The Palladium(II) Catalyzed Olefin Carbonylation Reaction. Mechanisms and Synthetic Utility[1]

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Received July 7, 1975

Abstract: The reaction of carbon monoxide with a variety of cyclic and acyclic olefins at 2-3 atm in methanol in the presence of palladium(II) chloride and copper(II) chloride as reoxidant was investigated. Linear α-olefins afforded predominantly β-methoxy esters under neutral conditions and diesters in the presence of base. Nearly quantitative yields (based on olefin) of these products were realized when greater than stoichiometric amounts of copper(II) were added. Carbonylation of cyclic olefins, either with or without added base, afforded predominantly diester products. The exception was cyclohexene which gave a low yield of the *trans*-β-methoxy ester in the absence of base. In each case, the 1,2- and 1,3-cycloalkanedicarboxylic esters obtained were the cis isomers. Product distributions and relative rates of reaction were consistent with cis carbomethoxypalladation, where the rate of the reaction was determined by the magnitude of the internal strain of the olefin. Carbonylation of selected methyl-substituted α-olefins in the presence of base yielded rearranged products. The relative rates of the competing hydride abstraction rearrangement process and the carbonylation reaction were dependent upon the nature of the alkyl substitution at or adjacent to the palladium-carbon σ-bond.

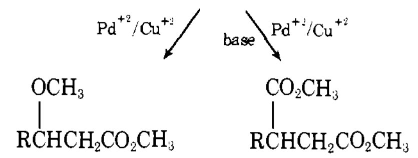
In general, the reaction of an olefin and carbon monoxide in a nucleophilic solvent catalyzed by a transition metal salt can take place to afford solvometalation derivatives and/or derivatives of α,β-unsaturated acids and diacids. The synthesis of succinic esters, β-alkoxy esters, and α,β-unsaturated esters from olefins by palladium-catalyzed carbonylation reactions have been reported.[3-6] These reactions are generally characterized by low yields and require high temperatures and pressures. Similar products have been obtained from the carbonylation of olefins in alcohol employing a stoichiometric quantity of palladium(II) in the presence of a mercury(II) salt.[7]

We have reported[8] that carbonylation of *cis*- and *trans*-2-butene in methanol, in the presence of catalytic amounts of palladium(II) chloride and stoichiometric amounts of copper(II) chloride, proceeds at low pressure (3 atm) and room temperature to afford predominantly the β-methoxy ester products, *threo*- and *erythro*-methyl 3-methoxy-2-methyl-butanoate, respectively. Under the same reaction conditions, except with the addition of sodium acetate, β-methoxy ester is not obtained, but a single diester is the only product. A reaction which produces β-alkoxy esters or diesters from olefins, carbon monoxide, and alcohol under mild reaction conditions therefore offers considerable synthetic potential. In order to explore the scope and utility of this reaction and to provide a study of the mechanism of the reaction, representative cyclic and acyclic olefins were allowed to react with carbon monoxide in methanol using a variety of conditions and reagents. In this paper, we report the results of the palladium(II)-catalyzed carbonylation of terminal and branched α-olefins and cycloolefins.

Results and Discussion

Linear α-Olefins. Carbonylation of linear α-olefins under standard reaction conditions (Table I) afforded β-methoxy esters and succinic esters as the major products (Scheme I).

Scheme I



$$R{-}CH{=}CH_2 + CO + CH_3OH \xrightarrow{Pd^{+2}/Cu^{+2}} RCH(OCH_3)CH_2CO_2CH_3$$

$$R{-}CH{=}CH_2 + CO + CH_3OH \xrightarrow[\text{base}]{Pd^{+2}/Cu^{+2}} RCH(CO_2CH_3)CH_2CO_2CH_3$$

The methoxypalladation reaction of 1-pentene gave a good yield (55%) of methyl 3-methoxyhexanoate and a small amount of the succinic ester (2%) via competitive carbomethyoxypalladation. Addition of an equimolar quantity of sodium acetate to the reaction resulted in the exclusive formation of dimethyl propylsuccinate in 53% yield. Similar products and yields were obtained from the carbonylation of 1-hexene and 1-decene. In the case of 1-decene, unreacted olefin was isolated and unisomerized from the reaction mixture.

Carbonylation of styrene in the presence of base similarly afforded dimethyl phenylsuccinate (51%). These yields represented a catalytic turnover of palladium(II) of approximately 10 times. In all reactions studied, the catalyst was precipitated as palladium(0) upon completion of the reaction.

Attack by uncoordinated nucleophile at the most substituted carbon atom of the double bond (Markownikoff addition) is the exclusive reaction path observed for the olefins studied and is consistent with the trans methoxypalladation mechanism proposed for the 2-butenes. As expected from steric requirements and initial π-complex stabilities, the α-olefins are more reactive than the internal olefins, *cis*- and *trans*-2-butene. The comparable reactivities of the α-olefins demonstrate, however, that the chain length of the olefin employed is sterically unimportant.

Deviation from standard reaction conditions has an important influence on the yields of β-methoxy ester as demonstrated for 1-pentene (Table II). Using a twofold excess of copper(II) chloride, the yield of β-methoxy ester based on olefin increased from 53 to 83%. This result and the fact that unreacted olefin was recovered unchanged after palladium(0) has precipitated from the reaction mixture suggested that other species successfully compete with the olefin for reaction with palladium(II).

One possible competitive reaction is the oxidation of carbon monoxide to carbon dioxide in the presence of water and palladium(II) chloride.[9,10]

$$CO + H_2O + PdCl_2 \rightarrow CO_2 + Pd^0 + 2HCl$$

$$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

The palladium(II) is reduced to palladium(0) during the course of the reaction, necessitating reoxidation by copper(II) and effectively decreasing the catalytic efficiency of the redox system with respect to olefin. Eliminating water from the reaction mixture by the use of pure, anhydrous copper-

Table I. Catalytic Carbonylation of Linear α-Olefins[a]

Olefin	NaOAc, mmol	Product(s)	% yield[b]
1-Pentene		Methyl 3-methoxyhexanoate	55
		Dimethyl propylsuccinate	2
1-Pentene	100	Dimethyl propylsuccinate	53
1-Hexene		Methyl 3-methoxyheptanoate	53
		Dimethyl butylsuccinate	2
1-Hexene	100	Dimethyl butylsuccinate	51
1-Decene		Methyl 3-methoxyundecanoate	52
		Dimethyl octylsuccinate	2
1-Decene	100	Dimethyl octylsuccinate	50
Styrene	100	Dimethyl phenylsuccinate	51

[a] Reaction conditions: 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, 3 atm of carbon monoxide, and 25 °C. [b] Yield ±0.5%, determined by VPC and based on olefin.

Table II. Carbonylation of 1-Pentene to Methyl 3-Methoxyhexanoate[a]

Olefin, mmol	Cu, mmol	$HC(OCH_3)_3$, ml	% yield[b]
25	50		55
25	100		83
25	50[c]		68
25	50[c]	3	74
25	100[c]	3	93

[a] Constant reaction conditions: 2.8 mmol of $PdCl_2$, 75 ml of anhydrous methanol, and 3 atm of carbon monoxide at room temperature. [b] Yield ±0.5%, determined by VPC and based on olefin. [c] Copper(II) chloride treated with dry hydrogen chloride gas at 150° (ref 11).

(II) chloride which had been treated with hydrogen chloride gas at 150° and trimethyl orthoformate as a water scavenger increased the yield of methoxy ester based on olefin (Table II). In this manner, a yield of β-methoxy ester of greater than 90% was realized by employing a twofold excess of copper(II).

The rate of carbon monoxide oxidation in the presence of water is much faster than the rate of the olefin carbonylation reaction. The competitive reaction of 50 mmol of water and 50 mmol of olefin (1-hexene) with a stoichiometric quantity (100 mmol) of copper (II) chloride afforded only a 2% yield of β-methoxy ester, and a near maximum concentration of carbon dioxide (74%) above the reaction mixture was established in only an hour (Table III). The catalytic reaction was complete and palladium(0) precipitated from the reaction in less than 24 h. By contrast, carbonylation of 50 mmol of olefin under anhydrous conditions in the presence of 100 mmol of copper(II) afforded a 70% yield of β-methoxy ester and required 48 h before loss of catalyst from the solution occurred. Slow oxidation of carbon monoxide was observed under the anhydrous conditions as well; a concentration of carbon dioxide (29%), nearly the maximum concentration, was obtained after approximately 36 h.

A second possible competing reaction is the oxidation of methanol by palladium(II) to methyl formate.[12,13]

$$2CH_3OH + PdCl_2 \rightarrow HCO_2CH_3 + Pd^0 + 3H^+ + 2Cl^-$$

Careful fractional distillation of the reaction mixture from the carbonylation of 1-decene indicated a minimum yield of 14% of methyl formate based on copper(II). The yield of β-methoxy ester from this reaction was 60% based on copper(II). The remaining copper(II) was probably consumed in the redox system (13 equiv) by oxidation of carbon monoxide.

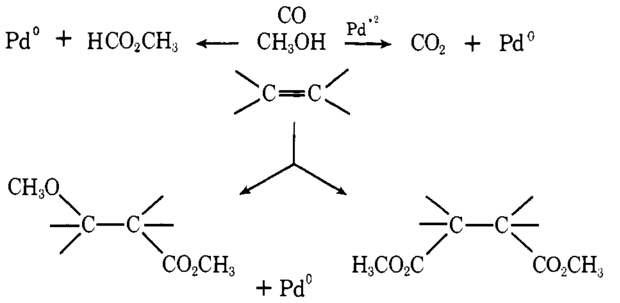
In all cases, therefore, at least two other molecular species are competing with the olefin for coordination and subsequent conversion to products by the catalytic species. The amount of palladium catalyst available for reaction, however, is strictly dependent upon the amount of copper(II) initially introduced into the system because all competing reactions result in reduction of palladium(II) to palladium(0) and deactivation of the catalyst. These observations suggest that the overall yield of products from reaction of the alkene will reflect the ability of the olefinic species to compete with methanol and carbon monoxide for the active metal catalyst, and that the overall yield of methoxy ester or diester will be determined by the ease of olefin to metal π-complexation and the rate of the ensuing metalation step (Scheme II).

Table III. Oxidation of Carbon Monoxide in the Carbonylation of 1-Hexene[a]

Time, h	% CO/% CO_2[b]	% CO/% CO_2[c]
0	100/0	100/0
1	26/74	99/1
2	24/76	99/1
4	23/77	97/3
10	23/77	94/6
24	23/77	86/14
36		73/27
48		71/29

[a] % composition of the atmosphere above the reaction mixture as determined by VPC analysis, ±0.5%. [b] Reaction conditions: 50 mmol of hexene, 50 mmol of water, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, and 3 atm of CO at 28 °C. [c] Reaction conditions: 50 mmol of hexene, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, 3 ml of trimethyl orthoformate, and 3 atm of CO at 28 °C.

