The peak at 8.5 min was identified as the starting material by coinjection. The larger peak was collected and identified as the cyclic vinyl ether **6b** by coinjection with a sample prepared according to the procedure described in the next section.

The crude material (about 3 g) from a run similar to the above was distilled under vacuum. A small amount of a substance, bp, 43–46° (0.025 mm), was collected. The ir spectrum had weak bands in the hydroxyl and carbonyl regions and the nmr spectrum showed that the dioxolane ring was present. This oil was apparently a mixture of the starting material and the desired ketoalcohol **6b**. As this low boiling fraction was distilled, white needles began to form in the column. The distillation was stopped and the residue in the distilling flask was taken up in 4 ml of petroleum ether. The solution was chilled in the freezer and seeded with the crystals which had formed in the column. After 24 hr, a crop of white needles (1.4 g) had separated. Two subsequent recrystallizations from petroleum ether gave 1.2 g, mp 59–60°, of analytically pure 2-(2′-methyl-2′-hydroxypropyl)-cyclohexanone (**6b**). Concentration of the mother liquors gave another 0.9 g, mp 57–60°; total yield was 68%. When a solution of the oil, in petroleum ether, which had not been subjected to distillation, was cooled in the freezer, white needles were obtained, mp 57–59°. The mmp 57–59.5° of the sample obtained from the distillation and that obtained from direct crystallization from petroleum ether showed no depression. The ir spectrum ($CHCl_3$) showed absorption at 3400 cm^{-1} (hydroxyl), 1710 (ketone), 1360 and 1375 (*gem*-dimethyl group), 1150, 1050, and 930 cm^{-1}. The ketone absorption was of moderate strength, while the hydroxyl band was strong. The nmr spectrum (CCl_4) had a doublet at 1.32 ppm (6 H, methyl protons), a complex envelope from 1.4 to 2.2 (10 H, ring and chain protons), a complex multiplet at 2.25 (1 H, tertiary proton α to carbonyl), and a broad absorption at 3.3 (1 H, hydroxyl proton).

When the crystalline solid was vaporized into the ionizing chamber of the mass spectrometer two substances were observed. The substance which vaporized first showed a molecular ion at *m/e* 170, which was verified by running the scan at 12 eV instead of the normal 70 eV. This is a molecular weight consistent with that expected for the desired ketoalcohol. The second substance which was vaporized showed a molecular ion of *m/e* 322. This second compound was not identified conclusively, but it was apparently a dimer of the keto alcohol **6b**, which is in equilibrium with the keto alcohol **6b** itself. The analysis reported below was performed on the crystalline solid above.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.30; H, 10.66.

2,2-Dimethyl-2,3,4,5,6,7-hexahydrobenzofuran (5b).—The crude oily product from the preceding experiment was distilled under reduced pressure (water pump). From the 3.0 g of **6b** which was distilled (bath temperature, 120°; pressure, 15 mm), 2.1 g (75%) of a colorless liquid was collected, bp 85° (15 mm). Vapor phase chromatography of this product on a 5 ft × 0.25 in. 25% QF-1 column (column temperature, 125°; flow rate, 60 ml of He/min) showed one peak at 5.3 min. This peak was collected and evaporatively distilled (bath temperature, 70°; pressure, 15 mm). The ir spectrum (liquid film) showed bands at 1710 cm^{-1} (enol ether), 1445, 1370, and 1385 (*gem*-dimethyl group), 1300, 1270, and 1220 (ether C–O), and 1195, 1150, 1095, 905, 870, and 785. There was also a weak band in the hydroxyl region of the spectrum, indicating that some alcohol was still present. The nmr spectrum (CCl_4) showed a singlet at 1.26 ppm (6 H, methyl groups), a multiplet at 1.65 (4 H, protons of the six-membered ring), a multiplet at 1.92 (4 H, allylic protons of the six-membered ring), and a multiplet at 2.25 (2 H, allylic protons of the five-membered ring). The mass spectrum of this compound was obtained from the single peak eluting from a 6 ft × 0.25 in. 1% SE-30 column. A satisfactory analysis was not obtained, probably owing to the presence of the keto alcohol, and the ease of hydrolysis of the enol ether.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 77.03; H, 10.41.

