

firmed as nearly quantitative under a variety of conditions. In conjunction with our earlier work with $\text{CHT}=\text{CO}$, such experiments should clarify the extent to which O_2 interrupts $^3\text{CH}_2$ reactions with 2-butene at the $^3\text{CH}_2$ or $^3\text{C}_3\text{H}_{10}$ stages. The possible contributions of reactions involved in these experiments should also be considered for such diverse other systems as those of recoil C^{11} in H_2 (the yield of C^{11}O_2 is enhanced by the introduction of O_2),¹⁸ the photooxidation of acetone,¹⁹ and the reactions of atomic O with C_2H_2 and O_2 mixtures, from which CO_2 has been observed.²⁰

(18) C. MacKay, J. Nicholas, and R. Wolfgang, *J. Am. Chem. Soc.*, **89**, 5758 (1967).

(19) See, for example, D. E. Hoare and G. S. Pearson, *Advan. Photochem.*, **3**, 83 (1964).

(20) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).

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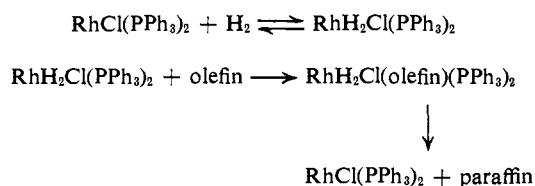
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The Mechanism of Isomerization of an Olefin and Its Possible Relation to the Mechanism of the Catalytic Hydrogenation with Tris(triphenylphosphine)rhodium Chloride

Sir:

The dihydride $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ derived from tris(triphenylphosphine)rhodium chloride is a versatile and useful reagent for the selective reduction of mono- and disubstituted double bonds in homogeneous media.¹ The mechanism of the hydrogenation of olefins with $\text{RhCl}(\text{PPh}_3)_2$ has been studied by Wilkinson and co-workers.^{1a} The hydrogenation is stereochemically a *cis* process, and kinetic studies indicate the following steps

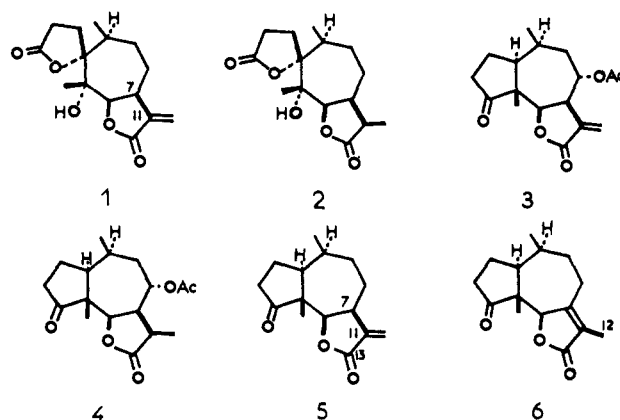


The rate-determining step appears to be the formation of olefin- $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ complex.^{1a} A simultaneous transfer of both hydrogens has been proposed.^{1a}

In this communication, we wish to present evidence for an alkyl-rhodium complex as an intermediate in the hydrogenation and, as a corollary, the stepwise transfer of hydrogen from rhodium to the olefin.

The methylene groups in psilostachyine (1) and confertiflorin (3) are smoothly reduced with $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$

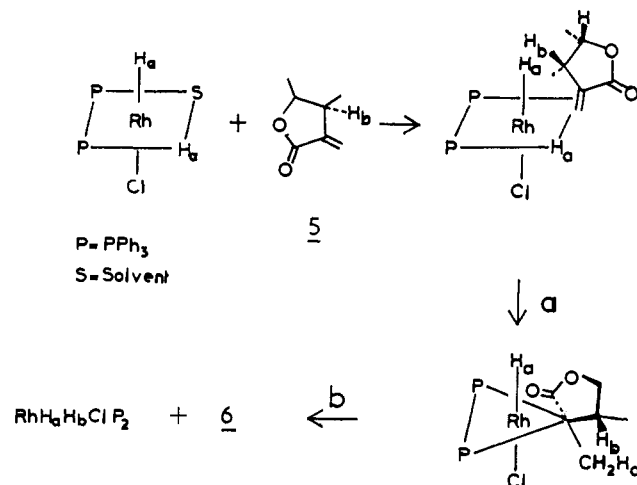
to yield the dihydro derivatives 2 and 4, respectively.^{2,3} In contrast, however, the main reaction of $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ with damsine (5) is not hydrogenation, but rather isomerization to isodamsine (6).



While the reason for this difference in behavior is not understood, it was felt that some connection might exist between the mechanism of reduction and the mechanism of this isomerization.

