Stereochemistry of Catalytic Hydrogenation of Alkenes Contrary to the Classical Model of Adsorption[1]

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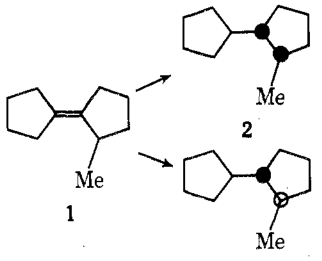
The stereochemistry of hydrogenation of 2-methylcyclopentylidenecyclopentane (**1**) on PtO_2, is examined to test the hypothesis that in the process of adsorption on a catalyst, an alkene experiences a change in geometry which is appreciable at the transition state for adsorption. The theory is supported by the formation of more *trans-* than *cis*-1-methyl-2-cyclopentylcyclopentane from **1** at high hydrogen pressures, a result which is contrary to expectation based upon traditional views of adsorption on surfaces. The stereochemistry of hydrogenating several isomers of **1** is determined to assess their possible role in the hydrogenation of **1**. At low pressures, the hydrogenation of tetrasubstituted ethylenes which have not been rigorously purified gives erratic stereochemical results; alkenyl peroxides or their decomposition products are implicated.

The classical interpretation of the stereochemistry of catalytic hydrogenation focuses attention upon the manner in which an unsaturated molecule can be fitted best to the catalyst's surface which is assumed to be flat (catalyst hindrance).[3,4] The transfer of hydrogen from the surface to the underside of the adsorbed molecule yields the product. According to current theory, the preceding view must be an oversimplification not only because the adsorption of the unsaturated species need not be the product-controlling step but even if it is, the geometry of the unsaturated molecule is altered upon adsorption.[2,5] The resulting change in torsional strain and intramolecular nonbonding interactions will depend upon which face of the double bond becomes attached to the catalytic site.[2] Because these effects can oppose "catalyst hindrance", the relative amount of the saturated stereoisomers which is obtained from a particular alkene can be the inverse of that predicted from classical theory. This kind of argument furnished an explanation for the fact that upon hydrogenation at high pressures over reduced platinum oxide, one of the more stereoselective catalysts, 2,3-dimethylcyclopentene, yields more *trans-* than *cis*-1,2-dimethylcyclopentane.[6] The observed effect in this instance is small; however, larger deviations from the classical norm can be anticipated.

To test the above ideas, we selected 2-methyl-1-cyclopentylidenecyclopentane (**1**) for this study because, clearly, the prediction based on classical theory is that more *cis*-(**2**) than *trans*-2-methyl-1-cyclopentylcyclopentane (**3**) will be formed.

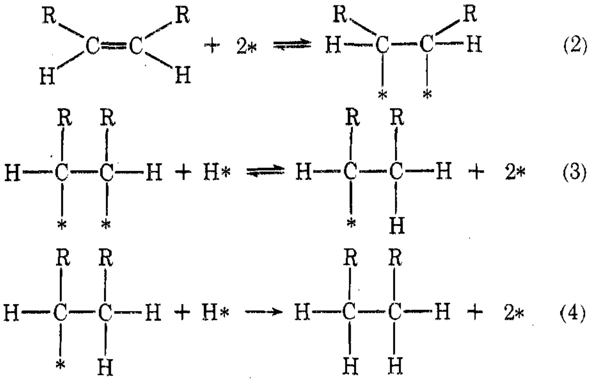


1 **2** **3**

We anticipated that the change in geometry of **1** on adsorption, however, would introduce repulsive interactions between the 2,2′ and 5,5′ ring positions which are much greater in the transition state which leads to the cis isomer than the transition state which leads to the trans isomer. Furthermore, the change in geometry would also tend to reduce "catalyst hindrance" involving the 2-methyl group. Our predictions drew support from the inspection of space filling models of the *α,β*-diadsorbed alkane which are represented in eclipsed conformations by the perspective diagrams in Figure 1.[2,5] Because they are not compressible the models overemphasize intramolecular steric hindrance; however, their use alerted us to the possible operation of the effects noted above. The hydrogenation of 2-cyclopentylidenecyclopentanol over a nickel catalyst gives mainly *trans*-2-cyclopentylcyclopentanol, but this result has been said to demonstrate the directive effect of the hydroxyl group.[7]

