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Racemization of (***R***)-(−)-10-methyl-$\Delta^{1(9)}$-octalin: Stereochemical requirements for double bond migration (isomerization) on metal catalysts

G.V. Smith*, Y. Wang, R. Song, M. Jackson

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale IL 62901-4409, USA

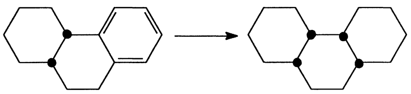
Abstract

(***R***)-(−)-10-methyl-$\Delta^{1(9)}$-octalin was synthesized in a mixture with *cis*- and *trans*-(***R***)-(−)-10-methyl-$\Delta^{1(2)}$-octalin in a five step sequence. After removal of the *cis*- and *trans*-(***R***)-(−)-10-methyl-$\Delta^{1(2)}$-octalins by hydrogenation over 5% Pt/C, 5% Rh/C, or 5% Pd/C, the remaining (***R***)-(−)-10-methyl-$\Delta^{1(9)}$-octalin was monitored for racemization (double bond migration) during continued hydrogenation. No racemization occurs over these catalysts. However, slow racemization does occur in increasing amounts during hydrogenations over a series of 1% Pd/SiO_2 catalysts with dispersions increasing from 36%D to 84%D. The ratio of *cis*- to *trans*-9-methyldecalin changes from 1.8 over 5% Rh/C, 1.6 over 5% Pt/C, 1.1 over 5% Pd/C, to 1.0 over the 1% Pd/SiO_2 catalysts. Since double bond migration does not occur over the 5% catalysts, it cannot be used to account for differences in the ratio of *cis*- to *trans*- products. Congestion around the double bond inhibits addition, but double bond migration seems to require the allylic hydrogens to be nearly perpendicular to the planes of the double bond and the surface.

Keywords: Hydrogenation; Double bond migration; Isomerization; Stereochemistry; Pt/C; Rh/C; Pd/C; Highly dispersed Pd/SiO_2

1. Introduction

Stereochemical requirements for hydrogenation (addition of hydrogen across π-bonds) originated with Vavon in 1926 [1] with the notion that steric hindrance between the catalyst and the substrate directs attack of hydrogen. This concept was greatly expanded with the detailed analytical work of Linstead et al. in 1942 [2] in which they carefully determined the stereoisomers produced from hydrogenations of *cis*-as-octahydrophenanthrene (**1**) and diphenic acid (**3**).[1] Each produced mainly *cis* isomers with *syn* ring junctions, which is easy to rationalize assuming that



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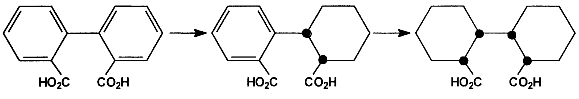

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*Corresponding author. Tel.: 001 618 453 7319; fax: 001 618 453 6408; e-mail: gvs@mols.siu.edu

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[1] The solid dot on the structure indicates a hydrogen atom on the side of the molecule above the plane of the paper.

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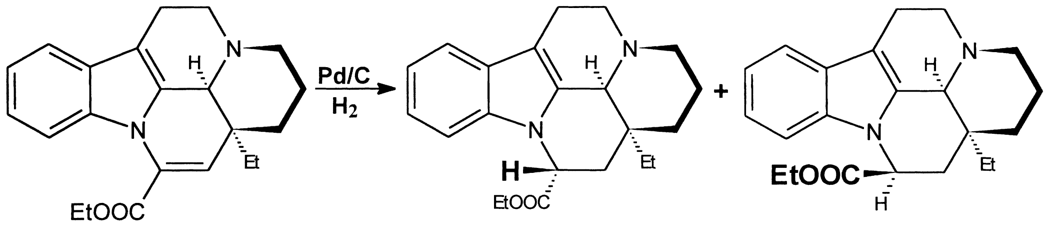
the molecules adsorb as flat as possible on a plane surface with minimum steric interference between the surface and the molecules, and that the hydrogens add from the surface to the side of the double bond facing the surface. Thus was born the now widely held understanding that hydrogenation occurs by addition of two hydrogen atoms from the surface to the same side of the adsorbed molecule, i.e., *cis* addition. What is not so widely understood is that this simple mechanism does not always predict stereochemistry. Sometimes addition appears to occur *trans*. Attempts to explain this apparent stereochemical anomaly have led to numerous studies [3,4].

