of small but significant hyperfine interaction with the protons. However, this conclusion must be regarded as tentative in view of the assumption and approximation involved.

The deduced structures of the Cu and Ag complexes examined in the present study are shown schematically in Table II. Recently, Upton and Goddard reported on the result of an ab initio theoretical study (GVB-CI) of π-coordinated $Ni(C_2H_2)$ and $Ni(C_2H_4)$ with geometry optimization. They found very little distortion of the acetylene and ethylene ligands from the respective linear and planar structures, and very little delocalization of the orbitals. The Ni atom was found to be essentially $Ni(3d^94s^1)$ with the 4s orbital hybridized as 4s-4p pointing away from the ligand. The formation of the complexes is attributed to the attractive interaction between the π electrons and the partially unshielded Ni atom. The same mechanism must be operative in the formation of $Cu(C_2H_2)$ and $Cu(C_2H_4)$. The geometry of bis(ethylene)nickel has been examined by Rösch and Hoffman using the extended Hückel-type MO method.[23] They found that the two extreme structures of $Ni(C_2H_4)_2$, D_{2d} and D_{2h}, are essentially degenerate in the total energy ($\Delta E = 0.07$ eV) with no rotational barrier. Inspection of the energy diagram determined for $Ni(C_2H_4)_2$ as a function of the torsional angle (Figure 5 in ref 23) shows that the $Ni(C_2H_4)_2^-$ or $Cu(C_2H_4)$ would be more stable in the D_{2h} structure by ~0.8 eV.

References and Notes

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A Convenient Synthesis of Cyclopentanones via Rhodium(I)-Catalyzed Intramolecular Hydroacylation of Unsaturated Aldehydes

R. C. Larock,*[1] K. Oertle, and G. F. Potter

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.

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Abstract: The rhodium(I)-catalyzed intramolecular hydroacylation of unsaturated aldehydes has been investigated. Three useful new catalyst systems have been developed. The catalysts are prepared by the addition of 2 equiv of tri-*p*-tolylphosphine, tri-*p*-anisylphosphine, or tris(*p*-dimethylaminophenyl)phosphine to chlorobis(cyclooctene)rhodium(I) in ethylene-saturated methylene chloride. 4,5-Unsaturated aldehydes afford good yields of substituted cyclopentanones. However, alkyl substitution in either the 2 or the 5 position substantially reduces the yield of ketone. Disubstitution in the 2 position gives rise to ethyl ketones instead. This procedure provides a valuable new route to spirocyclic and fused bicyclic ketones, but is not applicable to the synthesis of ketones of ring size other than five. Furthermore, it is tolerant of almost all important organic functionality except amines.

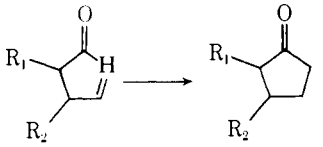
The transition metal catalyzed hydroformylation or oxo reaction is an extremely important industrial process which has been the subject of numerous studies (eq 1).[2-5] On the

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}H \qquad (1)$$

other hand, relatively few methods exist for the addition of aldehydes to olefins and each has severe limitations (eq 2).[6-12]

$$RCH{=}CH_2 + H\overset{O}{\overset{\|}{C}}R' \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}R' \qquad (2)$$

In this study we wish to report the development of several useful new catalysts for the intramolecular cyclization of 4,5-unsaturated aldehydes to cyclopentanones. Although numerous examples of the cationic cyclization of 5,6- and 6,7-unsaturated aldehydes to six- and seven-membered rings are known,[13-27] similar attempts to generate five-membered rings have generally failed.[27] However, Sakai and co-workers have reported that 2- and 3-substituted 4-pentenals could be cyclized to the corresponding cyclopentanones using *equivalent* amounts of either stannic chloride or Wilkinson's catalyst, $RhCl(PPh_3)_3$ (I) (eq 3).[28] Unfortunately, the yields were quite



(3)

low (0-57 and 17-34%, respectively) and the tin reaction, although highly stereospecific,[29] requires substitution α to the carbonyl. Lochow and Miller subsequently observed that 4-pentenal can be *catalytically* cyclized to cyclopentanone

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Table I. Effect of Various Transition Metal Complexes on the Cyclization of 4-Pentenal[a]

entry	complex	% yield of cyclopentanone[b]
1	$RhCl(PPh_3)_2$ (I)	47
2	$RhI(PPh_3)_3$	27
3	$Rh(NO)(PPh_3)_3$	0
4	$RhCl(PPh_3)_3 + AgClO_4$	11
5	$RhCl(PPh_3)_3 + AgBF_4$	0
6	$RhCl(CH_2{=}CH_2)[P(c\text{-}C_6H_{11})_3]_2$	trace
7	$RhCl(N_2)[P(c\text{-}C_6H_{11})_3]_2$	0
8	$RhCl(CO)(PPh_3)_3$	0
9	$RhCl(CO)[P(Ph\text{-}p\text{-}OMe)_3]_2$	0
10	$RhH(CO)(PPh_3)_3$	trace
11	$RhH(PPh_3)_4$	0
12	$RuCl(H)(PPh_3)_3$	0
13	$IrH(CO)(PPh_3)_3$	0
14	$IrCl(N_2)(PPh_3)_2$	0
15	$Pd(PPh_3)_4$	0
16	$PdCl_2(PPh_3)_2$	0

[a] 0.1 mmol of complex and 0.2 mmol of 4-pentenal in 5 mL of methylene chloride (no ethylene). [b] Maximum GLC yields.

using I and ethylene-saturated chloroform.[30] More recently Suggs has reported that the rhodium complex I promoted bimolecular hydroacylation of olefins when chelating aldehydes and imines are employed.[31,32] At this time we wish to report our work on the development of new catalysts for and extension of the intramolecular hydroacylation reaction of unsaturated aldehydes.

Results and Discussion

Effect of Solvent. Since many transition-metal reactions are highly solvent dependent, we first examined the effect of a large variety of solvents on the yield of cyclopentanone from the reaction of I and 4-pentenal. Since no dramatic effect was observed, methylene chloride at room temperature has been used in all subsequent work.