Scheme II



In order to determine the influence of base on the course of the reaction, 1-hexene was allowed to react in the palladium(II)/copper(II) catalyst system in the presence of a variety of bases (Table IV). As demonstrated for the reaction under neutral conditions, increasing the mole ratio of copper(II) to olefin increased the product yield relative to olefin. Reaction in the presence of the sodium salts of various carboxylic acids resulted in significant increases in the yield in the homologous series, going from sodium formate to sodium butyrate. Carbonylation of 1-hexene in the presence of a twofold excess of copper(II) and sodium butyrate afforded greater than a 90% yield of diester. Only a 32% yield was obtained in the presence of sodium formate; sodium propionate gave an 80% yield of diester.

Reaction in the presence of the nitrogen bases, triethylamine and 2,6-lutidine, produced low yields of diester. By contrast to the carboxylic acid salts, however, in which β-methoxy ester product was completely eliminated, reaction with these bases afforded a small amount of the methoxy ester. Sodium carbonate was the least effective base, giving only a 6% yield of diester based on olefin.

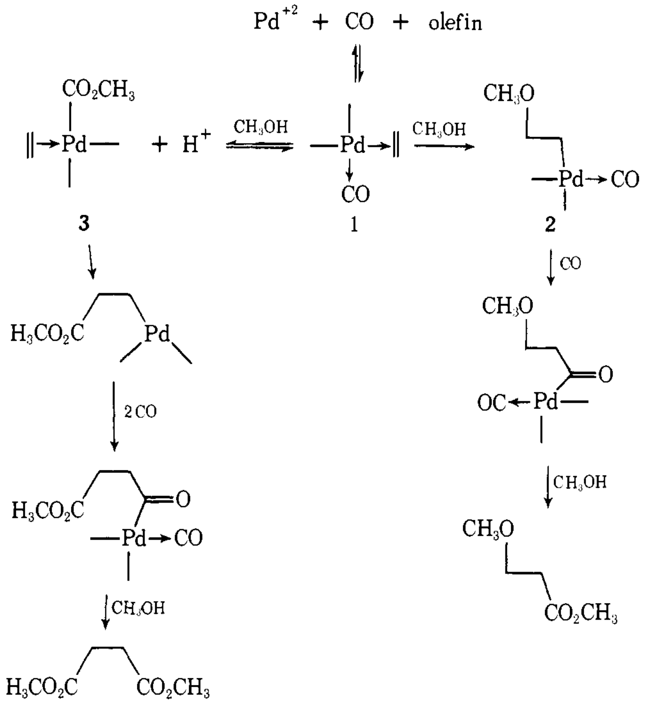
These results suggest that the effect of base is to catalyze the reaction which produces the carbomethoxypalladium adduct necessary for dicarbonylation (Scheme III). A common catalytic species in the system may be assumed to be a

Table IV. Carbonylation of 1-Hexene.[a] Effect of Base

Cu(II), mmol	Base, mmol	pK_a (H_2O)[b]	β-Methoxy ester, %[c]	Diester[c]
50	Sodium acetate (50)		0	50
100	Sodium formate (100)	3.75	0	32
100	Sodium acetate (100)	4.75	0	64
100	Sodium propionate (100)	4.87	0	80
100	Sodium butyrate (100)	4.82	0	94
100	Triethylamine (100)		3	22
100	2,6-Lutidine (100)		4	34
100	Sodium carbonate (100)		0	6

[a] Reaction conditions: 25 mmol of 1-hexene, 75 ml of methanol, and 3 atm of CO at 25 °C. [b] "Handbook of Chemistry and Physics", Vol. 51, R. C. Weast, Ed., Chemical Rubber Co., Cleveland, Ohio, 1970–1971, p D120. [c] Yield ±0.5%, based on olefin and determined by VPC.

Scheme III

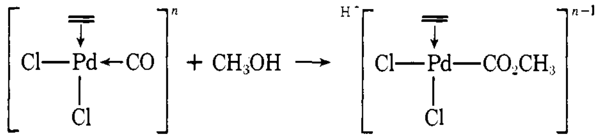


palladium(II) complex (**1**), containing coordinated olefin and carbon monoxide. Attack by methanol can then occur either at the olefin or at the carbonyl. Under neutral conditions, for α-olefins, reaction with the olefinic ligand is preferred, forming the σ-bonded β-methoxy alkyl complex **2**. Carbonyl insertion followed by methanolysis affords methoxy ester.

The reaction of methanol with the carbonyl to generate the carbomethoxypalladium complex **3** is base catalyzed;[14-17] the reaction does occur in neutral media as well, however, and forms a reactive intermediate. The influence of base on the carbonylation reaction of monoolefins therefore is to increase the concentration of the carbomethoxyl complex **3** to the extent that it is the predominant catalytic species (Scheme I). The effective base in the reaction may be a copper(II) methoxide species, as evidenced from the bright green precipitate formed upon addition of the carboxylate base to the copper(II) chloride–methanol solution. This is characteristic of the reaction which forms the copper(II) salt, $Cu(OCH_3)Cl$, from copper(II) chloride, methanol, and base ($LiOCH_3$).[18]

Rapid evolution of carbon dioxide upon addition of sodium carbonate to the copper(II)–methanol solution is consistent with the formation of $Cu(OCH_3)Cl$. The low yield of diesters in the presence of amine bases may be related in part to the ability of the nitrogen to coordinate to copper,[19] effectively eliminating the metal and/or the base from the catalytic cycle. Copper(II) also is known to undergo a facile reduction to copper(I) in the presence of trialkylamines,[20] which may also decrease the catalytic activity of the system.

The observation that β-methoxy ester production is eliminated in the presence of the carboxylate bases suggests that **3** cannot be further attacked by methanol at the olefinic ligand to form **2**, possibly as a result of a larger effective nuclear charge on the carbomethoxypalladium complex. Elimination of the amine base from the catalytic system by coordination may account for the production of the small amount of methoxy ester.



$$\left[\mathrm{Cl{-}Pd{\leftarrow}CO}\right]^{n} + CH_3OH \longrightarrow H^{+}\left[\mathrm{Cl{-}Pd{-}CO_2CH_3}\right]^{n-1}$$

Cyclic Olefins. Carbonylation of cyclic olefins under standard reaction conditions (in the absence of base) surprisingly afforded predominantly diester products (Table V). The exception was cyclohexene which gave a low yield (16%) of the *trans*-β-methoxy ester in the absence of base. A small amount of diester product, a mixture of the *cis*-1,2- and *cis*-1,3-diesters of cyclohexane in a ratio of 87 to 13, respectively, was formed coincidentally.

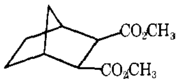
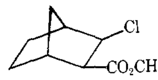
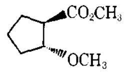
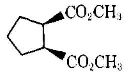
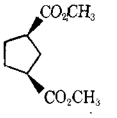
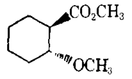
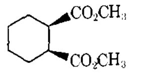
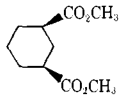
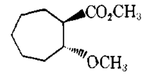
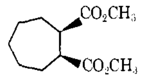
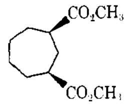
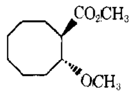
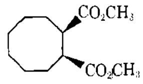
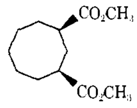
Norbornene underwent the carbonylation reaction quite rapidly to afford predominantly (80% yield) the *cis-exo*-diester. Also isolated from the reaction was a small quantity of the *cis-exo*-β-chloro ester. The stereochemical assignment of this compound was based on NMR coupling constants obtained from double irradiation techniques.

Cyclopentene, cycloheptene, and cyclooctene yielded a mixture of *cis*-1,2- and *cis*-1,3-diesters as the predominant products. The C_5 and C_7 cyclic olefins were considerably more reactive, however, and good conversions of cycloalkenes to products were realized. The conversion of cyclooctene was only 10%. The 1,2- to 1,3-diester distribution followed a similar trend. While the cis 1,3-isomer was the major product from carbonylation of cyclopentene and cycloheptene, cyclooctene gave predominantly the *cis*-1,2-diester. A small quantity of *trans*-β-methoxy ester was also obtained from each olefin.

The addition of equimolar quantities of sodium acetate had the predicted effect of eliminating methoxy ester production (Table VI). Increasing the basic strength of the reaction medium and utilizing greater than stoichiometric quantities of copper(II) chloride similarly enhanced the diester yields based on olefin. Carbonylation of cyclopentene, for example, in the presence of a twofold excess of copper(II) chloride and sodium butyrate produced the *cis*-1,2- and 1,3-diesters in greater than 90% yield based on olefin.

The ratio of 1,2- to 1,3-*cis*-diester was quite sensitive to reaction conditions. Stronger bases decreased the ratio of 1,2- to 1,3-diester. Increasing the carbon monoxide pressure fivefold effectively increased the amount of 1,2-diester at the expense of the 1,3-isomer (Table VII); however, the

Table V. Carbonylation of Cyclic Olefins[a]

Olefin	Products	Rel[b] amounts, %	% conversion[c]
Norbornene		98	82
		22	
Cyclopentene		4	60
		68	
		27	
Cyclohexene		95	17
		3.5	
		0.5	
Cycloheptene		2	58
		34	
		63	
Cyclooctene		4	10
		10	
		85	

[a] Reaction conditions: 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, and 3 atm of CO at 28°C. [b] Isomer ratios ±0.5%, determined by VPC. [c] % yield ±0.5%, determined by VPC and based on olefin.

Table VI. Carbonylation of Cyclic Olefins[a]

Olefin	Base	% yield[b]	Ratio[c] 1,3-:1,2-diester
Cyclopentene		57	71:29
	NaOAc	60	78:22
	NaOPr	75[d]	86:14
	NaOBu	95[d]	86:14
Cyclohexene		<1	13:87
	NaOAc	5	20:80
	NaOPr	5	20:80
Cycloheptene		55	65:35
	NaOAc	58	75:25
	NaOAc	73[d]	75:25
Cyclooctene		10	10:90
	NaOAc	30[d]	20:80
	NaOPr	40[d]	20:80

[a] Reaction conditions: 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 100 mmol of base, 75 ml of methanol, and 3 atm of CO at 28 °C. [b] Yield ±0.5%, determined by VPC and based on olefin. [c] Isomer distribution ±0.5%, determined by VPC. [d] Reaction conditions: 25 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 100 mmol of base, 75 ml of methanol, and 3 atm of CO at 28 °C.

Table VII. Carbonylation of Cyclic Olefins.[a] Effect of Pressure

Olefin	CO pressure, atm	Ratio[b] 1,3-:1,2-diester	% yield[c]
Cyclopentene	3	71:29	57
	15	28:72	32
Cycloheptene	3	65:35	55
	15	33:67	30

[a] Reaction conditions: 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, and 75 ml of methanol at 28 °C. [b] Isomer ratio ±0.5%, determined by VPC. [c] Yield ±0.5%, determined by VPC and based on olefin.

overall yield of diester products at 15 atm of carbon monoxide was reduced.