The preceding argument applies if adsorption of the alkene is virtually irreversible; however, other elementary processes may be product controlling. For example, if the addition of hydrogen proceeds via the Horiuti–Polanyi mechanism or one of its variations,[8,9,10] then the product-controlling reaction may be chemisorption (reaction 2), the formation of the "half-hydrogenated state" (reaction 3), or the combination of the latter with hydrogen to produce alkane (reaction 4).[2,5] Whether reaction 2 or 3 is product controlling, the change in intramolecular interactions, from alkene to the respective transition states, will affect the product ratios in the same direction, although not identically.[2,5] If reaction 4 is product controlling, however, alkene isomerization should be faster than the addition of hydrogen and the distribution of saturated products should approach the equilibrium value.[5,11]

$$H_2 + 2* \rightleftharpoons 2H* \qquad (1)$$



$$RHC{=}CHR + 2* \rightleftharpoons H{-}\underset{*}{\overset{R}{C}}{-}\underset{*}{\overset{R}{C}}{-}H \qquad (2)$$

$$H{-}\underset{*}{\overset{R}{C}}{-}\underset{*}{\overset{R}{C}}{-}H + H* \rightleftharpoons H{-}\underset{*}{\overset{R}{C}}{-}\underset{H}{\overset{R}{C}}{-}H + 2* \qquad (3)$$

$$H{-}\underset{*}{\overset{R}{C}}{-}\underset{H}{\overset{R}{C}}{-}H + H* \longrightarrow H{-}\underset{H}{\overset{R}{C}}{-}\underset{H}{\overset{R}{C}}{-}H + 2* \qquad (4)$$

The reduction of a tetrasubstituted alkene may proceed via isomerization to one which is less substituted so that the stereochemistry observed is characteristic of the hydrogenation of the products of isomerization rather than of the initial alkene.[12] Increasing the pressure of hydrogen, however, causes more of the tetrasubstituted alkene to be hydrogenated directly.[5,13] Accordingly, the stereochemistry of the hydrogenation of alkenes which might be formed by the double-bond isomerization of **1** and the effect of hydrogen pressure on the ratio of saturated stereoisomers which form also were examined.

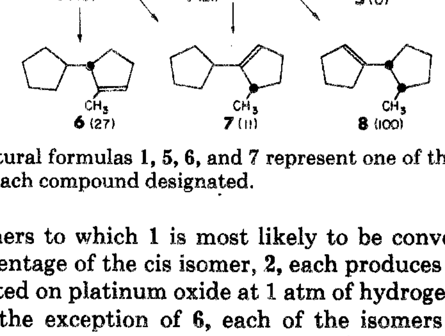
Although not anticipated from our previous experience, the ratio of stereoisomers obtained from 1 on hydrogenation over platinum oxide, particularly in the lower pressure range, seemed to be a function of the history of the alkene. Apparently, the effect is connected to the ease of peroxidation of the alkene because experiments conducted so as to mitigate exposure of the alkene to oxygen and with care to remove traces of peroxide, which might be present, lead to reproducible results.[14] In retrospect, the presence in alkenes of variable amounts of hydroperoxides or their decomposition products may account for some of the stereochemical anomalies which have been reported.[6,13,15]

