Kodak Co.) was distilled under 20-mm pressure, bp 60–62°. Potassium hydroxide pellets (198 g of 85%) (3.0 moles) were heated to 100–120°, and *trans*-1,4-dichloro-2-butene (125 g, 1.00 mole) was added slowly with stirring to the molten potassium hydroxide. *cis*-1-Chloro-1,3-butadiene was distilled, collected, and dried over calcium chloride. Distillation gave 47.1 g (53%) of material, bp 66°, $n^{20}\text{D}$ 1.4723. Treatment with maleic anhydride did not alter the physical properties of the *cis*-1-chloro-1,3-butadiene.

The 2-methoxybutadiene used was obtained in part as a gift from the late Dr. David Craig [bp 73.1–73.2° (730 mm), $n^{20}\text{D}$ 1.4448] and in part prepared by the method of Petrov.[15] The latter material had an infrared spectrum identical with that of the former and similar physical properties, bp 74°, $n^{20}\text{D}$ 1.4461.

The preparation of cyclic sulfones is illustrated by the reaction of the 3-methyl-1,3-pentadienes. A freshly distilled mixture (36.5 g) of the *cis* and *trans* isomers (0.445 mole, 27% *cis*, 73% *trans*), 250 g of sulfur dioxide (3.9 moles), small amounts of di-*n*-butylammonium picrate and pyrogallol, and 80 ml of absolute ether were sealed in a glass-lined steel autoclave. After 24 hr at room temperature the liquid part of the reaction mixture was separated from gummy material which was extracted subsequently with warm ether. From the combined ether solutions the solvent was removed; then at 125° bath temperature and 2-mm pressure, 10.2 g of a yellow oil was distilled which was shown by nmr (Table III) to consist of a single, fairly pure cyclic sulfone (16% of theoretical yield). Much decomposition occurred during the heating.

The recovery of the *cis* diene **16** from the cyclic sulfone **18** is also typical. Sulfone **18** (7.7 g) was heated to 150–180° and the products were distilled through a 5-cm Vigreux column, bp 67°. The yellow distillate was washed with aqueous sodium carbonate and water and dried, amounting to 1.65 g, 38%. Vpc (6, Table VI) showed the product to consist of *cis*-3-methyl-1,3-pentadiene (97%), *trans*-3-methyl-1,3-pentadiene (3%), and traces of lower boiling materials.

Rate Measurements.—The rate constant for addition of 1122 to 2,3-dimethylbutadiene was measured by observing the competition between this diene and isoprene in a mixture, the course of the reaction being followed by vapor chromatography. The solutions employed were prepared with a cooled (−20°), vacuum-jacketed, 15-ml volumetric flask. Portions (1 ml) of the solutions were transferred with a cooled syringe into heavy-walled ampoules (12.7-mm o.d., 2.3-mm wall thickness) cooled with ice water. To each of the ampoules 1 mg of di-*n*-butylammonium picrate had been added previously. The 1122 had been freshly distilled and was stored over molecular sieves, type 4A (Fisher). The dienes were also carefully distilled before use. The sealed ampoules were removed from the 82° bath at appropriate intervals 2–28 hr after immersion and stored at −20°. Analysis of 15–100-μl samples was carried out under conditions 14 and 14a of Table VI. Toluene was used as an internal standard. The F & M 300 gas chromatograph was equipped with a thermal conductivity detector and a Disc integrator which was employed to evaluate the peak areas.

To calculate the ratio of rate constants k_x/k_y the following formula was used

$$\frac{k_x}{k_y} = \frac{\log \dfrac{M_x{}^0 - F_x \dfrac{A_x}{A_{\text{standard}}} M_{\text{standard}}}{M_x{}^0}}{\log \dfrac{M_y{}^0 - F_y \dfrac{A_y}{A_{\text{standard}}} M_{\text{standard}}}{M_y{}^0}}$$

where $M_x{}^0$ designates the amount of competing species (x) in millimoles at the start of the experiment, F_x represents an experimentally determined conversion factor of x, and A_x is the measured peak area of the adduct of component x in integrator counts. Subscripts y and standard analogously refer to the second competing species y and to the standard (toluene), respectively. F takes into account the different thermal conductivities of the particular compound and the standard. Being defined by the equation

$$F_x = M_{\text{adduct x}}\, A_{\text{standard}},\, M_{\text{standard}} A_x$$

it represents the ratio of peak areas of the standard and of the cycloadduct of x for equimolar amounts of the two.