The product stereochemistry and isomer distributions are consistent with a mechanism which requires initial π-complexation of the olefin followed by a cis addition of a carbomethoxypalladium species (Scheme IV as shown for cyclopentene) to form the σ-bonded complex **4**. For the monocyclic olefins, two reaction pathways are available to complex **4**. Reaction with carbon monoxide (carbonyl insertion) and methanol will afford the 1,2-diester. However, because of a probable vacant coordination site available on the metal after the $Pd-CO_2CH_3$ addition, rearrangement may occur via a cis palladium hydride elimination mechanism to form the intermediate π-complex **5**. Olefin rotation followed by readdition of palladium hydride yields alkyl complex **6**. Carbonylation of **6** gives the 1,3-diester.

It is noteworthy that the cyclic olefins are structurally similar to *cis*-2-butene,[8] yet only cyclohexene mimics the reactions of this internal olefin, i.e., a poor yield of β-methoxy ester under neutral conditions and very low reactivity for the dicarbonylation reaction in the presence of base. Although the above mechanism adequately demonstrates the formation and stereochemistry of the observed products, it does not account for the predominant type of product, β-methoxy ester vs. diester, formed under neutral conditions, and the dissimilarities in the overall rates of conversion of olefin to product. The most appealing explanation consistent with the data is delicate balance between the ease of π-complex formation and the subsequent metalation step.

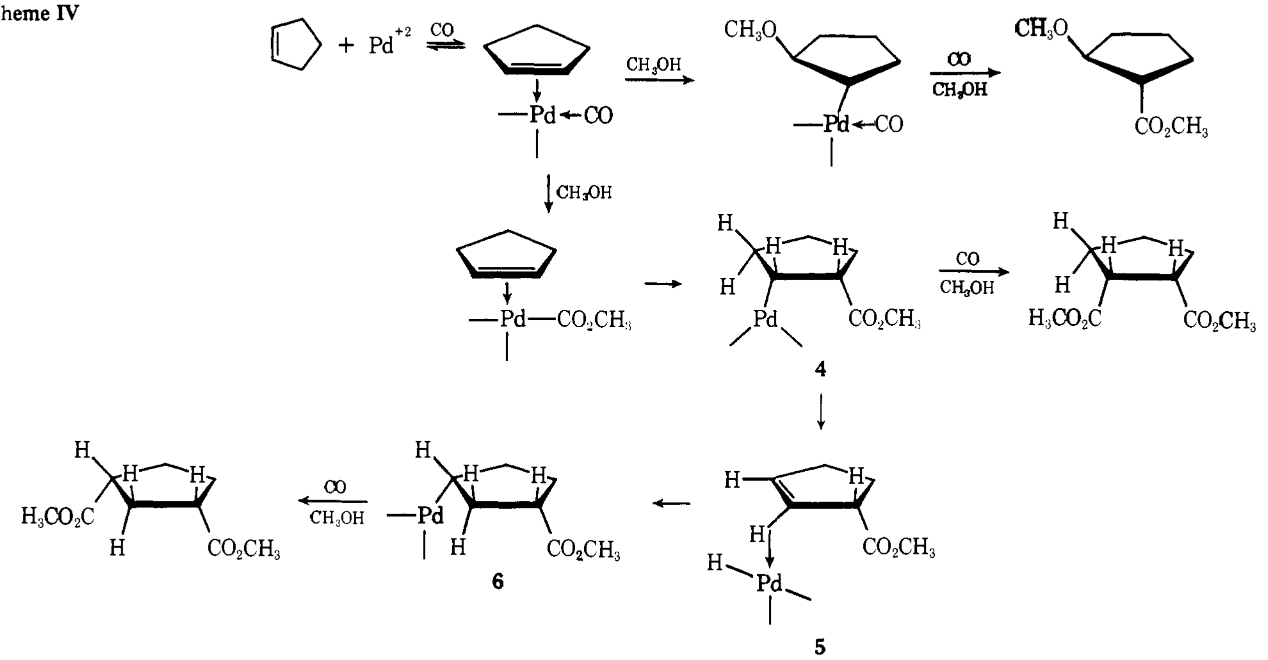
The predominant type of compound obtained from the catalytic carbonylation of cyclic olefins in neutral media may be considered a consequence of the ease of carbomethoxypalladation, which is reflected in the internal strain of the double bond. The fact that norbornene and the C_5, C_7, and C_8 cycloolefins react preferentially via the cis carbomethoxypalladium addition mechanism under neutral conditions is in contrast to cyclohexene and the linear acyclic olefins which favor the trans methoxypalladation pathway. This must be a consequence of the greater strain to which the double bond is subjected in these molecules (Table VIII) and indicates that relief of strain in proceeding from the π-complex to the transition state leading to the initial alkyl complex **4** is of considerable importance. For this interpretation to be acceptable, the transition state must be closely related to the olefin-carbomethoxypalladium structure. The slight weakening and lengthening of the

Table VIII. Comparison of Strain Energy (SE)[a] and the Carbonylation of Cyclic Olefins

Olefin	Predominant product type (%)[b]	% conversion to diester[c]	SE of cycloolefin[d]	SE of cycloalkane[d]
Norbornene	Diester (80)	82	27.2	17.55
Cyclopentene	Diester (57)	60	6.8	7.19
Cycloheptene	Diester (55)	58	6.7	7.57
Cyclooctene	Diester (10)	19	7.4	11.7, 9.98
Cyclohexene	Methoxy ester (16)	5	2.5	1.35

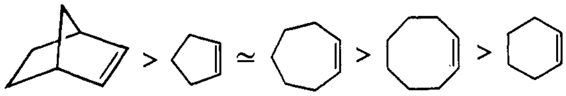
[a] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970). [b] Reaction conditions: 50 mmol of olefin, 2.8 mmol of $PdCl_2$ in 75 ml of methanol at 25 °C and 3 atm of carbon monoxide, yield based on olefin. [c] Reaction conditions: as for footnote *b* with the addition of 100 mmol of NaOAc; yield based on olefin. [d] In kcal/mol.

Scheme IV



multiple bond in proceeding to the activated complex relieves some of the strain present in the free olefin while the relatively longer bond lengths of the early transition state are favored on steric grounds.

The relative reactivity of the cyclic olefins with respect to diester formation shows the same order as that established for hydroformylation[21] and is similar to hydroboration with



disiamylborane[22] and the platinum(II)-catalyzed heterogeneous hydrogenation reaction.[23] Reaction of the C_5 to C_8 cycloalkenes with $XPdCO_2CH_3$ to yield unsaturated esters also gave a comparable order of reactivity.[24]

Because the olefin must compete with carbon monoxide and methanol for the palladium catalyst, the formation of the π-complex will be important in determining the overall yield of product in the carbonylation reactions. The reactivity of the cyclic olefins via the carbomethoxypalladation mechanism to form diesters is directly related to the π-complexation. On the basis of ring strain (Table VIII), the C_5, C_7, and C_8 cyclic olefins might be expected to be of nearly equal reactivity. However, cyclooctene gives a significantly lower yield of diesters than cyclopentene and cycloheptene, suggesting that cyclooctene does not form the π-complex as readily.

In order to test this, a competitive carbonylation was carried out using cyclopentene and cyclooctene. Equimolar quantities of the two olefins were allowed to react in the same reaction vessel with a catalytic amount of palladium(II) chloride and 3 atm of carbon monoxide in the presence of copper(II) chloride and sodium propionate (Table IX). The yield of cyclopentane diesters was relatively unchanged from the single olefin to the two olefin system, while the yield of cyclooctane diesters was substantially lower.

In this system there is effectively 50 mmol of palladium(II) catalyst available for reaction. The results of this reaction and the previous data indicate that 22 mmol of catalyst is consumed in the olefin carbonylation reaction and 28 mmol of catalyst is expended via the oxidation pathways (Table IX). In this reaction, however, the cyclic olefins must compete with one another as well as with carbon monoxide and methanol for catalyst. Although cyclooctene reacts with 20% of the theoretically available catalyst under standard conditions (Table IX), in competition with the more easily complexed olefin, cyclopentene, the amount of palladium(II) expended via cyclooctene carbonylation decreases to approximately 3%. Formation of a cyclooctene–palladium π-complex may be unfavorable because of steric considerations.[25]

The decreased reactivity of cyclooctene does not influence the favored reaction path of this strained cyclic olefin under neutral conditions, i.e., diester formation. The low reactivity of cyclohexene under basic conditions is therefore seen as a consequence of both low internal strain and decreased tendency for π-complex formation.

The ease of formation of the π-complex also can be related to the 1,2- to 1,3-diester ratios. The rearrangement is favored for the monoolefins which coordinate readily; cyclopentene and cycloheptene afford predominantly 1,3-diest-

Table IX. Competitive Carbonylation of Cycloolefins

Reactant	Pd(II) available, mmol	Oxidation	Catalyst (mmol) expended via carbonylation	
Cyclopentene[a]	50	31	19	
Cyclooctene[b]	50	40		10
Cyclopentene and cyclooctene[b]	50	28	19	3

[a] Reaction conditions: 25 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 100 mmol of sodium propionate, 75 ml of methanol, and 3 atm of CO at 28 °C (see Table VI). [b] Reaction conditions: 25 mmol of cyclopentene, 25 mmol of cyclooctene, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 100 mmol of sodium propionate, 75 ml of methanol, and 3 atm of CO at 28 °C.

Table X. Carbonylation of Isomeric 1-Olefins[a]

Olefin	% yield[b]	Products (ratio)
2-Methyl-1-pentene	4.5	One β-methoxy ester[c] (1) Four diesters[d] (1)
3-Methyl-1-pentene	50	Methyl 3-methoxy-4-methylhexanoate (98) Four diesters[d] (2)
4-Methyl-1-pentene	57	Methyl 3-methoxy-5-methylhexanoate (98) Dimethyl (2-methylpropyl)-succinate (2)

[a] Reaction conditions: 25 mmol of olefin, 1.4 mmol of $PdCl_2$, 50 mmol of $CuCl_2$, and 37.5 ml of methanol at 3 atm of CO pressure and room temperature. [b] Yield ±0.5%, determined by VPC and based on olefin. [c] Unidentified but probably methyl 3-methoxy-3-methylhexanoate. [d] Identified on Table XI.

ers. The rearrangement reaction is enhanced by the presence of base and is in agreement with the results obtained from the palladium-catalyzed isomerization of straight-chain olefins which proceeds via hydride abstraction and readdition.[26] The rearrangement process also is facilitated by the increased stability of the 1,3-disubstituted complex **6** compared to the 1,2-isomer **4** (Table VIII). Increased steric hindrance for carbon monoxide insertion into a palladium–carbon σ bond which is α to a tertiary carbon also promotes rearrangement (vide infra).

