then explained by a much smaller value of K (the complex association constant) in the latter case, when the Michaelis–Menten equation reduces to effective first order in peroxide. The electrophilic nature of the reaction, as indicated by the substituent effects in styrene, implies a strong polarization of the peroxide O–O bond by the catalyst, which suggests that the metal ion is in a comparatively high oxidation state. Correspondingly, one would expect an initial activation of the catalyst from its lower oxidation state, which explains the induction period observed in the case of molybdenum hexacarbonyl. Inhibition by *tert*-butyl alcohol, observed for the vanadium reaction, but not for the molybdenum, has been postulated as being due to competition for the catalyst by the alcohol.[7] In the molybdenum case presumably K_2 (the alcohol–catalyst association constant) is much smaller than K_1. Catalyst deactivation could be caused by catalyst complexing with further reaction products of the epoxidation. This deactivation has been observed in all cases except the molybdenum hexacarbonyl–octene system; in the latter case one suspects the octene further reaction products do not complex; this is borne out by the deactivation shown by molybdenum hexacarbonyl in the present work.

The mechanism shown (Scheme I) fits the experimental facts;[16] inevitably postulates have to be made regarding the relative values of the association constants of the various catalysts with the various reaction components; in the absence of direct experimental evidence concerning such complexes, however, the present scheme does satisfactorily explain the epoxidation observations.

Experimental Section

Materials.—*tert*-Butyl hydroperoxide (*i.e.*, Lucidol) was generally used as received, as a 90% aqueous solution; for some of the kinetic experiments samples were purified to greater than 99.5% peroxide by vacuum distillation, though this made no detectable difference to the kinetics. All other chemicals were purified and dried by standard means. In particular, vpc analysis of styrene and substituted styrenes failed to detect any impurities, using a variety of columns. Molybdenum naphthenate, 3% molybdenum by weight, was used as obtained from K & K Laboratories.

Analyses.—Peroxide concentrations were determined by refluxing an aliquot for 5 min with potassium iodide in 2-propanol–glacial acetic acid (2:1 v/v) followed by thiosulfate titration of the released iodine. Styrene oxide concentrations for the determination of stoichiometry were determined by vpc analysis on a 6 ft × 0.25 in. SE-54 column at 130°, using an F & M Model 700 gas chromatograph equipped with a Disc integrator. For example, in a given instance (Table I, run a), a sample in which 0.055 mmol of peroxide/g had reacted showed the presence of 0.053 mmol/g of styrene oxide.

Kinetic Experiments.—Typically, a solution of styrene (0.4 *M*), *tert*-butyl hydroperoxide (0.25 *M*), and di-*tert*-butyl-*p*-cresol (0.0002 g) (to inhibit homolytic reaction) in benzene (10.00 ml) was allowed to equilibrate at reaction temperature. The reaction was initiated by adding a solution of molybdenum naphthenate in benzene (freshly made up for each run), prewarmed to reaction temperature. Periodically, samples of about 1 g were withdrawn, weighed, and analyzed for peroxide as above.

Registry No.—*tert*-Butyl hydroperoxide, 75-91-2.

Transition Metal Complexes as Selective Isomerization Catalysts. Preparation of Compounds Having an Exocyclic Double Bond

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The selective isomerization of vinylcycloalkenes and vinylcycloalkanes to compounds having an exocyclic double bond has been studied using three metal complexes: $RuCl_2(Ph_3P)_3$ in the presence of air or hydroperoxides, $PtCl_2(Ph_3P)_2$ and $SnCl_2$ under hydrogen pressure, and $IrCl(CO)(Ph_3P)_2$. The reactions are highly selective for retaining the double bond in the exocyclic position in contrast to conventional acid- or base-catalyzed isomerizations and consequently have synthetic utility as a catalytic method for formation of the exocyclic double bond. The ruthenium(II) complex exhibits catalytic activity in the presence of small amounts of air or hydroperoxides but is quite inactive in their absence. A carbonyl complex having high catalytic activity is formed when air or hydroperoxides react with olefin solutions of $RuCl_2(Ph_3P)_3$. The cis/trans ratio of isomers formed varies with the catalyst used showing that in certain instances cis/trans isomerization is not rapid in comparison with double bond migration. A steric argument is offered to explain observed selectivity.

Advances in homogeneous transition metal catalysis during the past decade have provided many useful examples of the selective hydrogenation of unsaturated organic compounds.[1] It is also known that many of the same complexes used in olefin hydrogenation are effective catalysts for olefin isomerization.[2] This paper describes the selective migration of a double bond on a vinyl side chain of a cyclic hydrocarbon into a position exocyclic to the ring by three group VIII metal complexes well known for their ability to catalyze olefin hydrogenation: $RuCl_2(Ph_3P)_3$, shown by Wilkinson[3] and his coworkers to be a selective hydrogenation catalyst; the $PtCl_2(Ph_3P)_2$–$SnCl_2$–H_2 system studied extensively by Bailar;[4] and Vaska's complex,[5] $IrCl(CO)(Ph_3P)_2$. It appears that, as in the case of homogeneous hydrogenation, steric factors govern the course of the reaction and are the cause of the observed selectivity in retaining the exocyclic double bond.

The interconversions between semicyclic, exocyclic, and endocyclic olefins have been extensively studied

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[1] For a recent review of selective hydrogenation, see J. E. Lyons, L. E. Rennick, and J. L. Burmesiter, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 2 (1970).

[2] For reviews of olefin isomerization catalyzed by metal complexes, see C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, Chapter 3; M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

[3] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968), and references cited therein.

[4] (a) R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **90**, 6051 (1968). (b) J. C. Bailar, Jr., and H. Itatani, *ibid.*, **89**, 1592 (1967); H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 4300 (1967).

[5] (a) L. Vaska and J. DiLuzio, *ibid.*, **84**, 679 (1962); L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965), and references cited therein.

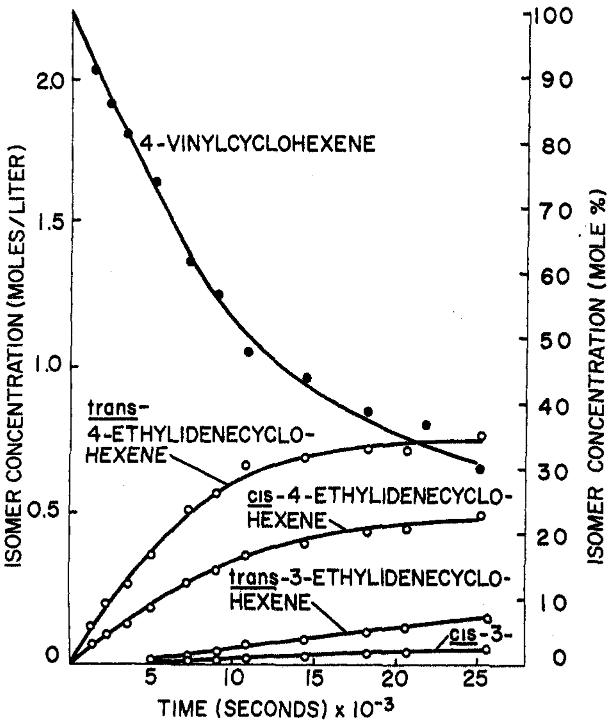
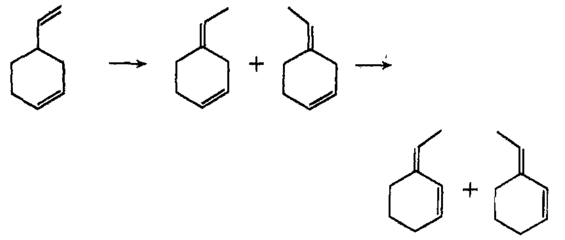