Results and Discussion

Platinum Oxide. In accord with our expectations, 2-methyl-1-cyclopentylidenecyclopentane (1) yields mainly the trans dialkylcyclopentane, 3, when hydrogenated over reduced platinum oxide, a catalyst which ordinarily exhibits a relatively high stereospecificity. However, several factors tend to limit the significance of this result. At pressures near atmospheric, the stereochemistry is sensitive to the history of the alkene, that is, samples of 1 which had been kept in the laboratory for several days yielded larger percentages of the trans isomer than the freshly prepared material. Generally, the older samples also hydrogenated more slowly. Apparently the effect is due to peroxides formed on exposure of the cycloalkene to the atmosphere because after the alkene was percolated through alumina in the manner recommended by Hussey, Kuelks, Nowak, and Baker, the ratio of saturated stereoisomers was the same as that given by a fresh sample.[14] Likewise, 2-methyl-1-cyclopentylcyclopentene (4) gave erratic results at low pressures of hydrogen; the more slowly reacting samples produced the *larger proportion* of the cis isomer 2 (Figure 2). Uncontrolled variations in stereochemistry have been reported for 1,2-dimethylcyclopentene and 9,10-octalin but without comment about the likely cause of the irregular behavior.[6,12]

At low pressures, the platinum-catalyzed hydrogenation of tetrasubstituted alkenes proceeds mainly via isomerization to more easily hydrogenated and generally less substituted alkenes.[5,12] The hydrogenation of 1 was always accompanied by the appearance of 4 although the concentration of the latter remained small, less than 2%. In competition, 4 reacts about twice as rapidly as 1. Chart I indicates the isomers to which 1 is most likely to be converted and the percentage of the cis isomer, 2, each produces when hydrogenated on platinum oxide at 1 atm of hydrogen.

Chart I
Isomers of 1 and the Percentage of *cis*-2-Methyl-1-cyclopentylcyclopentane (2) Formed from Each at 1 Atm (PtO_2)[a]



[a] Structural formulas 1, 5, 6, and 7 represent one of the epimeric forms of each compound designated.

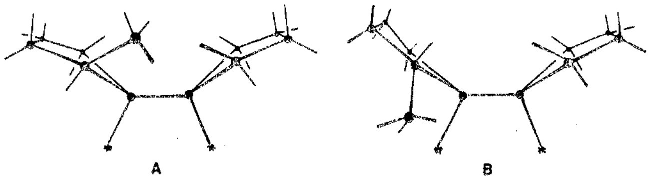


Figure 1. Diastereoisomeric adsorbed species of 1 represented as α,β-diadsorbed alkanes. A proceeds to give cis (2) and B to trans (3).

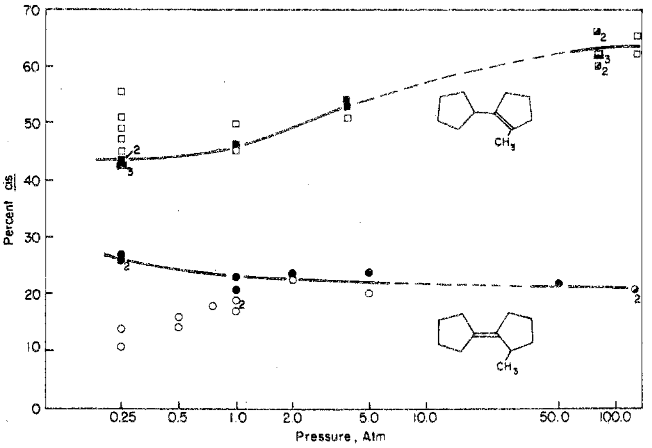


Figure 2. Percentage of cis isomer (2) which is formed over PtO_2 from 2-methyl-1-cyclopentylcyclopentene (4) or 2-methylcyclopentylidenecyclopentane (1) as a function of the hydrogen pressure. Darkened symbols represent experiments with freshly purified alkenes (see discussion): 4, □, ■; 1, ○, ●. The subscripts indicate the number of separate experiments which yielded the same result; symbols which lack a subscript represent the result of a single experiment.

