. The product possessed conjugated unsaturation and is presumed to be either 2- or 3-chloro-2,4-hexadiene. The position of the chlorine atom has not been determined.

Addition of Propylene to Butadiene. Propylene reacted with butadiene to give a 1:1 adduct identified as 2-methyl-1,4-hexadiene by its physical constants and infrared spectrum. The addition is a little slower than that of ethylene to butadiene and, accordingly, slightly greater quantities of catalyst and/or higher temperatures are required to obtain a given conversion. In this system, the primary product, *i.e.*, the 1,4-diene, apparently rearranges to the conjugated isomer less readily than does the ethylene–butadiene product. Since the conjugated isomer is required for the addition of a second molecule of olefin, multiple addition is repressed even under somewhat forcing conditions. Accordingly, 85% yields of the nonconjugated 1:1 adduct were obtained readily.

$$CH_2{=}CH + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$
$$\quad\ \underset{\displaystyle CH_3}{|}$$

$$CH_2{=}\underset{\displaystyle \underset{|}{CH_3}}{C}{-}CH_2{-}CH{=}CH{-}CH_3$$
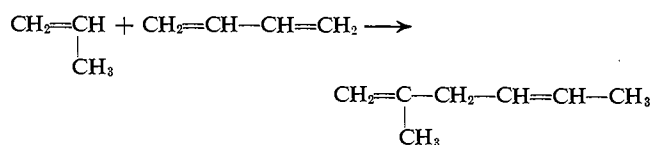
The product was separated into two isomers by gas chromatography. The major component was identified as *trans*-2-methyl-1,4-hexadiene by its infrared spectrum. Similarly, the minor component was shown to be the *cis* isomer.

Addition of Propylene to Isoprene. In contrast to the reaction between ethylene and isoprene, which was difficult to control so as to obtain the 1:1 product, the reaction between propylene and isoprene proceeded smoothly to give the 1:1 adduct. As discussed above, it appears that the branched structure of the propylene adducts resists isomerization and thus curtails the addition of a second molecule of olefin. With this combination, the 1:1 adduct was obtained in high conversion although appreciably more catalyst and higher temperatures were required to secure high conversions than in the reactions with ethylene. By analogy with the demonstrated structures of the ethylene–isoprene and the propylene–butadiene adducts, it is believed that this adduct is 2,4-dimethyl-1,4-hexadiene.

Addition of Ethylene to Styrene. The rhodium chloride catalyzed addition of ethylene to styrene proceeded smoothly at 50° to give 2-phenyl-2-butene in 40% conversion. The adduct was identified by means of its physical constants and by hydrogenation to 2-phenylbutane. In additional confirmation, the product
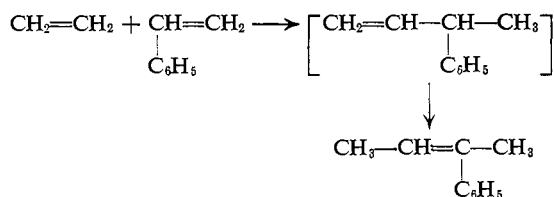
(10) G. Egloff, "Physical Constants of Hydrocarbons," Vol. V., Reinhold Publishing Corp., New York, N. Y., 1953, p. 426.

Table IV. Dimerization of Ethylene[a]

Rhodium chloride catalyst, g.	Solvent	Pressure of C_2H_4	Temp., °C.	Product
3	100 ml. CH₃OH	1000 atm.	45	178 g. of 2% 1-butene 77% trans-2-butene 20% cis-2-butene
0.3	100 ml. CH₃OH	1000 atm.	50	138 g. of butenes
0.3	100 ml. CH₃OH	1000 atm.	30	50 g. of 38% 1-butene[b] 44% trans-2-butene 18% cis-2-butene
2	None	500 atm.	55	234 g. of 3% 1-butene 69% trans-2-butene 27% cis-2-butene
2	100 ml. CH₃OH	34 atm.	50	115 g. of butenes
1	None	54 atm.	47	103 g. of butenes
1	None	27 atm.	47	13 g. of butenes
0.2	1 ml. C₂H₅OH	(181 g. C₂H₄)	52	36 g. of butenes
2 (ruthenium chloride)	100 ml. C₂H₅OH	1000 atm.	50	158 g. of butenes
0.62	100 ml. CH₃OH	700 atm.	130	120 g. of butenes 27 g. of hexenes 15 g. of octenes 11 g. of C_{10}- and C_{12}-olefins
0.44 (chloroplatinic acid)	100 ml. CH₃OH	1000 atm.	200	22 g. of butenes

