Electronic and Steric Effects in the Olefin Arylation and Carboalkoxylation Reactions with Organopalladium Compounds

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Abstract: The arylation and carboalkoxylation of olefins with aryl- and carboalkoxypalladium compounds to form styrene derivatives and unsaturated esters, respectively, has been further studied in order to better determine the factors affecting the direction of addition of the organic group to the olefin. Generally, the addition appears to be sterically controlled with the effectively larger organic group adding onto the least substituted carbon of the double bond and the palladium group going onto the more substituted carbon. Electronically the organic group appears to prefer addition to the more positive carbon but steric effects usually are considerably more important. Specific chelating effects may direct addition of the organic group to the more substituted carbon in appropriately substituted olefins. This effect was noted in the arylation of various methyl substituted allylic alcohols where 3-arylcarbonyl compounds were formed. Internal and cyclic olefins and organopalladium acetates give substantial amounts, or in some cases exclusively, 3-substituted olefins.

The remarkable ease of addition of some organopalladium compounds to olefins has led to the development of a series of useful synthetic reactions in which one of the vinylic hydrogens in the olefins is replaced by the organic group of the palladium compound.[1,2] The very reactive, unstable organopalladium compounds were prepared in the presence of the olefin to be treated by exchange reactions of palladium salts and organomercury, -lead, or -tin compounds. The reaction yields products in which the organic group had added predominantly or exclusively to the least substituted carbon of the double bond.[1] The reaction is stereospecific with

$$[RPdOAc] + R^1CH{=}CH_2 \longrightarrow RCH{=}CHR^1 + [HPdOAc]$$

internal olefins giving products consistent with a cis addition of the organopalladium reagent to the olefin followed by a cis elimination of a hydridopalladium species.[2] The results, of course, are also consistent with trans addition and trans elimination but several facts made this mechanism seem unlikely. Measurements of competitive reaction rate showed the following order of decreasing rates: ethylene > methyl acrylate > propylene > styrene > α-methylstyrene. This order of reactivity is not the one expected for radical or ionic additions but it is consistent with a cis covalent type addition. The reactions can be carried out in reactive solvents such as acetic acid, methanol, or acetone. These results also would be more consistent with a covalent addition. Recent studies of the palladium acetate oxidation of tetradeuteriocyclohexene have shown that palladium hydride additions and eliminations are very probably cis,[3] which means the organopalladium addition is also very probably cis.

In this paper, further results are reported bearing upon the influence of electronic and steric factors on the addition and subsequent elimination steps of the arylation and carboalkoxylation reactions. These results are of interest not only because they are useful in predicting products from the several promising synthetic applications referred to above, but because they

Table I. Reactions of Various "Arylpalladium Salts" with Propylene[a]

Mercurial used to prepare arylpalladium salt	Solvent	Products: Total yield, %	% *trans*-1-aryl-1-propene	% *cis*-1-aryl-1-propene	% 1-aryl-2-propene	% 2-aryl-2-propene	Internal addition/terminal addition
p-$CH_3OC_6H_4HgOAc$[b]	CH_3CN	74	50	3	4	43	1.3
p-$CH_3OC_6H_4HgCl$[b]	CH_3CN	7	54	10	~0	36	1.8
C_6H_5HgOAc[b]	CH_3CN	102	57	5	12	26	2.8
C_6H_5HgOAc[b]	CH_3OH	66	60	9	15	16	5.3
C_6H_5HgOAc[b]	CH_3COOH	87	63	7	14	16	5.3
C_6H_5HgOAc	THF	102	51	6	27	16	5.3
C_6H_5HgOAc	C_6H_6	95	48	7	29	16	5.3
C_6H_5HgOAc	CH_2Cl_2	122[c]	56	8	20	16	5.3
C_6H_5HgOAc	Monoglyme	96	52	7	24	17	4.9
C_6H_5HgOAc	Diglyme	71	54	7	22	17	4.9
p-$CH_3OCOC_6H_4HgOAc$	CH_3CN	95	58		18	24	3.2
p-$CH_3OCOC_6H_4HgCl$	CH_3CN	99	82			18	4.6

[a] Carried out at 30° with 30 psig of propylene for 1 hr. Mercurial and palladium salts always had the same anion in each reaction. [b] Data taken from ref 2. [c] High yield is because of some solvent evaporation during analyses.

