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THE ISOMERIZATION OF *cis,trans*-1,5-CYCLODECADIENE BY $RhCl_3 \cdot 3H_2O$ IN ETHANOL

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SUMMARY

The isomerization of *cis,cis*-1,6-cyclodecadiene to *cis,trans*-1,5-; and *cis,cis*-1,5-cyclodecadiene in the presence of their rhodium complexes seems to indicate an isomerization for which no thermal conversion has been reported. Evidences are presented for the functioning of ethanol as a hydride source in these polymerizations.

INTRODUCTION

The rhodium chloride isomerization of linear and cyclic olefins has been studied[1,2] and reviewed[3]. The following mechanisms have been proposed for double bond migration: (1) π-allyl hydride; (2) hydrido-π-olefin; and (3) addition and elimination of metal hydride[4]. We wish to report the identification of some of the organic components of a rhodium–chloride intermediate obtained during the isomerization of *cis,trans*-1,5-cyclodecadiene by $RhCl_3 \cdot 3H_2O$ in ethanol. Substituted cyclodecadienes have been obtained from the above reaction which tends to indicate that the addition and elimination of a metal hydride is important in rhodium chloride isomerization of olefins.

RESULTS

Recently Jonassen and coworkers[2] reported on the rhodium π-complex of *cis,cis*-1,6-cyclodecadiene formed by the metal-catalyzed isomerization of *cis,trans*-1,5-cyclodecadiene. A study of the reaction variables in this isomerization process was therefore of interest.

Rhodium trichloride trihydrate reacts with an excess of either *cis,trans*-1,5- or *cis,cis*-1,6-cyclodecadiene in 95% ethanol at 76–78° for 5–24 h with stirring to yield $[RhCl(C_{10}H_{16})]_2$. The amount of $[RhCl(C_{10}H_{16})]_2$ produced is dependent on the solvent but independent of reaction time (5–24 h) and diene. Cyanide displacement of the dienes in $[RhCl(C_{10}H_{16})]_2$ yields both *cis,cis*-1,5-[2] and *cis,cis*-1,6-cyclodecadiene.

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The composition of $[RhCl(C_{10}H_{16})]_2$ too is independent of reaction time for *cis,trans*-1,5-cyclodecadiene. For *cis,cis*-1,6-cyclodecadiene however it is time dependent and seems to involve a set of complex equilibria between *cis,cis*-1,6-, *cis,trans*-1,5-, and *cis,cis*-1,5-cyclodecadiene and its rhodium chloride complexes.

During this reaction with either diene, an intermediate polymeric product was isolated which with an excess of either diene in ethanol yielded $[RhCl(C_{10}H_{16})]_2$; in the absence of diene however reduction to rhodium metal occurred. The average composition of the intermediate polymer was $RhCl(C_{10}H_{16})(EtOH)_2$ as indicated by the elemental analysis of ten samples, purified by different techniques.

After cyanide displacement of the coordinated organic components this intermediate was found to contain: ethanol, *cis*-cyclodecene, *cis,cis*-1,6-, *cis,cis*-1,5-, and *cis,trans*-1,5-cyclodecadiene. A trace amount of water could also be present but none was detected by infrared or by gas chromatographic analyses.

A substituted cyclodecadiene of mass 196 containing an hydroxy and one ethoxy substituted double bond was also identified as a small component (5%). This composition was confirmed by the presence of vinyl protons at 5.8 and 6.1 τ^5 and OH proton at 8.6 τ and the typical ethyl pattern (quartet and triplet) superimposed on methylene protons. The presence of the EtO group was also indicated by C–O stretching frequencies at 1100 and 1160 cm^{-1}. One as yet not identified component (0.5%) of molecular weight 256 was also obtained. The infrared and nuclear magnetic resonance spectra of the intermediate are extremely complex and make it impossible to propose structural formulations. The positions of the double bonds in these substituted cyclodecadienes are not known at this time.

When the intermediate was prepared from 99% *cis,cis*-1,6-cyclodecadiene, the presence of *cis,trans*-1,5-cyclodecadiene was of interest since it seems to indicate an isomerization for which no thermal conversion has been reported.

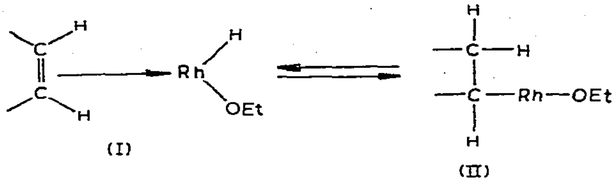
After concentration of the supernatant it was possible by preparative GLC to obtain eleven organic components—only two of these were better than 70% pure. These two could be fully identified as *cis*-cyclodecene and *cis,cis*-1,6-cyclodecadiene; they were the major components (90%) of the mixture. For the other components their IR and NMR spectra indicated that they were olefinic and contained EtO groups.