[a] Reactions were conducted in a 400-ml., silver-lined pressure vessel for 16 hr. [b] This product was held at 30° for 16 hr. with 2 g. of rhodium chloride in 100 ml. of MeOH. At the end of this treatment the product composition was 4% 1-butene, 68% trans-2-butene, and 27% cis-2-butene.

had a double bond conjugated with a benzene ring as indicated by its ultraviolet spectrum and the infrared spectrum showed the absence of terminal unsaturation. It is noteworthy that the ethylene residue became attached to the α-carbon atom of styrene. This is reminiscent of the addition of ethylene to the substituted

$$CH_2{=}CH_2 + \underset{\underset{C_6H_5}{|}}{CH}{=}CH_2 \longrightarrow \left[CH_2{=}CH{-}\underset{\underset{C_6H_5}{|}}{CH}{-}CH_3 \right]$$

$$\downarrow$$

$$CH_3{-}CH{=}\underset{\underset{C_6H_5}{|}}{C}{-}CH_3$$

atom (the 4-position) of 1,3-pentadiene. It is presumed that the primary adduct here was 3-phenyl-1-butene which rearranged to the conjugated isomer.

Addition of Ethylene to Methyl Acrylate. Reaction of methyl acrylate with excess ethylene at 150° in the presence of ruthenium chloride gave a high yield of methyl esters of linear monounsaturated acids. The principal product was methyl 3-pentenoate (47% yield). Esters of acids containing seven and nine carbon atoms

$$CH_2 = CH_2 + CH_2{=}CHCOOCH_3 \longrightarrow$$

$$[CH_2{=}CH{-}CH_2{-}CH_2COOCH_3]$$

$$\swarrow^{C_2H_4} \qquad \downarrow$$

$$[CH_2{=}CH{-}(CH_2)_4COOCH_3] \qquad CH_3{-}CH{=}CH{-}CH_2COOCH_3$$

$$\swarrow$$

etc.
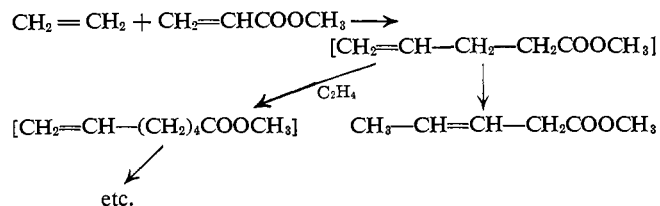
were also isolated in yields of 12 and 9%, respectively. Other products included the linear dimer of methyl acrylate (23% yield) and olefins formed by condensation of ethylene. The unsaturated esters were characterized by boiling point, refractive index, saponification equivalent, and infrared analysis. Hydrogenation of the product followed by fractional distillation yielded a series of saturated esters which were in turn identified

by their physical constants and saponification equivalents. Rhodium chloride as a catalyst for this reaction at 120° gave a mixture of esters similar to that obtained using ruthenium chloride.

Experimental Section

Dimerization of Ethylene with Rhodium Chloride Catalyst.[11] A 400-ml., silver-lined pressure vessel was charged with 100 ml. of methanol and 3 g. of rhodium chloride ($RhCl_3 \cdot 3H_2O$, Engelhard Industries, Inc.). The temperature was raised to 45°, agitation was commenced, and ethylene was injected to a pressure of approximately 400 atm. The pressuring was accompanied by a 10° rise in temperature. When the pressure had fallen to 200 atm., the vessel was repressured to 400 atm. The mixture was maintained at 45° over a 6-hr. period while the pressure was gradually increased to 1000 atm. Over 80% of the ethylene absorption occurred during the first 4 hr. The reaction vessel was cooled, and the product (178 g.) was condensed in a trap cooled with solid carbon dioxide. Analysis of the product by gas chromatography showed it to contain 2% 1-butene, 78% trans-2-butene, and 20% cis-2-butene. Under these conditions, the conversion of ethylene was apparently limited by the size of the reaction vessel since the quantity of butenes (178 g., 305 ml.) when added to that of the methanol (100 ml.) corresponds approximately to the volume of the container.

Other experiments on the dimerization of ethylene are summarized in Table IV.