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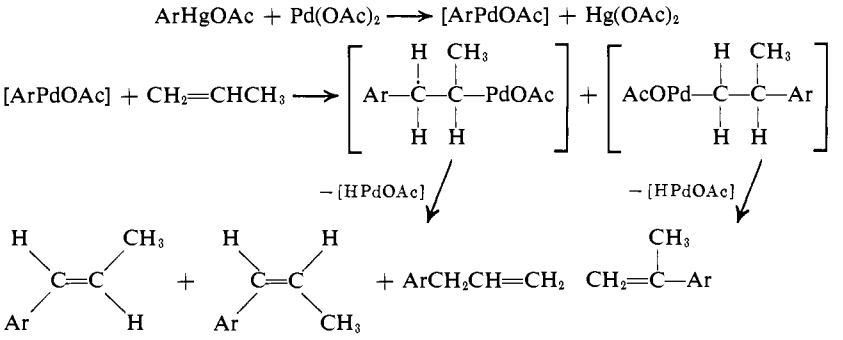
(1) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).
(2) R. F. Heck, *ibid.*, **91**, 6767 (1969).
(3) P. M. Henry and G. A. Ward, *ibid.*, **93**, 1494 (1971).

begin to give a complete picture of the behavior of these unusual new organometallic reagents which have received little attention in these respects previously.

Results and Discussion

1. Electronic Factors in the Organopalladium Compound. The products of the reaction of "phenyl- and *p*-anisylpalladium acetates" with propylene were reported previously.[2] The series has now been extended to include an electronegatively substituted example, "*p*-carbomethoxyphenylpalladium acetate" prepared as usual in the reaction mixture by the exchange reaction of *p*-carbomethoxyphenylmercuric acetate with palladium acetate. The results of these reactions are summarized in Table I.

The products obtained can be accounted for by the following equations



These additions have been referred to as anti-Markovnikov (terminal addition) and Markovnikov (internal addition) additions previously, but the terms have led to much confusion because the reagent is not obviously related to hydrogen chloride. Therefore, these labels will not be used here but each addition will be specifically described.

The data in Table I, in acetonitrile solvent, show an increase in the ratio of internal to terminal addition from 1.3 to 2.8 to 3.1 as the para substituent is changed from methoxyl to hydrogen to carbomethoxyl. The trend is the one expected on the basis of the usual electronic effects of these groups upon the position para to them. The magnitude of the effect is perhaps unexpectedly small, however, in view of the tremendous effect these changes have on the rates of electrophilic substitution reactions. Under the conditions of the reaction in Table I, the reaction of carbomethoxypalladium acetate with propylene yielded only terminal substitution product although the yields were not high because of competing palladium acetate oxidation of the olefin. Similarly, carbomethoxypalladium acetate and 1-hexene gave only terminal product, conjugated and nonconjugated ester,[2] while phenylpalladium acetate and 1-hexene gave the same internal to terminal addition ratio as was obtained with propylene. Thus, small electronic effects are seen but they do not exert a major influence on the direction of addition.

2. Solvent Effects upon the Arylation Reaction. Another factor in determining the direction of addition of the organopalladium compound to the olefin should be the ligands on the palladium during the reaction. Generally, Pd(II) compounds are four coordinate, but five and six coordination in solution probably occurs. We do not know what ligands are present during the reaction, but it seems quite likely that several of the ligands are solvent molecules. Therefore, large solvent effects might be expected to be observed. The phenylation of propylene has been investigated in a wide range of solvents under otherwise identical conditions, and the results are summarized in Table I. Seven solvents give the same ratio of *ca.* 5 of terminal to internal addition within experimental error. Acetonitrile on the other hand gave a ratio of 2.8. This is a significant but not a major difference. Even changing anions in the reactions from acetate to chloride had only small effects on the *p*-methoxy- and *p*-carbomethoxyphenylations. Thus, the relatively small molecules coordinated to the palladium in the examples of Table I do not seem to play a major role in determining directions of addition.

3. Electronic Factors in the Olefinic Compound. Many different, substituted olefins have already been investigated in the arylation reaction[1] and terminal addition predominated with 1-olefinic compounds in all of the reactions studied but minor amounts of internal addition products could have been missed. Therefore, some of the previously reported reactions have been reinvestigated and some reactions of other olefins were studied to get a more accurate measure of the proportion of internal substitution occurring. The reactions carried out with "phenylpalladium acetate" are summarized in Table II.