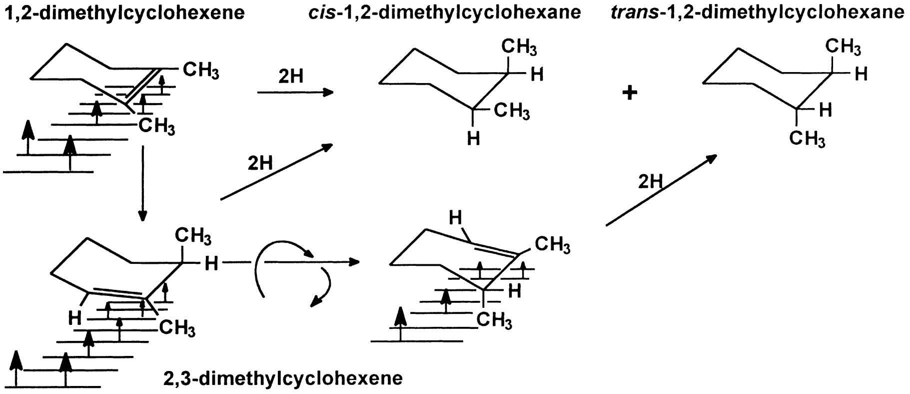
Apparent *trans* addition occurs most obviously during hydrogenations and deuteriumations of tetrasubstituted alkenes. Two examples of these are the plantinum catalyzed hydrogenation of 1,2-dimethylcyclohexene [5] and the deuteriumation of $\Delta^{9(10)}$-octalin [6]. Over Pt catalyst these substrates yield a significant amount of *trans* product, which has led to various mechanistic proposals. Essentially, four kinds of mechanistic proposals have been made; they are (A) turning the adsorbed alkene over while still attached to the surface so that after hydrogen has added to one face it can add to the other (not an explanation for $\Delta^{9(10)}$-octalin); (B) adding one hydrogen to the exposed face of the adsorbed alkene either from the bulk phase (if gaseous, involving dihydrogen; if liquid, involving dihydrogen or solvent), or from an adjacent protuberance on the catalyst surface, and then adding another hydrogen to the adsorbed face from the surface; (C) moving hydrogen from the bottom (adsorbed face) up onto the top of the adsorbed alkene; and (D) isomerizing the double bond to an adjacent position, desorbing the molecule and readsorbing it on its other face.



vinpocetin (**6**) (-)-dihydrovinpocetin (**7**) (+)-dihydrovinpocetin (**8**)

An example proposed for (A) is the formation of a 1,1-diadsorbed terminal alkene [7,8] which sits perpendicular to the surface and to which hydrogen or deuterium may add to either side, thus accomplishing *trans* addition.