Figure 1.—Isomerization of 4-vinylcyclohexene using $PtCl_2(Ph_3P)_2$–$SnCl_2$ under hydrogen pressure. Reaction run in a methanol solution which was 2.2 *M* in 4-vinylcyclohexene, 8.3×10^{-3} *M* in $PtCl_2(Ph_3P)_2$, and 8.8×10^{-2} *M* in $SnCl_2$ at 65° under 100 psi of hydrogen.

using both acids[6-8] and bases[9-11] as catalysts. Acid catalysts rapidly isomerize an exocyclic double bond into a more thermodynamically stable position inside the hydrocarbon ring.[6] Equilibration of methylenecyclohexane ($t_{1/2}$ <5 hr) and methylenecyclopentane ($t_{1/2}$ = 10 min) was accomplished by Cope[6] and coworkers using catalytic amounts of *p*-toluenesulfonic acid in acetic acid at 25°. The authors report endo/exo ratios of 99.9 and 99.6 for the six- and five-membered rings, respectively, at equilibrium. Benkeser[7] and Turner[8] have studied the acid-catalyzed isomerizations of vinylcyclohexane and ethylidenecyclohexane using the same catalyst system at higher temperatures and have found a preponderance (96%)[7] of the endocyclic isomer at equilibrium. Although examples of kinetic control in base-catalyzed isomerizations of cyclic monoolefins have been observed,[10] systems containing more than one double bond are more difficult to isomerize in a completely selective manner. For example, Bank, Rowe, Schriescheim, and Naslund[9] found that the isomerization of 4-vinylcyclohexene, catalyzed by potassium *tert*-butoxide in dimethyl sulfoxide (DMSO), gives the *cis*- and *trans*-3-ethylidenecyclohexenes (51%) and the isomeric ethylcyclohexadienes (9%) after reaction is 60% complete. Although this catalyst system is far more selective than conventional acidic or heterogeneous catalysts,[9] the *cis*- and *trans*-4-ethylidenecyclohexenes which would result from migration of *only* the vinyl double bond are not reported. The transition metal complexes which we have studied, on the other hand, catalyze the stepwise migration of a double bond in similar systems in a manner which is highly selective and in some cases exhibits a certain degree of stereospecificity.

Results

Isomerization of 4-Vinylcyclohexene. A. Reactions Catalyzed by $PtCl_2(Ph_3P)_2$–$SnCl_2$ under Hydrogen Pressure.—A mixture of $SnCl_2$ and $PtCl_2(Ph_3P)_2$ in a 10:1 molar ratio in methanolic solution under 100 psi of hydrogen is a very selective isomerization catalyst. The active catalytic species in this system is most probably $PtH(SnCl_3)(Ph_3P)_2$ which forms an olefin complex in solution.[4] Products of hydrogenation are not observed under the mild conditions of the isomerization. The isomerization of 4-vinylcyclohexene, readily available from butadiene by Diels–Alder dimerization, proceeds smoothly in this medium at 60–70°. The double bond migration occurs in a stepwise manner giving the four isomeric ethylidenecyclohexenes (eq 1) from which the *cis*- and *trans*-4-ethylidenecyclohexenes are obtained in over 65% yield and may be separated from the conjugated isomers by fractional distillation. Thus, high yields of the thermodynamically less stable unconjugated exocyclic olefins may be readily obtained by this method.



(1)

This catalyst system combines the desirable characteristic of rapid rate with a high degree of selectivity and consequently has considerable preparative utility in catalytic isomerization reactions. It can be seen (Figure 1) that the rates of isomerization of the 4-ethylidenecyclohexenes to the conjugated isomers are appreciably slower than the rate of isomerization of the starting material. Although *cis*- and *trans*-3-ethylidenecyclohexene[12] could be separated and isolated in the pure state using preparative gas chromatography, *cis*- and *trans*-4-ethylidenecyclohexene could not be isolated in a similar way. The unconjugated isomers could be separated adequately on a 150-ft capillary column, however, and tentative stereochemical assignments were made by inspection of the kinetic curve obtained for the isomerization (Figure 1). It was assumed that the isomer formed in higher yield was the precursor to *trans*-3-ethylidenecyclohexene and the isomer formed in lower yield was the precursor to *cis*-3-ethylidenecyclohexene. This assumption was consistent with an experiment which showed that geometrical isomerization of the *cis*- and *trans*-4-ethylidenecyclohexenes was very slow relative to double bond isomerization in the exocyclic dienes. The cis/trans

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[6] (a) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and J. Jacura, *J. Amer. Chem. Soc.*, **82**, 1150 (1960); (b) R. B. Bates E. S. Caldwell, and H. P. Klein, *J. Org. Chem.*, **34**, 2615 (1969).

[7] R. A. Benkeser and J. J. Hazdra, *J. Amer. Chem. Soc.*, **81**, 228 (1959).

[8] R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

[9] S. Bank, C. A. Rowe, Jr., A. Schriescheim, and L. A. Naslund, *J. Org. Chem.*, **33**, 221 (1968).

[10] Reviewed in D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

[11] (a) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **77**, 347 (1955); (b) H. Pines and H. E. Eschinayia, *ibid.*, **78**, 5950 (1956); (c) A. Schriescheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

[12] C. Cardenas, *Tetrahedron Lett.*, 4013 (1969).

ratio of the 4-ethylidenecyclohexenes remains fairly constant (0.5) during the initial stages of the reaction and the cis/trans ratio in the forming conjugated exocyclic dienes is somewhat lower than this.

Polar solvents are necessary for isomerizations using the platinum–tin system due to the insolubility of the inorganic species in the olefin. Both protic (alcohols) or aprotic (methylene chloride, *o*-dichlorobenzene) media are suitable for the reaction. Results are summarized in Table I.

B. Reactions Catalyzed by $RuCl_2(Ph_3P)_3$.—The selective isomerization of 4-vinylcyclohexene can be accomplished using 10^{-2}–10^{-3} *M* solutions of $RuCl_2(Ph_3P)_3$, I, in the neat diene (99% purity) at 90–100°. Again the double bond migration occurs in a stepwise manner but gives 90–95% yields of *cis*- and *trans*-3-ethylidenecyclohexene (eq 1). The remainder of the reaction product consists mainly of small amounts of unreacted starting material, *cis*- and *trans*-4-ethylidenecyclohexene, ethylbenzene, and the ethylcyclohexenes. Unlike the acid-[6] or base-catalyzed[9] isomerizations, the soluble transition metal complex exhibits little tendency to catalyze migration of the double bond into the ring under mild conditions. This method, therefore, affords a convenient way to obtain high yields of the *cis*- and *trans*-3-ethylidenecyclohexenes.