Registry No.—1,1-Dichloro-2,2-difluoroethylene, 79-35-6; **3**, 1735-42-8; **7**, 1986-85-2; **6**, 10033-78-0; **8**, 10033-79-1; **9**, 10033-80-4; **12**, 10033-81-5; **13**, 10038-82-6; **14**, 10033-83-7; **15**, 10033-84-8; **23**, 10033-85-9; **22**, 10033-86-0, **18**, 10033-87-1; **10**, 10033-88-2; **11**, 10033-89-3; **26**, 10033-90-6; **27**, 10033-91-7; **28**, 10033-92-8; **21**, 10033-92-8; **29a**, 10039-50-6; **2**, 10033-93-9; **16**, 2787-45-3; **17**, 2787-43-1; **20**, 926-56-7; **29b**, 10033-96-2; 2,2-dichloro-1,1-difluoro-3-(2-methylpropenyl)cyclobutane, 10033-97-3; **5**, 10033-98-4; *cis*-1-chloro-1,3-butadiene, 10033-99-5.

Acknowledgment.—We thank the B. F. Goodrich Co. for support of this work.

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The Reaction of Rhodium Trichloride with Dienes

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The reaction of ethanolic rhodium trichloride with dienes gives rise not only to various complexes of rhodium(III), but also to catalytic reactions involving the addition of ethanol to the diene. The results obtained by various workers on the interaction of rhodium trichloride with butadiene are rationalized.

The reduction of rhodium trichloride by ethanol in the presence of olefins[1-3] has frequently been employed for the preparation of π complexes of rhodium(I). In the cases of acrylonitrile[4] and cyclododecatriene,[5] σ and π complexes of rhodium(III) were obtained, respectively.

The interaction of ethanolic rhodium trichloride with butadiene has been investigated by a number of workers[6-8] with a variety of results. We now wish to report the catalytic and stoichiometric results we have obtained with conjugated dienes and rhodium trichloride.

Results

The Reaction of Rhodium Trichloride with Isoprene.—When rhodium trichloride is heated in ethanol with

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[2] R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

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[5] G. Paiaro, A. Musco, and G. Diana, *J. Organometal. Chem.*, **4**, 466 (1965).

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[7] L. Parri, G. Lionetti, G. Allegra, and A. Immerzi, *Chem. Commun.*, 336 (1965).

[8] J. Powell and B. L. Shaw, *ibid.*, 323 (1966).

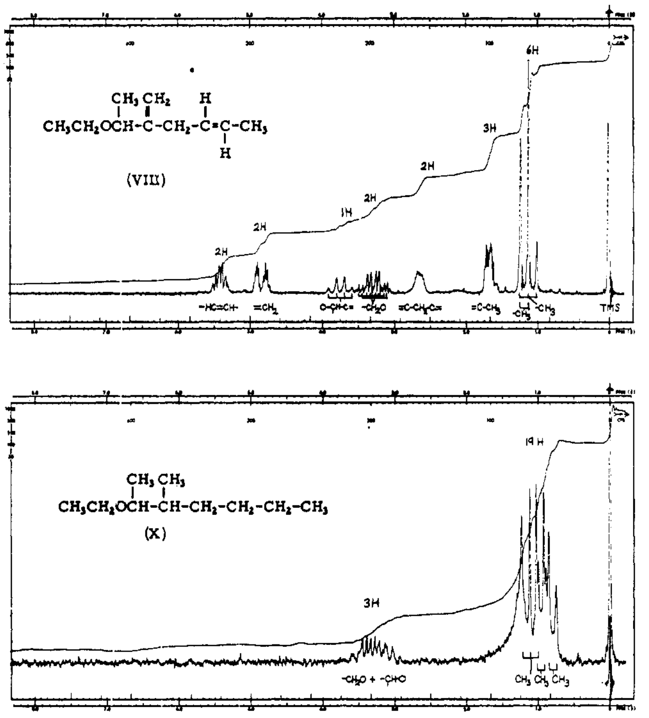
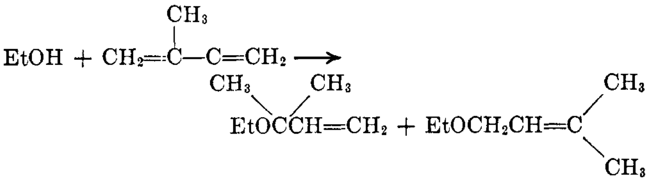


