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Selective Homogeneous Hydrogenation of Cycloocta-1,5, and Cycloocta-1,3-diene to Cyclooctene in the Presence of (η^4-cycloocta-1,5-diene)(η^6-Cycloocta-1,3,5-triene)ruthenium(0)

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Cyclooctadiene isomers (1,3- and 1,5-COD) are selectively, homogeneously hydrogenated to cyclooctene (C_8H_{14}) in tetrahydrofuran (THF) solution, under mild conditions of temperature (20 °C) and hydrogen pressure (1 atm), in the presence of catalytic amounts of (cycloocta-1,5-diene)(cycloocta-1,3,5-triene)ruthenium(0), [Ru(η^4-COD)(η^6-C_8H_{10})] (1). The rate of hydrogenation is higher when 1,3-COD is the substrate. Evidence for the isomerization 1,5-COD → 1,3-COD is reported. Similar studies carried out in several alcoholic solutions, although showing a decreased selectivity in the hydrogenation, confirm the isomerization 1,5-COD → 1,3-COD, and allow a discrimination between the isomerization and the hydrogenation. The nature of the alcohol strongly influences the isomerization process, to a lesser extent the hydrogenation process. Isomerization appears to be a necessary step for the catalytic hydrogenation of 1,5-COD, in the presence of 1. *Indeed, a non-isomerizable diene (bicyclo[2,2,1]hepta-2,5-diene, norbornadiene (NBD)) is not hydrogenated in the above experimental conditions.*

These results elucidate the mechanism of previously reported catalytic hydrogenation of conjugated trienes in the presence of 1.

Introduction

Homogeneous catalytic hydrogenation of polyenes to monoenes has been extensively studied [1–6]. Selectivity in these processes can be achieved by two types of catalytic systems: those which are completely inert with respect to the hydrogenation of the resulting monoenes, and those for which the selectivity is due principally to thermodynamic and/or kinetic factors that reduce the rate of formation of the saturated hydrocarbon. In the case of simultaneous formation of monoene and the corresponding saturated hydrocarbon the process can be regarded as occurring by the following steps:

$$\text{triene} \xrightarrow{k'} \text{diene} \xrightarrow{k''} \text{monoene} \xrightarrow{k'''} \text{saturated hydrocarbon}$$

or alternatively by two or more concurrent mechanisms catalysed by different metal complexes, with the direct hydrogenation to the saturated hydrocarbon being considered a side reaction [3]. Although the case more commonly involves thermodynamic and/or kinetic control in selectivity [7–10], examples are also known which show a selectivity due to the inert nature of the catalytic species to further hydrogenation of the monoenes. These catalysts include $[Co(CN)_5]^{3-}$ [1, 11, 12], $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ [13], $[VCl_2(\eta^5\text{-}C_5H_5)_2]/LiC_4H_9$ [14] and $[PdCl(PPh_3)(\eta^3\text{-allyl})]$ [15].

The synthesis, characterization and reactivity of metal complexes of cyclic polyolefins have received much attention [16], but there are only few reports on their application as homogeneous catalysts. The complexes $[Ru(PPh_3)_2(\eta^6\text{-COT})]$ [17] (COT = cycloocta-1,3,5,7-tetraene), $[Ru(\eta^4\text{-NBD})(\eta^6\text{-COT})]$ [17] (NBD = norbornadiene) and $[M(\eta^4\text{-}C_8H_{10})(\eta^6\text{-}C_8H_{10})]^+$ [18] (M = Rh, Ir; C_8H_{10} = cycloocta-1,3,5-triene) are active in the hydrogenation of monoenes under mild conditions. The complex $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene) produces a mixture (1 to 9 ratio) of 2- and 3-hexenoate in the homogeneous hydrogenation of methyl sorbate, at 100 °C and 30 atm of hydrogen pressure [13]. Recently, we reported the homogeneous hydrogenation of cycloheptatriene (C_7H_8) to cycloheptene (C_7H_{12}) in the presence of [Ru(η^4-