Dimerization of Propylene. The pressure vessel described above was charged with 100 ml. of ethanol, 3 g. of rhodium chloride, and 190 g. of propylene. The mixture was heated at 50° for 16 hr. with agitation. The propylene was cautiously vented, and the ethanol and reaction products were distilled from the catalyst.

(11) T. Alderson, U. S. Patent 3,013,066 (1961).

The distillate was washed twice with water and redistilled to give 6 g. of C_6-olefins, b.p. 62–67°, $n^{25}D$ 1.3921–1.3939. The infrared spectra of selected fractions showed the presence of *trans* unsaturation and also of terminal methylenic unsaturation ($CH_2=CRR'$). Comparison with spectra of known olefins suggested that 2-methyl-2-pentene was the major component.

In an experiment conducted in methanol at 207° (900 atm.) with ruthenium chloride as catalyst, propylene was converted to dimers and higher boiling olefins in 20% conversion. Fractional distillation of the product showed that over half of it was C_6-olefins and that C_9-olefins made up most of the remainder.

Addition of Ethylene to Propylene. A 400-ml., silver-lined pressure vessel was charged with 100 ml. of ethanol and 3 g. of rhodium chloride. Propylene (168 g., 4 moles) was condensed into the vessel which was then heated to 60° and pressured with ethylene (1000 atm.). This pressure was maintained by repressing with ethylene for 16 hr. while the mixture was agitated at 60°. (Repressurings totaling 580 atm. were required.) The mixture was cooled to room temperature and vented through a trap cooled in solid carbon dioxide to obtain 225 ml. of condensate. Distillation of this material through a low-temperature column gave propylene and butenes in a ratio of approximately 2:1. The residue, which consisted of the higher olefins and alcohol, was washed with aqueous calcium chloride to give 23 ml. of hydrocarbons. The amber liquid in the reaction vessel (177 ml.) was distilled under reduced pressure to give 160 ml. of distillate. This was washed twice with aqueous calcium chloride solution to give 90 ml. of hydrocarbons which was combined with the 23 ml. from the trap to give 113 ml. of product. Gas chromatography showed that this material contained equal quantities of C_5- and C_6-olefins and that these made up 95% of the total. Distillation at atmospheric pressure through a Podbielniak column gave C_5-olefins, b.p. 33–36°, $n^{25}D$ 1.3900–1.3950. The C_5- and C_6-fractions were hydrogenated, and the resulting alkanes were characterized by gas chromatography and examination of their infrared spectra. The C_5-alkanes comprised approximately equal amounts of *n*-pentane and 2-methylbutane. The C_6-fraction was shown to consist of approximately equal quantities of *n*-hexane and 2-methylpentane. This demonstrates that straight- and branched-chain isomers were formed to about equal extents.

Dimerization of Butadiene with Rhodium Chloride–Potassium Acetate. A 400-ml., silver-lined pressure vessel was charged with 100 ml. of methanol, 6 g. of potassium acetate, and 2 g. of rhodium chloride. Butadiene (216 g.) was condensed into the vessel, and the temperature was raised to 100°. A pressure of 190 atm. developed. The reaction mixture was held at 100° for 16 hr. with agitation, cooled to 25°, and the excess butadiene was distilled into a cold trap (88 g. recovered). The reaction mixture, 196 ml. of dark-colored liquid, was distilled to a pot temperature of 80° (5 mm.) to leave a still residue of 36 g. The distillate (140 ml.) was washed twice with aqueous calcium chloride solution to give 80 ml. of hydrocarbon, $n^{25}D$ 1.4621. This product had an absorption maximum at 2640 Å. ($k = 137$). Since 2,4,6-octatriene has $k = 430$ (see below), it is estimated that this material contains 32%

of the conjugated triene. This product was combined with products from similar experiments and fractionally distilled to give two principal fractions.