Figure 1.—Nmr spectral data for ethers VIII and X.

isoprene, a catalytic reaction set in to form ethers I and II. At room temperature I and II were obtained



$$\mathrm{EtOH + CH_2{=}\overset{CH_3}{C}{-}C{=}CH_2 \longrightarrow EtO\overset{CH_3\;CH_3}{C}CH{=}CH_2 + EtOCH_2CH{=}C(CH_3)_2}$$

I II

in 58 and 21% yields, respectively, while at 60° ether II is the dominant product. An examination of the reaction in progress revealed that ether I was formed initially, and slowly isomerized to II.

Methanol, propanol and isopropyl alcohol also undergo addition to isoprene, although more slowly and in diminished yield. In the cases of propanol and isopropyl alcohol, the oxidation products propionaldehyde and acetone, respectively, were detected in the reaction mixture. The reaction appears to be truely catalyzed by rhodium since it cannot be carried out in the presence of hydrochloric or sulfuric acid. The reaction is slowed by addition of water and inhibited by sodium carbonate.

When the reaction is carried out on a larger scale, air-stable complexes of composition III may be isolated in good yield. Careful chromatography of the mixture

$[(\mathrm{C_5H_8})_x\mathrm{RhCl_2}]_n$ III

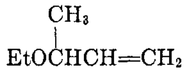
$\{[(\mathrm{C_6H_5})_3\mathrm{P}](\mathrm{C_5H_8})_x\mathrm{RhCl_2}\}_2$ IV

$(\mathrm{C_5H_5N})_2(\mathrm{C_5H_8})_x\mathrm{RhCl_2 \cdot H_2O}$ V

permitted the isolation of III, $x = 2$, 3, and 4, of molecular weights, 1080, 1750, and 7700, respectively. Treatment of III of average composition $x = 2.5$ with triphenylphosphine gave dimer IV, while treatment with pyridine gave monomer V. Catalytic hydrogenation of the complex mixture with a rhodium-on-carbon catalyst gave an oil which was shown by mass spectral analysis to contain only hydrocarbons of the type $(\mathrm{C_5})_n$ ($n = 1$–4).

Although these complexes must clearly contain π-allylic groups,[5,8] a detailed study of their nature was not undertaken.

The Reaction of Rhodium Trichloride with Butadiene.—Ethanolic rhodium trichloride reacts with butadiene in a manner similar to that of isoprene to give ethers VI and VII in 33 and 6% yields, respectively. In

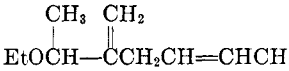


$\mathrm{EtO\overset{CH_3}{C}HCH{=}CH_2}$

VI

$\mathrm{EtOCH_2CH{=}CHCH_3}$

VII

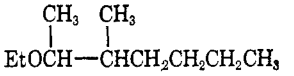


$\mathrm{EtO\overset{CH_3}{C}H{-}\overset{CH_2}{\overset{\|}{C}}CH_2CH{=}CHCH_3}$

VIII

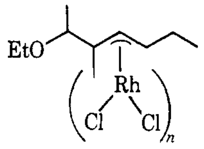
sharp contrast to the reaction with isoprene, however, a polymeric oil was also obtained from which ether VIII was isolated and characterized (*vide infra*).