The following observations have been made regarding the isomerization of 5: (a) no isomerization of 5 to 6 occurs with $\text{RhCl}(\text{PPh}_3)_2$ alone; addition of hydrogen causes the reaction $5 \rightarrow 6$; (b) in the presence of EtOD, no incorporation of deuterium atom takes place in the isomerization; (c) the system $\text{RhD}_2\text{Cl}(\text{PPh}_3)_2$ and damsine (5) in equivalent amounts leads to a 58% incorporation of one deuterium atom in 6 and 0% of two deuterium atoms in the presence of a catalytic amount of $\text{RhCl}(\text{PPh}_3)_2$, 70% of 6 contains no deuterium atom, 30% one, and 0% two deuterium atoms.⁴ These facts may be accommodated by Scheme I.

Scheme I



(1) (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, **A**, 1711 (1966); F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid.*, 1574 (1967); (b) J. F. Biellmann and H. Liesenfelt, *C. R. Acad. Sci., Paris, Ser. C*, **263**, 251 (1966); A. J. Birch and K. A. M. Walker, *Tetrahedron Lett.*, 4939 (1966); J. F. Biellmann and H. Liesenfelt, *Bull. Soc. Chim. Fr.*, 4029 (1966); C. Djerassi and J. Gutzwiller, *J. Amer. Chem. Soc.*, **88**, 4537 (1966); F. H. Jardine and G. Wilkinson, *J. Chem. Soc.*, **C**, 270 (1967); A. J. Birch and K. A. M. Walker, *ibid.*, 1894 (1966); *Tetrahedron Lett.*, 1935 (1967).

(2) T. J. Mabry, H. E. Miller, H. B. Kagan, and W. Renold, *Tetrahedron*, **22**, 1139 (1966); N. H. Fischer and T. J. Mabry, *ibid.*, **23**, 2529 (1967).

(3) For the synthetic viewpoint it is interesting to note that 1 and 2 are mainly isomerized under conditions of heterogeneous conditions.² We wish to thank Dr. Kagan for calling our attention to this problem and Professor Mabry for very kindly supplying the compounds.

(4) Determined by mass spectrometry measurements with MS-9 (Gif-sur-Yvette and National Institutes of Health at Bethesda, Md.) and THN 208 spectrometers (Thomson-Houston) (Strasbourg).

Several authors have proposed a similar reaction sequence for the isomerization of olefins by the metal catalysts. The essential steps are reaction of the olefin with the metal hydride to give an alkylmetal intermediate which decomposes to the metal hydride and isomerized olefin.⁵ In general, the alkyl-metal bond is attached to the least substituted carbon atom;^{5a} however, our results require the rhodium-carbon bond to be attached at C-11, and this is reasonable in terms of the stabilization afforded by the electron-withdrawing lactone group at C-13.⁶

According to this representation, use of $\text{RhD}_2\text{Cl}(\text{PPh}_3)_2$ in step a would lead to the introduction of one deuterium atom in damsine (5) with the formation in step b of $\text{RhHDCl}(\text{PPh}_3)_2$. The hydrogen transferred to rhodium would most reasonably come from the C-7 position of damsine (5). The reaction of $\text{RhHDCl}(\text{PPh}_3)_2$ with a second molecule of damsine (5) gives isodamsine (6) with one or no deuterium atom, and, as the reaction proceeds, $\text{RhD}_2\text{Cl}(\text{PPh}_3)_2$ is progressively replaced by $\text{RhClH}_2(\text{PPh}_3)_2$. These steps explain the fact that the isodamsine (6) produced is only 58% labeled.⁷ Furthermore, the absence of dideuterated isodamsine (6) implies the irreversibility of the initial hydrogen transfer. It has already been shown that the exchange reaction between gaseous hydrogen and $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ is extremely slow.^{1a}

The hydrogen requirement of this isomerization implies that the actual catalyst is $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$, the hydrogenation catalyst. The behavior with deuterium and with deuterated ethanol is similar to that in the hydrogenation where the reaction occurs under this condition almost without participation of protons from the solvent.¹ To explain our results, one may envision either a different mechanism for this isomerization from that of the hydrogenation of olefins or that a side reaction of the usual hydrogenation mechanism gains importance. A complex between olefin and $\text{RhCl}(\text{PPh}_3)_2$ as intermediate in the isomerization is excluded by the obligatory presence of hydrogen. Furthermore, the formation of a π -allyl complex between damsine (5) and $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ would require the unlikely coordination number of eight for the rhodium atom.⁸