Two examples have been proposed for (B). In one example, molecular deuterium from the gas phase (alternatively, presumably from the liquid phase also) was proposed to add in a *trans* fashion, one deuterium to the exposed face of an adsorbed π-allyl species (in a Rideal type mechanism [9]) and another deuterium from the surface to the adsorbed face [10]. In the other example, one hydrogen on an edge atom was proposed to add down to the top of an alkene adsorbed at the inside of a lower step or plane while another hydrogen adds up from the surface to the adsorbed face [11]. An interesting example of this mechanism has recently been proposed by Tungler et al. [12] to account for the formation of (−)-dihydrovinpocetin (**7**) from vinpocetin (**6**). (+)-Dihydrovinpocetine (**8**) would be expected if vinpocetin adsorbs on its less hindered face and if hydrogen adds from the surface to the adsorbed face. However, massive production of (−)-dihydrovinpocetin signals *trans* addition and prompted the authors to refer to recent work by McIntyre et al. [13] in which hydrogen is shown to be "activated" by the Pt tip of a scanning tunneling microscope. Although not elaborated by the authors [12], extrapolating these results to the vinpocetin hydrogenation implies that hydrogen can jump off an adjacent protuberance onto the exposed face of an adsorbed alkene to give "top side" addition. Alternatively, an arrangement might be envisioned within a pore where hydrogen jumps from the surface of one metal crystallite onto the exposed face of an alkene adsorbed on another metal crystallite on the opposite wall. Or if two metal crystallites are closely located, the same sort of jump could be envisioned. Surely, as must be the case for the scanning tunneling microscope experiment, the distance over which such a jump might occur must be short, so that the energy required to break the hydrogen–metal bond is regained by formation of the hydrogen–carbon bond. The maximum distance might be equivalent to that of two hydrogen bonds in water.



While this novel suggestion does alert us to the possibility that hydrogen atoms may posses the ability to move some distance through space (or solvent; an idea advanced by Izumi [14]) to attack adsorbed species, and hence, jump from an adjacent protuberance to the exposed face of an adsorbed species, caution must be observed in the case of vinpocetin, because its hydrogenations were run in methanol solvent. In a somewhat similar case of the hydrogenation of an α,β-unsaturated ester (in the presence of deuterated methanol and trifluoroacetic acid), van Bekkum and coworkers [15–18] his group showed that *trans*-addition involves hydrogen or deuterium addition from these solvents. This example and other *trans* hydrogenations, such as cholest-$\Delta^{8(14)}$-ene-3β-ol, are typically discounted as resulting from proton or deuteron addition from a strong acid or a solvent molecule to the top side of the adsorbed alkene. That being the case, one wonders whether hydrogen can also be transferred from various molecules in solution to an adsorbed alkene.

An example of (C) is a proposal of a 1,3-hydrogen shift over the top (exposed face) of an adsorbed alkene [19]. This latter proposal has recently been shown unlikely by findings that deuterium labeled apopinenes racemize by way of 1,3-deuterium shifts along the adsorbed face of the double bond [20].

But currently the most widely accepted mechanism for apparent *trans* addition is (D), which involves double bond migration followed by desorption, flipping, readsorption, and addition [21].

The mechanism explains the major products regardless of whether the active site is a plane atom, edge atom, corner atom, or some cluster of such atoms. It became strengthened by the discovery that a small amount of 2,3-dimethylcyclohexene is formed and desorbs during hydrogenation of 1,2-dimethylcyclohexene over platinum [21]. However, to accomplish this *trans* addition on platinum, the isomerization must proceed contrary to thermodynamics; it must proceed virtually completely from the more stable to the less stable isomer (the 2,3-isomer yields only 30% *trans* under comparable conditions). This problem, that the more stable 1,2-isomer is proposed to virtually completely isomerize to the less stable 2,3-isomers, is discounted by authors on the basis that the 1,2-isomer adsorbs weaker than the 2,3-isomers, so the 2,3-isomers displace the 1,2-isomer from the catalyst surface. Their argument is further strengthened by the fact that the proportion of *trans* product increases as the double bond isomerizing ability of various catalysts increases [22]. Moreover, the proponents urge, the reaction occurs within pores from which the newly formed 2,3-isomer does not escape before readsorption and hydrogenation. Nevertheless, while it is true that some 2,3-isomer is formed and escapes into the bulk liquid phase, it is also true that *trans* product forms from the very beginning of the reaction before the 2,3-isomer reaches steady state [21].