With the exception of 6, each of the isomers could be formed from 1 via a 1,3-hydrogen shift.[16] If the mechanism of isomerization involved an allylic intermediate as suggested by Smith and Burwell,[12] then the principal product of isomerization is likely to be 4 because it would be formed through the breaking and subsequent re-formation of a tertiary hydrogen to carbon bond. The intermediate adsorbed π-allylic structure could retain the planarity of the groups about the double bond in 1 and would include the 2-methyl group in the same plane. Adsorption of the alkene with this same orientation would also allow the formation of 7 and 8 by an analogous dissociative mechanism or lead to *cis*-2-methyl-1-cyclopentylcyclopentane (2) through the acceptance of hydrogen from the catalyst. Adsorption of 1 on its opposite face would permit the formation of 7 and 5 by a dissociative mechanism or the trans saturated isomer, 3, by the simple abstraction of hydrogen from the catalyst. Because 1 yields more trans (3) than does 4, the latter cannot be the only intermediate even though it is the only isomer of 1 which is observed to form. If any of the other isomers were produced as intermediates they would escape detection because being less substituted alkenes, in competition, they are hydrogenated more rapidly than 1 or 4. Clearly the observed product distribution obtained from 1 at low pressures can be accounted for as arising via isomerization to some combination of the alkenes 4, 5, 7, and 8.[16] In the section on catalysis by palladium on carbon, we shall return to this question.

More definite conclusions regarding the stereochemistry of the direct addition of hydrogen to 1 can be inferred from experiments conducted at high pressure. Evidently, increasing the pressure of hydrogen increases the fraction of an alkene, including tetrasubstituted alkenes, which add hydrogen directly without prior isomerization.[5,12,13] Thus, 4 gives 43% cis at 0.25 atm and 62% at 80–100 atm. In this instance, direct addition should yield only the cis isomer, **2**; the proportion of trans (**3**) actually formed is an indicator of the fraction of **4** which isomerizes to more easily hydrogenated alkenes such as **6** and **7**. Increasing the pressure causes **1** to yield more of the trans dialkylcyclopentane, **3**, and accordingly, **3** must be the principal direct reduction product of **1**. The product-limiting step at very high pressure is likely to be the adsorption of the alkene, reaction 1.

Some support for the preceding interpretation of stereochemistry may be gained from a comparison of catalytic hydrogenation at high pressure with reduction by diimide.[2] An alkene probably adopts a geometry in the transition state for adsorption on a catalyst which is quite similar to that attained in the transition state for the transfer of hydrogen from diimide to the carbon–carbon double bond. Differences in the ratios of geometrical isomers formed by these procedures can be attributed to the expected larger interactions between the catalyst and the alkene at the transition state for adsorption. The cis to trans ratios obtained from **1**, **6**, and **7** by catalytic hydrogenation at high pressure are remarkably like those obtained from diimide (Table I), indicating that intramolecular forces largely determine the ratio of stereoisomers under these conditions.[2] Not surprisingly, **5** yields only trans, **3**, with either reagent.

Table I
Comparative Stereochemistry of Catalytic (PtO_2) and Diimide Reductions of 1 and Its Isomers

	% cis (2)		
Compd	PtO_2 (1 atm)	PtO_2 (80 atm)	Diimide
1	23	21	24
4	46	62	100
6	27	20	24
7	11	12	26
5	0.0	0.0	0.0

Effect of Impurities. Apparently the impurities in the alkene affect the stereochemistry as well as the rate of hydrogenation of **1** and **4**, the effect being to *decrease* the ratio of cis (**2**) to trans (**3**) isomers obtained from **1** and *increase* the ratio of these products formed from **4**. At least for the latter, the effect is in the direction expected for an increase in the ratio of simple addition to isomerization–addition.[17] If the same explanation applied to the effect of impurities on **1**, then the simple addition of hydrogen to **1** at low pressures is more stereospecific [greater proportion of trans (**3**)] than addition at high pressures of hydrogen. This result would be expected if the mechanism were the same as that which we have postulated and supported with evidence obtained with less substituted alkenes, i.e., that the product-controlling step for the addition of hydrogen at low pressures is the formation of the "half-hydrogenated state" while the addition at high pressures is the adsorption of the alkene.[5,6] However, the fraction of saturated products which are formed via this mechanism cannot be determined from the stereochemical evidence alone. The dominant reaction path apparently involves isomerization to less substituted and more reactive alkenes.