Transition-Metal Catalysts. In a search for catalysts which might prove more effective than I, we have investigated a wide variety of transition-metal complexes as potential catalysts for the cyclization of 4-pentenal to cyclopentanone (Table I). In short, no complex examined proved as effective as I, which under the conditions utilized was not catalytic. Cationic coordinatively unsaturated complexes of rhodium[33] prepared from I and silver perchlorate or silver tetrafluoroborate proved ineffective (entries 4 and 5). Chloroethylenebis(tricyclohexylphosphine)rhodium(I) (entry 6) and chlorodinitrogenbis(tricyclohexylphosphine)rhodium(I) (entry 7) were investigated in the hope that the ethylene and the dinitrogen ligands would dissociate relatively easily from these complexes and that the bulky tricyclohexylphosphine ligand might sterically hinder decarbonylation of the aldehyde. Unfortunately, both reagents reacted very sluggishly and no more than traces of cyclopentanone were observed. Photolysis of the dinitrogen complex offered no improvements. In all of these reactions infrared absorptions characteristic of $RhCl(CO)[P(c\text{-}C_6H_{11})_3]_2$[34] were observed indicating that decarbonylation is a major reaction pathway.[35-37] Such chlororhodium(I) carbonyl complexes were found to be completely unreactive as catalysts (entries 8 and 9). A number of transition metal hydride complexes (entries 10-13) were also examined as potential catalysts, but no cyclopentanone was observed. The hope here was that hydrometalation of the olefin, intramolecular oxidative addition of the aldehyde, and subsequent reductive elimination of the starting metal hydride might afford the cyclic ketone. Such was not the case, although both rhodium hydride complexes examined did consume the starting aldehyde.

Table II. Effect of Ligands on the Rhodium-Catalyzed Cyclization of 4-Pentenal [a]

ligand	% yield of cyclopentanone[b] equiv of phosphine[c] 1	2	3
PPh_3	35	78	55
$P(p\text{-}C_6H_4F)_3$	47	82	70
$P(p\text{-}C_6H_4N(CH_3)_2)_3$	41	90	95
$P(p\text{-}C_6H_4CH_3)_3$	65	97	72
$P(o\text{-}C_6H_4CH_3)_3$	59	72	76
$P(p\text{-}C_6H_4OCH_3)_3$	70	98	88
$P(o\text{-}C_6H_4OCH_3)_3$	0	0	0
$P(CH_3)_2Ph$	13	22	5
$P(C_2H_5)_3$	24	37	19
$P(n\text{-}C_4H_9)_3$	25	45	
$P(c\text{-}C_6H_{11})_3$	55	37	68
$P(OC_2H_5)_3$	15	0	trace
$(CH_3)_2PCH_2CH_2P(CH_3)_2$	45	45	48
$Ph_2PCH_2CH_2PPh_2$		17	
$AsPh_3$		16	

[a] 50% rhodium per aldehyde in ethylene-saturated methylene chloride. [b] GLC analysis using an internal standard. [c] Relative to rhodium.

Effect of Added Olefins, Acetylenes, Water, and Air. In the midst of our work Lochow and Miller reported that saturating the reaction mixture with ethylene substantially improves the yield of cyclopentanone.[30] We have observed the same effect. Using 50% I the yield of cyclopentanone increases from 47 to 87%. No other added olefin or acetylene proved as effective: cyclooctene (26%), vinyl bromide (0%), acetylene (0%), and hexafluoro-2-butyne (4%). With acetylene and vinyl bromide the solution changed colors, but no ketone was observed. Added water was observed to have no effect on the yield, but air destroyed the catalyst.

Use of in Situ Prepared $RhClL_n$ Complexes. We next turned our attention to improving the original rhodium(I) catalyst by modifying the ligands attached to rhodium. Our initial attempts to prepare complexes of the type $RhClL_3$ with tertiary phosphines other than triphenylphosphine were generally unsuccessful. Major problems were encountered in isolation of the complexes owing to their increased solubility in a variety of solvents and their sensitivity toward oxygen. Consequently, we chose to prepare these complexes in situ by addition of the desired ligand to a solution of chlorobis(cyclooctene)rhodium(I) dimer in methylene chloride under ethylene:

$$\tfrac{1}{2}[RhCl(olefin)_2]_2 + nL \xrightarrow[n = 1\text{-}3]{} RhCl(olefin)_{3-n}L_n \quad (4)$$

Chlorobis(ethylene)rhodium(I) dimer gives identical results, but appears to be somewhat more difficult to store. This procedure allows one to vary the ratio of ligand to rhodium so as to optimize the yield of ketone.

In this manner a number of ligands were readily examined and the results are tabulated in Table II. With few exceptions the highest yield of cyclopentanone was obtained using 2 equiv of ligand per rhodium. It was observed later that, if the phos-

Table III. Rhodium-Catalyzed Cyclization of Unsaturated Aldehydes[a]