The higher boiling fraction, b.p. 65–66° (40 mm.), $n^{25}D$ 1.530–1.536, was 2,4,6-octatriene (lit.[6a] b.p. 43° (10 mm.), $n^{27}D$ 1.5131). It had an absorption maximum at 2660 Å. ($k = 430$); its infrared spectrum showed there was no terminal unsaturation. These data indicate that the compound is a conjugated triene with internal double bonds. Quantitative hydrogenation required 3 moles of hydrogen and gave exclusively *n*-octane, b.p. 119–123°, $n^{25}D$ 1.3952 (b.p. 125.66°, $n^{20}D$ 1.3974, is reported[12]), with an infrared spectrum identical with that of a known sample. When a sample of the 2,4,6-octatriene was treated with a trace of iodine, it was completely converted in 1 hr. to a white, crystalline solid, m.p. 52–54°. The solid, when dissolved in alcohol, still had the ultraviolet spectrum characteristic of a conjugated triene, λ_{max} 2630 Å. This solid is the all-*trans*-2,4,6-octatriene (lit.[6a] m.p. 52.5°). The 2,4,6-octatriene fraction obtained upon distillation is presumably a mixture of the several stereoisomeric conjugated octatrienes.

The lower boiling fraction, b.p. 41–48° (40 mm.), $n^{25}D$ 1.450–1.467, consisted chiefly of vinylcyclohexene and octatrienes in which the three double bonds were not all conjugated. Hydrogenation equivalents of selected samples varied from 41 to 57 (calcd. for C_8-triene, 36; for a C_8-diene, 54). A portion of this material was heated on a steam bath for 6 hr. with a solution of potassium hydroxide in 2-ethoxyethanol. Fractional distillation of the recovered hydrocarbons gave vinylcyclohexene, b.p. 35° (30 mm.), $n^{25}D$ 1.4580 (lit.[13] b.p. 125.8–126.5°, $n^{20}D$ 1.4624) and 2,4,6-octatriene, b.p. 34° (10 mm.), $n^{25}D$ 1.5330. The identification of the vinylcyclohexene was confirmed by comparing its infrared spectrum with that of a known sample.

Methyl Acrylate Dimerization. A. Rhodium Chloride Catalyst. A 400-ml. silver-lined pressure vessel was charged with 79 g. of methanol, 129 g. of methyl acrylate, 3 g. of rhodium chloride, and 2 g. of hydroquinone. The mixture was heated to 140° and held there for 10 hr. Distillation of the reaction mixture gave over 100 g. of recovered methyl acrylate and 9 g. of dimethyl α-dihydromuconate (dimethyl 2-hexenedioate), b.p. 102–105° (4 mm.), $n^{25}D$ 1.4497. Farmer[14] reported b.p. 127° (14 mm.). Only 0.6 g. of nonvolatile higher molecular weight products were formed.

The dimethyl α-dihydromuconate was characterized by its infrared and ultraviolet spectra. It was hydrogenated over a palladium catalyst at 80° to give dimethyl adipate. Saponification of the latter gave adipic acid, m.p. 147–150°, m.m.p. 149–151°.

B. Ruthenium Chloride Catalyst. In the pressure vessel was placed 40 g. of methanol, 144 g. of methyl acrylate, 2 g. of ruthenium chloride, and 2 g. of hydroquinone. The mixture was heated to 210° for 10 hr. Fractional distillation of the product gave a mixture of methyl acrylate and methyl propionate (65 g.), dimethyl α-dihydromuconate (35 g., 44%), b.p. 102–122° (3 mm.), $n^{25}D$ 1.4507, and nonvolatile residue (38 g., 47%).

(12) Reference 10, p. 101.
(13) O. Aschann, *Chem. Ber.*, **57**, 1959 (1924).
(14) E. H. Farmer and L. A. Hughes, *J. Chem. Soc.*, 1940 (1935).

The dimer was characterized by its ultraviolet and infrared absorption spectra.

C. Ethylene-Promoted Ruthenium Chloride. The reaction vessel was charged as in the preceding experiment except that no hydroquinone was employed. Ten grams of ethylene was added to the mixture which was heated to 150° and held there for 16 hr. Distillation of the products gave 83 g. of methyl acrylate, $n^{25}D$ 1.3940; 4 g. of methyl 3-pentenoate, b.p. 26–35° (2 mm.), $n^{25}D$ 1.4160, 34 g. (56% yield) of dimethyl α-dihydromuconate, b.p. 75–88° (2 mm.), $n^{25}D$ 1.4479; and 34 g. of higher boiling products not further characterized. The methyl pentenoate was characterized by its infrared spectrum, which showed nonconjugated carbon–carbon unsaturation, and by hydrogenation to methyl valerate was identified by its physical constants, saponification equivalent, and infrared spectrum.