It is interesting that, although the reaction is carried out in the neat diene, the ruthenium(II) complex is converted to a complex II having a CO ligand unless air or hydroperoxides have been scrupulously removed from the starting material. After reaction is complete, the new complex may be precipitated from solution in approximately 60% yield by the addition of excess pentane to the reaction mixture. This material is a tan solid having intense infrared absorptions at 1994 and 1092 cm^{-1} characteristic of ruthenium–carbonyl[13] and coordinated triphenylphosphine, respectively. Compound II has catalytic activity similar to the starting complex and is most probably an intermediate in the isomerization reaction. The elemental analysis and molecular weight is consistent with the formula, $RuCl_2(CO)(Ph_3P)_2(C_8H_{12})$. Although it was initially thought that the isolable intermediate II could have been a hydrido complex,[14] the elemental analysis, together with the absence of a detectable Ru–H signal in the nmr spectrum[15] and the failure of the material to undergo exchange reactions[15] with deuterium gas, all showed that the initial assumption was incorrect. A carbonyl complex II has been formed, perhaps by Ru(II)-catalyzed decarbonylation of hydroperoxide impurities in the olefin. Thus, when 4-vinylcyclohexene was freed of oxygen-containing impurities by percolation through activated silica gel, much of the $RuCl_2(Ph_3P)_3$, I, did not dissolve in the diene, the rate of isomerization was greatly diminished, and a yellow solid III (40% of the weight of complex used) having no infrared absorptions in the 2000-cm^{-1} region was recovered from the reaction mixture. The total yield of isomerization products using the purified olefin was less than 2% after 24 hr at 95°. On introduction of small amounts of air or *tert*-butyl hydroperoxide into the purified olefin, rapid rates of Ru(II)-catalyzed isomerization were again observed.

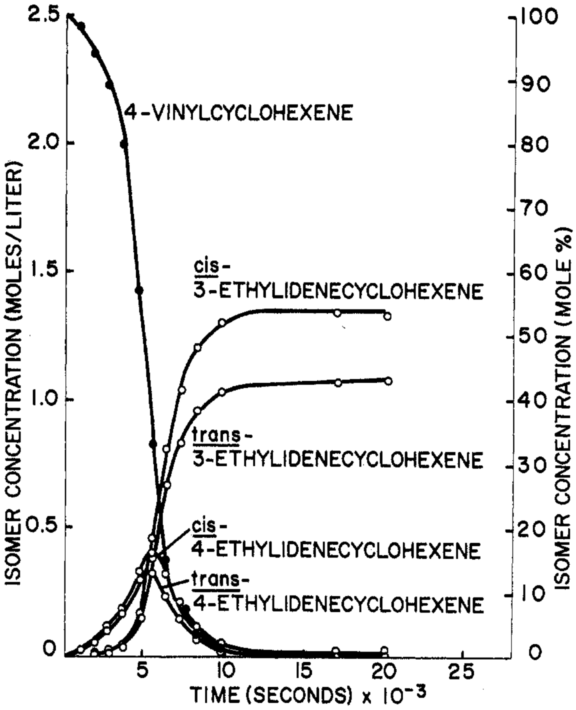

Figure 2.—Isomerization of 4-vinylcyclohexene using $RuCl_2(Ph_3P)_3$ as the catalyst. Reaction run in a 1:1 benzene–ethanol solution which was 2.5 *M* in 4-vinylcyclohexene and 6.5 × 10^{-3} *M* in $RuCl_2(Ph_3P)_3$ under nitrogen at 80°.

We have demonstrated, therefore, that, when the *pure* olefin is contacted with $RuCl_2(Ph_3P)_3$, *little or no isomerization occurs unless small amounts of air or hydroperoxides are added.* Furthermore, the carbonyl complex II is an isomerization catalyst in the neat diene even in the absence of air or hydroperoxides, indicating that *the introduction of air or hydroperoxides into the isomerization reaction results in formation of a catalytically active carbonyl complex.*[16]

Isomerization reactions catalyzed by I occur much more rapidly in 1:1 benzene–ethanol solution than in the neat diene and give a 97% yield of *cis*- and *trans*-3-ethylidenecyclohexene at completion. The reaction may be stopped at an intermediate stage, giving up to 29% yield of the unconjugated 4-ethylidenecyclohexenes. The overall stereochemistry is the reverse of what was observed using the platinum–tin catalyst system. The cis/trans ratio of the 3-ethylidenecyclohexenes was 1.3 at complete conversion and the cis/trans ratio of the 4-ethylidenecyclohexenes at their maximum value (29%) was 1.2.

The relatively slow initial rate of isomerization of 4-vinylcyclohexene (Figure 2) suggests an autocatalytic reaction wherein I is slowly converted to the active species. During this initial period the reaction mixtures change from dark red to orange or amber colored solutions. The reactions then became pseudo zero order in 4-vinylcyclohexene over the approximate range of 20–80% of reaction. Several reactions were run in

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[13] S. D. Robinson and G. Wilkinson, *J. Chem. Soc. A*, 300 (1966).

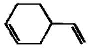
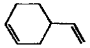
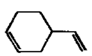
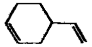
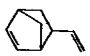
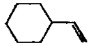
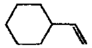
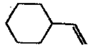
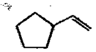
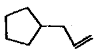
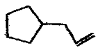
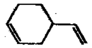
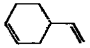
[14] Recently it has been reported that toluene reacts with $RuCl_2(Ph_3P)_3$ at 22° to give a solution which exhibits infrared bands at 1950–1985 cm^{-1}: J. Blum, *et al.*, *J. Chem. Soc. B*, 1000 (1969). This observation was cited as evidence for the insertion of Ru(II) into the benzyl–hydrogen bond. Our data show that infrared absorptions in the neighborhood of 2000 cm^{-1} are not sufficient to establish the existence of metal hydrides as reaction intermediates.

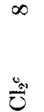
[15] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

[16] J. E. Lyons, *Chem. Commun.*, 562 (1971).

Table I

Formation of Olefins Having an Exocyclic Double Bond by Selective Homogeneous Isomerization of Unsaturated Cyclic Hydrocarbons

Complex used	Catalyst concn, $M \times 10^{-3}$	Substrate[a]	Solvent	Initial substrate concn, vol %	Temp, °C	Reaction time, hr	Isomerization of substrate, %	Exocyclic isomer yield, %	Exocyclic isomer(s) (product %)
$RuCl_2(Ph_3P)_3$	7.1		None	100	95	66	98	93	*cis*-3-Ethylidenecyclohexene (51.5) *trans*-3-Ethylidenecyclohexene (41.5)
	3.2		DMA	33	95	24	100	98.6	*cis*-3-Ethylidenecyclohexene (54.1) *trans*-3-Ethylidenecyclohexene (44.5)
	1.5		Benzene–ethanol[b]	33	80	6.5	99	97	*cis*-3-Ethylidenecyclohexene (54) *trans*-3-Ethylidenecyclohexene (43)
	5.2		*o*-Dichlorobenzene	33	100	1	39	31	*cis*-4-Ethylidenecyclohexene (12) *trans*-4-Ethylidenecyclohexene (10) *cis*-3-Ethylidenecyclohexene (5) *trans*-3-Ethylidenecyclohexene (4)
	2.6		Benzene–ethanol	33	80	21	7.3	3.6	*cis*- + *trans*-5-ethylidenebicyclo-[2.2.1]-2-heptene (3.6)
	8.6		None	100	95	46	70	70	Ethylidenecyclohexane (70)
	2.7		DMA	33	101	45	79	78	Ethylidenecyclohexane (78)
	1.6		Benzene–ethanol	33	80	4.2	99	99	Ethylidenecyclohexane (99)
	8.3		None	100	90	165	99	92	Ethylidenecyclopentane (92)
	5.8		None	100	95	45	74	0.5	Propylidenecyclopentane (0.5)
	8.3		Benzene–ethanol	33	70	20	>99	79	Propylidenecyclopentane (79)
$PtCl_2(Ph_3P)_2–SnCl_2$[c]	9.1		Methanol	9	65	5	86	81	*cis*-4-Ethylidenecyclohexene (28.5) *trans*-4-Ethylidenecyclohexene (36.5) *cis*-3-Ethylidenecyclohexene (4.5) *trans*-3-Ethylidenecyclohexene (11.5)
	8.3		Methanol	33	65	6	65	61	*cis*-4-Ethylidenecyclohexene (20) *trans*-4-Ethylidenecyclohexene (34) *cis*-3-Ethylidenecyclohexene (1.7) *trans*-3-Ethylidenecyclohexene (5.3)