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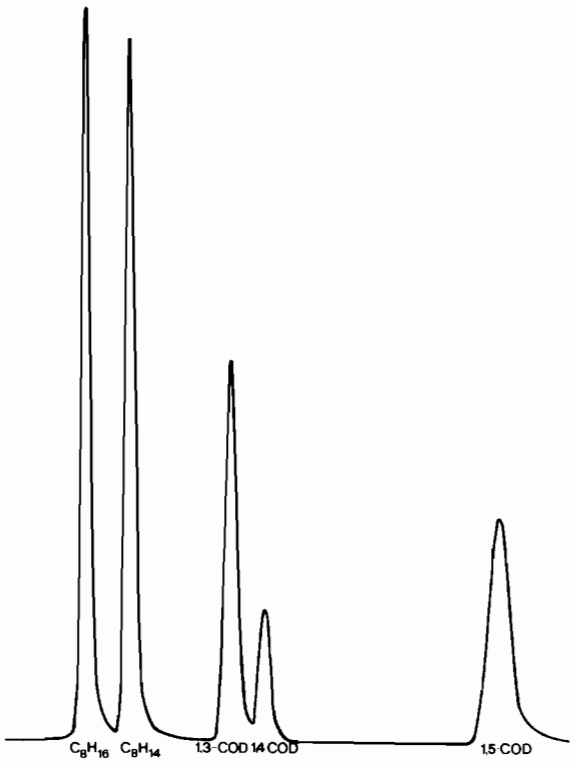


Fig. 1. Separation of the cyclooctadiene isomers and their hydrogenated derivatives by gas chromatographic analysis (the volume of 1,4-COD is about one third of that of other compounds).

1,5-COD)(η^6-C_8H_{10})] (*1*) and [Ru(η^4-1,5-COD)-(η^6-C_7H_8)] (*2*) (1,5-COD = cycloocta-1,5-diene), at room temperature and under one atmosphere of hydrogen pressure [19]. Although a mechanism has been suggested (see Scheme 1) to account for the experimental results, the position of the hydrogen addition to the η^6-coordinated polyolefin (in *1* and *2*) and the type of intermediates involved in the hydrogenation process were not established. With the hope of gaining more information on the stereochemistry involved, we decided to investigate the homogeneous hydrogenation of 1,3- and 1,5-COD, in the presence of *1*. The results of this study are reported and discussed here.

Experimental

Apparatus

I.R. Spectra were recorded on a Perkin-Elmer Mod. 580 spectrometer using KBr cells for liquids, previously evacuated and purged with pure nitrogen. ^{1}H NMR spectra were registered on a Bruker WP-80-SY spectrometer, in C_6D_6 solution and with TMS as internal reference. G.L.C. analyses were performed on a Perkin-Elmer Sigma 3 gas-chromatography instrument, equipped with a 2m/3mm column of 2½% OV-1 on G. AW. DMCS 33479 80–100 mesh (Supelco) for separation of mixtures in the hydrogenation of C_7H_8, and with a 2m/3mm column of 15% Dimethylsulfolane 80% Chromosorb WAW (Supelco) for separation of mixtures in the hydrogenation of 1,3- and 1,5-COD (Fig. 1).

Detection was obtained by flame ionization. Experimental conditions were: injector 50 °C; oven 50 °C, carrier gas He (35 ml/min); detector 150 °C, H_2 (1.2 atm) and air (2.5 atm); sample 0.01 μl. The areas of peaks were measured by a weighing procedure.

Catalytic hydrogenations were carried out according to previously published procedures [19]. The amount of *1* and concentration of dienes are given in the figure captions.

Materials

The synthesis of *1* was described previously [19]; the purity of *1* was checked each time before use by ^{1}H NMR spectra. 1,4-COD was prepared by published procedure [20]. Other polyolefins (Fluka) were purified by stirring with small pieces of sodium metal and were distilled under reduced pressure just before use. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride and then refluxed, under nitrogen, with sodium benzophenone ketyl and distilled before use. Alcohols were dried by refluxing over the appropriate magnesium or sodium alkoxide under nitrogen prior to distillation.