Therefore, this mechanism explains the major products and a substantial portion of the minor products, but one wonders how the unexplained portion of the minor products, the results of apparent *trans* addition, occurs. Are there circumstances under which hydrogen can add from the gas or liquid phase to the exposed face of an adsorbed double bond? Are there sites on the surface where the double bond can adsorb such that surface hydrogen on a step can jump onto its exposed face? And can double bond migration fully account for apparent *trans* addition to tetrasubstituted alkenes? To seek answers to these questions, we have focused initially on the issue of double bond migration.

If double bond migration fully accounts for *trans* products from the hydrogenation of 1,2-dimethylcyclohexene and $\Delta^{9(10)}$-octalin, then one might expect to find evidence for double bond migration in a relatively unsubstituted cyclohexene ring. But one of the problems with the 1,2-/2,3-dimethylcyclohexene system is: the daughter 2,3-isomer excludes the parent 1,2-isomer from the surface and lowers the probability of observing isomerization from 1,2- to 2,3-. Clearly double bond migration must be studied among isomers which do not exclude each other from the surface. Therefore, we have worked with enantiomers, which should have identical rates of double bond migration and addition on a symmetrical surface.

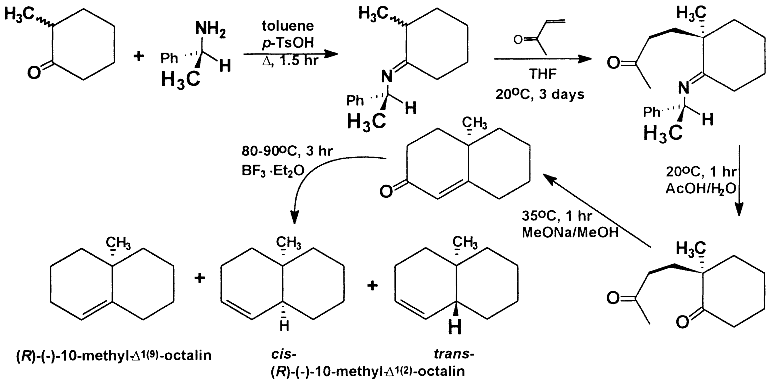
Our first enantiomeric pair was (+)-, and (−)-4-methylcyclohexene, which contains a double bond two positions away from the methyl substituent. Starting with virtually pure (−)-4-methylcyclohexene, we found that 2.55% double bond migration occurs over plantinum after approximately 32.9% deuteriumation [23]. Its relative rate of isomerization to addition was 0.078 over Pt. This rate of double bond migration does not seem to account for that required for the amount of *trans*-1,2-dimethylcyclohexane produced during hydrogenation of 1,2-dimethylcyclohexene according to mechanism D [5]. Results from deuteriumation of (−)-4-methylcyclohexene were in accord with those found by Dutton and coworkers [24,25] for double bond migration along the alkyl chain of oleic acid during hydrogenation. They found double bond migration proceeded only 28% of the rate of addition over platinum at 50°C, a temperature much higher than those employed to study the dimethylcyclohexene system. For comparison, double bond migration (racemization) in the apopinenes, our second enantiomeric pair, occurs very fast relative to addition [26,27]. Over Pt, double bond migration occurs 61% of the rate of addition. So the relative rates of double bond migration and addition are much different in different molecules. To learn what stereochemical factors control this, we have studied the hydrogenation of a new molecular probe, (***R***)-(−)-10-methyl-$\Delta^{1(9)}$-octalin. Preliminary results over Pt catalysts have been reported elsewhere [28]; here we report results over Pd and Rh catalysts.

2. Experimental

The catalysts, 5% Pd/C, 5% Pt/C, 5% Pt/Al_2O_3, and 5% Rh/C were purchased from Engelhard Industries. The 1% Pd/SiO_2 catalysts of dispersions 36.0, 49.7, 63.1, 77.8, and 84.0 were synthesized in our laboratories from one 1% Pd/SiO_2 precursor prepared by ion exchange and reduction in hydrogen at 300°C for various times [27,29]. Hydrogen and helium were purchased from GENEX company.