$PtCl_2(Ph_3P)_2$–$SnCl_2$[c]	8.3		Methylene chloride	33	65	5	81	72	*cis*-4-Ethylidenecyclohexene (23.1) *trans*-4-Ethylidenecyclohexene (41.5) *cis*-3-Ethylidenecyclohexene (1.6) *trans*-3-Ethylidenecyclohexene (6.0)
	8.3		*o*-Dichlorobenzene	33	65	5	84	80	*cis*-4-Ethylidenecyclohexene (23.6) *trans*-4-Ethylidenecyclohexene (45.5) *cis*-3-Ethylidenecyclohexene (1.8) *trans*-3-Ethylidenecyclohexene (9.4)
	8.3		*o*-Dichlorobenzene	33	95	1	61	40	*cis*- + *trans*-5-ethylidenebicyclo-[2.2.1]-2-heptene (40)
$IrCl(CO)(Ph_3P)_2$	7.7		None	100	105	170	72	60	*cis*-4-Ethylidenecyclohexene (28) *trans*-4-Ethylidenecyclohexene (20) *cis*-3-Ethylidenecyclohexene (8) *trans*-3-Ethylidenecyclohexene (12)
	6.2		None	100	100	41	9.5	9	Ethylidenecyclohexane (9)

[a] Purified by distillation under nitrogen. No attempt was made to remove peroxides with silica gel. [b] A 1:1 mixture of benzene and ethanol. [c] A 1:10 mole ratio of $PtCl_2(Ph_3P)_2$ and $SnCl_2$ were used. Reactions were run under 100 psi of hydrogen.

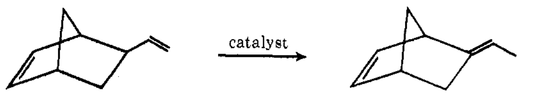
which the concentration of I was varied from 10^{-3} to 10^{-4} *M* which demonstrated that from 20 to 80% of reaction the isomerization is first order in ruthenium complex and has a pseudo-first-order rate constant of 4.6×10^{-2} sec^{-1}.

During the course of the isomerization in benzene–ethanol the original complex I was converted to an orange carbonyl complex IV which was precipitated by addition of excess pentane to the solution after reaction was complete. Although the infrared spectrum, elemental analysis, and catalytic activity of IV suggest that it is similar to II, the molecular weight and melting point are considerably higher.

The ruthenium(II)-catalyzed isomerization of 4-vinylcyclohexene may also be carried out in polar aprotic solvents such as *o*-dichlorobenzene or *N,N*-dimethylacetamide (DMA). In all cases high yields (92–99%) of the 3-ethylidenecyclohexenes can be achieved after long reaction times, and substantial quantities (22–28%) of the 4-ethylidenecyclohexenes may be obtained by interrupting the reaction at an intermediate stage. The results of these reactions are summarized in Table I.

C. Reactions Catalyzed by $IrCl(CO)(Ph_3P)_2$.—As in the previous case, Vaska's complex catalyzes the isomerization of 4-vinylcyclohexene in a selective and stepwise manner. The maximum attainable yield of the unconjugated 4-ethylidenecyclohexenes is 48% when the neat diene is isomerized at 105°. The cis/trans ratio of the 4-ethylidenecyclohexenes at their maximum value is 1.9, whereas the cis/trans ratio of the 3-ethylidenecyclohexenes is 0.81. The reaction may be run either in the neat diene or in solution (Table I). Rates are generally much slower than with the ruthenium or platinum catalysts. An induction period is observed during which the active species may form; however, when the reaction mixture is treated with excess pentane at the conclusion of the reaction, the starting complex, $IrCl(CO)(Ph_3P)_2$, is recovered in 80–90% yield. Ethylbenzene and the ethylcyclohexenes are minor products resulting from a slow disproportionation reaction[17] as in the ruthenium(II) system. Results of these reactions are summarized in Table I.

Isomerization of 5-Vinylnorbornene.—The isomerization of 5-vinylbicyclo[2.2.1]-2-heptene, a compound which is easily obtained from Diels–Alder dimerization of butadiene and cyclopentadiene, occurs in the presence of catalytic amounts of either $RuCl_2(Ph_3P)_3$ or the platinum-tin system under conditions similar to those used for 4-vinylcyclohexene (eq 2). When a



(2)

10:1 mixture of $SnCl_2$ and $PtCl_2(Ph_3P)_2$ in methanol was used under hydrogen pressure, a 40% yield of ethylidenenorbornene was obtained after 1 hr. This reaction was not so selective as the isomerization of 4-vinylcyclohexene since isomers other than ethylidenenorbornene were formed in 20% yield. The ruthenium(II) catalyst gave far slower rates in 1:1 benzene–ethanol than with 4-vinylcyclohexene. The

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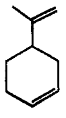
(17) J. E. Lyons, *Chem. Commun.*, 564 (1969).

yield of ethylidenenorbornene obtained after 21 hr at 80° was only 3.6%. The color change during reaction and the nature of the complex formed showed that when no effort was made to remove hydroperoxides a carbonyl complex was again formed. Presumably the steric requirements are such that the rate of isomerization of 5-vinylbicyclo[2.2.1]-2-heptene was slow even in the presence of the ruthenium–carbonyl complex. The carbonyl complex formed in 60% yield was an orange solid having an infrared spectrum similar to those of II and IV (ν_{Ru-Co} ~1980 cm^{-1}; ν_{PPh_3} ~1090 cm^{-1}). Attempts to selectively isomerize *d*-limonene V with both the ruthenium(II) catalyst and the platinum–tin system met with little success. The presence of a methyl substituent on the vinyl double bond apparently caused the reaction rate to be slow. This resulted in competitive double bond migrations both within the ring and of the exocyclic double bond which was being formed. In the case of the $RuCl_2(Ph_3P)_3$-catalyzed reaction, the carbonyl complex which was recovered was a bright orange solid having infrared absorption bands at 2030 (m), 1920 (s), and 1090 cm^{-1} (s).