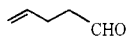
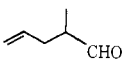
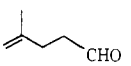
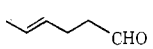
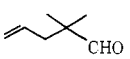
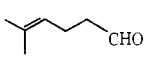
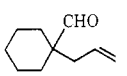
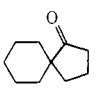
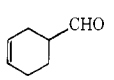
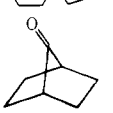
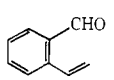
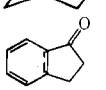
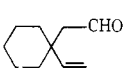
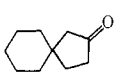
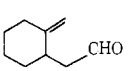
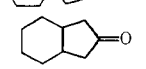
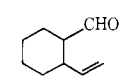
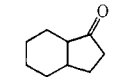
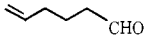
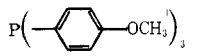
entry	aldehyde	ligand[b]	% catalyst[c]	product	% yield[d]
1		$P(C_6H_5)_3$	50		78
		$P(C_6H_4CH_3)_3$	50		97
			10		95
			1		20
		$P(C_6H_4OCH_3)_3$	50		98
			10		88
		$P(C_6H_4N(CH_3)_2)_3$	50		90
			20		**78**
			10		90
			1		10
2		$P(C_6H_4CH_3)_3$	50		51
			10		24
		$P(C_6H_4OCH_3)_3$	50		53
			10		37
3		$P(C_6H_4CH_3)_3$	50		90
		$P(C_6H_4OCH_3)_3$	50		95
		$P(C_6H_4N(CH_3)_2)_3$	50		98
4		$P(C_6H_4CH_3)_3$	50		59
			10		34
		$P(C_6H_4OCH_3)_3$	50		52
			10		40
5		$P(C_6H_4CH_3)_3$	50		0
		$P(C_6H_4OCH_3)_3$	50		0
		$P(C_6H_4N(CH_3)_2)_3$	50		0
6		$P(C_6H_4CH_3)_3$	50		0
		$P(C_6H_4OCH_3)_3$	50		0
		$P(C_6H_4N(CH_3)_2)_3$	50		0
7		$P(C_6H_4OCH_3)_3$	50		0
8		$P(C_6H_4OCH_3)_3$	50		0
9		$P(C_6H_4CH_3)_3$	50		6
		$P(C_6H_4OCH_3)_3$	50		8
10		$P(C_6H_4N(CH_3)_2)_3$	10		**93**
11		$P(C_6H_4N(CH_3)_2)_3$	50	 *cis-/trans-*, 64/36	**90**
12	 *cis-/trans-* 36/64	$P(C_6H_4N(CH_3)_2)_3$	50	 *cis-/trans-* 27/73	**89**

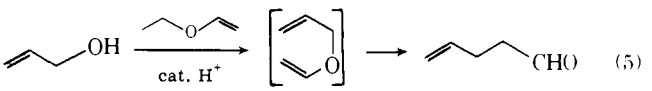
Table III. (*Continued*)

entry	aldehyde	ligand[b]	% catalyst[c]	product	% yield[d]
13			50		19
			20		19

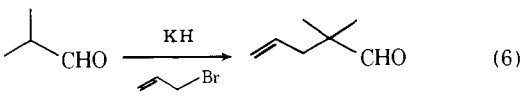
[a] Chlorobis(cyclooctene)rhodium(I) dimer at room temperature in methylene chloride saturated with ethylene. [b] 2 equiv per rhodium. [c] Mole percent rhodium per aldehyde. [d] GLC yields using an internal standard; isolated yields are in boldface type.

phine is old or impure, up to 3 equiv of phosphine is sometimes necessary to achieve the same yields obtained with only 2 equiv of pure phosphine. The basicity of the phosphine[38-40] appears to be the most significant factor in determining the yield of ketone, the less basic triarylphosphines giving better results than trialkylphosphines. Steric factors also appear to play an important role. While tri-*p*-anisylphosphine gives an excellent 98% yield of cyclopentanone, tri-*o*-anisylphosphine gave extensive decarbonylation and no ketone. Although both tri-*p*-tolylphosphine and tri-*o*-tolylphosphine give good yields of cyclopentanone, with the latter catalyst the ketone soon disappeared and two new unidentified products were observed upon GLC analysis. From the results of Table II, three new catalyst systems look particularly promising, those containing tri-*p*-tolylphosphine, tri-*p*-anisylphosphine, and tris(*p*-dimethylaminophenyl)phosphine.

Synthesis of Unsaturated Aldehydes. In order to determine the generality of this new approach to cyclic ketones, a variety of unsaturated aldehydes were required. Fortunately 4,5-unsaturated aldehydes are readily available by a variety of methods. Particularly useful among these is the highly versatile Claisen rearrangement[41] (eq 5). The allylation of aldehydes


(5)

by allyl bromide and potassium hydride (eq 6)[42] or allylation of the corresponding enamines (eq 7)[43] provide equally con-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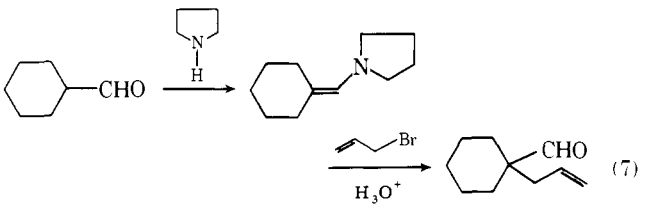
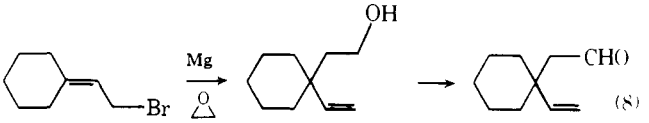
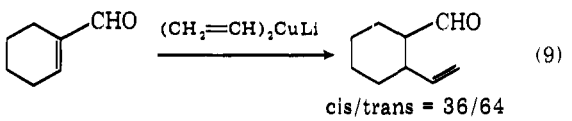

(7)

venient routes to the desired unsaturated aldehydes. 4,5-Unsaturated aldehydes are also available via reaction of allylic Grignard reagents with ethylene oxide[44] and subsequent oxidation to the aldehyde (eq 8). One other very versatile route


(8)

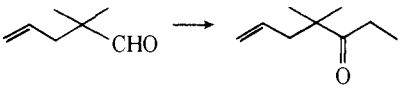
to the desired aldehydes involves the conjugate addition of vinyl cuprate reagents to α,β-unsaturated aldehydes (eq 9),[45]


(9)

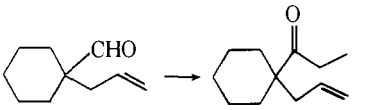
cis/trans = 36/64

Cyclization of Unsaturated Aldehydes. With a number of unsaturated aldehydes in hand, it remained for us to determine the generality of the rhodium-catalyzed cyclization reaction. Thus, we have examined the 4-pentenal cyclization with varying amounts of each of our new catalysts and applied the best procedures to the cyclization of a variety of other unsaturated aldehydes. The results are described in Table III.