Increasing the carbon monoxide pressure increases the rate at which the 1,2-addition intermediate **4** is trapped, reducing the amount of rearranged (1,3) product. At higher pressures, carbon monoxide may coordinate more efficiently to the vacant ligand site on palladium, therefore eliminating the rearrangement pathway. The observed effect is an increase in the rate of carbonylation of **4** while decreasing the rate of palladium hydride elimination. Saturation of the active palladium(II) species with carbon monoxide at high pressures can retard olefin coordination and accounts for lower product yields.

Methyl-Substituted Olefins. The isomeric, methyl-substituted α-olefins, 2-methyl-1-pentene, 3-methyl-1-pentene, and 4-methyl-1-pentene, and the dimethyl-substituted α-olefin, 3,3-dimethyl-1-butene, were carbonylated in methanol using the palladium(II) chloride–copper(II) chloride catalyst system. The 3-methyl and 4-methyl isomers gave a good yield of the 3-methoxyhexanoates with trace amounts (1–2%) of diester products under neutral conditions (Table X). The 2-methyl isomer, on the other hand, was quite unreactive and only a small amount of β-methoxy ester was obtained.

The predominant products in the palladium(II) catalyzed carbonylation of the methyl-substituted olefinic series in the presence of base (sodium acetate) were diesters. However, in these acyclic compounds, rearrangement takes place (Table XI). The carbonylation of 2-methyl-1-pentene afforded four diester products in a 37% yield based on olefin. The diesters were identified as two glutaric esters, an adipic ester, and a malonic ester. The major product (45% of the total) was dimethyl 2-ethyl-3-methylglutarate. Carbonylation of 3-methyl-1-pentene similarly yielded rearranged products, the major portion of which (50%) was dimethyl (1-methylpropyl)succinate. In addition, two adipic esters and a malonic ester were identified as products. No rearrangement occurred, however, in the reaction of 4-methyl-1-pentene. A single diester product, dimethyl (2-methylpropyl)succinate, was obtained in a 69% yield.

Rearrangement also occurred in the reaction of 3,3-dimethyl-1-butene (Table XII). However, in contrast to the other acyclic olefins studied, carbonylation under neutral conditions gave predominantly diester products: 29% β-methoxy ester, 46% malonic ester, 25% succinic ester. The reaction in basic media afforded only the two diesters in a 48% yield.

The products and yields of the carbonylation reaction of the three isomeric methyl-substituted olefins in neutral solution are consistent with the Markownikoff methoxypalladation mechanism proposed for the analogous reaction of straight-chain olefins. The yields, which approximate relative reactivities of the olefins, increase in the order: 2-methyl-1-pentene ≪ 3-methyl-1-pentene < 4-methyl-1-pentene, reflecting the decreasing steric demands for nucleophilic attack by methanol at the most substituted carbon of the double bond and the enhanced rate of formation of the π-complex.

The results obtained from carbonylation of the methyl-substituted α-olefins under basic conditions are best explained, as for the rearrangement observed with cyclic olefins, by a palladium hydride abstraction-readdition mechanism. While the propensity for rearrangement in cyclic olefins is facilitated by the proximity of cis hydrogens[24] in a conformationally restricted ring system, this argument is not necessarily valid for acyclic olefins, as rearrangement in unbranched, linear olefins is not important (vide supra).

The driving force for rearrangement in branched-chain olefins, however, is inferred from the products and product ratios. For the reaction of 2-methyl-1-pentene, quite significantly, no succinic ester was formed and nearly three-fourths of the products were derived from an initial hydrogen abstraction from C-4 of the initial σ complex **7** (Scheme V). Only 25% of the products involve palladium hydride abstraction from C-2 or the C-3 methyl group.

The major product obtained from the carbonylation of 3-methyl-1-pentene is the succinic ester **10** (Scheme VI). Rearrangement of the initial palladium–carbon σ-bonded complex **9** occurs however, to give complex **11** which further rearranges to yield, upon carbonylation, the adipic ester products. The major adipic ester (>75% of the total), dimethyl 2,3-dimethyladipate (**12**), is derived from hydrogen abstraction from the C-5 methylene rather than from the methyl group bonded to C-4 (the source of adipic ester **13**). Significantly, complex **11** is not carbonylated and no glutaric ester is obtained.

Two factors, therefore, are concluded to be important in the carbonylation reaction of the methyl-substituted α-olefins and are compatible with the anti-Markownikoff carbomethoxypalladation mechanism: (i) The rates of the competitive hydride abstraction rearrangement and carbonylation processes are dependent upon the nature of the alkyl substitution at the carbon σ-bonded to palladium, and (ii) hydride abstraction from the most highly substituted carbon atom adjacent to a palladium carbon σ bond is favored and is in the order tertiary > secondary > primary.

Table XI. Carbonylation of Isomeric 1-Olefins in the Presence of Base[a]

Olefin	% yield[b]	Product (ratio)
$CH_3CH_2CH_2C(CH_3){=}CH_2$	37	$CH_3CH_2CH(CO_2CH_3)CH(CH_3)CH_2CO_2CH_3{}^c$ (5)
		$CH_3CH(CO_2CH_3)CH_2CH(CH_3)CH_2CO_2CH_3{}^c$ (3)
		$CH_3CH_2CH_2CH(CH_2CO_2CH_3)CH_2CO_2CH_3$ (2)
		$CH_3CH_2CH_2CH(CH_3)CH(CO_2CH_3)_2$ (1)
		$CH_3CH_2CH{=}C(CH_3)CH_2CO_2CH_3$ (1)
$CH_3CH_2CH(CH_3)CH{=}CH_2$	39	$CH_3CH_2CH(CH_3)CH(CO_2CH_3)CH_2CO_2CH_3{}^c$ (14)
		$CH_3CH(CO_2CH_3)CH(CH_3)CH_2CH_2CO_2CH_3{}^c$ (10)
		$CH_3CH_2CH(CH_2CO_2CH_3)CH_2CH_2CO_2CH_3$ (3)
		$CH_3CH_2CH(CH_3)CH_2CH(CO_2CH_3)_2$ (1)
$CH_3CH(CH_3)CH_2CH{=}CH_2$	69	$CH_3CH(CH_3)CH_2CH(CO_2CH_3)CH_2CO_2CH_3$

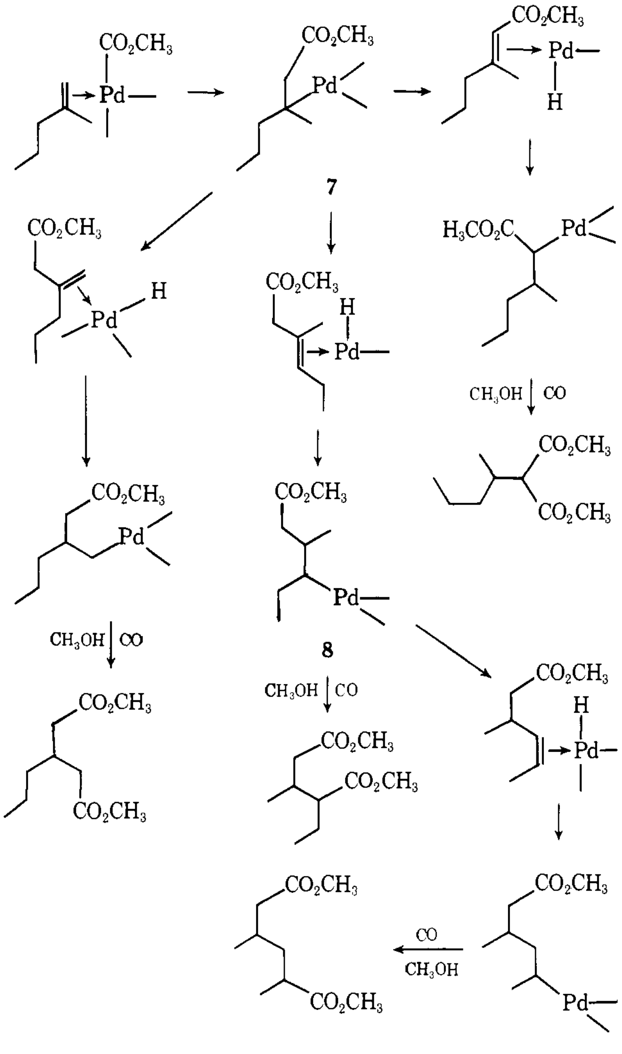
[a] Reaction conditions: 25 mmol of olefin, 1.4 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 100 mmol of NaOAc, and 75 ml of methanol at 3 atm of CO pressure and room temperature. [b] Yield ±0.5%, determined by VPC, and based on olefin. [c] Isomer ratio determined by VPC, ±0.5%.

Table XII. Carbonylation of 3,3-Dimethyl-1-butene

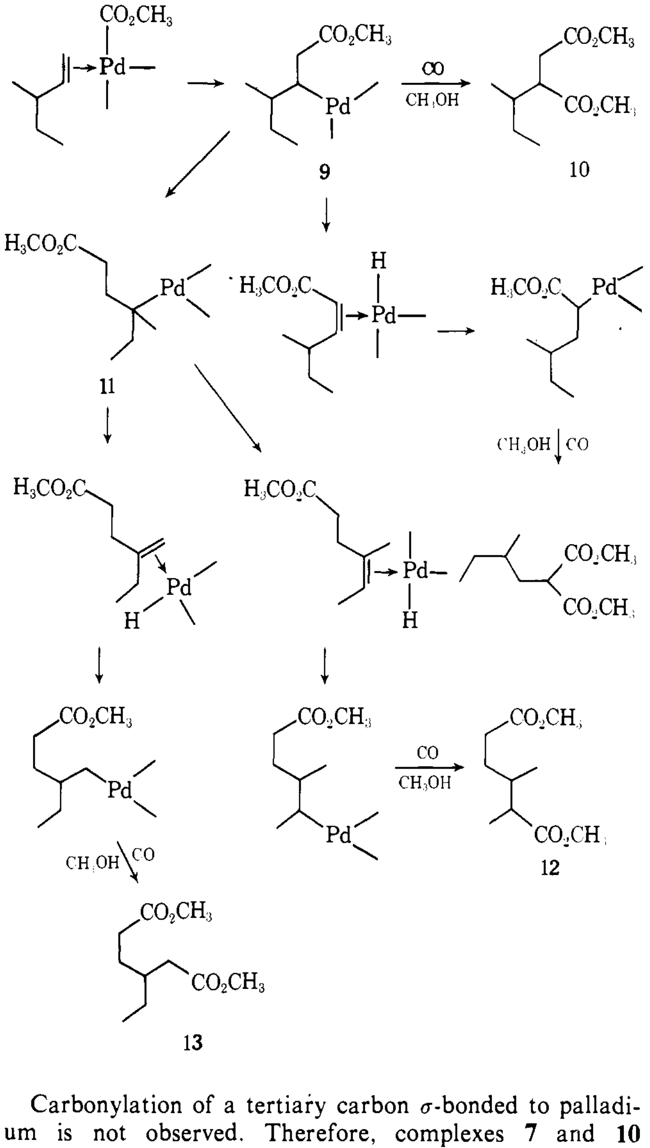
Reaction conditions	% yield	Products (ratio)[b]
Standard[a]	52	$(CH_3)_3CCH(OCH_3)CH_2CO_2CH_3$ (29)
		$(CH_3)_3CCH(CO_2CH_3)CH_2CO_2CH_3$ (25)
		$(CH_3)_3CCH_2CH(CO_2CH_3)_2$ (46)
NaOPr (100 mmol) added	50	$(CH_3)_3CCH(CO_2CH_3)CH_2CO_2CH_3$ (15)
		$(CH_3)_3CCH_2CH(CO_2CH_3)_2$ (85)

[a] Standard reaction conditions: 25 mmol of olefin, 2.8 mmol of $PdCl_2$, and 100 mmol of $CuCl_2$ in 75 ml of methanol at 3 atm of CO and room temperature. [b] Product ratio determined by VPC, ±0.5%.