Hydrolysis and recyclization of **5b** and **6b** were carried out as previously described for the monomethyl compounds **5a** and **6a**. The physical properties of the compounds obtained in this way were identical with the physical properties of the samples obtained earlier.

Registry No.—**5a**, 10198-31-9; **5b**, 22931-91-5; **6b**, 22931-92-6; **8**, 22931-93-7; **9**, 22931-94-8; ethylene ketal of **6b**, 22931-95-9.

Hydrogenation of Cycloalkenes Using Homogeneous Rhodium Complexes as Catalysts[1]

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Initial rates of hydrogenation and pseudo-first-order rate constants are reported for several cycloalkenes in different solvent systems at 25.0 ± 0.1° under 1 atm of hydrogen using rhodium complexes as homogeneous catalysts. None of the solvent systems investigated has been found to be more effective than 3:1 benzene–ethanol. 1,2-Dimethylcyclohexene (**1**) and 1,3-dimethylcyclohexene (**3**) are not hydrogenated with chlorotris(triphenylphosphine)rhodium(I), nor is 1-methylcyclohexene (**2**) with either a diphenylpiperidylphosphine or a phenyldipiperidylphosphine complex. Deuterium addition to bicyclo[2.2.1]heptene (**8**) is *exo,cis*. 2,3-Dimethylcyclohexene (**5**) and 2,4-dimethylcyclohexene (**6**) furnish 50% and 48% *cis* products, respectively, and their thermodynamically less stable product isomers are appreciably more exchanged than are their more stable counterparts when deuterium is used. These results permit refinements of the mechanistic details of this reaction.

Alkylcyclohexenes with trisubstituted double bonds are hydrogenated rather slowly relative to cyclohexene using Wilkinson's chlorotris(triphenylphosphine)rhodium(I) catalyst[2] in benzene–ethanol at 25° under 1 atm of hydrogen pressure.[3] We report here the use of this catalyst, as well as variants of it,[4,5] in the hydrogenation of 1,2-dimethylcyclohexene (**1**), 1-methylcyclohexene (**2**), 1,3-dimethylcylohexene (**3**), 1,4-dimethylcyclohexene (**4**), 2,3-dimethylcyclohexene (**5**), 2,4-dimethylcyclohexene (**6**), *p*-menthene (**7**), and bicyclo[2.2.1]hept-2-ene (**8**) in benzene and benzene–ethanol solution. The effect of several other solvent systems on the rates of hydrogenation of **2** has also been investigated.

Experimental Section

Apparatus and Procedures.—With chlorotris(triphenylphosphine)rhodium(I) as the catalyst, the procedures were described

(1) We make grateful acknowledgment for support of this research from the National Science Foundation (GP 4656 and 9250) and Teijin, Ltd. (Tokyo, Japan).

(2) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(3) A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, **91**, 672 (1969).

(4) R. Stern, Y. Chevallier, and L. Sajus, *C. R. Acad. Sci., Paris, Ser. C.*, **264**, 1740 (1967).

(5) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1054 (1968).

previously using the apparatus which had been already described.[3]

Other catalysts were prepared *in situ* from chlorodicyclooctenerhodium(I)[6] as follows. The reaction flask containing 3.88 mg (1.08×10^{-2} mmol) of chlorodicyclooctenerhodium(I) was purged with hydrogen and 3.00 ± 0.01 ml of a degassed benzene solution of $2.27–3.24 \times 10^{-2}$ mmol of a phosphine or an arsine ligand and 1.00 ± 0.01 ml of degassed absolute ethanol were added *via* hypodermic syringe. The system was first shaken gently under hydrogen for 5 min, then strongly agitated for an additional 5 min. Following the addition of 0.50 ± 0.01 ml of the alkene, the rest of the procedure was identical with that when an externally prepared catalyst was used.

Solvent effects were studied by substituting 4.00 ml of a second solvent for the 3.00 ml of benzene and 1.00 ml of ethanol.

Bromotris(triphenylphosphine)rhodium(I).—This catalyst was prepared in 50 ml of degassed absolute ethanol by the procedure of Wilkinson.[2]

Chlorodicyclooctenerhodium(I).—The procedure of Porri was followed[6] using rhodium(III) chloride hydrate in absolute ethanol containing distilled cyclooctene in a Schlenk tube under nitrogen.

Anal. Calcd. for $C_{16}H_{28}ClRh$: C, 53.6; H, 7.9. Found: C, 53.8; H, 8.0.