Samples of **4** which had not been percolated through alumina prior to use gave a ratio of cis to trans isomers which decreased with conversion, from 51% cis at 6% reduction to 38% cis at 37% reduction. Rigorously purified samples did not show this effect. This trend in stereochemistry corresponds to a decrease in the relative rates of addition to isomerization resulting from a progressive change in the catalyst, as if the impurities, which had tended to favor simple addition–hydrogenation, were being destroyed.[17] Tetrasubstituted alkenes appear to be more easily affected in this way by adventitious impurities, presumably peroxides, than are less substituted alkenes.

Reduction over Palladium. Alkene isomerization characteristically accompanies hydrogenation on palladium catalysts and the hydrogenation of **1** is unexceptional in this regard.[18] Isomerization yields mainly 2-methyl-1-cyclopentylcyclopentene (**4**) and *trans*-2-methyl-1-(1-cyclopentenyl)cyclopentane (**5**). The latter is more easily hydrogenated than either **1** or **4** and consequently the amount detected after less than 60% of **1** remains (Table II) must represent only a fraction of that actually formed initially. Smaller amounts of **7** and an unidentified product, possibly *cis*-2-methyl-1-(1-cyclopentenyl)cyclopentane, are also present at this stage of the reduction. Knowledge of the distribution of the product as a function of the fraction of **1** converted would have afforded a better measure of the initial distribution of products. Although this information is lacking, the principal alkene formed appears to be **5** rather than **4**, although the latter is likely to be an initial product too. Whether the mechanism of formation of **5** is dissociative or associative, the first step would require the adsorption of **1** on the face which, ordinarily, would be thought to be the more hindered side of the molecule.[19]

Table II
Survey Hydrogenations of 1 and 4[a]

Compd	Catalyst	P, atm	% redn	% cis[b]	% other products
1	5% Pt/C	0.25	29	15	1.6 (4)
		1.0	100	11	
		135	66	13	2.1 (4)
1	5% Pd/C	0.25	36	11	10 (4), 13 (5)
		1.0	47	10	11 (4), 9 (5)
		133	100	13	
1	5% Rh/C	134	100	45	
1	5% Ru/Al_2O_3	67	45	45	0.2 (4)
4	5% Pd/C	0.25	7	32	0.7 (7)
4	5% Rh/C	134	100	94	

[a] Temperature 27 ± 2°. [b] Percent of saturated product

In comparison, the initial product of isomerization of **4** appears to be **7** rather than **6**. Although **1** is not formed initially, it would undoubtedly appear later as the reaction proceeded, since isomerization is a dominant feature of the hydrogenations of alkenes on palladium catalysts. Usually the more stable isomers predominate in the products of hydrogenation when palladium catalysts are used, and in this respect the results in Table II are not unexpected.

Other Catalysts. Several other catalysts were used in a few experiments and the results are shown in Table II. With ruthenium and rhodium catalysts, **1** yields larger proportions of the cis product than is given by platinum at the same pressure. The fact that **1** gives 55% cis at high pressure may simply reflect the fact that **4**, a principal product of the isomerization of **1**, yields the cis isomer almost exclusively (94% cis) under the same conditions. The ratio of saturated isomers obtained with platinum on carbon is similar to the ratio obtained on reduced platinum oxide; however, too few experiments were done to warrant much comment. For comparison we note that Weitkamp reports that the hydrogenation of $\Delta^{9,10}$-octalin at 25°C and 25 atm of hydrogen gives 67, 95, and 85% *cis*-decalin with platinum, ruthenium, and rhodium catalysts, respectively; the metals were supported on charcoal.[13b]

Experimental Section[20]

2-Methyl-1-(1-cyclopentenyl)cyclopentene (9). The alkenes 1 and 4 were separated from a mixture obtained by hydrogenating the diene, 2-methyl-1-(1-cyclopentyl)cyclopentene (**9**), until the equivalent of 1 mol of hydrogen per mole of **9** had been adsorbed. The diene was prepared as follows.