Scheme V



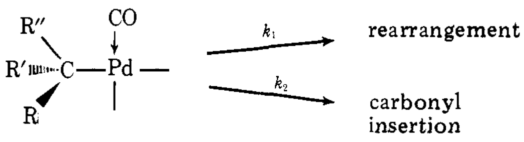
Scheme VI



Carbonylation of a tertiary carbon σ-bonded to palladium is not observed. Therefore, complexes **7** and **10** (Schemes V and VI) do not insert carbon monoxide before hydride abstraction occurs and no succinic ester is obtained from reaction of 2-methyl-1-pentene, while no glutaric ester is formed from carbonylation of 3-methyl-1-pentene. The lack of reactivity of the tertiary carbon-palladium σ bond toward carbonyl insertion is probably the result of steric factors which have been shown to be very important in the formation and reactions of palladium alkyl complexes;[24] analogous results have been obtained for the hydroformylation reaction.[27,28] The formation of the three-centered transition state necessary for the occurence of the ligand migration of the alkyl group from the metal to the carbonyl is effectively hindered by the three alkyl groups attached to the carbon bonded to the metal of the σ complex. The bulky tertiary alkyl may also restrict carbon monoxide coordination, a step necessary for carbonylation, and thus promote abstraction of hydride, a sterically less demanding function.

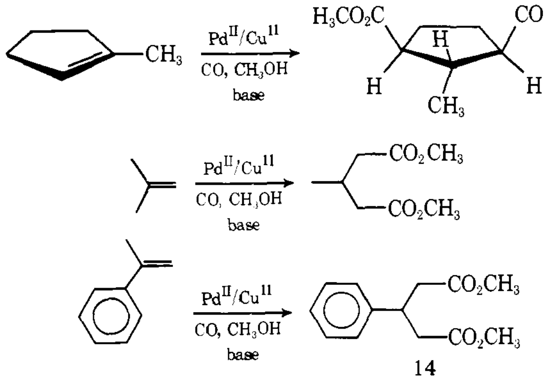
Similarly, the rate of hydride abstraction becomes competitive with carbonylation when a secondary carbon to palladium σ bond is α to a highly substituted alkyl group. For this reason, complex **9** (Scheme VI) rearranges to form malonic ester, a reaction not observed with straight-chain olefins. Likewise, further rearrangement of complex **8** to adipic ester is observed (Scheme V). These results are summarized in Scheme VII. Steric hindrance to π-complex formation and σ-bonded complex formation decrease the reactivity, giving lower yields of the 2-methyl and the 3-methyl isomers as compared with 4-methyl-1-pentene and the unbranched, linear α-olefins.

Scheme VII. Rate of Carbonyl Insertion vs. Rearrangement

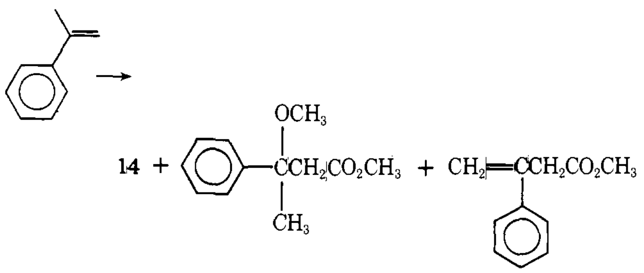


R = H; R′ = n-alkyl; R″ = H or n-alkyl $k_1 \ll k_2$
R = H; R′ = n-alkyl; R″ = secondary or $k_1 \sim k_2$
tertiary alkyl $k_1 \gg k_2$
R = R′ = R″ = alkyl

The stability of σ palladium tertiary carbon bonds to carbon monoxide insertion can be used to prepare symmetrical glutaric esters from disubstituted olefins.



Carbonylation of 1-methylcyclopentene in the presence of sodium propionate afforded dimethyl *trans*-2-methyl-*cis*-1,3-cyclopentanedicarboxylate. Reaction of isobutylene gave a 39% yield of two diesters, the glutaric ester (80% of the total) and a malonic ester (20%). The least reactive olefin via the decarbonylation mechanism was α-methylstyrene which produced the symmetrical glutaric ester, dimethyl 3-phenylglutarate (**14**, 12%). The reaction of this olefin under basic conditions was quite unusual in that the major product was the β-methoxy ester (27%), and methyl 3-phenyl-3-butenoate was also obtained.



The carbonylation reaction of 3,3-dimethyl-1-butene under neutral conditions is quite unusual by comparison to the other acyclic olefins studied. The nature of the product distribution of this reaction (30% β-methoxy ester and 70% diesters) is extremely informative, however, in that this reaction is intermediate between those of the acyclic olefins (and cyclohexene) and the strained cycloolefins. Acyclic olefins and cyclohexene afford preferentially β-methoxy ester (>95% of the total product), while predominantly diesters (>95% of the total product) are obtained from the strained cyclic olefins.

For the strained cyclic olefins, the favored formation of diesters via the dicarbonylation mechanism has been explained as the result of the strain to which the double bond is subjected in the molecule. This interpretation postulates that strain is relieved in proceeding from the π complex to the transition state which leads to the formation of the initial alkyl complex. The product of carbonylation of the cyclic olefins was attributed to ring strain. The fact that 70% of the product from the carbonylation of *tert*-butylethylene is diesters therefore implies that the double bond of this acyclic olefin must be subject to internal strain. It has been suggested, in fact, on the basis of ^{13}C-H coupling constants, that sizable steric interaction occurs between the *tert*-butyl

Scheme VIII

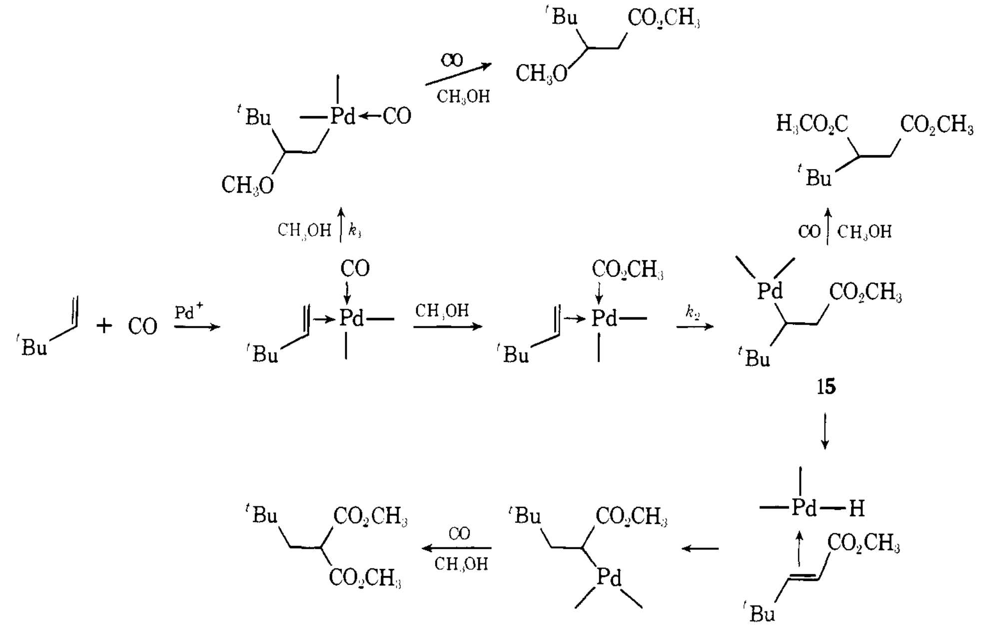


Table XIII. Analysis of the Products of the Palladium(II)-Catalyzed Olefin Carbonylation Reaction