Electron-withdrawing substituents at or near the double bond favored terminal substitution. Thus, acrylonitrile, methyl acrylate, acrolein, allyl chloride, styrene, and vinyl acetate give practically exclusive terminal substitution while propylene, 1-hexene, allyl alcohol, and allyl acetate give appreciable amounts of internal substitution. As the substituent is moved farther from the double bond, the olefinic compound generally reacts more like 1-hexene.

Clearly, the organopalladium acetate additions are only slightly effected by the electronic character of the substituent on the double bond. While additions of hydrogen halides to the same series of olefinic compounds would have changed from essentially completely terminal to completely internal halide addition, the addition of phenylpalladium acetate has gone from near 100% terminal to only 75% terminal. Thus, steric factors would seem to be more important than electronic ones. Apparently palladium is effectively the smallest part of the organopalladium acetate. The relatively long palladium–carbon bond and the square planar geometry about the palladium combine to produce a relatively small effective size for the palladium group compared with the usual trigonal or tetrahedral carbon groups. Apparently in the absence of steric effects, addition of the organic group of the organopal-

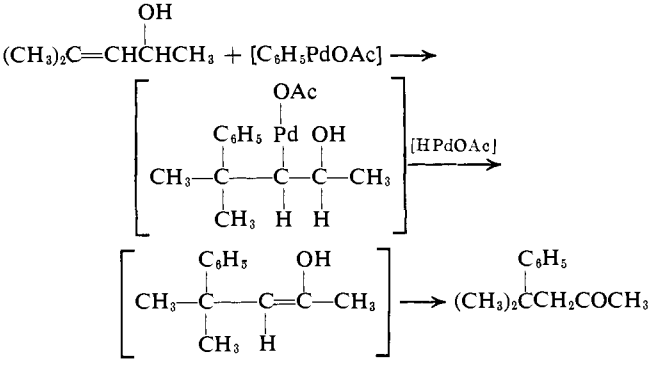
Table II. Reactions of Phenylpalladium Acetate with Various Olefinic Compounds[a]

Olefinic compound	Products, % yields — Terminal substitution	Internal substitution
CH_2=$CHCOOCH_3$	*trans*-C_6H_5CH=$CHCOOCH_3$, 84	~0
CH_2=CHCHO	*trans*-C_6H_5CH=CHCHO, 85	~0
CH_2=CHCN	*trans*-C_6H_5CH=CHCN, 26; *cis*-C_6H_5CH=CHCN, 17	~0
CH_2=$CHCH_2Cl$[b]	$C_6H_5CH_2CH$=CH_2, 37; *trans*-C_6H_5CH=$CHCH_3$, 11	~0
CH_2=CHOAc[c]	*trans*-C_6H_5CH=CHOAc, 31; *cis*-C_6H_5CH=CHOAc, 14	C_6H_5CH=CH_2, 0.2; *trans*-C_6H_5CH=CHC_6H_5, 4[d]
CH_2=CHC_6H_5	*trans*-C_6H_5CH=CHC_6H_5, 78; *cis*-C_6H_5CH=CHC_6H_5, <1	CH_2=$C(C_6H_5)_2$, <1
CH_2=$CHCH_3$[e]	*trans*-C_6H_5CH=$CHCH_3$, 57; *cis*-C_6H_5CH=$CHCH_3$, 5; $C_6H_5CH_2CH$=CH_2, 12	CH_2=$C(C_6H_5)CH_3$, 26
CH_2=$CH(CH_2)_3CH_3$	C_6H_5CH=$CH(CH_2)_3CH_3$, 47; $C_6H_5CH_2CH$=$CH(CH_2)_2CH_3$, 7	CH_2=$C(C_6H_5)(CH_2)_3CH_3$, 18
trans-C_2H_5CH=CHC_2H_5	$C_2H_5CH(C_6H_5)CH$=$CHCH_3$, 48; $C_2H_5C(C_6H_5)$=$CHCH_2CH_3$, 30	
CH_2=$CHCH_2OH$	$C_6H_5CH_2CH_2CHO$, 35; C_6H_5CH=CHCHO, 13[f]	CH_2=$C(C_6H_5)CHOH$, 5; $CH_3CH(C_6H_5)CHO$, 4
CH_2=$CHCH_2COOCH_3$	C_6H_5CH=$CHCH_2COOCH_3$, 54; $C_6H_5CH_2CH$=$CHCOOCH_3$ (?), 4	CH_2=$C(C_6H_5)CH_2COOCH_3$, 4
CH_2=$CHCH_2CN$	C_6H_5CH=$CHCH_2CN$, 45; $AcOCH_2CH$=CHCN, 55	~0
CH_2=$CHCH_2CH_2Cl$[b]	*trans*-C_6H_5CH=$CHCH_2CH_2Cl$, 36	~0
CH_2=$CHCH_2OAc$	*trans*-C_6H_5CH=$CHCH_2OAc$, 89; *cis*-C_6H_5CH=$CHCH_2OAc$, 5	CH_2=$C(C_6H_5)CH_2OAc$, 5
CH_2=$CHCH_2CH(OH)CH_3$	C_6H_5CH=$CHCH_2CH(OH)CH_3$, 59	Low
CH_2=$CH(CH_2)_3OH$	C_6H_5CH=$CH(CH_2)_3OH$, 28	CH_2=$C(C_6H_5)(CH_2)_3OH$, 18