Hydrogen was passed through a Hydro Purge tube, Coast Engineering Laboratory, Gardena, Calif., and maintained at a small positive pressure. The reaction temperatures were regulated using a Beckman thermometer in an oil bath.

Results and Discussion

The Ru(η^4-1,5-COD) unit in *1* appears to be maintained during the entire process, since good yields (80–85%) of *2* are recovered from the catalytic hydrogenation of C_7H_8 to C_7H_{12} [19, 21].

Our previous results on the reactivity of *1* towards carbon monoxide showed that the formation of the monocarbonyl derivative is accompanied by release of the metal–olefin bond in the 3,4 position of the coordinated cyclooctatriene [22]. If the weaker bonding of the C_3 and C_4 carbons to the metal is also assumed in the reaction with hydrogen, then the mechanism suggested for the selective hydrogenation should be that shown in Scheme I (pathway A) (where C_7H_8 is considered as substrate).

A different explanation is however dictated by the alternative attack of hydrogen at position 1

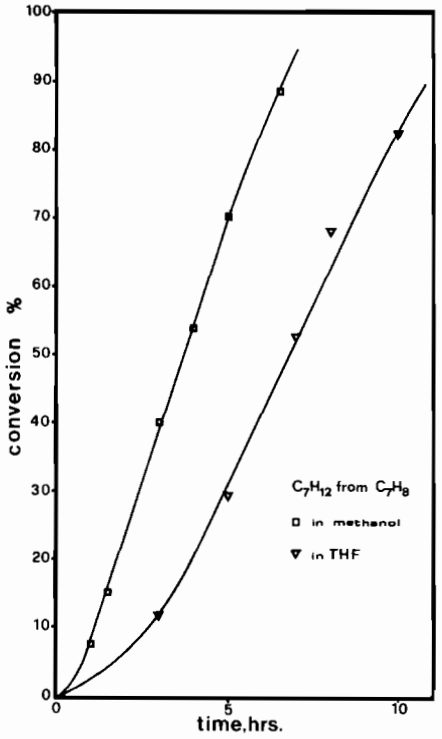


Fig. 2. Catalytic hydrogenation of cycloheptatriene to cycloheptane (at 20 °C). ([*1*] = 8.24 × 10^{-3} *M* in methanol; [*1*] = 2.09 × 10^{-2} *M* in THF; [C_7H_8]/[*1*] = 43).

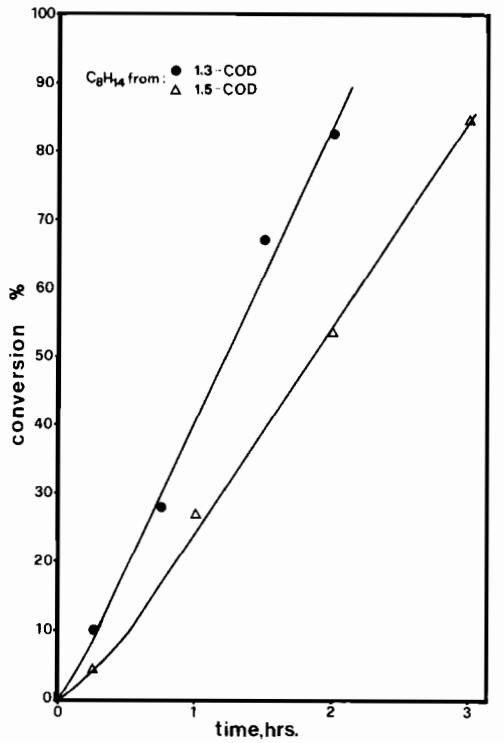
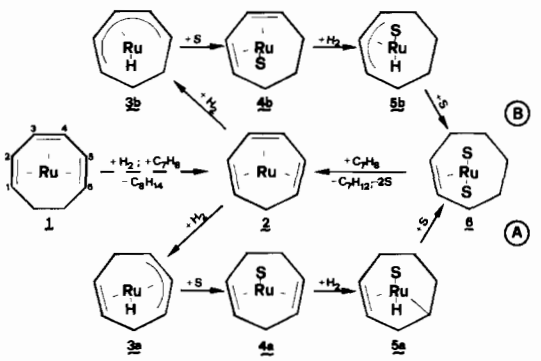


Fig. 3. Catalytic hydrogenation of 1,3-COD and 1,5-COD, in THF (at 20 °C). ([*1*] = 6.9 × 10^{-3} *M*; [COD]/[*1*] = 43).