In the cyclization of substituted 4-pentenals several generalizations can be made. All three ligands employed appear equally effective even at concentrations as low as 10%. However, yields drop off drastically with only 1% of the catalyst. Substitution of a methyl group in either the 2 or 5 position of 4-pentenal (entries 2 and 4) cuts the yield in half, but only the latter compound appears to react any slower. Substitution of two methyl groups in either the 2 or 5 positions (entries 5 and 6) affords neither the desired cyclic ketones, the starting material, nor the expected olefinic decarbonylation product. In fact no recognizable product is obtained in the case of 5-methyl-4-hexenal. However, disubstitution in the 2 position (entries 5 and 7) affords a most interesting side product, the corresponding ethyl ketone (eq 10 and 11). In some fashion


(10)

10–15%


(11)

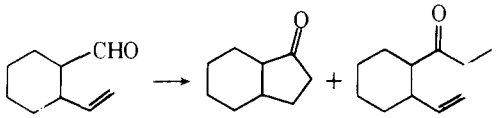
55%

ethylene is inserting into the carbon-hydrogen bond of the aldehyde in these cases. Unfortunately, this reaction does not appear to be general for aldehydes which do not contain unsaturation in the 4 position. Finally, substitution in the 3 and/or 4 positions of 4-pentenal (entries 3, 10, and 11) does not appear to affect the yield of the cyclization reaction at all and excellent yields are obtained.

We have also examined the possibility of preparing bicyclic ketones by our procedure. Since the failure of (1-allylcyclohexane)carboxaldehyde (entry 7) to provide the spirocyclic ketone appeared to be due to the fact that the ketone is disubstituted in the 2 position, we examined the cyclization of the isomeric aldehyde, (1-vinylcyclohexyl)acetaldehyde (entry 10). In this case cyclization proceeded in quantitative yield using only 10% of the tris(*p*-dimethylaminophenyl)phosphine catalyst. This approach would appear to have great promise for the synthesis of spirovetivanes, an interesting class of naturally occurring sesquiterpenes containing this same spiro[4.5]decane skeleton.[46]

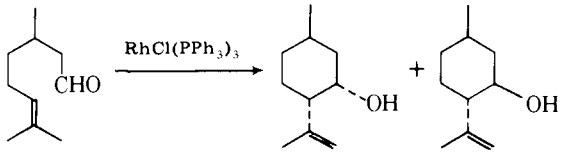
Isomeric hexahydroindanones can also be prepared by rhodium-catalyzed cyclizations. (2-Methylenecyclohexyl)-acetaldehyde cyclizes in essentially quantitative yield to a 64/36 cis/trans mixture of bicyclic ketones (entry 11). The stereochemical ratio was determined by gas chromatographic comparison with independently prepared authentic samples

of each isomer. The carbon-hydrogen bond of the aldehyde apparently adds predominantly to the more remote side of the double bond, forming the more stable cis-fused bicyclic ring system,[47] (2-Vinylcyclohexane)carboxaldehyde (entry 12) can be prepared by divinylcuprate addition to 1-cyclohexenecarboxaldehyde and low-temperature quenching with methanol. A 36/64 cis/trans mixture results as determined by gas chromatographic and spectral analysis. This aldehyde is cyclized in excellent yield to a mixture of the corresponding cis and trans bicyclic ketones and 5–10% of the ethylene insertion product (eq 12). The two ketones are easily separated, however, by column chromatography.



(12)

Quite clearly a large variety of cyclopentanones can be prepared by rhodium-catalyzed cyclizations. The question remained as to whether one might be able to prepare cyclobutanones or cyclohexanones in like manner. Unfortunately, 3-butenal is exceptionally difficult to prepare, thus precluding widespread application of this approach to the synthesis of cyclobutanones. In order to determine if 5,6-unsaturated aldehydes could be cyclized to cyclohexanones, the cyclization of 5-hexenal was investigated (entry 13). The product had a GLC retention time identical with that of 2-methylcyclopentanone and no peak was observed for cyclohexanone. There was extensive decarbonylation as indicated by a GLC peak with a retention time similar to that of pentene and the presence of a Rh-CO band in the infrared spectra of the residual complex. Rather interestingly, the presence or absence of ethylene had no effect on the yield of 2-methylcyclopentanone. It should be noted here that previous attempts to cyclize the 6,7-unsaturated aldehyde, (+)-citronellal, afforded neither of the originally anticipated cyclic ketones, but a mixture of unsaturated cyclohexanols instead (eq 13).[20]



(13)

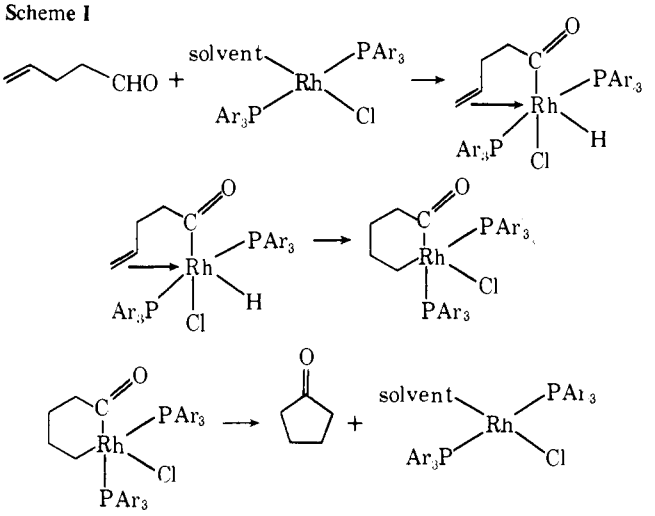
To ascertain if acetylenic aldehydes could be cyclized to α,β-unsaturated cyclic ketones, 4-pentynal, 5-hexynal, and 5-heptynal were treated with 50% of the triarylphosphine catalysts. With all three aldehydes, the reaction mixture became black after about 15 min and no new products were observed by GLC analysis. Approximately 50% of the aldehyde remained after 2 days. An infrared spectrum of the residual complex showed that a Rh-CO bond was present.