[a] All reactions carried out in acetonitrile solution at room temperature. [b] Treated with "phenylpalladium chloride" rather than the acetate. [c] Unpublished results. [d] Probably not a product of internal substitution. [e] Data taken from ref 2. [f] Probably not a primary product, but formed by reaction of acrolein produced by oxidation of the allyl alcohol with palladium acetate.

ladium compound would be preferential to the more positive carbon of the double bond.

4. Possible Chelation Effects in the Arylation of Allylic Alcohols. Trisubstituted olefins generally do not undergo arylation reactions in more than a few per cent yields. Major reactions are palladium acetate oxidation of the olefins and coupling of the arylating agent to form biaryls.[1] The trisubstituted double bond in 4-methyl-3-penten-2-ol, however, did phenylate under normal conditions producing 4-methyl-4-phenyl-2-pentanone in 29% yield. There was no indication of the



presence of an isomeric product in which the phenylpalladium acetate had added in the reverse direction although a few per cent of this product could have been missed. Electronic and not steric control of the addition could have given the observed product. A series of methyl substituted allylic alcohols was phenylated and all showed predominate addition of the phenyl group to the allylic position of the alcohol. The data are given in Table III. Hydride eliminations in the arylation of allylic alcohols generally occurred to produce enols which gave carbonyl products.[1] Even in the 2-phenylated derivatives formed, hydride shifts apparently occurred to produce substantial amounts of carbonyl products also. Since neither steric nor electronic factors appear to be the dominent force in directing the addition of phenylpalladium acetate to the allyl alcohol derivatives, another explanation is necessary. It is already well known that chelation can produce exclusive ortho palladation in aromatic compounds azobenzene[4] and *N*,*N*-dimethylbenzylamine[5] and coordination of the phenylpalladium acetate with oxygen in the allylic alcohols could result in specific 3-phenylation in the present examples. A four-membered ring would ultimately be formed but this is probably reasonable in these examples since both oxygen and palladium have bonding angles near 90°. Thus, in favorable situations, chelation effects probably can be more important than steric or electronic effects in determining direction of addition of organopalladium compounds.

Table III. Phenylation of Various Methyl-Substituted Allyl Alcohols[a]

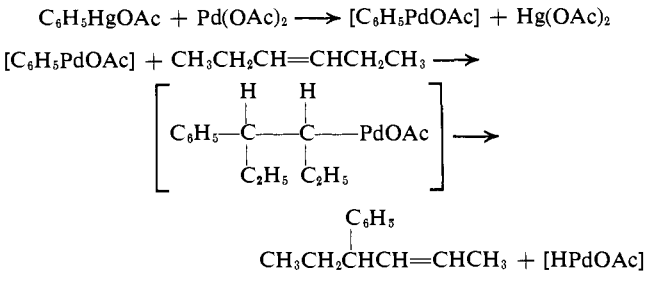
Allylic alcohol	3-Phenylated products	2-Phenylated products
CH_2=$CHCH_2OH$	$C_6H_5CH_2CH_2CHO$, 35; C_6H_5CH=CHCHO, 13[b]	CH_2=$C(C_6H_5)CH_2$-OH, 5; CH_3CH-$(C_6H_5)CHO$, 4
trans-CH_3CH=$CHCH_2OH$	$C_6H_5CH(CH_3)$-CH_2CHO, 38	$CH_3CH_2(C_6H_5)$-CHO, ~1
trans-CH_3CH=$CHC(OH)HCH_3$	$C_6H_5CH(CH_3)$-CH_2COCH_3, 44	<5%
$(CH_3)_2C$=$CHC(OH)HCH_3$	$(CH_3)_2C(C_6H_5)$-CH_2COCH_3, 29	<5%