Hydrogenations were conducted at ambient temperature (23–25°C) and 2.0 psig hydrogen in an apparatus previously described [27]. Essentially, it consists of a small glass slurry reactor (15 mm× 100 mm) containing double helical Vigreux indentations, with a neck at the top (for connection to the hydrogen handling system) adjacent to an injection port capped by a nylon bushing and a silicon septum. After introducing the catalyst, conducting several evacuations and purgings with hydrogen, the solvent and substrate are introduced and the reactor is rotated at its bottom in a vortex manner at 2500 revolutions per minute. Because hydrogenations of these compounds are so slow, there is little danger of mass transfer problems (with the improbable exception of pore diffusion) influencing results.

(***R***)-(−)-10-methyl-$\Delta^{1(9)}$-octalin was synthesized in a mixture with *cis*- and *trans*-(***R***)-(−)-10-methyl-$\Delta^{1(2)}$-octalin in a five step sequence shown in Scheme 1. The first four steps follow the procedure of Pfau [30]. The last step is a new example of the selective reduction of the carbonyl group of an aliphatic α,β-



Scheme 1. Synthesis of (***R***)-(−)-10-methyl-1,9-octalin.

unsaturated ketone. NMR spectra agreed with those published [31].

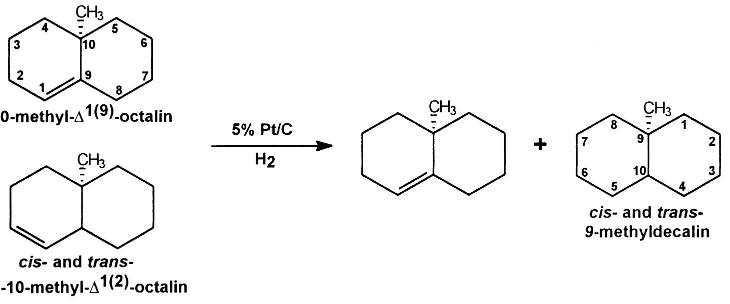
The 10-methyl-$\Delta^{1(2)}$-octalins were removed by hydrogenation (*n*-hexane solvent) over the various supported Pt, Rh, and Pd catalysts, and the resulting mixtures containing 10-methyl-$\Delta^{1(9)}$-octalin, now diluted with optically inactive *cis*- and *trans*-9-methyldecalin, were further hydrogenated to different extents over the Rh and different Pd catalysts, and their optical rotations measured. Gas chromatographic analyses of the reaction mixtures revealed the concentrations of the *cis*- and *trans*-9-methyldecalins and of the remaining 10-methyl-$\Delta^{1(9)}$-octalin and allowed calculation of its specific rotation. (See Scheme 2).

3. Results

On Pt we found virtually no racemization and, therefore, no double bond migration [28]. Now, also, on 5% Rh/C we find no racemization. At 63.5%, 76.8%, and 91.4% hydrogenation on 5% Rh/C, we found specific rotations of −67.2°, −66.8°, and −67.2°, respectively, for recovered 10-methyl-$\Delta^{1(9)}$-octalin. Likewise, 5% Pd/C did not catalyze double bond migration as shown in Fig. 1. Moreover, we continued to find more *cis*- than *trans*-9-methyldecalin in the products.

These results led us to do two things. We examined computationally optimized models of the 10-methyl-octalins to learn more about their structures and we conducted hydrogenations on 1% Pd/SiO_2 catalysts of a variety of decreasing particle sizes to see if higher proportions of edges and corners might increase racemization and influence the stereochemistry.

As the Pd particle size becomes smaller, the rates of addition and racemization increase. Fig. 2 shows a plot of the averages of at least two experiments for each of five different dispersions stopped at approximately 81% addition (19% 10-methyl-$\Delta^{1(9)}$-octalin



Scheme 2. Hydrogenation of synthetic mixture of 10-methyloctalins.