	Elemental analysis, %					
	Calculated		Found			
Compound	C	H	C	H	^{1}H NMR[a,b]	Mass spectrum (70 eV)[c]
Methyl 3-methoxyhexanoate[d]	59.98	10.07	59.96	10.27	0.92 (m, 3 H) 1.2–1.8 (complex band, 4 H) 2.26–2.67 (ABX m, 2 H) 3.33 (s, 3 H) 3.6 (m, 1 H) 3.67 (s, 3 H)	145 ($M^+ - CH_3$, 11) 117 ($M^+ - C_3H_7$, 49) 75 ($C_3H_7O_2$, B)
Methyl 3-methoxyheptanoate[d]	62.04	10.41	61.92	10.68	0.90 (m, 3 H) 1.1–1.7 (complex band, 6 H) 2.26–2.66 (ABX m, 2 H) 3.33 (s, 3 H) 3.6 (m, 1 H) 3.67 (s, 3 H)	159 ($M^+ - CH_3$, 10) 117 ($M^+ - C_4H_9$, 42) 75 ($C_3H_7O_2$, B)
Methyl 3-methoxyundecanoate	67.79	11.38	67.83	11.34	0.88 (m, 3 H) 1.2–1.8 (complex band, 14 H) 2.26–2.67 (ABX m, 2 H) 3.35 (s, 3 H) 3.60 (m, 1 H) 3.70 (s, 3 H)	215 ($M^+ - CH_3$, 7) 117 ($M^+ - C_8H_{17}$, 39) 75 ($C_3H_7O_2$, B)
Dimethyl *n*-propylbutanedioate[e]	57.43	8.57	57.11	8.79	0.91 (m, 3 H) 1.1–1.8 (complex band, 4 H) 2.18–2.95 (m, 3 H) 3.67 (s, 3 H) 3.69 (s, 3 H)	157 ($M^+ - CH_3O$, 25) 146 ($M^+ - C_3H_6$, 60) 128 ($M^+ - HCO_2CH_3$, 29) 114 ($157 - C_3H_7$, B)
Dimethyl *n*-butylbutanedioate[f]	59.39	8.97	59.37	9.27	0.89 (m, 3 H) 1.1–1.9 (complex band, 6 H) 2.24–2.99 (m, 3 H) 3.67 (s, 3 H) 3.69 (s, 3 H)	171 ($M^+ - CH_3O$, 30) 146 ($M^+ - C_4H_8$, 35) 142 ($M^+ - HCO_2CH_3$, 10) 114 ($171 - C_4H_9$, B)
Dimethyl *n*-octylbutanedioate[g]	65.09	10.14	64.82	10.38	0.88 (m, 3 H) 1.1–1.9 (complex band, 14 H) 2.24–2.99 (m, 3 H) 3.65 (s, 3 H) 3.68 (s, 3 H)	227 ($M^+ - CH_3O$, 20) 146 ($M^+ - C_8H_{16}$, 93) 114 ($227 - C_8H_{17}$, B)
Dimethyl phenylbutanedioate[h]					2.62 (d of d, 1 H, J_{gem} = 17 Hz, $J_{2,3}$ = 5 Hz) 3.18 (d of d, 1 H, J_{gem} = 17 Hz, $J_{2,3}$ = 10 Hz) 3.62 (s, 6 H) 4.06 (d of d, J = 10 Hz, 5 Hz) 7.2 (bs, 5 H)	191 ($M^+ - CH_3O$, 13) 162 ($M^+ - HCO_2CH_3$, 72) 121 (C_8H_9O, B)
Methyl *trans*-2-methoxycyclopentanecarboxylate[i]					1.56–2.29 (m, 6 H) 2.77 (m, 1 H) 3.32 (s, 3 H) 3.70 (s, 3 H) 4.04 (m, 1 H)	158 (M^+, 1) 143 ($M^+ - CH_3$, 25) 127 ($M^+ - CH_3O$, 12) 87 ($127 - C_3H_4$, B)
Methyl *trans*-2-methoxycyclohexanecarboxylate[j]	62.78	9.36	62.79	9.45	1.0–2.5 (complex band, 9 H) 3.31 (s, 3 H) 3.4 (m, 1 H) 3.68 (s, 3 H)	172 (M^+, 4) 157 ($M^+ - CH_3$, 14) 81 (C_6H_9, 41) 71 ($C_3H_3O_2$, B)
Methyl *trans*-2-methoxycycloheptanecarboxylate[i]						186 (M^+, 3) 171 ($M^+ - CH_3$, 15) 155 ($M^+ - CH_3O$, 9) 95 (C_7H_{11}, 43) 71 ($C_3H_3O_2$, B)
Methyl *trans*-2-methoxycyclooctanecarboxylate[k]					1.2–2.1 (complex band, 12 H) 2.6 (m, 1 H) 3.28 (s, 3 H) 3.69 (s, 3 H) 3.7 (m, 1 H)	
Dimethyl *cis*-*exo*-2,3-norbornanedicarboxylate[l]	62.25	7.60	62.04	7.77	1.07–1.74 (complex band, 5 H) 2.04 (m, 1 H) 2.55 (m, 1 H) 3.62 (s, 6 H)	181 ($M^+ - CH_3O$, 25) 153 ($M^+ - CO_2CH_3$, 14) 146 ($M^+ - C_5H_6$, 8) 145 ($M^+ - C_5H_7$, B)
Dimethyl *cis*-1,2-cyclopentanedicarboxylate[m]	58.05	7.58	58.16	7.71	1.75–1.80 (m, 6 H) 3.05 (m, 2 H) 3.68 (s, 6 H)	155 ($M^+ - CH_3O$, 47) 145 ($M^+ - C_3H_5$, 12) 126 ($M^+ - HCO_2CH_3$, 40) 67 (C_5H_7, B)

Table XIII (*Continued*)

	Elemental analysis, %					
	Calculated		Found			
Compound	C	H	C	H	^{1}H NMR[a,b]	Mass spectrum (70 eV)[c]
Dimethyl *cis*-1,3-cyclopentanedicarboxylate[n]	58.05	7.58	58.16	7.71	1.75–2.38 (m, 6 H) 2.81 (m, 2 H) 3.69 (s, 6 H)	155 ($M^+ - CH_3O$, 33) 127 ($M^+ - CO_2CH_3$, 26) 67 (C_5H_7, B)
Dimethyl *cis*-1,2-cyclohexanedicarboxylate[o]	59.98	8.05	60.23	8.32	1.2–2.2 (complex band, 8 H) 2.73 (m, 2 H) 3.68 (s, 6 H)	169 ($M^+ - CH_3O$, 34) 140 ($M^+ - CO_2CH_3$, 69) 81 (C_6H_9, B)
Dimethyl *cis*-1,3-cyclohexanedicarboxylate[o]	59.98	8.05	60.23	8.32	1.0–2.6 (complex band, 10 H) 3.68 (s, 6 H)	169 ($M^+ - CH_3O$, 19) 140 ($M^+ - HCO_2CH_3$, 42) 81 (C_6H_9, B)
Dimethyl *cis*-1,2-cycloheptanedicarboxylate[i]	61.66	8.47	61.46	8.45	1.1–2.3 (complex band, 10 H) 2.99 (m, 2 H) 3.68 (s, 6 H)	183 ($M^+ - CH_3O$, 55) 154 ($M^+ - HCO_2CH_3$, 96) 95 (C_7H_{11}, B)
Dimethyl *cis*-1,3-cycloheptanedicarboxylate[i]	61.66	8.47	61.46	8.45	1.4–2.7 (complex band, 12 H) 3.68 (s, 6 H)	183 ($M^+ - CH_3O$, 33) 160 ($M^+ - C_4H_6$, 14) 154 ($M^+ - HCO_2CH_3$, 42) 95 (C_7H_{11}, B)
Dimethyl *cis*-1,2-cyclooctanedicarboxylate[i]	63.14	8.83	63.03	9.07	1.2–2.3 (complex band, 12 H) 2.95 (m, 2 H) 3.67 (s, 6 H)	197 ($M^+ - CH_3O$, 44) 168 ($M^+ - HCO_2CH_3$, 79) 109 (C_8H_{13}, B)
Dimethyl *cis*-1,3-cyclooctanedicarboxylate[i]	63.14	8.83	63.03	9.07	1.4–2.7 (complex band, 14 H) 3.67 (s, 6 H)	197 ($M^+ - CH_3O$, 6) 168 ($M^+ - HCO_2CH_3$, 26) 109 (C_8H_{13}, 53) 67 (C_5H_7, B)
Methyl *cis-exo*-3-chloro-2-norbornanecarboxylate[p]	57.30	6.95	56.92	7.10	1.0–2.9 (complex band, 9 H) 3.69 (s, 3 H) 3.95 (d of d, 1 H, $J_{2,3}$ = 7.3 Hz, $J_{2,7}$ = 3.1 Hz)	159 ($M^+(^{37}Cl) - CH_3O$, 6) 157 ($M^+(^{35}Cl) - CH_3O$, 15) 153 ($M^+ - Cl$, 17) 152 ($M^+ - HCl$, 71) 131 ($M^+(^{37}Cl) - CO_2CH_3$, 4) 129 ($M^+(^{35}Cl) - CO_2CH_3$, 13) 124 ($152 - C_2H_4$, B) 123 ($M^+(^{37}Cl) - C_5H_7$, 4) 121 ($M^+(^{35}Cl) - C_5H_7$, 12)
Methyl 3-methoxy-3-methylhexanoate[q]						159 ($M^+ - CH_3$, 7) 143 ($M^+ - CH_3O$, 5) 131 ($M^+ - C_3H_7$, 12) 81 ($142 - H_2CO_2CH_3$, B)
Methyl 3-methoxy-4-methylhexanoate[d]	62.04	10.41	61.97	10.55	0.8–1.9 (complex band, 9 H) 2.4 (m, 2 H) 3.34, 3.35 (2s, 3 H) 3.6 (m, 1 H) 3.70 (s, 3 H)	159 ($M^+ - CH_3$, 4) 117 ($M^+ - C_4H_9$, 49) 75 ($C_3H_7O_2$, B)
Methyl 3-methoxy-5-methylhexanoate[d]	62.04	10.41	61.93	10.63	0.94 (d, 6 H, J = 7 Hz) 1.0–1.9 (complex band, 3 H) 2.25–2.67 (ABX m, 2 H) 3.36 (s, 3 H) 3.6 (m, 1 H) 3.70 (s, 3 H)	159 ($M^+ - CH_3$, 8) 117 ($M^+ - C_4H_9$, 35) 75 ($C_3H_7O_2$, B)
Methyl 3-methyl-3-hexenoate[r]					0.95 (t, 3 H) 1.7 (m, 3 H) 2.0 (m, 2 H) 3.00 (m, 2 H) 3.68 (s, 3 H) 4.7–5.5 (complex band, 1 H)	142 (M^+, 29) 127 ($M^+ - CH_3$, 11) 111 ($M^+ - CH_3O$, 10) 83 ($M^+ - CO_2CH_3$, 67) 82 ($M^+ - HCO_2CH_3$, B) 69 ($M^+ - CH_2CO_2CH_3$, 58)

Table XIII (*Continued*)