The cyclization of allyl formate was also examined using both Wilkinson's catalyst and the complex prepared from tri-*p*-anisylphosphine. Unfortunately, no color change was observed and no allyl formate was consumed. No butyrolactone could be detected after 2 days reaction time.

It is evident that rhodium-catalyzed cyclizations afford a very valuable new method for the synthesis of cyclopentanones. However, they do not appear applicable to the formation of cyclic ketones of other ring sizes.

Effect of Other Functional Groups. In order for the rhodium cyclization procedure to find widespread application in organic synthesis, and particularly in the synthesis of complex natural products, the reaction must be tolerant of a diversity of functional groups. To examine this question we have investigated the cyclization of 4-pentenal in the presence of a number of

Scheme I



important organic functional groups. Each of the following compounds (1 equiv) was added to the 4-pentenal reaction [10% tris(*p*-dimethylaminophenyl)phosphine] and the yield of cyclopentanone determined: isovaleric acid (100% yield of cyclopentanone), ethyl acetate (95%), acetonitrile (97%), methyl isobutyl ketone (100%), *n*-hexyl bromide (88%), 1-hexanol (82%), and triethylamine (22%). The reaction is clearly tolerant of carboxylic acids, esters, nitriles, ketones, primary bromides, and alcohols, but tertiary amines provide sharply reduced yields.

Mechanism. The mechanism of the rhodium-catalyzed cyclization reaction can be inferred from known mechanisms for hydroformylation, hydrogenation, decarbonylation and other well-established transition metal promoted processes.[30] Mechanistically, the reaction appears to follow the pathway outlined in Scheme I. The active catalyst is probably a coordinately unsaturated bisphosphine complex in which either the solvent or ethylene occupies one coordination site. The stoichiometry indicated for the catalyst is supported by the greater yields of cyclopentanone obtained when using a 2:1 ratio of ligand to rhodium. The aldehyde presumably oxidatively adds to the catalyst forming an acylhydridorhodium(III) complex analogous to one recently reported by Suggs and shown to react with olefins to give ketones.[31] In the reaction of 5-hexenal, rhodium hydride addition to form the six-membered ring metallacycle is apparently strongly favored over formation of a seven-membered ring species. A similar six-membered ring acylalkyl metallacyclic complex has been isolated by Casson and co-workers and shown to reductively eliminate a cyclopentanone when treated with a stoichiometric amount of triphenylphosphine.[48] The decarbonylation side reaction presumably follows a previously established mechanism for this transformation.[36,37,49,50] The role of ethylene in these two competing reactions is not clear.

Conclusions

4,5-Unsaturated aldehydes can be catalytically cyclized to cyclopentanones using catalysts prepared from chlorobis(cyclooctene)rhodium(I) dimer and 2 equiv (per rhodium) of tri-*p*-tolylphosphine, tri-*p*-anisylphosphine, or tris(*p*-dimethylaminophenyl)phosphine in methylene chloride saturated with ethylene. Substitution in the 2 and 5 positions tends to reduce the yield of cyclic ketone and the corresponding ethyl ketones begin to appear as side products. This procedure is applicable to the synthesis of spirocyclic and fused bicyclic ketones and appears tolerant of a wide range of functional groups. It is not applicable, however, to the synthesis of cyclic ketones of ring size greater than five.

Experimental Section

All reagents were used directly as obtained commercially unless otherwise noted. The solvents were dried over molecular sieves, distilled, and degassed before use. All infrared spectra were obtained on a Beckman IR 4250 spectrophotometer. ^{1}H NMR spectra were obtained on Varian A-60 and HA-100 instruments and the ^{13}C NMR spectra on a JEOL FX 90 Q. A Varian 920 gas chromatograph with a thermal conductivity detector was used for most GLC analyses, more difficult separations being determined on a Varian 3700 gas chromatograph. Mass spectra were recorded on an AEI MS 902 and a Finnegan 4023 GC/MS combination.

Transition-Metal Complexes. The following complexes were used as obtained commercially: $RhH(CO)(PPh_3)_3$ (Strem), $RhCl(CO)(PPh_3)_2$ (Alfa Inorganics—Ventron), $RuCl(H)(PPh_3)_3$(ROC/RIC), $IrCl(N_2)(PPh_3)_2$ (Alfa Inorganics—Ventron), and $IrH(CO)(PPh_3)_2$(ROC/RIC). $RhCl(PPh_3)_3$,[51] $RhI(PPh_3)_3$,[52] $RhCl(CH_2{=}CH_2)[P(c\text{-}C_6H_{11})_3]_2$,[34,53] $RhCl(N_2)[P(c\text{-}C_6H_{11})_3]_2$,[34,53] $RhH(PPh_3)_4$,[54] $RhCl(CO)[P(Ph\text{-}p\text{-}OMe)_3]_2$,[55] $Rh(NO)(PPh_3)_3$,[56] $[RhCl(C_8H_{14})_2]_2$,[57] $[RhCl(CH_2{=}CH_2)_2]_2$,[58] $Pd(PPh_3)_4$,[59] and $PdCl_2(PPh_3)_2$[60] were prepared according to published procedures.

Phosphines. The following phosphines were used as obtained commercially from Strem: tri-*o*-anisylphosphine, tri-*p*-anisylphosphine, tri-*o*-tolylphosphine, tri-*p*-tolylphosphine, tri(*p*-fluorophenyl)phosphine, tris(*p*-dimethylaminophenyl)phosphine, tricyclohexylphosphine, 1,2-bis(dimethylphosphino)ethane, and 1,2-bis(diphenylphosphino)ethane. Tri-*n*-butylphosphine (Aldrich), triphenylphosphine (Aldrich), triethylphosphine (Aldrich), dimethylphenylphosphine (Pfaltz and Bauer), triethyl phosphite (Aldrich), and triphenylarsine (Aldrich) were purified by distillation or recrystallization before use.