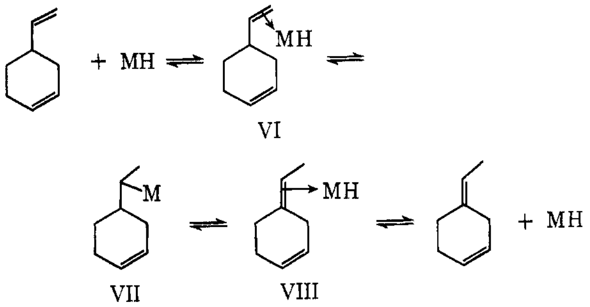

V

Isomerization of Vinyl- and Allylcycloalkanes.— Vinylcyclohexane and vinylcyclopentane were isomerized to give high yields of ethylidenecyclohexane[18] and ethylidenecyclopentane, respectively, in the presence of catalytic quantities of $RuCl_2(Ph_3P)_3$ (I). A 10^{-3} *M* solution of the ruthenium(II) complex in neat vinylcyclohexane was warmed at 100° for 112 hr. After this time, the reaction mixture contained vinylcyclohexane (5%), ethylidenecyclohexane (94%), and an unidentified product (1%). A similar experiment using vinylcyclopentane gave ethylidenecyclopentane (92%), three unidentified products (7%), and starting material (1%). These reactions occur at a somewhat faster rate in *N*,*N*-dimethylacetamide than in the neat olefin. Vinylcyclohexane reacts to form ethylidenecyclohexane in 99% yield after 4 hr in benzene–ethanol at 80° in the presence of I. An induction period is observed followed by an interval, from 20 to 60% of reaction, where the reaction appears to be pseudo zero order in olefin. Vaska's complex is a catalyst for the reaction as well; however, rates are much slower than with the ruthenium complex. In cases where I was used, traces of oxygen or oxygen-containing impurities promoted reaction, and whenever high catalytic activity was observed, ruthenium carbonyls were isolated after reaction. The results of these experiments appear in Table I. Allylcyclopentane was isomerized in benzene–ethanol solutions containing I over a 22-hr period to a mixture of propylidenecyclopentane (79%) and propylcyclopentene (21%). Allylcyclohexane, however, yielded the *cis*- and *trans*-propenylcyclohexanes (92%), and isomer which might be propylidenecyclohexane (3%) and unreacted starting material (5%) under similar conditions.

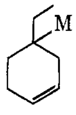
Discussion

The selective formation of an exocyclic double bond in isomerization reactions of vinyl-substituted ring compounds using transition metal complexes is an example of a rather high degree of kinetic control. The type of selectivity which we have observed, in contrast to what is found in acid- and base-catalyzed isomerizations, may be largely the result of steric interactions in the organometallic intermediates which are formed during the course of the reaction.

The first step in the transition metal catalyzed isomerization is presumed to be abstraction of hydrogen from the medium to produce a metal hydride[4,19] which may form a π bond[20] with the olefin. It has been argued that, although the presence of alkyl substituents on a double bond need not have a large effect on the rate of π-complex formation with a hydrido complex, the alkyl groups can have a profound effect on the rate of the subsequent hydrogen transfer step to form a square planar alkyl complex due to interactions with the bulky phosphine ligands.[3,21] For this reason it is possible to selectively hydrogenate the vinyl group of 4-vinylcyclohexene using either $RuCl_2(Ph_3P)_3$[3] (I) or the $PtCl_2(Ph_3P)_2$–$SnCl_2$ catalyst system.[4] The probable mechanism of the selective isomerization of 4-vinylcyclohexene by transition metal complexes is schematically represented in eq 3. It is felt that the essential feature that determines the selectivity which we have observed in this system is the reluctance of intermediate VIII to rearrange to the metal alkyl IX, a transformation which is expected to be sterically unfavorable.[3,21] In addition, the π complex VIII should be somewhat more hindered and perhaps less stable than VI. Electronic effects apparently operate in the same direction as steric effects since it is known that electron-releasing alkyl substituents on an olefinic double bond tend to decrease the stability of platinum–olefin complexes.[22] In support of this reasoning, it is known that the equilibrium constants for formation of silver nitrate–olefin complexes with vinylcyclohexane, ethylidenecyclohexane, and 1-ethylcyclohexene



VI VII VIII (3)



IX

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[18] Iron carbonyl has been found to catalyze this reaction in an unselective manner: T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[19] J. Halpern, *Discuss. Faraday Soc.*, 13 (1968).

[20] B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Wells, *ibid.*, 37 (1968), and references cited therein.

[21] C. O'Connor and G. Wilkinson, *J. Chem. Soc. A*, 2265 (1968).

[22] M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen & Co., London 1968, p 21.

are 5.9, 1.6, and 0.5 l./mol, respectively.[23] Thus, it is evident that coordination of an olefin to a metal center is quite sensitive to the degree of alkyl substitution even when the metal is not surrounded by bulky phosphine ligands. Nonetheless, it seems that bulky ligands substantially enhance the selectivity of the catalytic isomerization of vinylcycloalkanes. This is apparent from a comparison of $Fe(CO)_5$ and the catalysts reported in Table I. Iron carbonyl isomerizes vinylcyclohexane to a mixture of ethylcyclohexene and ethylidenecyclohexane,[16] whereas complex I is highly selective for formation of ethylidenecyclohexane in 99% yield.[24]

It should be emphasized that eq 3 is only a schematic representation and not a precise mechanism. Although it is known that in reactions of 4-vinylcyclohexene with rhodium(I)[25] and platinum(II)[26,27] chlorides the diene behaves as a bidentate ligand, it is not certain whether platinum(II) and ruthenium(II) *phosphine* complexes would incorporate 4-vinylcyclohexene as a monodentate or a bidentate ligand. Since reaction initially occurs at the vinyl group, a second coordinate π bond is omitted in eq 3.

Finally, our observation that air and hydroperoxides enhance the rate of olefin isomerization in the presence of $RuCl_2(Ph_3P)_3$, I, and that a carbonyl complex, II, $RuCl_2(Ph_3P)_2(CO)(C_8H_{12})$, is formed in 40–60% yield, requires additional comment. The addition of small amounts of oxygen has been found to promote extensive double bond isomerization during the hydrogenation of olefins catalyzed by $RhCl(Ph_3P)_3$ in benzene–ethanol.[28] An oxidized rhodium complex having an infrared band at 850 cm^{-1} characteristic of metal peroxide has been implicated in the double bond isomerization reaction.[28] We have observed small amounts of solids formed in the $RuCl_2(Ph_3P)_3$-catalyzed reactions whose infrared spectra indicate the presence of metal peroxide; however, the carbonyl complexes which we isolate are usually free of infrared bands in the region from 800 to 900 cm^{-1}. In the case of the $RuCl_2(Ph_3P)_3$-catalyzed isomerizations in neat olefin which we have examined, the reaction rate when air was added was rapid compared with reactions run in the absence of air. The recovery of a carbonyl complex II when air was added but only an olefin complex III when air was absent strongly suggest that the CO arises from an interaction between oxygen and the olefin. It is known that rhodium(I) complexes catalyze (a) oxidation of olefins in the allylic position,[29] (b) decomposition of hydroperoxides to form alcohols,[30] (c) rearrangement of allyl alcohol to give propionaldehyde,[31] and (d) decarbonylation of aldehydes to form CO and hydrocarbons.[32] A series of similar reactions occurring at the ruthenium center could be offered as a tentative explanation for the formation of CO complexes on addition of air or hydroperoxides to olefin solutions of $RuCl_2(Ph_3P)_3$. A complex in which CO has replaced a phosphine ligand would be expected to be more reactive toward olefin on steric grounds. Not only would the metal center be more accessible to entering olefin but the trans-directing influence of a CO is somewhat greater than that of a phosphine ligand[33] and reactions of hydride or alkyl ligands (eq 3) trans to CO would occur at an accelerated rate. It is reasonable, therefore, that complex II is capable of forming the active species, possibly a metal hydride (eq 3), more readily than complex I. Speculation regarding the origin of II as well as the rationale for its greater catalytic activity must be regarded as highly tentative at this point.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Infrared spectra were determined on Perkin-Elmer infrared spectrophotometers Models 137-B and 21. Nmr spectra were run using Varian T-60 and A-60 spectrometers. Gas chromatographic analyses were carried out on a Perkin-Elmer Model 226 instrument equipped with a 150-ft capillary column coated with UCON 550-X. Fractional distillations were performed on a Nester-Faust 18-in. semimicro spinning-band column equipped with a stainless steel band. Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weights were determined by vapor pressure osmometry using a Hewlett-Packard Mechrolab Model 302 osmometer.