Addition of Ethylene to Butadiene. A 400-ml. pressure vessel was charged with 0.5 g. of rhodium chloride, 1 ml. of ethanol, 175 g. (2.34 moles) of butadiene, and 75 g. (2.68 moles) of ethylene. The temperature was raised to 50° and held there for 16 hr. while the pressure vessel was agitated. At the end of this time the vessel was cooled to room temperature and vented through a trap to obtain 30 ml. of liquid condensate that was principally butadiene. The pressure vessel contained 295 ml. of clear orange liquid that was distilled to a pot temperature of 50° (5 mm.) to leave a residue of 7 g. The distillate, 270 ml. (189 g.), $n^{25}D$ 1.4209, was assayed by gas chromatography. It contained 8% butadiene, 67% 1,4-hexadiene, and 22% 2,4-hexadiene.

The above product was combined with those from similar experiments and distilled at atmospheric pressure through a Podbielniak column. Two main fractions were obtained. The larger fraction, b.p. 65°, $n^{25}D$ 1.4070–1.4100, was 1,4-hexadiene (lit.[15] b.p. 65–66°, $n^{20}D$ 1.4151). This fraction was separated by gas chromatography into two components. The one with the shorter elution time had $n^{25}D$ 1.4060 and was shown by infrared spectroscopy to be the *trans* isomer. The other component had $n^{25}D$ 1.4110 and was shown to be the *cis* isomer. It was noted that the *cis* isomer was somewhat higher boiling than the *trans* since later portions of the 1,4-hexadiene fraction had higher contents of the *cis* isomers than did the earlier parts. Also the refractive index of the fraction rose as the distillation proceeded.

The smaller fraction, b.p. 82–84°, $n^{25}D$ 1.4467–1.4542, was 2,4-hexadiene (lit.[16] b.p. 80–82°, $n^{20}D$ 1.4518). It was separated by gas chromatography into three components. Here again the elution times paralleled the boiling points.

1. The lowest boiling 2,4-hexadiene, $n^{25}D$ 1.4462, was assigned the *trans,trans* structure on the basis of its infrared spectrum. It had an ultraviolet maximum at 2260 Å., (log ϵ 4.42). This maximum had two shoulders.

2. The middle boiling 2,4-hexadiene, $n^{25}D$ 1.4523, was assigned the *cis,trans* structure on the basis of its infrared spectrum. It had an ultraviolet maximum at 2290 Å., (log ϵ 4.27).

3. The highest boiling 2,4-hexadiene, $n^{25}D$ 1.4557, was assigned the *cis,cis* structure on basis of its infrared

(15) R. Paul and S. Tchelitcheff, *Compt. rend.*, **223**, 1136 (1946).
(16) Reference 10, p. 413.

spectrum. It had a broad ultraviolet maximum at 2310 Å., (log ϵ 4.35).

Both the 1,4-hexadiene and the 2,4-hexadiene gave exclusively hexane upon catalytic hydrogenation.

The addition of ethylene to butadiene was conducted similarly to the above procedure except that 1 g. of rhodium chloride was employed as catalyst and 1.2 moles of ethylene per mole of butadiene was used. Under these conditions, in addition to the hexadienes described above, approximately 25% of the product was C_8-dienes, b.p. 110°, $n^{25}D$ 1.4203–1.4217. The infrared spectrum of this material showed that it contained both terminal and internal double bonds, and the ultraviolet spectrum showed that these bonds were not conjugated. Gas chromatography separated the C_8-dienes into two components in approximately equal amounts. The material that eluted first had $n^{25}D$ 1.4201. Catalytic hydrogenation gave 3-methylheptane, identified by its infrared spectrum. The other component, $n^{25}D$ 1.4211, was catalytically hydrogenated to give 3-ethylhexane which was identified by its infrared spectrum. From these data it is concluded that the two C_8-diolefins were 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene.

When the addition of ethylene to butadiene was conducted at 100° using over 2 moles of ethylene per mole of butadiene, only a trace of hexadienes was obtained. The two principal products were C_8-diolefins. One, b.p. 109°, $n^{25}D$ 1.4208–1.4214, was nonconjugated C_8-diolefins (see above). The other, b.p. 72–75° (100 mm.), $n^{25}D$ 1.4622–1.4649, was C_8-diolefins in which the double bonds were conjugated. The ultraviolet spectrum of the latter corresponds to that of a trialkylbutadiene. Hydrogenation of the nonconjugated diolefin fraction gave a material which infrared spectroscopy indicated to be almost pure 3-ethylhexane. Hydrogenation of the conjugated diolefins gave a mixture containing approximately 70% 3-methylheptane and 30% 3-ethylhexane. Thus, at the higher temperatures employed in this experiment, considerable isomerization of the 1,4-C_8-dienes to the conjugated isomers occurred. The 3-methylheptadiene appears to isomerize more readily than does the 3-ethylhexadiene.