Unsaturated Aldehydes. 4-Pentenal was prepared by three different procedures. Collins oxidation[61] of 4-penten-1-ol (Chemical Samples) gave a 44% yield of 4-pentenal, while the procedure of Sharpless and Akashi[62] afforded a 41% yield of the aldehyde. The low yields were due mainly to the high water solubility of the product. The majority of the 4-pentenal was prepared by Claisen rearrangement of allyl vinyl ether (Columbia Organic Chemicals).[63] 4-Pentenal was obtained in 65% yield, bp 102–103 °C (lit.[63] bp 105 °C).

The following aldehydes were prepared using literature procedures: 2-methyl-4-pentenal,[64] 18% yield, bp 115–116 °C (lit. bp 118°C); 3-cyclohexenecarboxaldehyde,[65] 29% yield, bp 55–57 °C (17 Torr) (lit. bp 51–52 °C (13 Torr)); 4-hexenal,[66] bp 129–132 °C (lit.[67] bp 42–44 °C (15 Torr)); *o*-formylstyrene,[68] 42% yield, bp 77–82 °C (1.7 Torr) (lit. bp 70–75 °C (1 Torr)); 4-methyl-4-pentenal,[69] 21% yield, bp 68 °C (95 Torr) (lit. bp 100–103 °C (758 Torr)); 5-methyl-4-hexenal,[70] 20–30% yield, bp 90 °C (100 Torr) (lit. bp 90 °C (100 Torr)).

5-Hexenal, 4-pentynal, and 5-hexynal were obtained by oxidizing the appropriate alcohols (Chemical Samples, Farchan, and Farchan, respectively) using the procedure developed by Sharpless:[62] 5-hexenal, 31% yield, bp 124–126 °C (lit.[71] bp 128–129 °C); 4-pentynal, 21% yield, bp 61–63 °C (43 Torr) (lit.[72] bp 70 °C (50 Torr)); 5-hexynal, 25% yield, bp 52–54 °C (20 Torr) (lit.[73] bp 61–62 °C (30 Torr)).

5-Heptynal[74] was prepared by protection of 5-hexyn-1-ol (Farchan) (dihydropyran, catalyst *p*-TsOH), methylation (*n*-BuLi, CH_3I), deprotection to 5-heptyn-1-ol[75] (catalyst *p*-TsOH/CH_3OH), and oxidation (pyridinium chlorochromate[76]). An overall yield of 64–72% was obtained, bp 70–80 °C (50 Torr). The infrared, nuclear magnetic resonance, and mass spectra were identical with the literature values.[74]

2,2-Dimethylpentenal was prepared from isobutyraldehyde, allyl bromide, and potassium hydride according to the literature procedure,[42] except for the following modifications. A 6:1 ether to hexamethylphosphoramide solvent mixture was employed instead of tetrahydrofuran, and an aqueous workup was avoided by filtering and then distilling the product directly from the reaction mixture, 30% yield, bp 65 °C (90 Torr) (lit.[77] bp 124–125 °C (760 Torr)).

The following procedure was used to prepare (1-allylcyclohexane)carboxaldehyde. *n*-Butyllithium (0.1 mol) in hexane was added to diisopropylamine (0.1 mol) in tetrahydrofuran (THF) in a three-neck 250-mL round-bottom flask cooled in an ice bath. *N*-(Cyclohexylmethylene)-*tert*-butylamine[78] (0.1 mol) in THF was added and refluxed for 22 h. The mixture was cooled to room temperature and allyl bromide (0.11 mol) was added. The resulting mixture, which contained a precipitate, was refluxed for 20 h. After cooling to room temperature, 10% aqueous HCl was added and the resulting clear solution was refluxed for an additional 3 h. (Most of the heating is unnecessary.) The solution was saturated with solid NaCl. The organic layer was separated and the aqueous layer was washed with ether. The combined organic phase was washed once with 5% HCl and repeatedly with saturated aqueous NaCl until the washings were neutral. After drying with anhydrous Na_2SO_4 and removal of ether, (1-allylcyclohexane)carboxaldehyde was obtained in 41% yield, bp 93–96 °C (20 Torr) (lit.[77] bp 105–107 °C (32 Torr)).

(2-Methylenecyclohexyl)acetaldehyde was prepared as follows. 1-Hydroxymethylcyclohexene was synthesized from cyclohexanone according to literature procedures[79,80] in 47% overall yield, bp 83–85 °C (13 Torr) (lit.[79] bp 96 °C (18 Torr)). Conversion to the corresponding vinyl ether was accomplished by heating with ethyl vinyl ether and a catalytic amount of mercuric acetate,[81] 50% yield, bp 61–68 °C (15 Torr) (lit.[82] bp 69 °C (17 Torr)). Cope rearrangement of the vinyl ether at 200 °C in a sealed tube afforded after distillation a 37% yield of the desired aldehyde: bp 81–85 °C (12 Torr) (lit.[82] bp 82 °C (14 Torr)); ^{1}H NMR (CCl_4) δ 1.2–2.85 (11 H, m), 4.52 (1 H, br s, vinyl), 4.66 (1 H, br s, vinyl), 9.65 (1 H, t, J = 1.5 Hz, CHO); IR (max) (CCl_4) 3080, 2940, 2860, 2710, 1730, 1645, 1445, 885 cm^{-1}; MS *m/e* 138.104 49 ± 0.14 ppm (calcd for $C_9H_{14}O$, 138.104 47).