DISCUSSION

The identification of cyclodecadiene substituted at the double bond positions by hydroxy and ethoxy groups respectively makes it possible to draw some conclusions about the isomerization mechanism. Rh^{III} is reduced by ethanol to Rh^{I} and the ethanol oxidized to CH_3CHO thus accounting for the redox scheme. Ethanol was detected in the intermediate and is assumed to be coordinated to the metal ion. As was observed by Cramer[1] who found that protonic solvents may function as a hydride source in olefin isomerization, the OH bond in ethanol can be split homolytically by the metal ion to give a hydridoethoxyrhodium (I) species with solvent, chloride, or olefin occupying the other coordination positions.

The rhodium ion may then react with the olefin to form an alkylethoxyrhodium intermediate (II).

The alkyl intermediate can revert back to the original olefin complex or yield the isomerized olefin complex with isomerization, the normal pathway in this reaction system.


(I)
(II)

A hydride is then re-abstracted from the alkyl moiety present on the Rh–OEt unit to give the isomerized olefin and a hydridoethoxyrhodium unit which can again yield EtOH coordinated to the metal ion. Since a certain amount of water from $RhCl_3 \cdot 3H_2O$ is present even in the absolute ethanol medium used, the addition of hydroxy groups to the olefin will occur in a way similar to the ethoxy group.

However, if in the formation of a σ-bonded alkylrhodium complex, the OEt group instead of H becomes attached to the olefin a different reaction product will result. The amount of ethoxylated olefin observed is quite small compared to the amount of diene isomerized and thus represents only a by-product in this reaction. To postulate a hydridoethoxyrhodium species as the reactive intermediate seems very reasonable on the basis of Cramer's deuteration work. It is enforced by this work which found ethanol in the intermediate and ethoxy and hydroxy groups on some of the C_{10} molecules isolated from this reaction.

The addition of an alcohol to an olefin can occur either in a basic[6] or acidic medium[7]—a mechanism which could also account for the observed substituted cyclodecadiene. In the preparation of $[RhCl(C_{10}H_{16})]_2$, the liberation of HCl makes the medium acidic; but this does not appear to be a critical factor.

Oxygen does not seem to affect the olefin distribution in $[RhCl(C_{10}H_{16})]_2$. However the reaction was not attempted under elevated oxygen pressure since this could lead to the formation of an epoxide which would decompose in an acidic medium to give an OH group[8] on the cyclic ring.

Some cyclodecene was found both in the intermediate and supernatant. Obviously some hydrogenation process for the unsaturated cyclic dienes occurs in this reaction. The route by which this occurs is under investigation.

EXPERIMENTAL

A Perkin–Elmer 810 Flame Ionization gas chromatograph containing a stream splitter (1/3 ratio) with a Speedomax 0–1 mV scale recorder was used for the analytical work. Cyclic diolefins were separated by an improved silver nitrate GLC column[9]. Small samples of the dienes were collected for IR, NMR, and mass spectrometry.

Infrared spectra were obtained using the Beckman IR-8 and IR-5 Double Beam Spectrophotometers in the 2.5 to 16 micron region.

Nuclear magnetic resonance spectra of olefins trapped by a GLC technique were scanned on a Varian Associate A-60 NMR using a 50–75 μl microtube; tetramethylsilane (TMS) was used as the internal standard.

A Hitachi RMU-68 double focusing mass spectrometer was used to obtain mass spectra of the olefins.

Preparation of $[RhCl(C_{10}H_{16})]_2$

A typical preparation of $[RhCl(C_{10}H_{16})]_2$ involved treating 500 mg of

$RhCl_3 \cdot 3H_2O$ with a 6 to 7 molar excess of either *cis,trans*-1,5- or *cis,cis*-1,6-cyclodecadiene in 95% ethanol (8 to 40 ml) at 76–78° from 5 to 24 h with stirring. The solution was filtered and the precipitate was washed with absolute ethanol and air dried.

Preparation of the intermediate

Various amounts of $RhCl_3 \cdot 3H_2O$ (0.5 to 1 gram) were dissolved in 12 to 40 ml of 95% or absolute ethanol containing 1 to 2.5 ml of either diene. The solution was stirred and heated for 1–2 h; reaction time begins with the first sign of a precipitate in the reaction mixture. At the end of the reaction, the solution was rapidly cooled in an ice bath. The resultant precipitate was filtered, washed with absolute ethanol, and air dried.

Reaction medium

The combined filtrates from several reactions used in the synthesis of $[RhCl(C_{10}H_{16})]_2$ were reduced in volume by use of a rotary evaporator (1 mm and room temperature). The residue was treated with aqueous KCN to decompose any rhodium olefin complexes. The organic components were extracted with hexane and the solution was reduced in volume. Gas liquid chromatographic scans during the concentration process indicated no apparent reduction or decomposition. The organic components were separated by preparative gas liquid chromatography.

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