Ethyldiphenylphosphine.—This material, prepared as described,[7] distilled at 148–149° (4 mm). It was stored under purified nitrogen.

Phenyldipiperidylphosphine.—Redistilled phenyldichlorophosphine was added to 4 equiv of piperidine in dry benzene with cooling as described[8] to furnish phenyldipiperidylphosphine in 73% yield. It melted at 79.0–80.5°, twice recrystallized from ethanol.

Diphenylpiperidylphosphine.—Redistilled diphenylchlorophosphine was added to 2 equiv of piperidine in benzene with cooling. The crude crystals, recovered by evaporation of the solvent from the washed benzene solution, were obtained in 93% yield, mp 53.0–54.0°, when twice recrystallized from ethanol.[9]

Solvents and Substrates.—Benzene was distilled from potassium metal under nitrogen. Ethanol was distilled from ethyl phthalate and sodium ethoxide. Immediately before use it was redistilled under nitrogen. Other solvents were distilled under nitrogen immediately before use.

Commercial samples of cyclohexene, 1-methylcyclohexene (**2**), and 1,3-dimethylcyclohexene (**3**) (all 99%) were further purified by preparative glpc (Dow Corning DC 200, 20% on firebrick), and then distilled from potassium metal under nitrogen.

The dehydration of 2,3-dimethylcyclohexanol mixed isomers [from the hydrogenation of 2,3-dimethylphenol at 170° (2400 psig) with nickel kieselguhr] using commercial alumina at 330° furnished a mixture of 2,3-dimethylcyclohexene (**5**, 40 ± 1%), *cis*- and *trans*-3,4-dimethylcyclohexenes (50 ± 1%), and 1,2-dimethylcyclohexene (**1**, 10 ± 1%). This mixture was separated by a glpc procedure using silver nitrate–ethylene glycol (28% on firebrick) into a 3,4-dimethylcyclohexene fraction and an 80:20 mixture of **5** and **1**. The latter furnished a mixture of 90.0% **5** and 10.0% **1** by a glpc procedure using Dow Corning DC 200. Further rectification of the mixture was not practical; it was distilled from potassium under nitrogen as a final purification step.

Only component **5** of this mixture was subject to hydrogenation and there was no increase in component **1** as a result of the isomerization of **5** in the course of the hydrogenation.

The dehydration of 1,3-dimethylcyclohexanol (from 3-methylcyclohexanone and methylmagnesium bromide) with 100% phosphoric acid at 150° (115 mm) furnished a mixture of 1,3-dimethylcyclohexene (**3**) and 2,4-dimethylcyclohexene (**6**). The mixture was 50 ± 5% by nmr and was not practical of further separation. It was distilled from potassium under nitrogen before use. There was no detectable isomerization of **6** to **3** in the course of the hydrogenation of this mixture, during which only **6** disappeared.

Bicyclo[2.2.1]hept-2-ene (**8**) was twice resublimed under nitrogen.

(6) L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965).

(7) J. Meisenheimer, J. Casper, H. Hoering, W. Lauter, L. Lichtenstadt, and W. Samuel, *Justus Liebigs Ann. Chem.*, **449**, 213 (1926).

(8) A. W. Frank, *J. Org. Chem.*, **26**, 850 (1961).

(9) H. H. Sisler and N. L. Smith, *ibid.*, **26**, 611 (1961).

Results

Initial rates for the absorption of hydrogen by cyclohexene and the several other cycloalkenes which have been the concern of this study are summarized in Table I (3:1 benzene–ethanol), Table II (benzene), Table III (1-methylcyclohexene in various solvents), and Table IV (cyclohexene and 1-methylcyclohexene with various catalysts in 3:1 benzene–ethanol).

The exchange patterns for the two product isomers from **5** and **6** are given in Table V. These patterns are similar to those reported earlier[8] for the product isomers from **4** and **7**, and for the product from **2**.