(2-Vinylcyclohexane)carboxaldehyde was synthesized by the following procedure. 1-Hydroxymethylcyclohexene was oxidized to the corresponding aldehyde in 71% yield using pyridinium chlorochromate[76] in methylene chloride, bp 67–71 °C (15 Torr) (lit.[83] bp 61–63 °C (10 Torr)). Lithium divinylcuprate was added to this aldehyde as follows.[45] Cuprous bromide–dimethyl sulfide complex (20.9 mmol, 4.28 g) was suspended in 7 mL of dimethyl sulfide and 15 mL of THF. At −78 °C 18 mL of 2.35 M vinyllithium was slowly added while stirring vigorously. After 15 min the reaction mixture was warmed to −15 °C for 30 min and then cooled again to −78 °C. 1-Cyclohexenecarboxaldehyde (20.9 mmol, 2.30 g) dissolved in 50 mL of THF was added, and the reaction mixture stirred for 15 min at −78 °C, 90 min at −30 °C, and 35 min at −20 °C, before quenching at −78 °C with 3 mL of methanol. Extraction with ether, washing the organic layer with ammonium chloride/ammonia, evaporation of the solvent, chromatography on 100 g of silica gel with 4:1 hexane/ether, and distillation afforded 1.44 g (50%) of the desired aldehyde, bp 70 °C (11 Torr). GLC analysis (OV-101 30-m capillary column) of the product showed two peaks in a ratio of 36:64, determined by infrared, nuclear magnetic resonance, and GC–mass spectroscopy to be a cis–trans mixture of the desired unsaturated aldehydes: ^{1}H NMR ($DCCl_3$) δ 1.15–2.9 (10 H, m), 4.85–6.3 (3 H, m, vinyl), 9.55 (1 H, d, J = 2 Hz, CHO), 9.68 (1 H, d, J = 1 Hz, CHO) (the ratio of the 9.55 peak to 9.68 peak was approximately 7:3); IR (max) (CCl_4) 3080, 2930, 2860, 2705, 1730, 1450, 920 cm^{-1}; MS *m/e* 138.104 393 ± 0.5 ppm (calcd for $C_9H_{14}O$, 138.104 468). The lesser aldehyde was determined to be the cis isomer by rhodium-catalyzed cyclization to *cis*-1-hexahydroindanone, which was identical with an authentic sample prepared by an independent route.[84–86]

(1-Vinylcyclohexyl)acetaldehyde was prepared as follows. 1-Ethynylcyclohexanol (Farchan) was reduced with $LiAlH_4/NaOCH_3$ to 1-vinylcyclohexanol,[87] which gave upon treatment with phosphorus tribromide an overall 79% yield of β-cyclohexylideneethyl bromide, bp 80–85 °C (11 Torr) (lit.[88] bp 78–83 °C (11 Torr)). 2-(1-Vinylcyclohexyl)ethanol was synthesized by preparation of the Grignard reagent corresponding to the above bromide and treatment with ethylene oxide as follows.[44] The bromide (65 mmol, 12.3 g) in 40 mL of THF was added over a period of 5 h to 4.5 g of magnesium turnings in 30 mL of THF at 15 °C. After stirring for 1 h, the Grignard reagent was added over a period of 30 min to 5 mL of ethylene oxide in 15 mL of THF at −25 °C. The mixture was maintained at −20 °C for 30 min and then warmed to 10 °C before hydrolysis. A standard workup, chromatography on 30 g of silica gel (1:1 hexane/ether), and distillation provided 3.40 g (34%) of the desired alcohol: bp 107–112 °C (11 Torr); ^{1}H NMR (CCl_4) δ 1.25–1.75 (12 H, m), 3.48 (2 H, t, J = 7 Hz, CH_2O), 4.90 (1 H, dd, J = 2, 17 Hz, vinyl), 5.03 (1 H, dd, J = 2, 11 Hz, vinyl), 5.68 (1 H, dd, J = 11, 17 Hz, vinyl); IR (max) (CCl_4) 3640, 3080, 2930, 2850, 1450, 910 cm^{-1}; MS *m/e* 154.135 37 ± 2.6 ppm (calcd for $C_{10}H_{18}O$, 154.135 77). The alcohol was oxidized to the corresponding aldehyde with pyridinium chlorochromate[76] in methylene chloride in 89% yield: bp 80–90 °C (11 Torr); ^{1}H NMR (CCl_4) δ 1.3–1.8 (10 H, m), 2.27 (2 H, d, J = 3 Hz, CH_2CHO), 5.03

(1 H, dd, J = 2, 17 Hz, vinyl), 5.14 (1 H, dd, J = 2, 11 Hz, vinyl), 6.02 (1 H, dd, J = 11, 17 Hz, vinyl), 9.63 (1 H, t, J = 3 Hz, CHO); IR (max) (CCl_4) 3080, 2930, 2860, 2730, 1730, 1680, 1640, 1455, 920 cm^{-1}; MS m/e 152.120 27 ± 1.0 ppm (calcd for $C_{10}H_{16}O$, 152.120 12).

Solvent and Transition Metal Complex Studies under N_2 Atmosphere. The following procedure was used when studying the effects of various solvents and transition-metal complexes on the yield of cyclopentanone. The complex (0.10 mmol) was placed in a 25-mL round-bottom flask equipped with a septum inlet tube and was flushed with N_2. The solvent (5 mL) containing 4-pentenal (0.20 mmol) and the GLC internal standard, *n*-undecane, was added by syringe. If the reaction mixture was to be heated, the flask was equipped with a reflux condenser. The flask was lowered into a preheated oil bath after addition of the solvent and the system closed once equilibrium was reached as indicated by an attached mercury bubbler.

The progress of the reaction was followed by GLC analysis at various time intervals (10-ft 10% Carbowax 20M, 100 °C). The various transition-metal complexes investigated along with the yields of cyclopentanone are listed in Table I.

Cyclization Reactions with In Situ Prepared Complexes in an Ethylene Atmosphere. The following is a typical procedure used when the cyclization reaction was run under ethylene. In a 25-mL round-bottom flask equipped with a septum inlet tube were placed the rhodium complex and an appropriate amount of phosphine. A methylene chloride solution (5 mL) containing the aldehyde (1.0 mmol) and GLC internal standard was added by syringe and the flask flushed with argon and cooled in liquid N_2. Ethylene was then admitted into the flask until a distinct layer of liquid ethylene was present on the frozen methylene chloride. The flask was allowed to warm to room temperature with the excess ethylene escaping through a mercury bubbler. After warming to room temperature, the flask was sealed. The determination of yields by gas chromatography was carried out exactly as described above for cyclopentanone. The results are summarized in Table II.

All GLC yields of cyclic ketones reported in Table III were determined exactly as described here using an appropriate internal standard.