	Elemental analysis, %					
	Calculated		Found			
Compound	C	H	C	H	^{1}H NMR[a,b]	Mass spectrum (70 eV)[c]
Dimethyl (1-methylbutyl)propanedioate[s]	59.39	8.97	59.19	9.16	0.89 (m, 3 H) 0.96 (d, 3 H, J = 7 Hz) 1.1–1.6 (complex band, 4 H) 2.0–2.5 (m, 1 H) 3.27 (d, 1 H, J = 7 Hz) 3.73 (s, 6 H)	171 (M$^+$ – CH$_3$O, 16) 159 (M$^+$ – C$_3$H$_7$, 3) 143 (M$^+$ – CO$_2$CH$_3$, 4) 133 (M$^+$ – C$_5$H$_9$, 11) 132 (M$^+$ – C$_5$H$_{10}$, B)
Dimethyl 2-ethyl-3-methylpentanedioate[t,u]	59.39	8.97	59.19	9.16	0.7–1.1 (complex band, 6 H) 1.3–1.8 (complex band, 2 H) 1.9–2.6 (complex band, 4 H) 3.68 (s, 6 H)	171 (M$^+$ – CH$_3$O, 44) 142 (M$^+$ – HCO$_2$CH$_3$, 79) 129 (M$^+$ – CH$_2$CO$_2$CH$_3$, 36) 113 (142 – C$_2$H$_5$, 32) 102 (M$^+$ – C$_3$H$_5$CO$_2$CH$_3$, B)
Dimethyl 3-propylpentanedioate[v]	59.39	8.97	59.19	9.16	0.89 (m, 3 H) 1.1–1.6 (m, 4 H) 2.35 (bs, 5 H) 3.68 (s, 3 H)	171 (M$^+$ – CH$_3$O, 50) 159 (M$^+$ – C$_3$H$_7$, 3) 142 (M$^+$ – HCO$_2$CH$_3$, 22) 129 (M$^+$ – CH$_2$CO$_2$CH$_3$, B)
Dimethyl 2,4-dimethylhexanedioate[u,w]	59.39	8.97	59.19	9.16	0.92, 0.95 (2d, 3 H, J = 8 Hz) 1.2–2.7 (complex band, 6 H) 3.67 (s, 6 H)	171 (M$^+$ – CH$_3$O, 26) 142 (M$^+$ – HCO$_2$CH$_3$, 39) 129 (M$^+$ – CH$_2$CO$_2$CH$_3$, 82) 115 (M$^+$ – C$_2$H$_4$CO$_2$CH$_3$, 23) 101 (M$^+$ – C$_3$H$_6$CO$_2$CH$_3$, 30) 88 (M$^+$ – C$_4$H$_7$CO$_2$CH$_3$, B)
Dimethyl (2-methylbutyl)propanedioate[x]	59.39	8.97	59.19	9.21	0.7–2.1 (complex band, 11 H) 3.45 (m, 1 H) 3.73 (s, 6 H)	173 (M$^+$ – C$_2$H$_5$, 5) 171 (M$^+$ – CH$_3$O, 12) 145 (M$^+$ – C$_4$H$_9$, 19) 132 (M$^+$ – C$_5$H$_{10}$, B)
Dimethyl (1-methylpropyl)butanedioate[u,x]	59.39	8.97	59.19	9.21	0.8–2.0 (complex band, 9 H) 2.14–3.03 (m, 3 H) 3.67 (s, 3 H) 3.69 (s. 3 H)	171 (M$^+$ – CH$_3$O, 22) 146 (M$^+$ – C$_4$H$_8$, 41) 129 (M$^+$ – CH$_2$CO$_2$CH$_3$, 27) 114 (171 – C$_4$H$_9$, B)
Dimethyl 2,3-dimethylhexanedioate[u,x]	59.39	8.97	59.19	9.21	0.88, 0.92 (2d, 3 H, J = 7 Hz) 1.09, 1.14 (2d, 3 H, J = 7 Hz) 1.3–2.1 (complex band, 3 H) 2.16–2.59 (m, 3 H) 3.69 (s, 6 H)	171 (M$^+$ – CH$_3$O, 17) 142 (M$^+$ – HCO$_2$CH$_3$, 33) 129 (M$^+$ – CH$_2$CO$_2$CH$_3$, 23) 115 (M$^+$ – C$_2$H$_4$CO$_2$CH$_3$, 58) 88 (M$^+$ – C$_4$H$_7$CO$_2$CH$_3$, B)
Dimethyl 3-ethylhexanedioate[x]	59.39	8.97	59.19	9.21	0.89 (m, 3 H) 1.2–2.0 (complex band, 5 H) 2.16–2.41 (m, 4 H) 3.68 (s, 6 H)	171 (M$^+$ – CH$_3$O, 31) 142 (M$^+$ – HCO$_2$CH$_3$, 47) 115 (M$^+$ – C$_2$H$_4$CO$_2$CH$_3$, 63) 88 (M$^+$ – C$_4$H$_8$CO$_2$CH$_3$, B)
Dimethyl (2-methylpropyl)butanedioate[x]	59.39	8.97	59.28	9.02	0.89 (d, 3 H, J = 6 Hz) 0.93 (d, 3 H, J = 6 Hz) 1.1–1.9 (complex band, 3 H) 2.14–3.06 (m, 3 H) 3.67 (s, 3 H) 3.69 (s, 3 H)	171 (M$^+$ – CH$_3$O, 29) 159 (M$^+$ – C$_3$H$_7$, 7) 146 (M$^+$ – C$_4$H$_8$, 34) 114 (171 – C$_4$H$_9$, B)
Methyl 4,4-dimethyl-3-methoxypentanoate[x]					0.88 (s, 9 H) 2.01–2.93 (ABX m, 2 H) 3.3 (m, 1 H) 3.38 (s, 3 H) 3.68 (s, 3 H)	159 (M$^+$ – CH$_3$, 1) 143 (M$^+$ – CH$_3$O, 2) 117 (M$^+$ – C$_4$H$_9$, 26) 75 (C$_3$H$_7$O$_2$, B)

Table XIII (*Continued*)

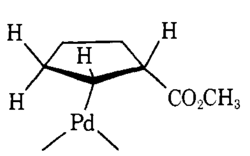
Compound	Elemental analysis, %				^{1}H NMR[a,b]	Mass spectrum (70 eV)[c]
	Calculated		Found			
	C	H	C	H		
Dimethyl (2,2-dimethylpropyl)propanedioate[x]					0.88 (s, 9 H) 1.92 (d, 2 H, J = 6 Hz) 3.41 (t, 1 H) 3.72 (s, 6 H)	187 ($M^+ - CH_3$, 19) 171 ($M^+ - CH_3O$, 21) 145 ($M^+ - C_4H_9$, 8) 127 (187 – HCO_2CH_3, 75) 57 (C_4H_9, B)
Dimethyl (1,1-dimethylethyl)butanedioate[x]					0.96 (s, 9 H) 2.3–3.1 (m, 3 H) 3.67 (s, 3 H) 3.69 (s, 3 H)	171 ($M^+ - CH_3O$, 19) 147 ($M^+ - C_4H_7$, 46) 128 ($M^+ - CH_3CO_2$-CH_3, 13) 114 (171 – C_4H_9, B)
Dimethyl *trans*-methyl-*cis*-1,3-cyclopentanedicarboxylate[i]	58.98	8.05	59.77	8.31	1.13 (bd, 3 H) 1.8–2.6 (complex band, 7 H) 3.70 (s, 6 H)	169 ($M^+ - CH_3O$, 15) 140 ($M^+ - HCO_2CH_3$, 47) 125 (140 – CH_3, 7) 81 (C_6H_9, B)
Dimethyl (1-methylethyl)propanedioate[x]					0.99 (d, 6 H, J = 7 Hz) 2.0–2.8 (m, 1 H) 3.15 (d, 1 H, J = 8 Hz) 3.72 (s, 6 H)	143 ($M^+ - CH_3O$, 34) 132 ($M^+ - C_3H_6$, B) 114 ($M^+ - HCO_2CH_3$, 13)
Dimethyl 3-methylpentanedioate[x]					1.02 (m, 3 H) 2.1–2.7 (m, 5 H) 3.68 (s, 6 H)	143 ($M^+ - CH_3O$, 56) 115 ($M^+ - CO_2CH_3$, 33) 114 ($M^+ - HCO_2CH_3$, 71) 59 (CO_2CH_3, B)
Dimethyl 3-phenylpentanedioate[y]					2.2–3.0 (ABX m, 4 H) 3.68 (s, 6 H) 3.7 (m, 1 H) 7.0–7.2 (m, 5 H)	236 (M^+, 9) 177 ($M^+ - CO_2CH_3$, 11) 176 ($M^+ - HCO_2CH_3$, 99) 118 (177 – CO_2CH_3, B) 77 (C_6H_5, 47)
Methyl 3-phenyl-3-butenoate[z]					3.51 (m, 2 H) 3.64 (s, 3 H) 5.22 (m, 1 H) 5.53 (bs, 1 H) 7.2–7.6 (m, 5 H)	176 (M^+, 46) 145 ($M^+ - CH_3O$, 15) 118 ($M^+ - CO_2CH_2$, B) 117 ($M^+ - CO_2CH_3$, 61) 103 ($M^+ - CH_2CO_2CH_3$, 25) 77 (C_6H_5, 23)
Methyl 3-methoxy-3-phenylbutanoate[x]					1.73 (s, 3 H) 2.78 (s, 2 H) 3.08 (s, 3 H) 3.53 (s, 3 H) 7.1–7.5 (m, 5 H)	177 ($M^+ - CH_3O$, 9) 176 ($M^+ - CH_3OH$, 55) 118 (177 – CO_2CH_3, 87) 115 (176 – $H_2CO_2CH_3$, B) 77 (C_6H_5, 30)

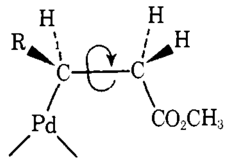
[a] In ppm downfield from TMS, multiplicity and relative peak area in parentheses. [b] For a compilation of ^{13}C NMR data, see D. E. James and J. K. Stille, *J. Org. Chem.* in press. [c] *m/e*, relative intensities in parentheses. [d] Compared to an authentic sample prepared by methylation (ref 8) of the β-hydroxy ester obtained from the Reformatsky reaction (ref 33). [e] Hydrolyzed to the known diacid; mp 96–96.5° (lit.[34] mp 94°). [f] Hydrolyzed to the known diacid; mp 84–84.5° (lit.[35] mp 82.5–83.5°). [g] Hydrolyzed to the known diacid; mp 90–91° (lit.[36] mp 90°). [h] Mp 58–59° (lit.[37] mp 57.5–58.5°). [i] Assignment based on analytical data and the known stereochemical course of the reaction. [j] Identified by comparison with an authentic sample (ref 38). [k] Identified by comparison with an authentic sample (ref 39). [l] Hydrolyzed to the known diacid; mp 154° (lit.[40] mp 152–153°). [m] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 41). [n] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 42). [o] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 43). [p] Coupling constants and stereochemical assignment based on double irradiation experiment. [q] See Table **X**. [r] Cis–trans mixture. [s] Identified by comparison with an authentic sample prepared by the malonic ester synthesis (ref 33). [t] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 44). [u] Diastereomeric mixture. [v] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 45) [w] Identified by comparison with an authentic sample prepared by esterification (methanolic HCl) of the known diacid (ref 46). [x] Structure elucidation based on analytical data. [y] Mp 87–88° (lit.[47] mp 85–87°). [z] Identified by comparison with the ^{1}H NMR spectrum of an authentic sample (ref 48).

group and the vinyl proton of the 3,3-dimethyl-1-butene molecule.[30] This interaction causes double bond deformation and results in internal strain. Because approximately 30% of the product from the carbonylation of *tert*-butylethylene is methoxy ester, it is possible to postulate that the internal strain energy of this molecule is intermediate between that of cyclohexene and cyclopentene, from 3 to 7 kcal/mol (Table VIII). This intermediate strain energy thus allows the methoxypalladation and carbomethoxypalladation steps to be mutually competitive, i.e., $k_2 \geq k_1$ (Scheme VIII).