TABLE I

INITIAL RATES OF HYDROGENATION IN 3:1 BENZENE–ETHANOL[a]

Substrate[b]	Alkene, *M*	Initial rate, mol min^{-1} × 10^6	k', min^{-1}
C_6	1.10	180	17[c]
1-MeC_6 (**2**)	0.94	5.3	0.49[d]
1,3-Me_2C_6 (**3**)	0.82	0	...
1,4-Me_2C_6 (**4**)	0.82	1.7[e]	0.16
2,3-Me_2C_6[f] (**5**)	0.74	2.1	0.20
2,4-Me_2C_6[g] (**6**)	0.41	1.7	0.16
1-Me-4-*i*-PrC_6 (**7**)	0.67	2.7[e]	0.25
4-MeMeC_6 (**9**)	0.87	78[e]	7.2

[a] At 25.0 ± 0.01° (760 ± 1 mm), 4.50-ml solution, chlorotris(triphenylphosphine)rhodium(I) at 2.40 m*M*. [b] C_6, cyclohexene: 1,4-Me_2C_6, 1,4-dimethylcyclohexene; etc. [c] With 2.40 m*M* bromo complex, 27. [d] With 2.40 m*M* bromo complex, 0.49. [e] Data from ref 3. [f] Contains 10.0% 1,2-dimethylcyclohexene, which is inert. [g] Contains 50% 1,3-dimethylcyclohexene, which is inert.

TABLE II

INITIAL RATES OF HYDROGENATION IN BENZENE[a]

Substrate[b]	Alkene, *M*	Initial rate, mol min^{-1} × 10^6	k', min^{-1}
C_6	1.10	148	13.7
1-MeC_6 (**2**)	0.94	1.4	0.13
1,4-Me_2C_6 (**4**)	0.82	1.0	0.09
1-Me-4-*i*-PrC_6 (**7**)	0.67	1.2	0.11
Bicyclo C_7 (**8**)	1.22	48	4.4

[a] At 25.0 ± 0.01° (760 mm), 4.50-ml solution, chlorotris(triphenylphosphine)rhodium(I) at 2.40 m*M*. [b] Abbreviations as in Table I; **8** is bicyclo[2.2.1]heptene.

TABLE III

RATES OF HYDROGENATION OF 1-METHYLCYCLOHEXENE IN SELECTED SOLVENTS[a]

Solvent	Initial rate, mol min^{-1} × 10^6	k', min^{-1}
Benzene–ethanol (3:1)	5.3	0.49
Benzene	1.4	0.13
Dichloromethane	0.81	0.075
Chloroform	0	...
1,2-Dichloroethane	0.41	0.038
Chlorobenzene	0.27	0.025
Benzonitrile	0	...
Nitrobenzene	4.8	0.45
Cyclohexanone	4.2	0.39

[a] At 25.0 ± 0.1° (760 ± 1 mm), 4.5-ml solution, chlorotris(triphenylphosphine)rhodium(I) at 2.40 m*M*.

SCHEME I

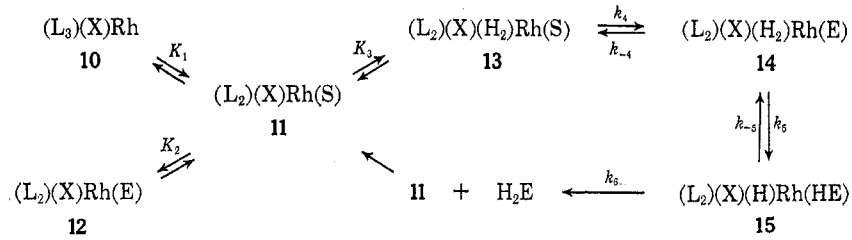

TABLE IV

RHODIUM COMPLEXES AS CATALYSTS FOR THE HYDROGENATION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE[a]

Ligand	Registry no.	Ratio[b]	Initial rate, mol min^{-1} × 10^6: Cyclohexene	1-Methylcyclohexene
Ph_3As	14973-92-3	3.0	1.2	0
		2.5	2.0	0
$EtPh_2P$	14973-91-2	2.7	94	3.2
		2.1	166	3.5
Ph_3P	14694-95-2	3.0	233	5.3
		2.5	405	8.8
$PhPip_2P$[c]	22979-14-2	3.0	300	0
Ph_2PipP	22979-15-3	3.0	670	0

[a] At 25.0 ± 0.01° (760 mm), 4.50-ml solution, catalyst (2.40 m*M*) prepared *in situ via* chlorodicyclooctenerhodium(I). [b] Mole ratio of ligand to metal atom. [c] $PhPip_2P$, phenyldipiperidylphosphine.