As in the case of isoprene, an orange butadiene–rhodium complex (IX) was also isolated in good yield. Hydrogenation of IX gave ether X (identified by comparison with an authentic sample prepared by hydrogenation of VIII) as the principal product, with lesser quantities of an unidentified compound $\mathrm{C_{10}H_{20}O}$. Treatment of rhodium trichloride with ether VIII gave an orange complex whose analysis and physical properties were very similar to those of IX. Although a detailed analysis was again difficult, a π-complex of type XI seems highly likely.



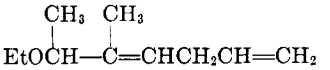
$\mathrm{EtO\overset{CH_3}{C}H{-}\overset{CH_3}{C}HCH_2CH_2CH_2CH_3}$

X



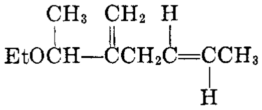
XI

The Structure of Ether VIII.—Ether VIII was assigned the structure *trans*-2-ethoxy-3-methylidene-5-heptene on the basis of the following data. (1) Palladium-catalyzed hydrogenation of VIII gave $\mathrm{C_{10}H_{22}O}$ (X) and 3-methylheptane. (2) The infrared spectrum (neat) shows two strong bands at 910 and 970 cm^{-1}, indicative of either $\mathrm{CH{=}CH_2}$ or $\mathrm{{>}C{=}CH_2}$ + $_{\mathrm{H}}{>}\mathrm{C{=}C}{<}^{\mathrm{H}}$. (3) The mass spectrum shows two strong peaks at m/e 45 and 108, indicative of the partial structure $\mathrm{EtOC(CH_3)HC_6H_9}$. (4) The nmr spectrum (Figure 1) shows the presence of four olefinic protons, two protons adjacent to two double bonds, three protons adjacent to one double bond, and three protons adjacent to oxygen. These data are consistent with either structure VIIIa or VIIIb. From a detailed consideration of the splitting patterns (see Figure 1 for assignments), structure VIIIb is strongly preferred.



$\mathrm{EtO\overset{CH_3}{C}H{-}\overset{CH_3}{C}{=}CHCH_2CH{=}CH_2}$

VIIIa

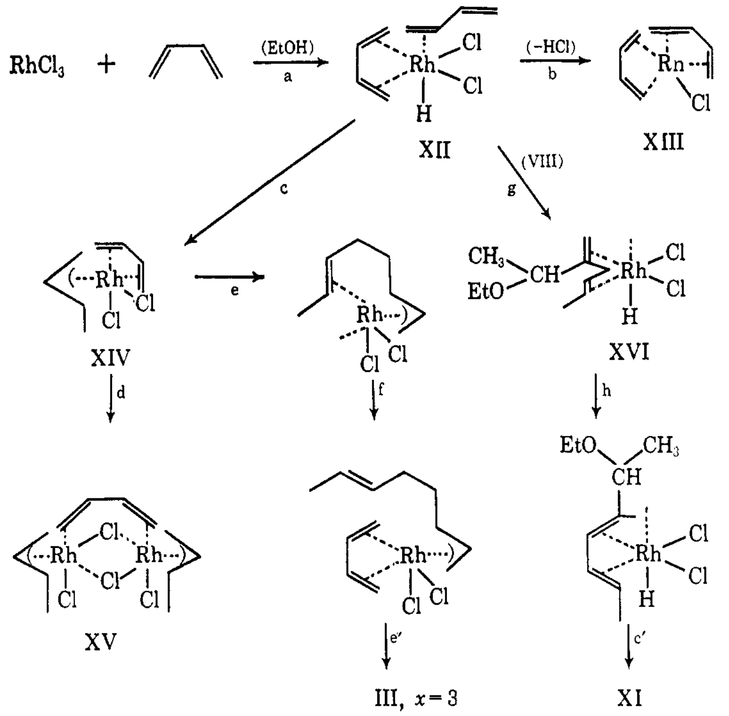


$\mathrm{EtO\overset{CH_3}{C}H{-}\overset{CH_2}{\overset{\|}{C}}CH_2\overset{H}{C}{=}\underset{H}{C}CH_3}$

VIIIb

As may also be seen from Figure 1, the nmr spectrum of the hydrogenated ether X is also consistent with the proposed structure.