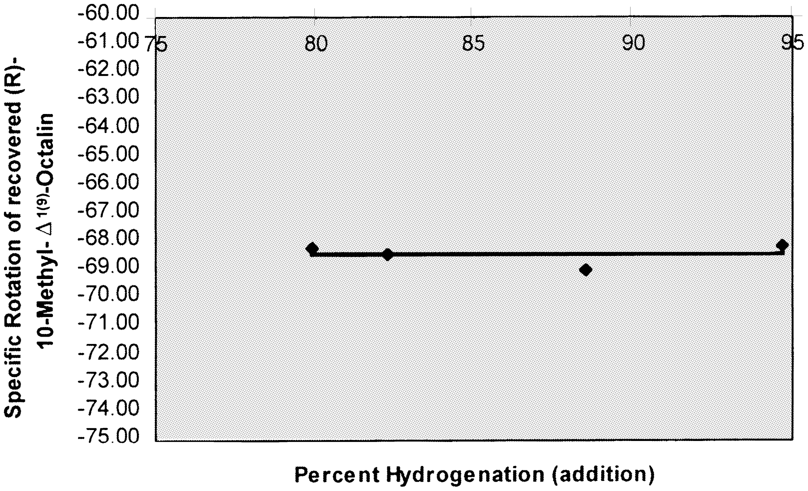


Fig. 1. Hydrogenation of (***R***)-10-methyl-$\Delta^{1(9)}$-octalin over 5% Pd/C.

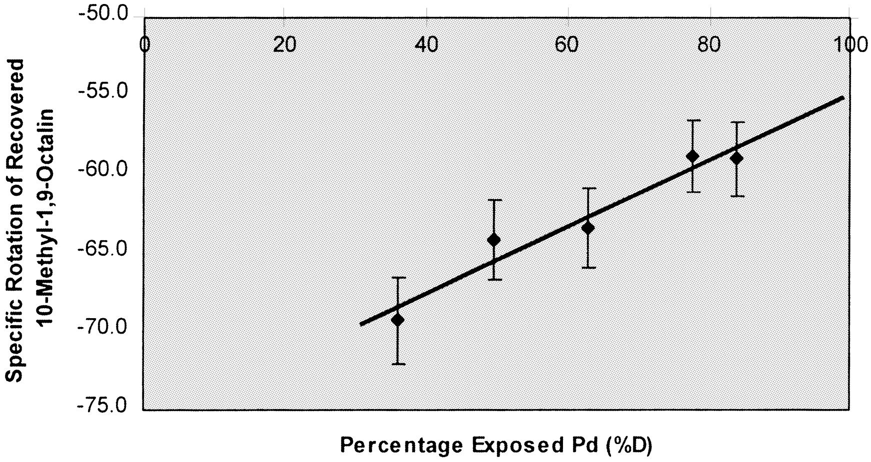


Fig. 2. Hydrogenation of (***R***)-(−)-10-methyl-1,9-octalin over variously dispersed Pd/SiO_2 at an average 81% hydrogentation.

remaining). Error bars (4%) are included as an estimation of maximum error and a trend line has been added.

The approximate ratios of *cis* to *trans* saturate are shown in Table 1. These were obtained after subtracting for the *cis* and *trans* saturates produced from the mixture of *cis*- and *trans*-10-methyl-$\Delta^{1(2)}$-octalins in the initial stage of the hydrogenation. The proportions of *cis*- and *trans*-products are roughly the same on Pt and Rh but different on Pd. Although the data go through a minimum at 63% dispersion on the 1% Pd/SiO_2 catalysts, the experimental error for these data, which may be as high as 20% in some cases, restricts mechanistic conclusions.

Optimized 3D structures of (***R***)-10-methyl-$\Delta^{1(9)}$-octalin are shown in Fig. 3 as both space filling and ball and stick models in the same orientation. The view is at the front with the 10-methyl group at the back showing the downward protrusion of C_7, the in-plane position of the equatorial allylic hydrogen at C_8, and the congestion on top caused by the 10-methyl group.