TABLE V

DEUTERIUM EXCHANGE PATTERNS IN *cis* AND *trans* PRODUCTS FROM 2,3- AND 2,4-DIMETHYLCYCLOHEXENE[a]

	cis-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3
d_0	0.5	0.6	1.9	2.1
d_1	2.5	2.6	2.5	3.4
d_2	84.1	96.1	94.6	83.6
d_3	12.7	0.6	0.9	10.8
d_4	0.2	0.1	0.1	0.1
d_{av}	2.09[b]	1.97[b]	1.96[c]	2.03[c]

[a] At 10–12% reduction, 25.0 ± 0.01° (760 mm), 99% deuterium, 4.5-ml solution, chlorotris(triphenylphosphine)rhodium(I) at 2.40 m*M*. [b] Recovered cycloalkene contained 0.5% d_1 species. [c] Recovered cycloalkene contained 0.2% d_1 species.

Finally, the *cis/trans* product composition from these homogeneous catalyst systems are compared in Table VI with results reported using heterogeneous platinum catalysts.

TABLE VI

PER CENT *cis* ISOMERS USING HOMOGENEOUS RHODIUM AND HETEROGENEOUS PLATINUM CATALYSTS

Substrate	$(Ph_3P)_3ClRh$[a]	Pt[b]
1,4-Me_2C_6 (4)	50[c]	57
2,3-Me_2C_6 (5)	50	77
2,4-Me_2C_6 (6)	48	47
1-Me-4-*i*-Pr (7)	30[c]	43
4-MeMeC$_6$ (9)	67[c]	74

[a] In benzene–ethanol. [b] See S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082 (1960); J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960). [c] Reference 3.

Discussion

The several steps of the overall reaction are summarized in Scheme I. This scheme embodies the steps originally proposed by Wilkinson[2] but also accommodates more recent evidence concerning the details of this reaction.[3,5,10]

Thus this scheme implies an influence of the solvent S, the ligand L, and the ligand/rhodium ratio upon the dissociation of the catalyst **10** to **11**, as well as variable effects of the alkene E on the overall rates through diversion of **11** to **12**. The concentrations of the dihydro complex **13** and the π complex **14** are seen to be functions of the hydrogen tension and the coordination potential of E *vs.* S. The two-step transfer of hydrogen (**14** → **15** → H_2E product) becomes observable as k_{-5} approaches k_6 in magnitude.

A steady-state treatment[11] of the steps of Scheme I leads to the rate expression

$$\text{rate} = \frac{k_4 k_5 k_6 K_3 [H_2][E][\text{cat}]}{(1 + [L]/K_1 + K_2[E] + K_3[H_2])(k_{-4}k_{-5} + k_{-4}k_6 + k_5 k_6)} \quad (1)$$

where $[H_2]$, [E], and [cat] are the molar concentrations of hydrogen, alkene, and catalyst (added as **10**), respectively. Notice that if k_{-4} is very small, eq 1 becomes the equivalent of Wilkinson's rate expression for cyclohexene[2] except for the additional term in the denominator for the reassociation of **10**.

The data of Tables I–VI will be discussed in terms of the steps of Scheme I and rate expression 1.

Variation of Rates with Alkene and Solvent Systems.—For a particular solvent system, the formation of the π-complex species (**14**, Scheme I) requires the displacement of solvent, S, from hexacoordinate **13** by alkene, E;[12] hence a very strongly coordinating solvent or a weakly π-complexing alkene will lead to a very slow hydrogen addition reaction. At the same time, the formation of **11**, hence of **13**, depends upon the displacement of a ligand molecule, L, by S; hence a solvent system may be a more or a less effective one for one of two contrary reasons. Finally, the transfer of the second hydrogen atom in the pentacoordinate alkyl–rhodium σ complex, **15**, may involve prior formation of a hexacoordinate species (**15′**) containing S; hence the solvent may promote the last step of the process by demoting the return of **15** to **14** (*i.e.*, by reducing k_{-5} [**15**]).

The optimum solvent system, then, has an intermediate coordinating power which tends to promote

(10) A. L. Odell, J. B. Richardson, and M. J. Jung, *J. Catal.*, **8**, 393 (1967); J. B. Biellmann and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968).

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 104.