We think that the second explanation is more reasonable and we propose the formation of an alkylrhodium hydride as an intermediate in the isomerization of damsine (5) as well as in the hydrogenation of olefins with $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$. The reverse reaction, $\text{alkyl-RhHCl}(\text{PPh}_3)_2 \rightarrow \text{olefin} + \text{RhH}_2\text{Cl}(\text{PPh}_3)_2$, has a much smaller rate than the transfer of the second hydrogen in the usual cases, so that no isomerization can be detected. The stereochemical outcome of the reaction scheme involving an alkylrhodium is expected to be a *cis* process: *cis* addition of rhodium hydride to the double bond, followed by a cleavage of the rhodium-carbon bond with retention. On the basis of this evidence one may not

distinguish between the simultaneous transfer of both hydrogens or the reaction scheme involving alkylrhodium hydride as intermediate.

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The Structure of Sirenin¹

Sir:

Sirenin is a sperm attractant, active at concentrations of 10^{-10} M, produced by the female gametes of the water mold *Allomyces*. The production, isolation, and characterization of sirenin and its 4-(4-nitrophenylazo)-benzoate (NABS) esters have been described.² We now present the complete structure of sirenin (I) which becomes the first structurally characterized plant sex hormone.

Bis-NABS-sirenin (II) had nmr signals³ at 0.95 (3 H, s, tertiary CH_3), 1.78 (3 H, broadened s, $\text{C}=\text{CCH}_3$), 4.75 (4 H, s, two NABS- $\text{OCH}_2\text{C}(\text{C})=\text{C}$), 5.59 (1 H, t, $J = 7$ Hz, $\text{C}=\text{CHCH}_2$). Partial ozonolysis at -60° gave three products, purified by tlc on silica gel. One was the NABS ester of hydroxyacetone, identical with an authentic sample.

A second product (III), mol wt 447 (mass spectroscopy), retained nmr signals attributed to the tertiary methyl, one NABS- $\text{OCH}_2\text{C}(\text{C})=\text{C}$, and the vinyl proton at 5.98. New signals appeared at 9.79 (1 H, t, $J = 1.45$ Hz) and 2.55 (2 H, "t"). The 2.55 "triplet" was composed of two overlapping doublets, $J = 6.90$ and 7.85 Hz. Each peak of the "triplet" was further split into a doublet with coupling constant corresponding to the 9.79 peak which collapsed to a singlet upon irradiating the signal at 9.79. This product thus results from loss of hydroxyacetone-NABS ester from bis-NABS-sirenin with concomitant formation of an aldehyde, ir⁴ peak at 2736 and enhanced absorption at 1722. A propionaldehyde residue attached to an asymmetric center would make the adjacent methylene protons nonequivalent⁵ and result in unequal coupling to the methylene group α to the carbonyl. A 5-hydroxy-4-methyl-3-pentenyl moiety in sirenin accounts for these observations.

The third product (IV) retained nmr absorptions characteristic of the pentenyl double bond in II. New signals at 2.53 (2 H, t, $J = 6.35$ and 6.60 Hz for low- and high-field portions) and 4.95 (2 H, s, identical in chemical shift with NABS-hydroxyacetone) reflected the

(5) (a) N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967); (b) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966); (c) P. S. Hallmann, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 305 (1967); H. A. Tayim and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 3420 (1967).

(6) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

(7) According to the low rate of exchange of the two positions of both hydrogen atoms in $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$,^{1a} the hydrogen introduced during the isomerization of the first molecule of damsine (5) by $\text{RhD}_2\text{Cl}(\text{PPh}_3)_2$ may be used for the reaction of a second molecule of damsine, producing $\text{RhDHCl}(\text{PPh}_3)_2$ and isodamsine (6) containing no deuterium atom.

(8) R. V. Parish, *Coordination Chem. Rev.*, **1**, 439 (1966).

(1) Financial support in part by the National Science Foundation is gratefully acknowledged.

(2) L. Machlis, W. H. Nutting, M. W. Williams, and H. Rapoport, *Biochemistry*, **5**, 2147 (1966).

(3) All nmr data are δ values, recorded at 60 and 100 MHz in CDCl_3 with internal TMS (δ 0) unless otherwise stated.

(4) All ir spectra were taken in CHCl_3 unless otherwise stated and are given in reciprocal centimeters, cm^{-1} .

(5) See M. L. Martin and G. J. Martin, *Bull. Soc. Chim. France*, 2117 (1966). Dimethyl (+)-*trans*-homocarbonate exhibits a multiplet for its methylene group: L. R. Subramanian and G. S. K. Rao, *Tetrahedron*, **23**, 4167 (1967).