Scheme I

(or 6) of the coordinated ring (Scheme I, pathway B)*.

Polyolefinic eight membered rings η^5-coordinated to ruthenium [16] are known in cationic complexes both in the form *3a* (*cf.* [$Ru(CO)_3(\eta^3, \eta^2\text{-}C_8H_9)$]$^+$ [23, 24] and [Ru(η^6-arene)(η^3,η^2-C_8H_9)]$^+$ [25]) and *3b* (*cf.* [Ru(η^6-arene)(η^5-C_8H_9)]$^+$ [25]) in which a double bond of the ring is not bonded to the metal. In the absence of this additional double bond and with polyolefinic seven membered rings η^5-coordination appears more common (*cf.* [Ru(η^5-C_8H_{11})$_2$] [21, 26, 27] and [Ru(η^5-C_7H_7)(η^5-C_7H_9)] [28]).

Irrespective of the actual nature of intermediates *3*, and consequently *4* and *5*, the catalytic hydrogenation of C_7H_8 to C_7H_{12} is believed to start from *2*. The formation of *2* from *1* is indicated by an induction period in the hydrogenation of C_7H_8, which disappears when *2* is used as catalyst [19]. Exchange of a free ligand in solution for one coordinated to a metal is indeed a key step for catalytic processes occurring in the presence of transition metal complexes [29].

A good combination of selectivity and conversion for the homogeneous hydrogenation of C_7H_8 to C_7H_{12}, in the presence of *1* or *2* [19], was obtained in THF. Further studies, however, show that even better rates can be obtained in methanol (Fig. 2).

Therefore the hydrogenation studies of 1,3- and 1,5-COD are carried out in these solvents, in the presence of *1*. In addition, ethanol, isopropanol

*The presence of hydrido complexes of ruthenium is shown by IR spectroscopy.

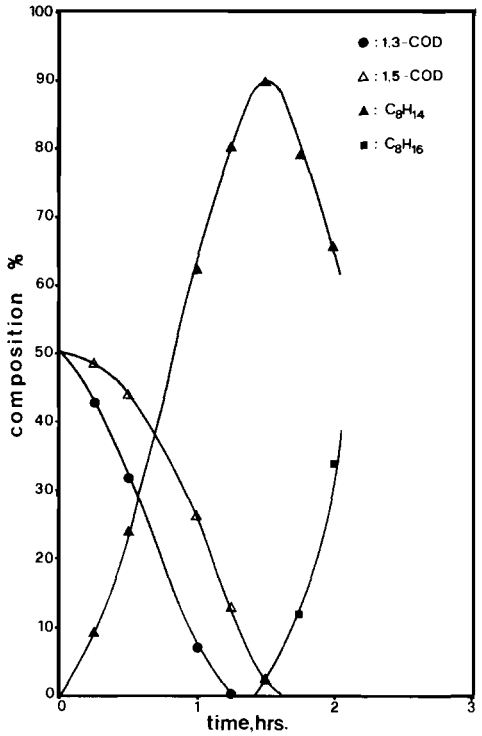


Fig. 4. Catalytic hydrogenation of equimolar mixture of 1,3-COD and 1,5-COD in THF (at 20 °C). ([*I*] = 6.9 × 10^{-3} *M*; [1,3-COD + 1,5-COD]/[*I*] = 50).