Materials.—Vinylcyclopentane, vinylcyclohexane, allylcyclopentane, allylcyclohexane, and 4-vinylcyclohexene all in 99% purity or greater were obtained from Aldrich Chemical Co. Vinylnorbornene was obtained from Union Carbide Corp. Dichlorobis(triphenylphosphine)platinum(II) and chlorocarbonylbis(triphenylphosphine)iridium(I) were purchased from Strem Chemical Co. and dichlorotris(triphenylphosphine)ruthenium(II) was prepared according to the method of Wilkinson.[3]

Isomerizations Using $RuCl_2(Ph_3P)_3$ as Catalyst. Isomerization of 4-Vinylcyclohexene in Benzene–Ethanol.—A solution of benzene (16.0 ml), ethanol (16.0 ml), and 4-vinylcyclohexene (16.0 ml) was stirred magnetically at 80 ± 1° under nitrogen. Each of the components of the solution had been deaerated by bubbling a rapid stream of nitrogen through them for 30 min prior to mixing and all transfers were made in a nitrogen atmosphere. $RuCl_2(Ph_3P)_3$, 0.3004 g, was added and dissolved within 3 min to give a dark red solution. Aliquots were syringed from the stirred solution at 15-min intervals and analyzed by gas chromatography.[34] Isomerization was complete within 6 hr giving *cis*-3-ethylidenecyclohexene, 54%, and *trans*-ethylidenecyclohexene, 43%, as the major products (Table I, Figure 1). From the linear portion of the kinetic curve (Figure 1), a pseudo-first-order rate constant of 4.15×10^{-2} sec^{-1} was calculated.

The reaction mixture, a clear orange solution, was allowed to cool to room temperature and then poured into 300 ml of deaerated *n*-pentane which had been percolated through activated silica gel under nitrogen. The pentane solution was vigorously stirred under nitrogen and within several seconds an orange solid began to precipitate. The solid was allowed to settle over a 2-hr period, and then the mixture was filtered through sintered glass using nitrogen pressure. An orange solid, IV, 0.16 g, mp ~190° dec, was collected, washed with 5 ml of deaerated pentane,

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[23] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

[24] In further support of this reasoning, it has recently been shown that, in the absence of phosphine ligands, $RhCl_3$ in refluxing ethanol catalyzes the *unselective* isomerization of 4-vinylcyclohexene to give a mixture of products including the ethylcyclohexadienes and products of disproportionation: C. J. Attridge and P. J. Wilkinson, *Chem. Commun.*, 620 (1971).

[25] (a) G. Winkaus and G. Singer, *Chem. Ber.*, **99**, 3602 (1966); (b) J. F. Young, R. D. Giilard, and G. Wilkinson, *J. Chem. Soc.*, 5177 (1964).

[26] R. Palumbo, A. Penzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969).

[27] E. Kuljian and H. Frye, *Z. Naturforsch., B*, **20**, 204 (1965).

[28] R. L. Augustine and J. F. VanReppen, *Chem. Commun.*, 495 (1970); *ibid.*, 497 (1970).

[29] J. E. Baldwin and J. C. Swallow, *Angew. Chem., Int. Ed. Engl.*, **8**, 601 (1969).

[30] B. Bierling, K. Kirschke, H. Oberender, and M. Schuly, *Z. Chem.*, **9**, 105 (1969).

[31] J. E. Lyons, unpublished results.

[32] J. Tsuji and K. Ohno, *Syn.*, 157 (1969).

[33] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., p 355.

[34] It was established using pure standards that no isomerization of products or starting material occurred during glpc analysis of product mixtures. Standardization was performed with the chromatograph used for analysis of reaction mixtures containing dissolved complexes, as well as with an instrument which had not been used for analysis of solutions containing metal complexes. Results were identical. Thus, the possibility of appreciable isomerization in the injection port due to decomposed complexes was eliminated.

and dried under vacuum. An ir of IV (25% solution in deaerated methylene chloride) exhibited sharp, strong bands at 1994 (ν_{Ru-CO}) and 1092 cm^{-1} (ν_{Ph_3P}). The nmr spectrum (Varian T-60) of a 25% solution of IV in deuteriomethylene chloride showed an intense signal at δ 7.3 due to aromatic protons and several broad multiplets from δ 3.0 to 0.8 attributed to allylic and other aliphatic protons. No signal was observed which could be assigned to vinyl protons; however, the area around δ 5.3 was obscured by the residual protons of deuteriomethylene chloride. The ratio of aromatic to aliphatic protons was approximately 3.5:1. No signal was observed in the region τ 10–30, whereas a 25% solution of $RuHCl(Ph_3P)_3$ in deuteriomethylene chloride showed a well-defined quartet at τ 28. It is concluded that the complex IV is not a ruthenium hydride but a carbonyl complex.

Anal. Calcd for $C_{45}H_{42}Cl_2OP_2Ru$: C, 64.90; H, 5.08; Cl, 8.51; P, 7.44; Ru, 12.14; mol wt, 833. Found: C, 64.79; H, 5.14; Cl, 9.02; P, 7.90; Ru, 12.18; mol wt. 1022.

The pentane solution was flash evaporated away from a small amount of dissolved solid at room temperature under vacuum and the clear volatile material distilled on a semimicro spinning band column giving 12.0 g [bp 147° (lit.[9] 146–148°), >99% glpc purity] of a mixture of *cis*- and *trans*-3-ethylidenecyclohexene. The pure isomers were isolated by gas chromatography (30 ft × 0.25 in. column packed with 10% cyanopropylphenylsilicone on 60–80 mesh Chromosorb P). The configurations were assigned by a comparison of infrared, uv, and nmr spectra with literature[9,12] values. For the cis isomer we observed a uv absorption maximum at 234 mμ (ϵ 17,200) [lit.[9] 237 mμ (ϵ 17,400)] and an nmr signal at δ 3.6 (doublet) (lit.[12] δ 3.63, d) characteristic of the internal vinyl proton of the cis structure.[12] The rest of the nmr and the infrared spectrum are identical with those reported in the literature.[9] The trans isomer exhibited uv maxima at 228 mμ (ϵ 15,000) and 234 (15,500) [lit.[9] 229 mμ (ϵ 15,600), 235 (15,100)]. The nmr spectrum showed a signal at δ 4.0 (lit.[12] δ 4.00) attributed to the internal vinyl proton of *trans*-3-ethylidenecyclohexene and the rest of the spectrum was consistent with this assignment. Similar experiments were run using 0.0381, 0.0500, and 0.2968 g of $RuCl_2(Ph_3P)_3$. From plots of the linear portions of the kinetic curves (*i.e.*, Figure 2), pseudo-first-order rate constants of 4.55 × 10^{-2}, 4.81 × 10^{-2}, and 4.64 × 10^{-2} sec^{-1}, respectively, were calculated. The average rate constant for the four runs was 4.6 × 10^{-2} sec^{-1}.