To a solution of methylmagnesium iodide (0.8 mol in 250 ml of ether) was added dropwise an equal volume of an ethereal solution of 2-cyclopentylidenecyclopentanone (120 g, 0.80 mol) which had been prepared by the self-condensation of cyclopentanone.[21] The solution was refluxed on a hot water bath for 20 min. The flask was cooled; the contents were poured over 800 g of ice and 120 ml of concentrated hydrochloric acid was added. The ether layer, containing the product, was separated from the water layer, washed with a sodium bicarbonate solution until neutral, and dried over magnesium sulfate. The ether was removed by distillation and the remainder was distilled through a short fractionating column, bp 73–74° (2 mm), 226–227° (730 mm). The product consisted of three hydrocarbons from which 2-methyl-1-(1-cyclopentenyl)cyclopentene (**9**) was separated by preparative chromatography using a 15 ft × 0.375 in. o.d. column filled with 20% Carbowax 20M on 30/60 mesh Chromosorb P at 165 or 130°. The yield of **9** was 47 g (40%): n^{25}D 1.5351; d^{25} 0.9264; λ_{max} (C_2H_5OH) 238 nm (ϵ 27000) (conjugated double bond); ^{1}H NMR τ 4.58 (s, 1 H, vinylic), 7.65 (m, 8 H, allylic, 8.20) (m, 7 H, ring hydrogen plus terminal allylic methyl); ir (neat) 3040 (m, vinylic C–H stretch) 2590, 2840, (s, C–H stretch), 1640 and 1595 (w and very w, C–C stretch, conjugated diene), 1440, 1380, 1315, 1295, 1025, 960 (C–H bending), 800 (trisubstituted double bond C–H bending), and 565 cm^{-1}.[22,23]

Anal. Calcd for $C_{11}H_{16}$: C, 89.11; H, 10.98. Found: C, 88.70; H, 10.98.

The above data do not exclude unequivocally 2-methyl-3-cyclopentylidenecyclopentene (**10**); however, when the diene is half reduced with diimide, the alkene remaining is **4**. Diimide selectively reduces trisubstituted double bonds in preference to tetrasubstituted;[24] if the diene were **10**, reduction of the trisubstituted double bond would leave alkene **1**.

2-Methyl-1-cyclopentylidenecyclopentane (1). Diene **9** was selectively hydrogenated in glacial acetic acid at 1 atm hydrogen over 5% Pd/C. The isomers were separated on a 30 ft × 0.375 in. o.d. column containing 20% Carbowax 20M on 45/60 mesh Chromosorb P (Wilkens Instrument Co.) or a 35 ft × 0.375 in. o.d. column containing 30% Carbowax 20M on the same support. The product was approximately 45% 2-methyl-1-cyclopentylidenecyclopentane (**1**): bp 202° (721 mm); n^{25}D 1.4944; d^{25} 0.8817; ^{1}H NMR τ 9.02 (d, J = 7 Hz, 3 H, methyl), 8.35 (m, 8 H, ring hydrogens), and 7.86 (m, 7 H, allylic hydrogens).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.68; H, 12.11.

The remainder was the endo isomer, 2-methyl-1-cyclopentylcyclopentene (**4**): bp 199.5° (721 mm); n^{25}D 1.4925; d^{25} 0.8906; ^{1}H NMR τ 8.42 (m, 13 H, ring hydrogens plus terminal allylic methyl) and 7.78 (m, 5 H, allylic hydrogens).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.93; H, 12.19.

The exo olefin (**1**) used for hydrogenation experiments was a minimum of 98.2% pure, although, for most reductions, the purity was 99.4% or better, the main impurity being 2-methyl-1-cyclopentylcyclopentene. The 2-methyl-1-cyclopentylcyclopentene (**4**) was at least 98.5% pure.