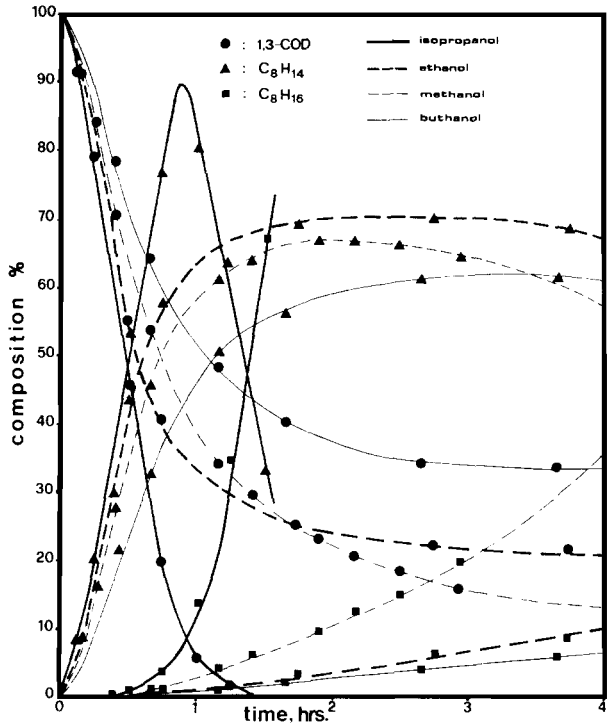


Fig. 5. Catalytic hydrogenation of 1,3-COD in alcoholic solution (at 20 °C). ([*I*] = 6.9 × 10^{-3} *M*; [COD]/[*I*] = 50).

and butanol* are used to compare the influence of different alcohols.

Both the COD isomers are selectively hydrogenated in THF, since cyclooctane is detected only when the diene substrate is completely transformed to monoene. 1,3-COD is hydrogenated faster than 1,5-COD (Fig. 3).

However, in the gas chromatographic tests of the experiments carried out on 1,5-COD at any stage of hydrogenation, together with the various amounts of 1,5-COD and cyclooctene, there is practically a constant amount (0.2–0.3%) of 1,4-COD and 1,3-COD. These findings, coupled with the higher rate of hydrogenation of 1,3-COD, support an isomerization of 1,5-COD to coordinated 1,3-COD. The failure of the attempted hydrogenation, under analogous conditions, of a non-isomerizable diene, such as bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) is in agreement with an isomerization of 1,5-COD to 1,3-COD as essential for the formation of cyclooctene from 1,5-COD. Therefore, the detection of the small amount of 1,3-COD and 1,4-COD is attributed mostly to decomposition of the catalyst intermediates in the chromatographic column*.

In the chromatograms of the reaction mixtures obtained by hydrogenation of 1,3-COD about 2% of 1,5-COD is detected, due to the decomposition of the various Ru(η^4-1,5-COD) unities of the intermediates**.

Further support of the isomerization 1,5-COD → 1,3-COD is achieved by similar experiments carried out on equimolar amounts of 1,3- and 1,5-COD isomers (Fig. 4).

The conjugated diene disappears more rapidly, but the high selectivity is maintained during the hydrogenation. Traces of 1,4-COD are detected in the chromatograms of the reaction mixtures.

The isomerization 1,5-COD → 1,3-COD is confirmed by the experiments carried out in alcoholic solutions. As found previously [19] for hydrogenation of cycloheptatriene in the presence of *I*, selectivity decreases since formation of cyclooctane ini-

*The use of butanol in place of propanol is due to some superimposition of the peaks of propanol and cyclooctene in the gas chromatographic analysis in our experimental conditions.

*See later for some considerations on the types of intermediates involved.

**Solutions of *I* in THF, before additions of dienes and hydrogen, gave only 1,5-COD and C_8H_{10} in the chromatographic analysis.

TABLE I. Turnover Numbers* for Selective Hydrogenation and Isomerization Reactions, at 20 °C.