Table 1
Approximate ratios of *cis*/*trans* obtained over different catalysts

Catalyst	*cis*/*trans*
5% Pt/C	1.6 [28]
5% Pt/Al_2O_3	1.7
5% Rh/C	1.8
5% Pd/C	1.1
1% Pd/SiO_2 84.0%D	1.0
1% Pd/SiO_2 77.8%D	0.90
1% Pd/SiO_2 63.1%D	0.84
1% Pd/SiO_2 49.7%D	0.97
1% Pd/SiO_2 36.0%D	1.1

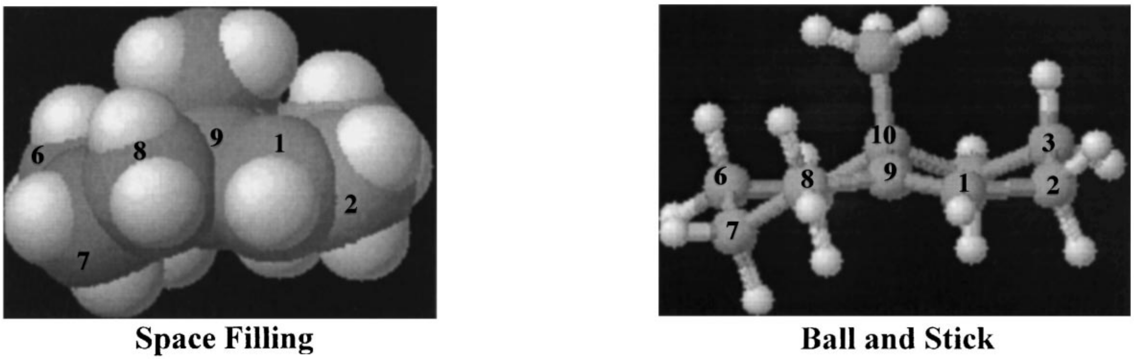
4. Discussion

Our aim in preparing (***R***)-10-methyl-$\Delta^{1(9)}$-octalin was two-fold. First, we wanted a molecule in which double bond migration would occur outside a cyclohexene ring in a convex manner, like the $\Delta^{7(8)}$ to $\Delta^{8(14)}$ isomerization in the cholest-$\Delta^{7(8)}$-ene-3β-ol system [21]. We wondered whether double bond migration might be more facile in this arrangement than within a cyclohexene ring in a concave manner. In the former case, hydrogen would migrate outside the ring system, but in the latter, it would migrate inside the ring system, as in the apopinenes [20]. Second, we wanted a molecule which had the topside blocked, as in the apopinenes. We reasoned that the 10-methyl group would sufficiently hinder adsorption on its side of the double group as the bridgehead methyl group appear to do in the cholestene system [19]. We were to be surprised in both cases.

First, racemization in (***R***)-10-methyl-$\Delta^{1(9)}$-octalin is best characterized as extremely slow. Second, not only does the 10-methyl group not prevent adsorption on its side of the double bond, but that side is also the dominant side of addition. What do these data suggest about the stereochemistry of double bond migration and addition.

That racemization is virtually nonexistent on large metal crystallites but occurs increasingly on smaller and smaller metal crystallites, suggest a minor role played by plane sites and a major role played by edge and corner sites [27,32]. In a qualitative way, these data also suggest the same roles for addition.