[a] All reactions were carried out in acetonitrile solution with phenylmercuric acetate and a stoichiometric amount of palladium acetate at 0° with completion at room temperature. [b] Probably not a primary product, but formed by reaction of acrolein produced by oxidation of the allyl alcohol with palladium acetate.

5. Arylation and Carbomethoxylation Reactions Forming Allylic Derivatives. In many of the reactions in Tables I and II and in other reactions reported pre-

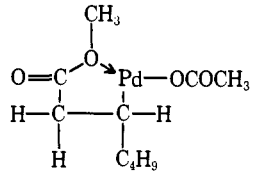
(4) A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3273 (1965).
(5) A. C. Cope and E. C. Friedrich, *ibid.*, **90**, 909 (1968).

viously,[2] where allylic hydrogens are available, considerable amounts of the thermodynamically less stable allylic derivatives are obtained in addition to the more stable vinyl derivatives. In the phenylation of *cis*- or *trans*-3-hexene the products were more than half the allylic derivatives. A similar result has been observed



in the palladium acetate oxidation of 2-octene where 3-octen-2-yl acetate is the major product.[6]

Several reasons why allylic elimination should occur can be suggested. Chelating effects in the intermediate organopalladium–olefin adducts may tend to cause allylic elimination to be preferred. For example, in the reaction of 1-hexene with carbomethoxypalladium acetate, the intermediate shown below could be formed and elimination would be directed toward the 4-methylene group in order to avoid the strain of producing a smaller ring. Such intermediates, however, seem less



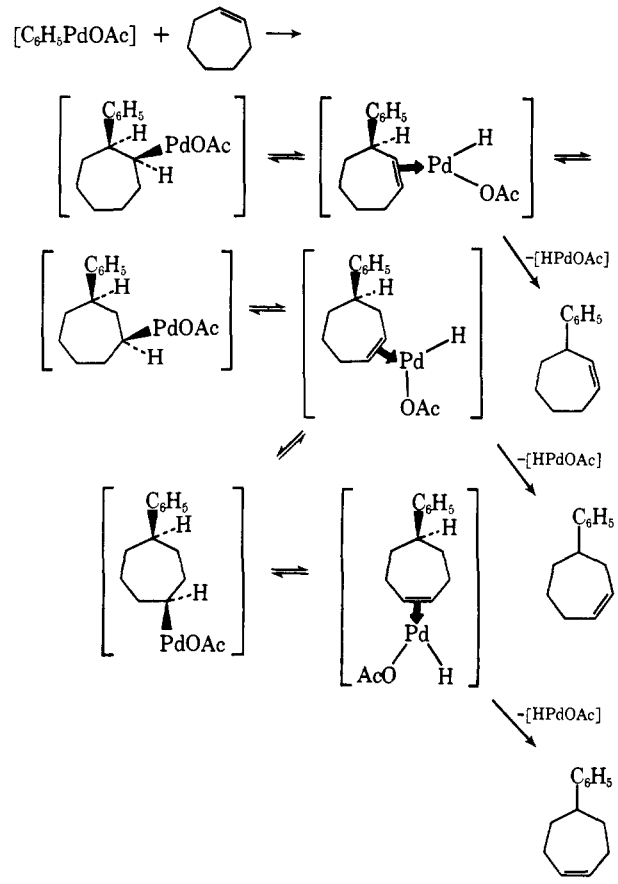
likely in arylation reactions. Even without a specific interaction, conformational effects may tend not to have the palladium group cis to the α hydrogen (β to palladium), a condition thought necessary for the elimination to occur.[2] Another possible explanation is that since cis addition of the organopalladium compound probably occurs,[2] a cis elimination of hydrogen from the other carbon of the original double bond cannot occur until carbon–carbon bond rotation takes place. If hydride elimination is rapid compared with the carbon–carbon bond rotation, then allylic elimination would be preferred. A third reason may be just the result of there being more strain in the transition state leading to the conjugated isomers. Presumably loss of hydridopalladium acetate from the organopalladium acetate–olefin adduct involves the intermediate formation of a hydridopalladium acetate–olefin π complex. For steric reasons, the formation of the least substituted olefinic complex may well be preferred.