2-Methyl-3-cyclopentylcyclopentene (6), 3-Methyl-2-cyclopentylcyclopentene (7), and *trans*-2-Methyl-1-(1-cyclopentyl)cyclopentane (5). 2-Cyclopentylidenecyclopentanone was hydrogenated over 5% palladium on carbon (without solvent) to 2-cyclopentylcyclopentanone,[25] which was then combined with methylmagnesium bromide to give 2-cyclopentyl-1-methylcyclopentanol (**11**), bp 105° (8 mm). When heated with 85% phosphoric acid, the alcohol gave a mixture, bp 105–107° (45 mm), consisting of **4**, **5**, **6**, **7**, and unidentified alkenes in the proportion 56:13:11:5:15.[26] If **11** is converted to the chloride[27] which, in turn, is heated with potassium *tert*-butoxide,[28] the alkenes **4**, **5**, **6**, and **7** are obtained in the proportion 61:5:12:17 with 5% unidentified material. Chromatography of either mixture of alkenes through a 20 mm × 950 mm column containing 25% silver nitrate supported on basic alumina (Woelm activity grade 1) using a 95:5 volume mixture of 30–60° petroleum ether–benzene as eluent, gave pure **4** and **7** and a mixture of **5** and **6**. The order of elution was **4**, **6**, and **5**, followed by **7**. Alkenes **5** and **6** were separated by preparative GLC at 175° on a 35 ft × 0.375 in. column containing 30% Carbowax 30M on 45/60 mesh Chromosorb P. On analytical columns of either Carbowax 1000 or Apiezon L, the order of elution was **5**, **7**, **4**, and **6**, although **4** and **6** were not resolved. Compounds **6**, **7**, and **5** were characterized and their structures assigned as follows.

2-Methyl-3-cyclopentylcyclopentene (6) is a clear liquid: ir (10% in CCl_4) 3030 (=CH), 2960, 2870, 1740 (C=C), 1450, 1370, 1280, 1240, 1150, 1120, 1065, 1015, and 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 8.0–9.0 (m, 14 H, ring and allylic methyl), 7.25–8.0 (m, 3 H, allylic), 4.76 (m, 1 H, vinylic); mass spectrum (70 eV) *m/e* (rel intensity) 150 (6, M$^+$), 81 (100), 80 (30).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.98; H, 11.93.

3-Methyl-2-cyclopentylcyclopentene (7) is a clear liquid: ir (10% in CCl_4) 3050 (=CH), 2960, 2780, 1740 (C=C), 1450, 1370, 1115, and 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 8.99 (d, 3 H, J = 7 Hz, methyl), 8.0–8.99 (m, 9–10 H, ring), 7.3–7.9 (m, 4–5 H, allylic), 4.80 (m, 1 H, vinylic); mass spectrum (70 eV) *m/e* (rel intensity) 150 (30, M$^+$), 135 (43), 82 (32), 81 (100), 80 (22), 79 (33), 67 (53).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.89; H, 11.94.

***trans*-2-Methyl-1(cyclopentyl)cyclopentane (5)** is a clear liquid: ir (10% in CCl_4) 3050 (-CH), 2950, 2870, 1740, (C=C), 1455, 1380, 1115, 1065, 1080, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 9.08 (d, 3 H, J = 5.5 Hz, methyl), 8.0–8.5 (m, 9–10 H, ring), 7.6–8.0 (m, 4–5 H, allylic), 4.78 (m, 1 H, vinylic); mass spectrum (70 eV) *m/e* (rel intensity) 150 (39, M$^+$), 135 (44), 83 (22), 82 (100), 81 (36), 80 (21), 79 (82), 77 (27), 68 (29), 67 (91).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.08. Found: C, 88.00; H, 11.93.