(12) We used (−)-menthone as the solvent in a single experiment using (±)-3-methylcyclohexene. The recovered cycloalkene was inactive. See, however, W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968), for a partial asymmetric hydrogenation using a catalyst having chiral ligands.

the formation of **11**, **13**, and (perhaps) **15'**, but not to demote the formation of **14**. Of course, the solvent system should also have an optimum ability to dissolve hydrogen. Additional research is called for to discover improved solvent systems for this reaction.

The variation in rates among the several alkenes is appreciably greater than that observed with heterogeneous catalysts.[13] The inertness of **1** and **3** seems likely to be the result of their failure to form the π complexes, **14**. π complexes of **1** are very weak.[14] Scale models of the catalyst suggest that there is steric crowding within the coordination sphere between the methyl groups of **1** and **3** and the triphenylphosphine ligands, but that these steric effects are not nearly so severe when **5** and **6** are the substrates.[15]

The slow rates of hydrogenation of **2**, **4**, **5**, **6**, and **7**, compared with that of cyclohexene, can probably be ascribed to the lesser stability of their π complexes.[14] However, **8** does not exhibit the enhanced rate relative to cyclohexene which is observed with heterogeneous catalysts,[13] although the π complex of **8** is probably particularly stable.[14] Here, the transition from the π complex, **14**, to the bicyclo[2.2.1]heptylrhodium intermediate, **15**, may be demoted (or k_{-5} promoted) because of the *endo* hydrogen interactions which develop in the transition of **14** to **15**. With heterogeneous catalysts, in contrast, hydrogen addition is most likely to a surface species which is already σ bonded.[16]

Variations of Rates with Ligand.—Wilkinson has reported the rate-slowing effect of an increase in ligand rhodium ratio.[5] Likewise, variations in rate with the basicity of L, such as we also observe with the ethyldiphenylphosphine and the piperidylphosphine complexes (Table IV), have been reported.[4,5] Note the striking difference in response of **2** to such changes compared with that of cyclohexene (or styrene[4]). We ascribe the inertness of **2** when the piperidylphosphine complexes are the catalysts to steric crowding within the coordination sphere between the methyl group of the substrate and these bulkier ligands.[15] These variants of Wilkinson's catalyst may prove to be most useful ones for the completely selective hydrogenation of mono- or disubstituted double bonds in the presence of trisubstituted ones.

Deuterium Addition.—Deuterium addition to **8** followed by nmr studies shows the addition *via* homogeneous rhodium catalysts to be *exo,cis*, the bridgehead/-*exo* proton signals being 1:1[17] *vs.* 1:2 when hydrogen is used. Thus the addition reaction to cycloalkenes, as to acyclic ones,[2] is *cis*.

The data of Table V show the exchange patterns for **5** and **6** to be similar to those observed earlier for **2**, **4**, and **7**.[3] Notice, however, that neither **5** nor **6** can form tertiary cycloalkylrhodium intermediates; such a tertiary intermediate from **5** would have to pass through the π complex of **1** in the exchange pathway suggested earlier.[3] The olefin of this complex would certainly dissociate.[14] No **5** was observed to isomerize to **1** in these experiments, however.

Likewise, the tertiary cycloalkylrhodium intermediate from **6** would have to pass through a π complex of **3** in the exchange process, but **3** is also inert (Table I), probably because of steric repulsions inherent in its *cis* and *trans* π complexes;[15] hence **6** would also be observed to isomerize to **3** were this pathway to be followed.

Consequently, we must add a second pathway for exchange to that offered earlier[3] to explain why the complex which has the cycloalkene in a geometry leading to the less stable product isomer undergoes appreciably greater exchange than its geometrical counterpart. It seems clear that a secondary hydrogen must be involved in the exchange pathways of **5** and **6** (*i.e.*, the *cis* π complex of **5** must isomerize to the π complex of *exchanged cis*-3,4-dimethylcyclohexene, and the *trans* π complex of **6** to the π complex of *exchanged trans*-3,5-dimethylcyclohexene, but their geometric counterparts must do so only to a very small extent).

We believe that the greater exchange observed in the *cis* complex of **5** and the *trans* complex of **6**, compared with their geometrical counterparts, comes about because of closely similar energy states within each *cis–trans* pair of π complexes (**14**) *as well as* of the transition states between these π complexes and their cycloalkylrhodium counterparts (**15**). The last must have the complete dimethylcyclohexane structures however, hence must differ by *ca.* 2 kcal.[18] By the same argument, the transition states between both members of the *cis–trans* pair of σ complexes and their corresponding saturated products should also differ by *ca.* 2 kcal; hence k_6 for both geometrical isomers of **15** should be about the same.