Exclusive allylic elimination would be expected in additions to small cyclic olefins if a cis addition–cis elimination mechanism is operating.[2] Arylation and carbomethoxylation of cyclopentene, -hexene, -heptene, and -octene have been studied and indeed little or no conjugated products are formed. The results are summarized in Table IV. The observed products, however, are not generally the pure allylic substitution products but mixtures of allylic and other isomers with the double bonds further removed from the substituent added.

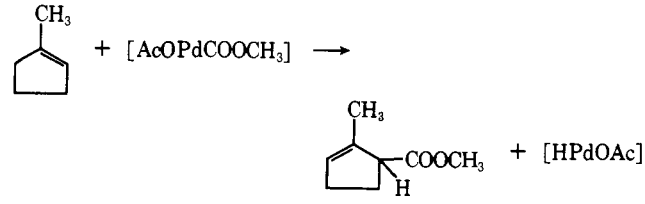
(6) T. Matsuda, T. Mitsuyasu, and Y. Nakamura, *Kogyo Kogaku Zasshi*, 72 (8), 1751 (1969).

Apparently, double bond migration in the cyclic olefins, presumably by palladium hydride addition–elimination reactions, is very favorable because the hydrogens are more often cis to the palladium group. Since little or no conjugated isomer is produced, the hydride addition–elimination reactions probably occur intramolecularly with the palladium hydride group always remaining on the same side of the carbon ring.

The reaction is exemplified below with the phenylation of cycloheptene

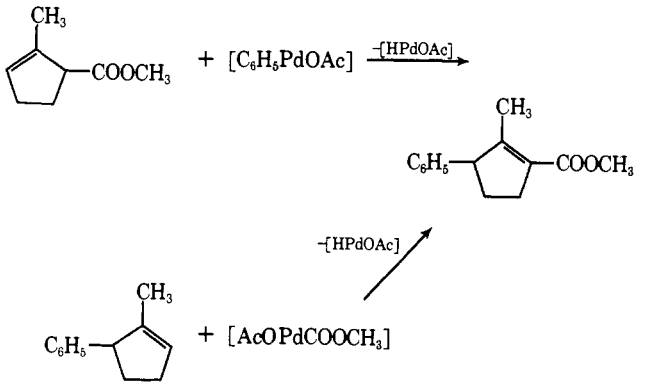


Carbomethoxylation and phenylation of 1-methylcyclopentene, on the other hand, led to the formation of only allylically substituted product. The methyl substituent on the double bond probably makes dissociation of the initial hydride π complex much more favorable compared with readdition in the reverse direction



Additions to disubstituted cyclic olefins, other than 1,2 derivatives which are not reactive, become complicated since additions may occur to either side of the ring with respect to the substituents and in some cases cis hydride eliminations are not possible. Apparently, trans elimination can occur if there is no alternative. Two pertinent examples with disubstituted cyclopentenes were investigated. The phenylation of methyl 2-methyl-2-cyclopentenoate proceeded as expected giving exclusively the allylic isomer, while the complementary re-

action, the carbomethoxylation of 5-phenyl-1-methylcyclopentene, unexpectedly produced the same product.



The results of these reactions are also summarized in Table IV. In Table IV, isomers were not specifically identified in most cases since they were clearly shown to be isomers by elemental analyses and nmr spectra. The major side products in these reactions were cyclic unsaturated acetates formed from the olefin and palladium acetate.