Solvent	Hydrogenation of 1,3-COD	Hydrogenation of 1,5-COD	Isomerization** 1,5-COD → 1,3-COD
Tetrahydrofuran	0.304	0.215	0.730
Isopropanol	1.010	0.920	11.490
Ethanol	0.931	0.431	0.801
Methanol	0.730	0.083	0.093
Butanol	0.621	0.054***	0.059***

*Calculated as mol of diene hydrogenated or isomerized per mol of catalyst per minute, from the slope of the curves (in the max. rate region) of Figs. 3, 5, and 6. **Calculated assuming that the rate of hydrogenation of 1,5-COD is given by the addition of the rate of isomerization (1,5-COD → 1,3-COD) and the rate of hydrogenation of 1,3-COD. Since, during the isomerization of 1,5-COD, 1,3-COD remains coordinated to the metal, turnover numbers calculated for the isomerization have theoretical meaning and can be used only to compare the rate of isomerization in the various solvents. Indeed the isomerization process cannot be separated from the hydrogenation process. ***The turnover numbers for hydrogenation of 1,5-COD and hence for isomerization, in butanol are estimated with 5–10% of error, because of a non-perfect separation of the peaks due to 1,5-COD and to the solvent in the chromatograms, under our experimental conditions.

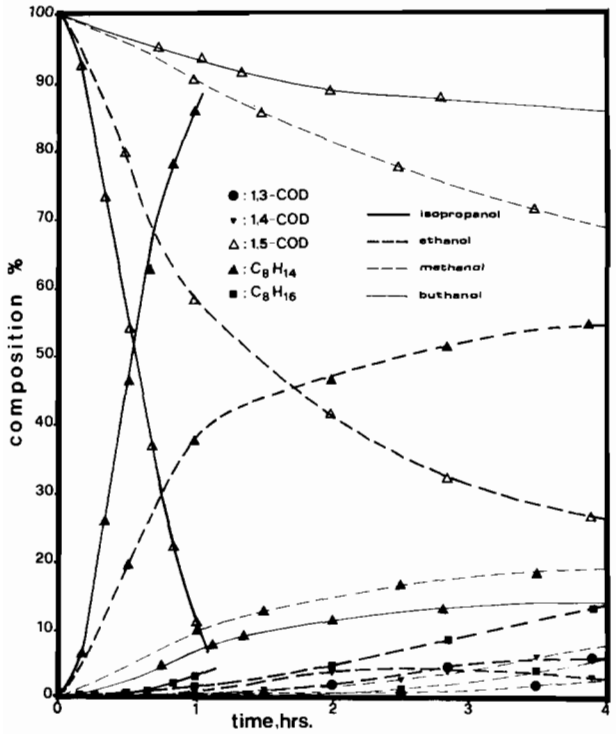


Fig. 6. Catalytic hydrogenation of 1,5-COD in alcoholic solution (at 20 °C). ($[I] = 6.9 \times 10^{-3}$ *M*; [COD]/[*I*] = 50).

tiates before hydrogenation of 1,3-COD (Fig. 5) and 1,5-COD (Fig. 6) is accomplished. The decrease in selectivity depends upon the type of alcohol.

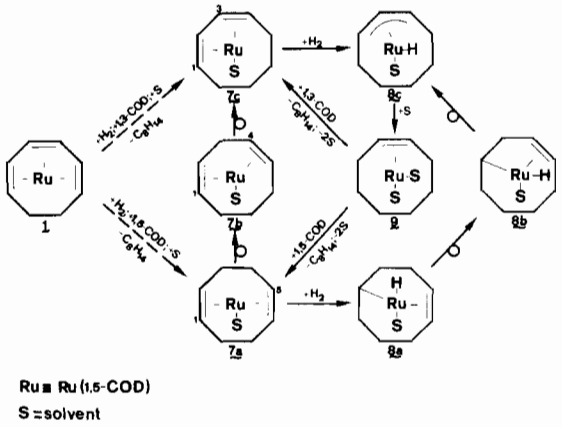
The initial rate of hydrogenation of 1,3-COD is higher in alcoholic solutions than in THF, with the following order of increasing rate: THF < Bu-n-OH < Me-OH < Et-OH < Pr-i-OH (Table I). However hydrogenation does not occur in the absence of hydrogen, although there are cases in which transfer hydrogenation of olefins in alcoholic solution is promoted by ruthenium(II) complexes such as $[RuH_2(PPh_3)_4]$ [30] and $[RuHCl(PPh_3)(\eta^6\text{-}C_6Me_6)]$ [31]. The latter complex is also active in transfer hydrogenation of cyclooctadienes in phenyl ethanol.