In contrast, the return of the *higher* energy member of each pair of **15** isomers to their isomerized and *exchanged* π complexes (*cis*-**15** from **5** to its isomerized and exchanged *cis*-**14** and *trans*-**15** from **6** to its isomerized and exchanged *trans*-**14**) can occur the more frequently because the transition states for the return of both members of the pair are closely the same in energy.

It is a corollary of the above argument that the transition state between **14** and **15** must closely resemble the π complex in structure.

Isomer Composition of the Products.—The *cis/trans* product compositions summarized in Table VI suggest that homogeneous rhodium catalysts are somewhat less selective than heterogeneous platinum when the double bond is endocyclic and the substituents are small. However, with the exception of **5**, the same trends are observed and one might point to this as support for a π-bonded surface species[19] as an intermediate in heterogeneous catalysis. The dissimilarity of **5** can probably be ascribed to the extra stress in the *surface* species leading to the *trans* product. This has the C-3 methyl group facing the platinum surface.

With homogeneous catalysts, the *cis–trans* pair of products form in the ratio of two corresponding rate expressions, in which several terms of both expressions cancel.

(13) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968); A. S. Hussey and G. P. Nowack, *ibid.*, **34**, 439 (1969).

(14) J. G. Traynham and M. F. Sehnert, *J. Amer. Chem. Soc.*, **78**, 4024 (1956); M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4696 (1962).

(15) Models constructed using the bond lengths and bond angles for hydridocarbonyltris(triphenylphosphine)rhodium(II) [S. J. Laplaca and J. A. Ibers, *ibid.*, **85**, 3501 (1963)] and pseudochair dimethylcyclohexenes to the same scale suggest this to be so.

(16) See S. Siegel, *Advan. Catal.*, **16**, 123 (1966), for a recent review of the mechanism of hydrogenation using heterogeneous catalysts.

(17) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

(18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 214.

(19) J. J. Rooney, F. G. Gault and C. Kemball *Proc. Chem. Soc.* 407 (1960).

When k_{-5c} and k_{-5t} are very small relative to k_{6c} and k_{6t}, as the exchange data suggests they are for **9**, eq 2 further simplifies to eq 3.

$$\frac{d[cis]}{d[trans]} = \frac{k_{4c}k_{5c}k_{6c}(k_{-4t}k_{-5t} + k_{-4t}k_{6t} + k_{5t}k_{6t})}{k_{4t}k_{5t}k_{6t}(k_{-4c}k_{-5c} + k_{-4c}k_{6c} + k_{5c}k_{6c})} \quad (2)$$

$$\frac{d[cis]}{d[trans]} = \frac{k_{4c}k_{5c}(k_{-4t} + k_{5t})}{k_{4t}k_{5t}(k_{-4c} + k_{5c})} \quad (3)$$

Further, if $k_{5c} \cong k_{5t}$, as we have suggested above, and if $k_{-4c} \cong k_{-4t}$ or are small relative to k_5 and k_6 for **9**,[20] then eq 3 further simplifies to eq 4.

$$d[cis]/d[trans] = k_{4c}/k_{4t} \quad (4)$$

The product ratio from **9** is mostly a kinetic result, not a consequence of an equilibrium.

We have proposed the same to be true for hydrogenations at platinum surfaces, and suggest that the similarity of the results in Table VI for **9** are in support of our previous proposal.

Registry No.—Cyclohexene, 110-83-8; **2**, 591-49-1; **3**, 2808-76-6; **4**, 2808-79-9; **5**, 1759-64-4; **6**, 2808-77-7; **7**, 5502-88-5; **8**, 498-66-8; **9**, 14072-86-7; chlorodicyclooctenerhodium(I), 12112-71-9.

(20) The data tell us nothing about the magnitude of k_{-4} for **9**. However, the exchange studies show that k_{-4} [**14**] for **4–7** is smaller than k_5 [**14**] and that k_{-5} [**15**] (or the rate of the D_2–HD exchange step) is smaller than k_6 [**16**] particularly so for the intermediates leading to the more stable product isomer. The π complexes of **9** are much more stable than those of **4–7** (ref 14); hence these requirements for **9** are not unreasonable.