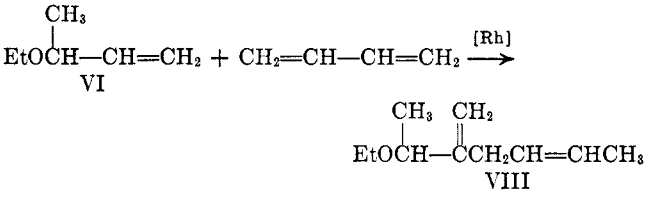
Scheme I



Discussion

The formation of all of the complexes which have been obtained from rhodium trichloride and butadiene may be easily rationalized by means of the general scheme presented in Scheme I. The initial formation of an unstable hydride XII by ethanolic reduction of rhodium(III) is assumed.[4] Stable complexes of a similar nature have been isolated with iridium,[3,9] however. In the present case of conjugated dienes, the susceptibility to hydride addition would be expected to lie somewhere in between those of cyclooctadiene and acrylonitrile, which give rise to π complexes of rhodium(I) and σ complexes of rhodium(III),[4] respectively. Thus at relatively low temperatures, the loss of hydrogen chloride from XII (process b) would be expected to give rise to the observed[7] complex (XIII). At higher temperatures (the conditions used by Shaw[8] unfortunately were not published) hydride addition should become relatively more important and lead by processes c and d to the observed allyl complex (XV). Under yet more vigorous conditions of high temperature and excess diene, addition of the π-allyl group to coordinated diene (routes e and e′) to form oligomeric π-allylic complexes might be expected. Indeed in the case of isoprene this appears to be the type of product reported in the present communication. In the case of butadiene, however, the catalytic formation of butadiene telomers such as VIII presents yet another possibility. Thus in contrast to the monoolefins formed in the case of isoprene, the *dienes* formed in the case of butadiene might well displace butadiene from complex XII (process g) to form a new complex of the type XVI, which then by isomerization[10] (process h) and hydride addition (process c′) would give rise to the observed product (XI).

The mechanism of formation of allylic ethers I, II, VI, and VII is not understood, although the products are just what one would expect from acid catalysis. The formation of telomer VIII probably arises from VI,



$$\underset{\text{VI}}{\mathrm{EtO\overset{CH_3}{\overset{|}{C}}H{-}CH{=}CH_2}} + \mathrm{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{[\mathrm{Rh}]} \underset{\text{VIII}}{\mathrm{EtO\overset{CH_3}{\overset{|}{C}}H{-}\overset{CH_2}{\overset{\|}{C}}CH_2CH{=}CHCH_3}}$$

however, since the same mode of addition was observed in the rhodium trichloride catalyzed cross reaction of propylene and butadiene.[6]

Experimental Section

Reaction of Rhodium Trichloride with Isoprene.—To a solution of 1.5 g of rhodium trichloride trihydrate in 300 ml of dry ethanol (nitrogen atmosphere) was added 27 g of isoprene. The reaction was carried out at 60° and followed by gas-liquid partition chromatography. A new peak appeared rapidly, followed by a second at longer emergence time which became dominant at the end of the reaction. After 3 hr the reaction stopped and quantitative analysis showed 63% of the charged isoprene had been converted. The mixture was cooled, poured into ice water, and extracted with pentane. The pentane extracts were washed with bicarbonate and water, dried, and fractionally distilled to give 6.3 g (22%) of 2-ethoxy-2-methyl-3-butene (I),[11] bp 98°, and 8.0 g (28%) of 4-ethoxy-2-methyl-2-butene (II),[12] bp 125°, $n^{28}\mathrm{D}$ 1.4165. The structures of these materials were confirmed by analysis and nmr spectroscopy.

The reaction was repeated at room temperature for 2 days to give ethers I and II in 58 and 21% yields (53% conversion), respectively.

In a similar run with 3.0 g of rhodium trichloride trihydrate, the alcoholic reaction mixture was stripped *in vacuo* to give 2.9 g of reddish brown solid (III), mp 250° dec. This material is initially soluble in benzene, but on drying becomes almost insoluble.