Although possible, 16-electron ruthenium(0) intermediates do not explain the different hydrogenation rate in the various alcohols. Therefore the mechanism proposed (Scheme II) considers 18-electron intermediates, by coordination of one or two molecules of solvent.

The initial rate of hydrogenation of 1,5-COD* in isopropanol and ethanol is higher than in THF (Fig. 6) but becomes slower in methanol and butanol A comparison of the rates of hydrogenation of the COD isomers indicates a marked influence of the type of alcohol upon isomerization of 1,5-COD to 1,3-COD (Table I). For instance, the hydrogenation rate of 1,3-COD in isopropanol is less than two times the rate in methanol but the isomerization rate is about 120 times higher.

Hydrogenation of 1,5-COD does not occur in the absence of hydrogen, but this is no proof of a participation of hydrogen in the isomerization cycle, since it was established that each substitution of cycloocta-1,3-5-triene in *1* [21] occurs only in hydrogenation conditions. When 1,5-COD and a molecule of solvent have substituted the triene to give *7a* the

*It must be noted that the 'hydrogenation of 1,5-COD' means in this paper formation of cyclooctene through two processes: isomerization of 1,5-COD to 1,3-COD followed by hydrogenation of coordinated 1,3-COD. (See also notes to TABLE I).



Scheme II

isomerization to *7c* could be possible in the absence of hydrogen (Scheme II). When 1,3-COD is the substrate hydrogenation to cyclooctene should start from *7c*. The presence of an induction period in all the solvents (Figs. 2–6) can be attributed to the production of the active organometallic species from the catalyst precursor *1*.

The traces of 1,4- and 1,3-COD in the gas chromatographic analyses of hydrogenation reactions of 1,5-COD are only an indirect proof of an isomerization process; 1,4-COD and 1,3-COD could be generated in the chromatographic column by dehydrogenation of intermediates *8b* and *8c*, respectively (Scheme II). It is well known that dehydrogenation is catalysed by hydrogenation catalysts, at higher temperatures [32, 33]. Therefore the presence of small amounts of 1,4- and 1,3-COD in hydrogenations of 1,5-COD carried out in THF, butanol and isopropanol can be explained equally well by a mechanism involving *7a* ↔ *7c* or *8a* ↔ *8c* intermediates. However when methanol and ethanol are the solvents the relative large amount of 1,4- and 1,3-COD (≅10% together, *cf.* Fig. 6) reflects a production of these isomers. The concurrent formation of cyclooctane suggests a competition of the cyclooctene formed for the same coordination sites of the dienes in *7b* and *7c*, to give intermediates such as [Ru(η^4-1,5-COD) S_n(η^2-C_8H_{14})$_{3-n}$] (*10*; n = 0, 1). A complex of the type [Ru(PPh_3)$_2$(C_6H_{10})$_3$] (C_6H_{10} = cyclohexene) has been proposed [34] as intermediate in the catalytic disproportionation of cyclohexene to benzene and cyclohexane. Addition of hydrogen to *10* eventually produces cyclooctane. The different proportion of 1,4 and 1,3-COD in methanol and ethanol might result from the different stability of the intermediates *7b* and *7c* having methanol or ethanol as coordinated solvent. These results are consistent with an isomerization mechanism involving ruthenium(0) intermediates (*7b*, *7c*). Moreover the isomerization 1,5-COD → 1,3-COD strongly supports that in the hydrogenation of cycloheptatriene in the presence of *1* [19] the attack of hydrogen occurs at position 1 (or 6) of the coordinated triene. Consequently the mechanism depicted in pathway B of Scheme I should be operative.

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