Perhydroindan Derivatives. XII.[1] 6-Methoxyindanone and Its Derivatives

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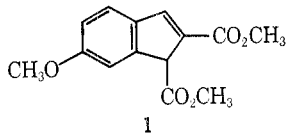
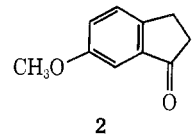
An optimum procedure for cyclizing *p*-methoxyhydrocinnamoyl chloride (**3b**) to 6-methoxyindanone (**2**) in 94% yield is described; the cyclization is conducted in dilute CH_2Cl_2 solution with no excess $AlCl_3$ present. When other procedures are employed, by-products resulting from solvent attack (**3c**) or intermolecular acylation (**5** and **6**) are produced and may become the major products. Several transformations of 1-indanone (**12**) and 6-methoxy-1-indanone (**2**) are described.

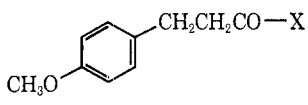
In seeking alternative routes to the indene diester **1**[2] and related compounds, the desirability of 6-methoxy-1-indanone (**2**) as an intermediate was apparent. Although a seemingly simple synthesis of this ketone **2** by an $AlCl_3$-catalyzed cyclization of the acid chloride **3b** had been reported,[3] at least three published attempts to repeat this cyclization have led to poor yields of the expected ketone **2**.[4] We have reinvestigated this cyclization in detail and describe here both a satisfactory method for forming the ketone **2** and the nature of the by-products when this cyclization is conducted under other than optimum conditions. We presume that the optimum conditions described for this cyclization will also be applicable to other Friedel–Crafts acylations *meta* to a methoxyl functions where difficulties have been noted.[3b]



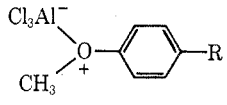
1



2



3a, X = OH
b, X = Cl
c, X = C_6H_5



4

In earlier work[4b] the *addition of the acid chloride to* a benzene solution containing excess $AlCl_3$ (1.7 equiv) (the procedure of ref 3) yielded a mixture of the indanone **2** (21%) and the phenyl ketone **3c** formed by attack of the acid chloride **3b**–$AlCl_3$ complex on the solvent. It seemed likely that these conditions (excess $AlCl_3$ throughout the reaction) served to deactivate the methoxyphenyl ring as a result of the excess $AlCl_3$ complexing with the methoxyl function (as in structure **4**).[5] Confirmation of this idea was readily obtained by the slow addition of an equimolar portion of $AlCl_3$ to a solution of the acid chloride **3b** in a relatively large volume of benzene. Under these circumstances the major product was the indanone **2** (90% yield) which was accompanied by only 8.3% phenyl ketone **3c**. Presumably, the formation of the indanone **2** in poor yield when the acid **3a** was added to excess polyphosphoric acid is also attributable to a similar deactivation by protonation of the methoxyl function. Seemingly, the above difficulties could be solved by following the normal Friedel–Crafts addition sequence in which only 1 equiv of $AlCl_3$ is added to a solution of the acid chloride in an inert solvent (*e.g.* CH_2Cl_2 rather than C_6H_6). However, when this procedure was followed, the crude indanone product **2** was accompanied by substantial amounts (15–40%) of a relative insoluble by-product from which we were able to separate the cyclic tetramer **5** (Scheme I) and a higher molecular weight polymer in

(1) This research has been supported by Public Health Service Grant 1-R01-CA-10933 from the National Cancer Institute and by Grant 68-1518 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) H. O. House, J. K. Larson, and H. C. Müller, *J. Org. Chem.*, **33**, 961 (1968).

(3) (a) W. S. Johnson and W. E. Shelberg, *J. Amer. Chem. Soc.*, **67**, 1853 (1945); (b) W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949).

(4) (a) J. Sam and J. N. Plampin, *J. Amer. Chem. Soc.*, **82**, 5205 (1960); (b) H. O. House and J. K. Larson, *J. Org. Chem.*, **33**, 448 (1968); (c) R. V. Heinzelmann, H. G. Kolloff, and J. H. Hunter, *J. Amer. Chem. Soc.*, **70**, 1386 (1948).

(5) It is likely that the reaction is also complicated by cleavage of the ether when excess $AlCl_3$ is present.