Table IV. Phenylation and Carbomethoxylation of Cyclic Olefins[a]

Cyclic olefin	Mercurial	Product	Bp (mm), °C	Isomeric composition by glc	% yield
	C_6H_5HgOAc		47–52 (1)	47 29	76
			47–52 (1)		5
	$CH_3OCOHgOAc$			53 25	78
					0.5
	$CH_3OCOHgOAc$		70–75 (14)	8 7	15
	C_6H_5HgOAc		70–80 (1.5)	29 21 10	60
	$CH_3OCOHgOAc$		70–75 (5.5)	48 15	63
	$CH_3OCOHgOAc$		56–58 (3)	24 29	53
	C_6H_5HgOAc		60–67 (2)		83
	$CH_3OCOHgOAc$		65–75 (17)		76
	C_6H_5HgOAc				62
	$CH_3OCOHgOAc$				20

[a] All reactions were carried out in acetonitrile solution with stoichiometric amounts of palladium acetate. Reactions were begun at 0° and after 30 min continued at room temperature for 15 hr. [b] Satisfactory carbon, hydrogen analyses and nmr spectra were obtained from these products. [c] Products were identified by glc retention times and nmr spectra.

6. Conclusions. Three factors appear to be important in determining the direction of addition of organopalladium compounds to olefins: (1) steric, (2) electronic, and (3) specific chelating effects. Generally, steric control seems to predominate leading to addition of the effectively larger organic group of the organopalladium compound to the least substituted carbon of the double bond and the palladium group to the more substituted carbon atom. Electronically, the organic group tends to add to the more positive carbon of the double bond but this effect is generally overshadowed by the steric effects. Specific chelating effects apparently can dominate and direct the addition in certain cases such as in the arylation of allylic alcohols. In these examples, 3-arylcarbonyl compounds are the major products regardless of which carbon is more substituted. Solvent effects upon the addition reaction are minor, at least with the seven solvents investigated.

Experimental Section

Analytical data, nmr spectra, and boiling points for all new compounds are given in the microfilm edition (Table V).[7]

Reagents. Palladium acetate and chloride were obtained from Engelhard Industries, Inc. Phenylmercuric chloride and acetate were purchased from the Aldrich Chemical Co., Inc. Olefinic compounds were all obtained from commercial sources and were used without further purification. Acetonitrile was dried by passage over molecular sieves before use. *p*-Methoxyphenylmercuric acetate and chloride were obtained by the method of Dimroth.[8]

***p*-Carbomethoxyphenylmercuric Chloride and Acetate.** A mixture of 20 g of powdered *p*-chloromercuribenzoic acid (Aldrich Chemical Co., Inc.), 100 ml of methanol, and 1.0 ml of concentrated sulfuric acid was prepared in a heavy-walled Pyrex bottle. A magnetic stirring bar was added, and the bottle was capped with a neoprene rubber-lined cap. The mixture was stirred magnetically in a steam bath overnight. After cooling in ice water the bottle was opened and the insoluble product was filtered from the solution and washed several times with fresh, cold methanol. The colorless powder obtained was dried in a vacuum desiccator. There was obtained 16.2 g of *p*-carbomethoxyphenylmercuric chloride.

The acetate was obtained by stirring 14.8 g (40 mmol) of the chloride with 6.80 g (40 mmol) of silver acetate in 80 ml of acetonitrile for about 15 hr. The reaction mixture was then evaporated to dryness at 50° under reduced pressure, and the product was extracted from the solid residue with about 2 l. of boiling benzene in several portions. The solution was filtered through Celite and concentrated to about 700 ml. After cooling overnight, 9.75 g of colorless crystals were obtained, mp 201°. Two further crystallizations from methyl ethyl ketone gave a purer product as colorless needles, mp 199°.

The nmr spectrum in deuteriochloroform at 60 MHz showed peaks at 1.95 Hz (singlet, 3 protons, acetate protons), 3.85 (singlet, 3 protons of methyl ester group), and at 7.75 (quartet from 4 aromatic protons). The product was found to contain 51.6% mercury by analyses; calcd, 50.81% Hg.

Arylation of Propene. The reactions summarized in Table I were carried out as described previously.[2] The products from the *p*-carbomethoxyphenylmercuric salt reactions were identified by their nmr spectra and analyses. Two products were also prepared in

(7) Table V will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(8) O. Dimroth, *Ber.*, 35, 2867 (1902).

other ways. Methyl *p*-allylbenzoate was obtained as described previously[9] from *p*-carbomethoxyphenylmercuric chloride, allyl chloride, and palladium chloride while methyl *p*-isopropenylbenzoate was obtained by brominating cumic acid in chloroform and then esterifying the product with methanol and distilling. The nmr spectra of the synthetic samples were the same as the products of the above reaction.