A 4.0-g sample of this material was dissolved in benzene and adsorbed on a column of activated Davidson silica gel. Elution with 50% benzene–pentane gave 0.93 g of $(C_5H_8)_4Cl_2Rh$ (IIIa),

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

[11] P. B. D. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 2504 (1954).

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TABLE I

ANALYTICAL DATA FOR RHODIUM–ISOPRENE COMPLEXES (III)

		Anal., %							
		Carbon		Hydrogen		Rhodium		Chlorine	
Compd	Mol wt	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
IIIa	7700	53.8	51.4	7.2	6.2	15.9	16.3	23.2	23.1
IIIb	1750	47.6	46.9	6.3	5.7	18.8	18.2	27.3	28.5
IIIc	1080	38.7	36.6	5.2	4.6	22.9	22.4	33.2	35.3

mp 254° dec; elution with 10% ether–benzene gave 0.8 g of $(C_5H_8)_3Cl_2Rh$ (IIIb), mp 248° dec; elution with 50% ether–benzene gave 0.77 g of $(C_5H_8)_2Cl_2Rh$ (IIIc), mp 254° dec; and elution with methanol gave 1.2 g of a mixture of complexes of higher chlorine content. The purity of IIIa was reasonably well established by rechromatographing into several fractions and comparing their infrared spectra. The analyses are reported in Table I. Although difficulties were encountered in the purification of most of these compounds, the crude analyses obtained coupled with the exact analysis for the pyridine derivative leave little doubt as to the correctness of the assignments.

Treatment of Complex III with Pyridine.—Complex III was prepared as above and chromatographed to give a mixture of average composition $(C_5H_8)_{2.5}RhCl_2$. To a solution of 1.2 g of this complex in 25 ml of benzene was added 0.75 ml of anhydrous pyridine (nitrogen atmosphere). The mixture was warmed to 40° for 1 hr, cooled, filtered, and evaporated to give complex V (x = 2.5).

For analysis, the material was repeatedly dissolved in benzene and precipitated with pentane, mp *ca.* 118° dec. This material is diamagnetic, $X_g = 0.46 \times 10^{-6}$ emucgs.

Anal. Calcd for $C_{17.5}H_{22}Cl_2N_2ORh$: C, 51.9; H, 6.1; Cl, 13.6; N, 5.4; Rh, 19.8; mol wt, 520. Found: C, 52.2; H, 5.6; Cl, 13.0; N, 4.5; Rh, 20.9; mol wt (vapor pressure osmometric in dichloroethane), 600.

Treatment of Complex III with Triphenylphosphine—Complex IIIc (0.42 g), 0.85 g of triphenylphosphine, and 15 ml of benzene were heated together under nitrogen for 2 hr. The reaction mixture was evaporated, and the residue was dissolved in benzene and chromatographed on silicic acid. Elution with 10% ether–methylene chloride gave complex IV, mp *ca.* 175° dec.

Anal. Calcd for $C_{56}H_{62}Cl_4P_2Rh_2$: C, 58.8; H, 5.4; Cl, 12.4; Rh, 18.1; mol wt, 1144. Found: C, 56.4; H, 4.5; Cl, 12.7; Rh, 18.8; mol wt (ebullioscopic in benzene), 1150.

Hydrogenation of Complex III.—The crude mixture of complex III (4.5 g) was slurried with ethanol and hydrogenated in the presence of 5% rhodium–carbon at 1000 psig, and room temperature for 3 hr, and then at 60° overnight. The colorless solution was filtered, diluted with water, and extracted with pentane. The pentane extracts were washed with bicarbonate and water, dried, and chromatographed on neutral alumina to give 0.4 ml of hydrocarbon oil, n^{26}D 1.4612. Gas–liquid partition chromatography confirmed the presence of isopentane and showed several peaks at emergence times compatible with C_{10}, C_{15}, and C_{20} hydrocarbons. This was confirmed in the mass spectrum, which additionally indicated the hydrocarbons to be preponderantly cyclic. The nmr spectrum showed the material to be highly branched (60% methyl groups).