Isolation of Ketones. The following preparation of 2-spiro[4.5]-decanone is representative of the procedure used in determining the isolated yields reported in Table III. (1-Vinylcyclohexyl)acetaldehyde (5.13 mmol, 781 mg) in 5 mL of methylene chloride was added to chlorobis(cyclooctene)rhodium(I) dimer (0.535 mmol, 192 mg) and tris(*p*-dimethylaminophenyl)phosphine (1.07 mmol, 420 mg) in 20 mL of methylene chloride under argon in a 100-mL round-bottom flask. After the flask was cooled under argon with liquid nitrogen, ethylene was admitted and allowed to condense until a clear layer of ethylene was observed on top of the frozen methylene chloride. The reaction mixture was allowed to slowly warm to room temperature while the excess ethylene escaped through a mercury bubbler. The reaction mixture was sealed and allowed to run for 5 days. The solvent was removed on a rotary evaporator and the residue dissolved in pentane and filtered through 20 g of silica gel. After collection of cyclooctene, the eluant was changed to 1:1 pentane/ether and the ketone (R_f 0.8) eluted: 727 mg (93%); bp 85–90 °C (10 Torr) (lit.[89] bp 112–113 °C (13 Torr)); ^1H NMR (CCl_4) δ 1.35–2.25 (m); ^{13}C NMR ($DCCl_3$) δ 22.93, 25.99, 34.57, 36.20, 37.17, 39.97, 50.76, 219.39; IR (max) (CCl_4) 2930, 2860, 1745, 1450, 1410, 1275, 1265, 1160, 905 cm^{-1}; MS m/e 152.119 87 ± 1.6 ppm (calcd for $C_{10}H_{16}O$, 152.120 11).

The following ketones were isolated in identical fashion.

Cyclopentanone: 10.1-mmol scale; ether eluant; 777 mg (92%), 666 mg distilled (78%), bp 85 °C (200 Torr). All spectra were identical with those of an authentic sample.

***cis*- and *trans*-2-Hexahydroindanone:** 5.11-mmol scale; 1:1 pentane/ether (R_f 0.64); 683 mg (97%); bp 85 °C (10 Torr) (lit.[91] bp *trans*- 90 °C (11 Torr), *cis*- 110 °C (20 Torr). A 64:36 cis/trans mixture was observed by GLC analysis (10-ft 10% Carbowax 20M, 160 °C). The isomers were separated by GLC, compared with authentic samples of each isomer of 2-hexahydroindanone prepared from 2-decalone according to a literature procedure,[90] and characterized as the oximes. *cis*-2-Hexahydroindanone; n_D^{20} 1.4830 (lit.[91] $n_D^{16.7}$ 1.4846); oxime mp 75–77 °C (lit.[91] mp 80 °C); ^1H NMR (CCl_4) δ 1.20–2.45 (m); IR (max) (CCl_4) 2930, 2860, 1750, 1465, 1455, 1410, 1165 cm^{-1}, *trans*-2-Hexahydroindanone; n_D^{20} 1.4759 (lit.[92] n_D^{20} 1.4763); oxime mp 161–162 °C (lit.[91] mp 161 °C); ^1H NMR (CCl_4) δ 1.1–2.4 (m); IR (max) (CCl_4) 2915, 2845, 1750, 1450, 1410, 1175, 1145 cm^{-1}.

***cis*- and *trans*-1-Hexahydroindanone:** 5.09-mmol scale; 1:1 pentane/ether (R_f 0.8); 625 mg (89%); bp 80 °C (10 Torr) (lit.[86] bp *cis*- 81.5–86.5 °C (10 Torr)); ^1H NMR (CCl_4) δ 0.95–2.45 (m); ^{13}C NMR ($DCCl_3$) δ 22.55 (*cis*-), 22.87 (*cis*-), 24.01 (*cis*-), 25.04, 25.63 (*cis*-, *trans*-) 25.91, 27.64, 28.18 (*cis*-), 32.68, 34.79 (*cis*-), 36.15 (*cis*-), 36.96, 43.55, 49.53 (*cis*-), 55.59, 217.95 (the cis carbonyl carbon at 219.63 was not observed owing to its low intensity); IR (max) (CCl_4) 2940, 2870, 1750, 1450, 1410, 1355, 1290, 1185, 1155, 1085, 1025, 955, 940, 925 cm^{-1}; MS m/e 138.104 47 ± 0.01 ppm (calcd for $C_9H_{14}O$, 138.104 47). The product was determined to be approximately a 27:73 cis/trans mixture by GLC analysis (OV-101, 30-m capillary column). The cis isomer was identified by comparison of an authentic sample prepared according to literature procedures.[84-86] An ethyl ketone corresponding to the starting material has also been isolated in low yield. Gas chromatography–mass spectrometry indicates approximately a 15:85 mixture here also.

1-Allylcyclohexyl Ethyl Ketone: 3.6-mmol scale, isolated by preparative GLC (10-ft 10% Carbowax 20M); ^1H NMR ($DCCl_3$) δ 1.10 (3 H, t, J = 7 Hz, $-CH_3$), 1.44 (10 H, m, CH_2's), 2.30 (2 H, d, J = 7 Hz, $CH_2CH{=}CH_2$), 2.52 (2 H, q, J = 7 Hz, $COCH_2$), and 5.04, 5.64 (3 H, m, $CH{=}CH_2$); IR (max) (neat) 3080, 2980, 2935, 2860, 1705, 1640, 1455, 1415, 1375, 1365, 1340, 1105, 990, and 915 cm^{-1}; MS m/e 180.150 34 ± 6 ppm (calcd for $C_{12}H_{20}O$, 180.151 24).

Effect of Functional Groups on the Cyclization of 4-Pentenal. The effect of various functional groups on the cyclization of 4-pentenal was determined using the procedure described earlier for examining the effect of various ligands. Tris(*p*-dimethylaminophenyl)phosphine (10%) was employed in all reactions. One equivalent of each functionally substituted compound was added to the flask immediately after addition of the 4-pentenal. All cyclopentanone yields were determined by GLC analysis as described earlier.

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