Addition of Ethylene to 1,3-Pentadiene. A pressure vessel was charged with 0.2 g. of rhodium chloride, 1 ml. of ethanol, 68 g. (1 mole) of 1,3-pentadiene, and 42 g. (1.5 moles) of ethylene. The mixture was heated at 50° with agitation for 16 hr., cooled to room temperature, and vented to remove excess ethylene. Distillation of the light yellow, liquid product (125 ml.) to a pot temperature of 78° (8 mm.) gave 110 ml. of distillate, $n^{25}D$ 1.4150, and 1.7 g. of residue. Redistillation through a packed column at atmospheric pressure gave 9 ml. of lower boiling product and 89 ml. of 3-methyl-1,4-hexadiene, b.p. 84°, $n^{25}D$ 1.4132. The infrared spectrum of the material showed that it contained a terminal and an internal double bond. A portion of the product was hydrogenated at atmospheric pressure and room temperature over platinum catalyst to give a saturated hydrocarbon which was identified by its infrared spectrum as 3-methylhexane.

Addition of Ethylene to 2,4-Hexadiene. A pressure vessel was charged with 0.2 g. of rhodium chloride, 1 ml. of ethanol, 118 ml. (1 mole) of 2,4-hexadiene, and 42 g. (1.5 moles) of ethylene. The reaction was car-

ried out at 50° with agitation for 16 hr. The reaction vessel was cooled to room temperature, and the excess ethylene was vented. The reaction mixture (143 ml.) was distilled to a pot temperature of 74° (10 mm.) to obtain 130 ml. of distillate and 1 g. of residue. The distillate was fractionally distilled at atmospheric pressure, whereupon 35 ml. of 2,4-hexadiene was recovered and 60 ml. of unconjugated C_8-dienes, b.p. 109–110°, $n^{25}D$ 1.4210, was obtained. A portion of this diolefin mixture was hydrogenated over platinum catalyst to give a mixture of saturated hydrocarbons demonstrated by infrared spectroscopy to be a mixture of 3-methylheptane and 3-ethylhexane.

Addition of Ethylene to Isoprene. A mixture of 1 g. of rhodium chloride, 2 ml. of ethanol, 300 ml. of isoprene, and 80 g. of ethylene was agitated at 50° for 16 hr., cooled to room temperature, and the excess ethylene was vented through a trap. The vessel contained 271 ml. of a clear, orange liquid which was distilled to a pot temperature of 75° at 5 mm. leaving a residue of 3 ml. The distillate (250 ml.) was redistilled to a pot temperature of 99° at atmospheric pressure. The distillation residue, 86 ml., had $n^{25}D$ 1.4439. The principal component of the residue, shown by gas chromatography to make up 46% of the mixture, was the unconjugated diene formed from one molecule of each of the reactants (see below). The next product in abundance, 35%, was a conjugated diolefin. Four other minor components were present.

The above distillation residue was combined with those of similar runs and fractionally distilled at atmospheric pressure. The principal fraction had b.p. 91–92° and $n^{25}D$ 1.4220. Gas chromatography of this material showed it to have a purity of 98%. The infrared spectrum showed the product to be an unconjugated diolefin having both terminal and internal unsaturation. Hydrogenation over a platinum catalyst gave a saturated hydrocarbon characterized by its infrared spectrum as 3-methylhexane. The second fraction, b.p. 109–110.5°, $n^{25}D$ 1.4615, was a conjugated diene believed to have the same carbon skeleton as the diolefin characterized above.