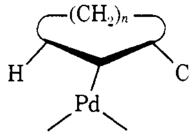
Carbonylation of 3,3-dimethyl-1-butene affords two diester products, the major one of which is obtained via rearrangement as a consequence of a high steric barrier to carbonyl insertion presented by the *tert*-butyl group adjacent to the alkylpalladium σ bond of **15**.

Finally, it is important to contrast the rearrangements of acyclic and cyclic olefins. Two important differences deserve comment: (i) Malonic esters are not formed in the carbonylation of cyclic olefins, and (ii) ultimate, 1,4-additions, which are common for the acyclic compounds, are not observed for cyclic olefins. Cis addition of the carbomethoxypalladation adduct to a cyclic olefin affords a σ complex with no cis hydrogens α to both palladium and the ester function. However, free rotation in the alkyl complex formed from the acyclic olefin makes available hydrogens for this cis elimination process and malonic esters can be formed.

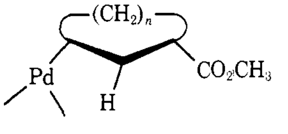




The absence of 1,4-dicarboalkoxylation products in the reaction of cyclic olefins can also be attributed to steric effects. The initial σ complex **16** formed by the cis addition of



16



17

the carbomethoxypalladium species contains a tertiary carbon β to the palladium–carbon σ bond. The results from the carbonylation of the methyl-substituted olefins suggest (Scheme VII) that for this system the rate of rearrangement will be competitive with the rate of carbonylation, and the relative rates of the two competing reactions will be dependent upon the stability of the intermediate π complex and the ability of the ring system to conformationally remove steric interactions. Thus, cyclopentene and cycloheptene favor rearrangement and formation of **17** while the C_6 and C_8 cycloolefins favor carbonylation of **16.**

Further rearrangement of **17** does not occur because of the absence of steric effects. Complex **17** contains a secondary carbon to palladium σ bond and is adjacent to two secondary carbons. The results suggest (Scheme VII) that for this system the rate of carbonylation is faster than the rate of rearrangement. In fact, under the reaction conditions studied, palladium migration in this type of σ complex, either formed from an acyclic or a cyclic olefin, was never observed.

Experimental Section

General Procedure for the Catalytic Carbonylation of Monoolefins under Neutral Conditions. To 35 ml of methanol in a 250-ml pressure bottle were added in succession, with stirring, 13.44 g (100.0 mmol) of cupric chloride, 10 ml of methanol, 50 mmol of olefin, 10 ml of methanol, 0.50 g (2.8 mmol) of palladium(II) chloride, and 20 ml of methanol (total methanol, 75 ml). The reaction vessel was then placed on the carbonylation apparatus[8] and was pressurized with 3 atm of carbon monoxide. Alternatively, as for cyclopentene and cycloheptene, the bottle was placed in a 500-ml autoclave and pressurized to 15 atm. The reaction was allowed to proceed with stirring at room temperature until palladium(0) had precipitated from solution (~72 h). Upon completion, the solvent was removed under reduced pressure and the residue was stirred with several portions of pentane. The pentane extracts were combined, filtered, and the concentrated under diminished pressure until all of the solvent was removed.

Separation, quantitative analysis, and product purification were achieved by VPC using one of three columns: a 10 ft × ⅜ in. 20% FFAP-Chromosorb W (60–80 mesh) column, a 10 ft × ⅜ in. 30% DEGS-Chromosorb-W (30–60 mesh) column, or a 10 ft × ⅜ in. 20% SE-30-Chromosorb-W (30–60 mesh) column. The FFAP column was the column of choice and gave the best product separations; unless otherwise specified this column was used for all analytical determinations and purifications. The SE-30 column was used in conjunction with the FFAP column and for separations which required column temperatures in excess of 220°. In all cases, the major products were separated by boiling points and eluted in the order: unsaturated ester > β-methoxy ester > diester. The order of elution of isomeric diesters from the FFAP column was, in general: malonic > succinic > glutaric > adipic.

General Procedure for the Catalytic Carbonylation in the Presence of Base. To 35 ml of methanol in a 250-ml pressure bottle was added in succession, with stiring, 13.44 g (100 mmol) of cupric chloride, 10 ml of methanol, 100 mmol of base, 10 ml of methanol, 50 mmol of olefin, 10 ml of methanol, 0.50 g (2.8 mmol) of palladium(II) chloride, and 10 ml of methanol (total methanol, 75 ml). The reaction vessel was then placed on the carbonylation apparatus and was pressurized with 3 atm of carbon monoxide. The reaction was allowed to proceed at room temperature until palladium(0) had precipitated from the mixture (24–72 h). After reaction, the precipitate was removed by gravity filtration and washed with methanol. The combined methanol filtrates were concentrated under reduced pressure and the residue was extracted with several portions of pentane. The pentane extracts were filtered, combined, and then concentrated under diminished pressure until all of the solvent was removed. Separation, quantitative analysis, and product purification were achieved by VPC as given above.

General Procedure for the Determination of Percent Yield. Unless otherwise specified, the percent yields based on olefin were obtained by VPC analysis.[31] Prior to reaction, a readily available and inert compound (usually a diester which eluted after the product) was chosen as an internal standard. A solution of known composition (usually a 1:1 mole ratio) was prepared and analyzed by VPC in order to determine the response factor relationship between the product(s) and the standard. The response factor was calculated from relative peak areas and was the average of at least five injections. Upon completion of the reaction studied, a given amount (based on an anticipated yield approximated from a previous reaction so as to be near to a 1:1 molar relationship) of internal standard was added to the reaction mixture. The usual work-up procedure was followed and the product with standard was analyzed by VPC. The percent yield was calculated using the previously obtained conversion factor and the peak areas of the product and internal standard from the reaction. The reported yields are the average of at least three injections from two separate runs. Standard deviations of 0.5% were attained. Alternatively, the internal standard could be added prior to carbonylation.

Catalytic Carbonylation of 1-Hexene in the Presence of Various Bases. A slurry of 2.11 g (25.0 mmol) of 1-hexene, 0.50 g (2.8 mmol) of palladium(II) chloride, 13.44 g (100.0 mmol) of cupric chloride, and 75 ml of methanol in the presence of 100 mmol of base was prepared in the usual manner. The color of the slurry formed was always bright green for the carboxylic acid salts (the intensity of the color increased from formate to butyrate) and yellow-brown for the amines. Addition of sodium carbonate to the cupric chloride–methanol solution resulted in rapid evolution of gas and uncontrollable foaming of the reaction mixture. The mixture was allowed to react with carbon monoxide (3 atm) for 72 h at room temperature and the percent yield of product was determined by VPC analysis after the usual work-up procedure. The results of these reactions are summarized in Table IV.

Oxidation of Carbon Monoxide in the Carbonylation of 1-Hexene. Two reactions were started simultaneously and the atmosphere above each mixture was analyzed by VPC for carbon dioxide content using the 20 ft × ⅛ in. 35% propylene carbonate column.[32] Both reactions contained 4.22 g (50.0 mmol) of 1-hexene, 0.50 g (2.8 mmol) of palladium(II) chloride, and 13.44 g (100.0 mmol) of specially treated cupric chloride in 75 ml of methanol. To one of the reaction mixtures was added 0.90 g (50 mmol) of water and the carbonylations were allowed to proceed until completion. The usual work-up, followed by VPC analysis, showed that a 2% yield of β-methoxy ester based on olefin was obtained from the reaction containing added water. The yield of the β-methoxy ester from the usual reaction was 70% based on olefin. The results of analysis for carbon dioxide are given in Table III.

Catalytic Carbonylation of 1-Decene. Isolation of Methyl Formate. A solution of 7.01 g (50.0 mmol) of 1-decene, 0.50 g (2.8

mmol) of palladium(II) chloride, and 13.44 g (100.0 mmol) of cupric chloride in 75 ml of methanol was allowed to react with carbon monoxide (3 atm) for 72 h at room temperature. Before depressurization, the reaction vessel was cooled to ~−10 °C by immersion in an ice-salt bath. The pressure was then released slowly and the cold mixture was transferred immediately to a fractional distillation apparatus. The temperature of the reaction mixture was raised slowly to 60° and the low-boiling distillate collected in a tared trap surrounded by a dry ice-2-propanol bath. This procedure afforded 0.82 g of a liquid which was shown by VPC analysis on the FFAP column to contain two components. The components, in order of elution, were identified as methyl formate (50% of the peak area) and methanol (50%). These results were confirmed by ^1H NMR analysis and suggest that a minimum yield of 14% (7 mmol) of methyl formate based on copper(II) was formed. The usual work-up which followed provided a 60% yield based on copper(II) of β-methoxy ester as determined by VPC analysis.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this research.

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Gas-Phase Alkylation of Xylenes by t-$C_4H_9^+$ Ions

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Abstract: The gas-phase alkylation of xylenes by t-$C_4H_9^+$ ions from the radiolysis of neopentane has been investigated in the pressure range from 20 to 771 Torr. The gaseous cation is entirely unreactive toward *p*-xylene and alkylates *o*-xylene, yielding exclusively 1,2-dimethyl-4-*tert*-butylbenzene. Reaction with *m*-xylene yields a mixture of 1,3-dimethyl-4-*tert*-butylbenzene and 1,3-dimethyl-5-*tert*-butylbenzene, whose isomeric ratio depends on the experimental conditions, ranging from the 8:92 value observed at 20 Torr in the absence of added bases to the 89:11 value measured at 770 Torr in the presence of NH_3. The *substrate* selectivity of the gaseous electrophile has been studied by competition experiments with respect to toluene. The observed $k_{o\text{-xylene}}:k_{\text{toluene}}$ ratio of 2.0 ± 0.2 appears fairly independent of the experimental conditions, while the apparent $k_{m\text{-xylene}}:k_{\text{toluene}}$ ratio is considerably affected by the nature and the concentration of gaseous bases, ranging from 0.65 ± 0.1 in the absence of NH_3 to 1.9 ± 0.2 in the presence of excess NH_3. These results are interpreted assuming the reversible *tert*-butylation at the ring positions ortho to one methyl group of *m*-xylene in order to explain both the effect of the pressure and of NH_3 on the isomeric composition of products and the apparent changes of the reactivity of *m*-xylene with respect to that of toluene. The reaction provides an example of an aromatic alkylation by a gaseous, unsolvated carbenium ion and allows the direct evaluation of the reactivity and the steric requirements of the electrophile, unaffected by the complicating effects of the solvent and the counterion invariably present in solution. The unusual *substrate* and *positional* selectivity of the gaseous t-$C_4H_9^+$ reagent, in particular the remarkable extent of the substitution ortho to one methyl group of *m*-xylene, are discussed in comparison with the conventional Friedel–Crafts alkylation.

The extension of the classical kinetic methods of solution chemistry to the gas-phase ionic reactions has been recently undertaken by new experimental approaches[1–3] that allow the actual isolation of the reaction products and the determination of their structure and isomeric composition.

Previous investigations on the reactivity of gaseous cat-