Examining the models in Fig. 3 reveals clues about the low rate of racemization. Should the molecule adsorb with the 10-methyl side away from the surface, the equatorial hydrogen at C_8 is not aimed at the surface. Rather, it is aimed parallel to the surface in a poor position to be abstracted to form a π-allyl species. Also, should it be removed, substantial rearrangement of the C_7 carbon would be required to form the π-$C_{1\text{-}8}$-allyl system. In fact, the axial hydrogen at C_8 is in much better position to be abstracted, providing the molecule sits down on the 10-methyl side. However, severe congestion occurs between the 10-methyl group and the axial hydrogen at C_8, so it may not be able to get close enough to the surface to be abstracted. Also, substantial rearrangement of C_7 would be required. However, the data do not exclude the possibility that double bond migration occurs to the $\Delta^{1(2)}$ position by way of a π-$C_{9\text{-}2}$-allyl surface species (methyl towards the surface) and that final addition occurs at C_1 and C_2. Such an isomerization



Space Filling

Ball and Stick

Fig. 3. Models of (***R***)-10-methyl-$\Delta^{1(9)}$-octalin.

would relieve methyl-surface interactions and not lead to racemization. However, this seems improbable since the axial hydrogen at C_2 is on the side of the ring system opposite the methyl. Nevertheless, baring this last possibility, we suggest the data reveal the importance of the stereochemistry of the allylic hydrogens in metal catalyzed double bond migrations. Apparently, double bond migration occurs most readily when abstractable hydrogens are axial and minimum structural rearrangement of the adjacent carbons are required to form an adsorbed π-allyl system. The apopinenes fit this description admirably; 10-methyl-$\Delta^{1(9)}$-octalins do not. As to its interactions with the surface, the smaller metal crystallites present more edge and corner sites on which this congested molecule can fit.

On the other hand, if the 10-methyl-$\Delta^{1(9)}$-octalins cannot adsorb on their 10-methyl side, why is the *cis* product dominant? The data do not clearly answer this question, but suggest that the requirements for removal and replacement of hydrogens in double bond migration are different from those required for addition to produce saturated products. Instructive is the different ratios of *cis/trans* on the different catalysts. Earlier, we mentioned that the argument for mechanism (D) was strengthened by the fact that those metals which catalyze most *trans* product, also catalyze most double bond migration. However, for the 10-methyl-$\Delta^{1(9)}$-octalins, no double bond migration (even on Pd) is observed on any of the 5% carbon-supported catalysts, yet the ratio is clearly lower on Pd. Since this ratio cannot be a result of double bond migration, desorption, flipping, and readsorption, mechanism (D) must not be operating and the different ratio must be some other property of the metal and substrate. Perhaps it reflects subtle differences in energies of adsorption on the different metals or some surface reconstruction of Pd which can more easily accommodate the 10-methyl-$\Delta^{1(9)}$-octalin structure. Perhaps *trans* addition does occur after all.

Can we eliminate any more *trans* addition mechanism? Certainly, aspects of mechanism (B) can be questioned. If *trans* addition were occurring by hydrogen jumping from a step down onto the top of an adsorbed molecule on a lower step, such opportunities should decrease as the metal particle size decreases. Yet, we find virtually unchanged *cis/trans* ratio as the particle size decreases. So if such a mechanism is occurring, it must occur between adjacent metal particle or between close metal particle on the opposite walls of small diameter pores. However, 1% Pd loadings do not place many metal crystallites close to one another, so this aspect of mechanism (B) has a low probability. Mechanism (A) cannot be eliminated by these data. Indeed, a 1,1-diadsorbed 10-methyl-$\Delta^{1(9)}$-octalin might occur. Mechanism (C) cannot be eliminated without deuterium labeling experiments. Again, mechanism (D) seems unlikely because of the lack of double bond migration between C_1 and C_8. However, we cannot exclude adsorption with the methyl up, double bond migration to the $\Delta^{1(2)}$-position, desorption, flipping, and readsorption with the methyl down followed by addition of hydrogen.

5. Conclusions

We can conclude, therefore, that congestion around the double bond inhibits addition, but that stereochemistry of the allylic hydrogens and their ability to move into a position nearly perpendicular to the planes of the double bond and the surface is critical. The mechanism of *trans* addition is still unresolved. Mechanism (A) remains a possibility, mechanism (B) is unlikely, mechanism (C) in not addressed, and mechanism (D) seems unlikely.

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