Reaction of Rhodium Trichloride with 1,3-Butadiene.—Butadiene, (18.5 g) was dissolved in a solution of 0.9 g of rhodium trichloride trihydrate in 150 ml of ethanol and heated in a sealed tube at 60° overnight. Gas–liquid partition chromatography showed a butadiene conversion of 53%. The reaction mixture was cooled and stripped *in vacuo*, and the distillate was diluted with water and extracted with pentane. The pentane extract was dried and distilled to give 6 g (33%) of 3-ethoxy-1-butene (VI,[13] bp 75.5–76.0°, n^{23}D 1.3863), 1 g (6%) of *trans*-1-ethoxy-2-butene (VII,[13] bp 98–100°, n^{23}D 1.4020), and a smaller quantity of *trans*-2-ethoxy-3-methylidene-5-heptene [VIII, bp 95–110° (137 mm)].

For analysis, VIII was purified by preparative gas chromatography and redistillation, bp 96° (100 mm).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.9; H, 11.7; mol wt, 154. Found: C, 77.3; H, 11.7; mol wt (mass spectrometry), 154.

The nmr spectrum of this material is shown in Figure 1.

The residue obtained when the original reaction mixture was stripped was diluted with pentane and filtered to give 0.7 g of orange rhodium–butadiene complex (IX).

Anal. Calcd for $C_{10}H_{10}ClORh$: C, 36.5; H, 5.8; Cl, 21.6; Rh, 31.4. Found: C, 35.6; H, 5.2; Cl, 22.6; Rh, 34.1.

The pentane filtrate was distilled to give an additional quantity of oil, bp 40–90° (0.5 mm). The infrared spectrum (neat) of this mixture showed the presence of unsaturated ethers.

Hydrogenation of Complex IX.—Complex IX (2.8 g) was mixed with 10 ml of ethanol and 0.1 g 5% rhodium–carbon and hydrogenated at 100 psig and room temperature for 2 hr, then at 60° overnight. The reaction mixture was filtered, diluted with water, and extracted with pentane. The pentane extract was passed through a short column of neutral alumina, evaporated, and chromatographed on a 10-ft Dow 710 silicone column at 130° to give 2-ethoxy-3-methylheptane (X), bp 169°, and a smaller quantity of unknown compound, bp 186°.

Anal. Calcd for $C_{10}H_{22}O$ (X): C, 76.4; H, 13.9; mol wt, 158. Found: C, 76.0; H, 13.6; mol wt (mass spectrometry, leak rate), 156 ± 5.

The nmr spectrum of this compound is shown in Figure 1.

Anal. Calcd for $C_{10}H_{20}O$ (unknown): C, 76.8; H, 12.8; mol wt, 156. Found: C, 76.1; H, 12.8; mol wt (mass spectrometry), 156.

Nmr and mass spectroscopy indicated that the material is cyclic and highly branched, but could not predict a unique structure.

Hydrogenation of *trans*-2-Ethoxy-3-methylidene-5-heptene (VIII).—Palladium-catalyzed hydrogenation of diene VIII in a low-pressure apparatus gave 3-methylheptane (identified by gas–liquid partition chromatography) and 2-ethoxy-3-methylheptane (X), identical with that obtained above from rhodium and butadiene.

Treatment of *trans*-2-Ethoxy-3-methylidene-5-heptene (VIII) with Rhodium Chloride.—Diene VIII (220 μl) was dissolved in a solution of 150 mg of rhodium trichloride trihydrate in 4 ml of ethanol and refluxed under nitrogen for 1 hr, cooled, and evaporated *in vacuo*, and the residue was dissolved in benzene, filtered, and precipitated with pentane to give 100 mg of an orange solid. The infrared spectrum of this material is similar to that of IX.

Anal. Calcd for $C_{10}H_{10}Cl_2ORh$: C, 36.5; H, 5.8; Cl, 21.6; Rh, 31.4. Found: C, 37.6; H, 4.8; Cl, 22.2; Rh, 33.1.

Registry No.—Rhodium trichloride, 10049-07-7; X, 7745-48-4; VIII, 7745-49-5.

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[13] M. Lepingle, *Bull. Soc. Chim. France*, **39**, 865 (1926).