Addition of Ethylene to 2-Chloro-1,3-butadiene. The reaction vessel was charged with 100 ml. of ethanol, 2 g. of rhodium chloride, 186 ml. (2 moles) of freshly distilled 2-chloro-1,3-butadiene, and 56 g. (2 moles) of ethylene. The mixture was maintained at 50° for 16 hr. with agitation. It was then cooled to room temperature, the excess ethylene was vented, and the reaction mixture (325 ml.) was distilled under reduced pressure to give 280 ml. of distillate and 20 g. of residue. The distillate was washed twice with aqueous calcium chloride solution to give 197 ml. of alcohol-free products. These were distilled through a 13-mm. Podbielniak column. Approximately 32 ml. of 2-chloro-1,3-butadiene was recovered. The main fraction (34 ml.) of the product had b.p. 58–60° (60 mm.), $n^{25}D$ 1.4869. This product is a conjugated diolefin obtained from one molecule each of ethylene and chloroprene λ_{max} 2300 Å (log ϵ 4.37).

Anal. Calcd. for C_6H_9Cl: C, 61.81; H, 7.78; Cl, 30.41. Found: C, 61.24; H, 7.81; Cl, 30.90.

Addition of Propylene to Butadiene. A mixture of 2 g. of rhodium chloride, 100 ml. of ethanol, and 126 g. of propylene was heated at 50° while 87 g. of butadiene

was injected gradually over a 6-hr. period. The temperature was held at 50° for an additional 10 hr. and then lowered to room temperature. The pressure vessel was vented through a trap to obtain 100 ml. of condensate. This liquid started to boil at −45°, and at a temperature of 10° approximately 40 ml. remained. This residue was added to the 310 ml. of orange liquid in the pressure vessel. Distillation to a head temperature of 30° at 30 mm. gave a first fraction of 290 ml. After two washings with aqueous calcium chloride solution, 205 ml. (142 g.), $n^{25}D$ 1.4181, remained. A second fraction, 14 g., b.p. *ca.* 35° (2 mm.), $n^{25}D$ 1.4540, was obtained. The first fraction was found by gas chromatography to contain 94% of the 1:1 adduct. Redistillation of this material gave 2-methyl-1,4-hexadiene, b.p. 90–91°, $n^{25}D$ 1.4182. Gas chromatography revealed that this diolefin comprised 93% of one component and 7% of another. These components were isolated by gas chromatography, and it was shown by infrared spectroscopy that the major component was the *trans* diene and the minor component the *cis* diene.

Addition of Propylene to Isoprene. A 400-ml. pressure vessel was charged with 5 g. of rhodium chloride, 10 ml. of ethanol, 260 ml. of isoprene, and 102 g. of propylene. The mixture was heated to 70° for 16 hr., cooled to room temperature, and the propylene was vented into a trap. The reaction vessel contained 325 ml. of a dark red liquid and some red solid. Distillation gave 49 ml. of recovered isoprene, 225 ml. of product, b.p. 60 (atm.) to 70° (1 mm.), and a residue of 18 g. Redistillation of the product at atmospheric pressure gave a principal fraction (155 ml., b.p. 110–114°, $n^{25}D$ 1.4310) that was C_8-diolefin containing nonconjugated double bonds. The infrared spectrum showed that one of the double bonds was in a terminal methylene group ($CH_2=CR_1R_{11}$) and that the other double bond was internal.

Addition of Ethylene to Styrene. A 400-ml. pressure vessel was charged with 2 g. of rhodium chloride, 100 ml. of ethanol, and 173 ml. of styrene. It was pressured with ethylene to 1000 atm. at 50°, and ethylene was repressured as consumed. The pressure drop in the first 3 hr. totaled 340 atm. After 16 hr. the mixture was cooled and vented through a trap. The liquid in the reaction vessel (315 ml.) gave two fractions upon distillation under reduced pressure. The first (224 ml.), after two washings with aqueous calcium chloride solution, yielded 116 ml. of recovered styrene, $n^{25}D$ 1.5262, and the second (72 g.) had b.p. 30–50° (1 mm.), $n^{25}D$ 1.5367. A residue of 8.6 g. remained. Redistillation of the second fraction gave 50 ml. of 2-phenyl-2-butene, b.p. 85–90° (20 mm.), $n^{25}D$ 1.5365 (lit.[17] b.p. 187–189°, $n^{25}D$ 1.53496). The ultraviolet spectrum showed that the product possessed a double bond conjugated with a benzene ring. The infrared spectrum showed the absence of terminal unsaturation. Hydrogenation gave 2-phenylbutane which was identified by its boiling point, refractive index, and infrared spectrum.

(17) K. V. Auwers and F. Eisenlohr, *J. prakt. Chem.*, [2] **82**, 91 (1910).