Isomerization of 4-Vinylcyclohexene in Aprotic Solvents.—Using a procedure and quantities of 4-vinylcyclohexene and $RuCl_2(Ph_3P)_3$ similar to those in the above example, isomerizations were carried out in 32.0 ml of DMA at 95° and in 32.0 ml of *o*-dichlorobenzene at 100°. The results of the glpc analyses are listed in Table I.

Isomerization of 4-Vinylcyclohexene in the Absence of Solvent.—A solution of 0.700 g of $RuCl_2(Ph_3P)_3$ in 100 ml of 4-vinylcyclohexene was stirred under nitrogen for 20 hr at 100°. Gas chromatographic analysis of the reaction mixture showed the formation of *cis*-3-ethylidenecyclohexene (52%) and *trans*-3-ethylidenecyclohexene (42%). Addition of the cooled orange solution to 300 ml of deaerated *n*-pentane with stirring caused a tan solid to precipitate. The mixture was filtered after standing under nitrogen 2 hr giving a tan solid II which was washed with *n*-pentane and dried in a stream of nitrogen, 0.405 g, mp 115–116°. The ir spectrum (ν_{Ru-CO} ~1990, ν_{Ph_3P} ~1090 cm^{-1}, Nujol) and nmr spectrum in CD_2Cl_2 are similar to those of IV. The elemental analysis and molecular weight are consistent with the structure $RuCl_2(CO)(Ph_3P)_2(C_8H_{12})$.

Anal. Calcd for $C_{45}H_{42}Cl_2OP_2Ru$: C, 64.90; H, 5.08; Cl, 8.51; P, 7.44; Ru, 12.14; mol wt, 833. Found: C, 64.74; H, 5.13; Cl, 8.94; P, 7.45; Ru, 12.69; mol wt, 833.

Effect of Air and *tert*-Butyl Hydroperoxide on the $RuCl_2(Ph_3P)_3$-Catalyzed Isomerization of 4-Vinylcyclohexene. Isomerization of Peroxide-Free Olefin.—4-Vinylcyclohexene was distilled under nitrogen and then passed through a column of freshly activated (190° at 1 mm for 18 hr) silica gel under nitrogen. The olefin, 40 ml, was transferred through a syringe into a clean dry reaction flask under nitrogen containing 0.251 g of $RuCl_2(Ph_3P)_3$ and the mixture heated at 100° for 18 hr. After this time a large amount of a dark brown complex had still not dissolved and the olefin solution was yellow. Analysis by gas chromatography showed that nearly 99% of the starting 4-vinylcyclohexene had remained unchanged. The reaction mixture was filtered giving 0.06 g of dark brown complex having an infrared spectrum similar to that of the starting complex. The yellow solution was allowed to stand at room temperature for 2 hr during which time a gold solid (III) crystallized. It was filtered, washed, and dried under vacuum for 3 hr. III, 0.12 g, mp 110–113°, exhibited bands in the ir at 6.4 ($\nu_{olefin\ ?}$) and 9.1 μ (ν_{Ph_3P}) but no bands attributable to Ru–CO. The elemental analysis was consistent with a ruthenium–phosphine complex having a ratio of Cl/P of >1.

Anal. Found: C, 65.90; H, 5.74; Cl, 10.33; P, 7.01; Ru, 11.73.

Isomerization Using Peroxide-Free Olefin with Added Air.—A reaction was carried out in a manner identical with that described in the above example except that air was bubbled through the olefin for 2 min just prior to contact with the catalyst. The complex fully dissolved to give a deep orange solution and after 18 hr at 100°, isomerization was at least 98% (glpc analysis) complete. The products were mainly *cis*- and *trans*-3-ethylidenecyclohexene. Addition of excess pentane to the cool orange solution precipitated 0.10 g of a tan solid, mp 115–117°, exhibiting bands in the infrared at ~1990 and ~1090 cm^{-1} (Nujol mull).

Isomerization Using Peroxide-Free Olefin with Added *tert*-Butyl Hydroperoxide.—A reaction was run similar to those cited above using distilled, chromatographed 4-vinylcyclohexene to which 0.20 ml of *tert*-butyl hydroperoxide had been added. The complex dissolved slowly over several hours to give an orange solution. After 22 hr reaction was 90% complete and a tan complex, 0.09 g, mp 115–119°, ν_{Ru-CO} 1990 cm^{-1} (Nujol), was recovered as before.

Isomerization of Peroxide-Free Olefin by Complex II.—Distilled, silica gel treated 4-vinylcyclohexene, 10 ml, and complex II, 0.070 g, were heated under nitrogen at 100° for 18 hr. The complex dissolved to give a deep orange solution from which II, mp 115–120°, ν_{Ru-CO} 1990 cm^{-1}, could be precipitated with excess pentane. Analysis of the reaction mixture showed at least 99% of the olefin had isomerized. The major products were *cis*- and *trans*-3-vinylcyclohexene (94%). In similar experiments, complex IV was shown to be catalytically active both in benzene–ethanol and in the neat diene.

Isomerization of Other Vinyl Compounds.—Vinylcyclohexene, vinylcyclopentane, and 5-vinylnorbornene were isomerized either neat or in DMA or benzene–ethanol solutions. Reactions were carried out in the same way as with 4-vinylcyclohexene. Conditions and results are summarized in Table I.

Isomerization of Allylcyclopentane.—The catalyst, $RuCl_2(Ph_3P)_3$, 0.062 g, was added to a solution of allylcyclopentane, 3.0 ml, benzene, 3.0 ml, and ethanol, 3.0 ml, all components of which had been deaerated by bubbling nitrogen through them for 30 sec. The solution was stirred for 22 hr under nitrogen at 70°. Flash evaporation of volatiles left 0.1 g of a gummy solid exhibiting a deep ir band at ~1980 cm^{-1} (Nujol). Gas chromatographic analysis of the volatiles showed two reaction products, propylidenecyclopentane (79%) and an unidentified product, possibly 1-propylcyclopentene (21%). Microdistillation gave 1.0 ml of an olefinic material whose nmr spectrum confirmed that it was propylidenecyclopentane.

Isomerizations Using $IrCl(CO)(Ph_3P)_2$ as Catalyst.—Reactions were carried out in the neat olefins in a manner analogous to reactions described above. Conditions and results are given in Table I. Addition of excess pentane to reaction mixtures resulted in recovery of only $IrCl(CO)(Ph_3P)_2$ in 80–90% yield.

Isomerizations Catalyzed by $PtCl_2(Ph_3P)_2$–$SnCl_2$ under Hydrogen Pressure.—A mixture of $PtCl_2(Ph_3P)_2$, 0.0656 g, $SnCl_2$, 0.167 g, deaerated methanol, 7.0 ml, and deaerated 4-vinylcyclohexene, 3.0 ml, was stirred magnetically in a Fisher-Porter aerosol tube connected to a hydrogen pressure line. Fitted to the Fisher-Porter tube was a capillary sampling device permitting periodic removal of liquid samples under pressure. Solution occurred when the stirred reaction mixture was heated at 65° under 100 psi of hydrogen. Samples were removed periodically and analyzed by gas chromatography (Figure 1). After 6 hr the reaction mixture contained *cis*-4-ethylidenecyclohexene (22%), *trans*-4-ethylidenecyclohexene (33%), *cis*-3-ethylidenecyclohexene (3%), *trans*-3-ethylidenecyclohexene (7%), and 4-vinylcyclohexene (35%).