***cis*- (2) and *trans*-2-Methyl-1-cyclopentylcyclopentane (3).** When saturated with hydrogen (Adams' PtO_2 in acetic acid), each of the above cyclopentenes, other than **5**, yielded a mixture of two hydrocarbons which were separated by GLC on 35 ft × 0.375 in. 30% Carbowax 20M on 45/60 mesh Chromosorb P at 130°. Samples of each isomer (0.15 ml in 0.5 ml of cyclohexane) were placed with 0.02 g of 5% palladium on carbon in separate 8 mm × 15 cm Pyrex tubes and sealed. The tubes were heated at 250° for 180 hr, cooled to room temperature, and opened, and the contents were analyzed by GLC.[29] The proportion of the isomers present in each tube was identical: 86.6% of the compound with the shorter retention time. The more stable isomer was assumed to be *trans*-2-methyl-1-cyclopentylcyclopentane (**3**): ir (neat) 2950, 2870, 1450, 1370, 905 w, 890 cm^{-1} w; ^{1}H NMR ($CDCl_3$) τ 9.02 (d, 3 H, J = 9 Hz, methyl), 8.1–8.9 (m, 17 H, ring); mass spectrum (70 eV) *m/e* (rel intensity) 152 (41, M$^+$), 83 (50), 82 (100), 81 (44), 69 (28), 68 (40), 67 (88).

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.97; H, 12.92.

The less stable isomer (longer retention time) is the only product of the reduction of **4** by diimide and is accordingly *cis*-2-methyl-1-cyclopentylcyclopentane (**2**): ir (neat) 2950, 2870, 1455, 1370, 905 cm^{-1} w; ^{1}H NMR ($CDCl_3$) τ 9.29 (d, 3 H, J = 8 Hz, methyl), 8.1–8.9 (m, 17 H, ring); mass spectrum (70 eV) *m/e* (rel intensity) 152 (28, M$^+$), 83 (53), 82 (100), 81 (47), 69 (28), 68 (41), 67 (90).

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 87.15; H, 13.19.

Reagents. Reagent grade acetic acid, cyclohexane (99.8% pure Phillips Petroleum Co.), and triethylamine (Matheson Coleman and Bell) were used as obtained. Diglyme, bis(2-methoxyethyl) ether (Matheson Coleman and Bell), was distilled over lithium aluminum hydride before use as solvent in diimide reductions.

Platinum oxide (Adams' catalyst) and 5% palladium on powdered charcoal (batch no. 6457) were purchased from Matheson Coleman and Bell. Rhodium, 5% on calcium carbonate (batch no. C2200), was purchased from Englehard Industries, Inc. The catalysts were used as obtained.

Procedures. With the exception of the additional attention given to the condition of the alkene prior to its use in an experiment (see below) the hydrogenations were performed in the manner previously described;[5b] the acidic solvent was extracted from the hydrocarbon mixture before the latter was analyzed. Mixtures obtained from hydrogenations in other solvents were analyzed directly. On a 19 ft × 0.25 in. column packed with 20% Carbowax 1000 on 60/80 mesh Chromosorb P, the relative retention times at 130° were 1.00 (**3**), 1.08 (**5**), 1.13 (**2**), 1.43 (**7**), 1.55 (**4**), 1.56 (**6**), 1.72 (**1**).

Reductions by diimide generated in diglyme by the action of triethylamine on benzenesulfonylhydrazide followed the procedure of Garbisch, Schildcrout, Patterson, and Sprecher.[30]

Because the first series of hydrogenations of **1** and **4** gave inconsistent results the experiments were repeated with alkenes which were chromatographed over basic alumina (Woelm's activity grade 1), using pentane as eluent, immediately before it was used.[17] The solution of alkene in pentane under a nitrogen atmosphere was concentrated to a volume of about 0.5 ml (approximately 10% alkene by volume) and added to the reaction chamber containing the reduced catalyst (1.5 mg) and the acetic acid (5 ml).

Registry No.—**1**, 56761-48-9; **2**, 935-80-8; **3**, 935-81-9; **4**, 51874-03-4; **5**, 56761-49-0; **6**, 51874-04-5; **7**, 56761-50-3; **9**, 56761-51-4; 2-cyclopentylidenecyclopentanone, 825-25-2; methyl iodide, 74-88-4.

References and Notes

(1) (a) Financial support by the National Science Foundation is gratefully acknowledged (NSF-GP-7466 and NSF-GP-36119X). (b) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968.

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