A similar reaction was run on a scale 10 times the size of the above experiment. Results were nearly identical and are reported in Table I. The reaction mixture was distilled on a semimicro spinning-band column under nitrogen. A constant-boiling fraction (4.5 ml, bp 141°, $n^{20}D$ 1.4812, >99% glpc purity) was shown by nmr to be *cis*- and *trans*-4-ethylidenecyclohexene: δ 5.63 (singlet, 2 protons, $H{>}C{=}C{<}H$), 5.23 (quartet, 1 proton $>C{=}C{<}H$), 2.70 (singlet, 2 protons $=CCH_2C=$), 2.17 (broad, 4 protons, $=CCH_2$), 1.58 (doublet, 3 protons, CH_3); all signals showed some fine structure. Although it was possible to separate the *cis*- and *trans*-4-ethylidenecyclohexanes using a 150-ft capillary column coated with UCON 550-X, the packed column used for collecting pure *cis*- and *trans*-3-ethylidenecyclohexene was not efficient enough for collection of the pure isomers of 4-ethylidenecyclohexene. Stereochemical assignment was made by inspection of the kinetic curve of the $PtCl_2(Ph_3P)_2$–$SnCl_2$-catalyzed isomerization. It was assumed that the isomer formed in higher yield was the precursor to *trans*-3-ethylidenecyclohexene and the isomer formed in lower yield was the precursor to *cis*-3-ethylidenecyclohexene. This assumption was consistent with an experiment which showed that geometrical isomerization of the *cis*- and *trans*-4-ethylidenecyclohexenes obtained from the Ru(II)-catalyzed isomerizations was very slow relative to double bond isomerization to the 3-ethylidenecyclohexenes.

Registry No.—$RuCl_2(Ph_3P)_3$, 15529-49-4; 4-vinylcyclohexene, 100-40-3; $RuCl_2(CO)(Ph_3P_2)_2(C_4H_{12})$, 12521-89-0; allylcyclopentane, 3524-75-2; $IrCl(CO)(Ph_3P)_2$, 14871-41-1; $PtCl_2(Ph_3P)_2$, 10199-34-5; *cis*-4-ethylidenecyclohexene, 30318-84-4; *trans*-4-ethylidenecyclohexene, 30319-25-6; 5-vinylnorbornene, 3048-64-4; vinylcyclohexane, 695-12-5; vinylcyclopentane, 3742-34-5.

Acknowledgment.—The author gratefully acknowledges the assistance of Miss Caroline Link who carried out much of the experimental work, and Mrs. Ruth Jenkins and Mr. Arthur Raymond for gas chromatographic analyses.

The Condensation of α Olefins with Paraformaldehyde, Acetylating Agents, and Hydrogen Chloride[1]

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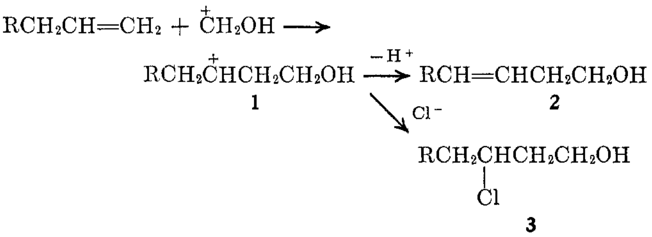
Reaction of 1-hexene, paraformaldehyde, and either acetonitrile, acetic anhydride, or acetyl chloride, with hydrogen chloride at −60 to −70° gave principally acyclic materials. The major component (30–50% yield) was identified as a *cis*- and *trans*-3-heptenyl acetate (**8**) mixture, and smaller quantities of *cis*- and *trans*-4-chloro-3-propyltetrahydropyran (**9**) and 3-chloro-1-heptyl acetate (**11**) were found. In addition, 20–40% yields of 2-chlorohexane (**4**) were obtained and minor amounts of 2-methyl-3-hexen-1-yl acetate (**7**) and 3-chloro-2-methyl-1-hexyl acetate (**10**) were separated and identified. Similar product mixtures were obtained from propylene. This procedure provides a convenient one-step synthesis of homoallylic acetates from readily available 1 olefins.

Recent articles[2-5] have described a modification of the Prins reaction in which various types of olefins were condensed with paraformaldehyde and hydrogen halides at low temperatures. The nature of the product was dependent on the structure of the starting olefin, but in each case it appeared that it was derived from initial electrophilic attack of protonated formaldehyde upon the double bond. Cyclic deprotonation[2] of the adduct **1** led to the homoallylic alcohol **2**, a precursor to other observed products, while chloride ion capture gave the corresponding 3-chloro-1-alkanol (**3**).



$$RCH_2CH{=}CH_2 + \overset{+}{C}H_2OH \longrightarrow$$

$$\underset{\mathbf{1}}{RCH_2\overset{+}{C}HCH_2CH_2OH} \xrightarrow{-H^+} \underset{\mathbf{2}}{RCH{=}CHCH_2CH_2OH}$$

$$\xrightarrow{Cl^-} \underset{\mathbf{3}}{RCH_2\underset{Cl}{\underset{|}{C}}HCH_2CH_2OH}$$

During the study of extensions of the modified Prins reaction it has been observed that, if the reaction is carried out in the presence of acetylating agents, predominantly linear materials are produced. In the initial experiment it was found that 1-hexene, paraformaldehyde, and acetonitrile reacted smoothly with hydrogen chloride in methylene chloride at −60 to −70°. Glpc analysis of the reaction mixture after an aqueous work-up showed that, in addition to low yields of a mixture of *cis*- and *trans*-4-chloro-3-propyltetrahydropyran (**9**), 3-chloro-1-heptyl acetate (**11**), and 40% of 2-chlorohexane (**4**), a rather substantial quantity of still another compound was formed (40% yield). This was purified by fractionation and identified as 3-heptenyl acetate (**8**) by elemental analysis and infrared, nmr, and mass spectra. Analogous experiments substituting acetyl chloride or acetic anhydride for the acetonitrile gave similar reaction mixtures. Treatment of a solution of acetonitrile in methylene chloride with hydrogen chloride, followed by addition of the other reactants and again introducing hydrogen chloride, gave a product mixture indistinguishable from that obtained using free acetonitrile. Similar experiments with propylene gave mixtures containing 3-butenyl acetate, 4-chlorotetrahydropyran, and 3-chloro-1-butyl acetate in somewhat lower yields, presumably due to losses because of greater water solubility during the aqueous work-up. Although the yields of unsaturated esters are moderate by this procedure, it does represent a simple one-step synthesis of homoallylic acetates from readily available starting materials.

In the condensations with 1-hexene, several minor components were consistently present in varying amounts depending on the reaction conditions. These were separated by preparative glpc and identified by nmr, infrared, and mass spectra. Scheme I summarizes the compounds observed in a typical experiment and Table I shows typical product distributions under identical conditions with the different acetylating agents.

A single sharp peak (on both UCON and Carbowax glpc columns) appeared to be a mixture of chloromethyl acetate (**5**) and 2-hexyl acetate (**6**), in approximately

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29–April 2, 1971.

[2] P. R. Stapp, *J. Org. Chem.*, **34**, 479 (1969).

[3] P. R. Stapp, *ibid.*, **34**, 1143 (1969).

[4] P. R. Stapp and D. S. Weinberg, *ibid.*, **34**, 3592 (1969).

[5] P. R. Stapp and J. C. Randall, *ibid.*, **35**, 2948 (1970).