Arylation and Carbomethoxylation of Liquid Olefinic Compounds. These reactions were carried essentially as described previously.[2] Generally, 5 mmol of the mercurial, 10 ml of acetonitrile or other solvent, and 2 ml of the olefinic compound were stirred magnetically in a 50-ml erlenmeyer in an ice bath while 5 mmol of powdered palladium acetate or chloride was added. After about 30 min at 0° the reaction mixtures were allowed to warm up and stir at room temperature from 1 to 20 hr. Analyses of the reaction mixtures were usually made by glc on a 12-ft Apiezon "N" or Carbowax 20M on Chromosorb W column. Internal standards of biphenyl or methyl benzoate were used. The reaction mixtures were usually filtered through Celite and concentrated on the steam bath if samples of products were to be isolated for nmr or C and H determinations. The isomeric carbomethoxy and phenyl cyclic olefin derivatives were separated on a 12-ft 1,2,3-tris(2-cyanoethoxy)-propane on Gas Chrom Z column. In examples where the products were well-known compounds, identification was made by comparison of retention times and nmr spectrum with known materials.

1-Phenyl-1-hexene was obtained by the sodium bisulfite dehydration of the alcohol prepared from phenylmagnesium bromide and *n*-hexaldehyde. The other two isomeric phenylhexenes were obtained by Wittig reactions, one from valerophenone and the reagent from methyltriphenylphosphonium iodide and *n*-butyllithium and the other from 2-phenylethyl(triphenyl)phosphonium bromide with *n*-butyllithium and *n*-butyraldehyde. Only single product peaks were seen by glc on a 12-ft Apiezon "N" column for each of these products even though cis and trans mixtures may have been present.

In other cases where the products were either new compounds or difficult to obtain in other ways, nmr spectra were the basis for identification while analyses were obtained for all major products and some minor ones which could be conveniently purified by glc. In some examples larger scale reactions were carried out to obtain enough products for definite identification. Two examples of larger scale reactions are given below.

4-Phenyl-3-butenonitrile. A 500-ml, three-necked, round-bottomed flask was equipped with a mechanical stirrer, condenser, and a thermometer. A mixture of 33.6 g (0.10 mol) of phenylmercuric acetate, 200 ml of acetonitrile, and 20 ml of 3-butenonitrile was placed in the flask. The reaction mixture was then stirred in an ice bath for a few minutes and 22.4 g of powdered palladium acetate was added. The mixture was stirred for 30 min at 0° and then allowed to warm up to room temperature. Stirring was continued overnight. Initially the reaction mixture was cooled slightly to keep the temperature from rising above 30°.

The reaction mixture was diluted with 100 ml of ether and poured onto 100 g of ether-wet alumina (Woehlm Activity Grade 1) in a 1-in. diameter chromatography column and washed through with 1 l. more of ether. The eluate was concentrated on the steam bath and the residue was distilled under reduced pressure through a 6-in. Vigreux column. The fraction, bp 87–103° (3 mm), 7.2 g, was mainly a mixture of *cis*- and *trans*-3-cyanoallyl acetate and the material of bp 123–200° (3 mm), a yellow liquid which solidified on cooling, 7.4 g, was mainly the expected product. Several recrystallizations from benzene–hexane gave about 3 g of colorless plates, mp 60–61°, which was the pure trans isomer.

trans-**4-Chloro-1-phenyl-1-butene.** In the same reaction vessel as was used in the previous example was placed 31.3 g (0.10 mol) of phenylmercuric chloride, 200 ml of acetonitrile, and 20 ml of 4-chloro-1-butene. The reaction mixture was stirred at 0° and 17.7 g (0.1 mol) of powdered palladium chloride was added. The reaction was continued and the product isolated as in the preceding example. Distillation of the product under reduced pressure gave 5.2 g of colorless liquid, bp 86–95° (2 mm), which was about 95% pure.

trans-**4-Chloro-1-phenyl-1-butene.** The analytical sample was further purified by passage through a short column of silica gel to remove an impurity causing low carbon analyses.

Carbomethoxylation of Propylene. In a heavy-walled Pyrex bottle was placed a magnetic stirring bar, 1.60 g (5 mmol) of carbomethoxymercuric acetate,[10] and 1.12 g (5 mmol) of powdered palladium acetate. The bottle was capped with a neoprene rubber-lined cap with two small holes in the metal cap for "hypodermeric" injections. The air in the bottle was replaced, first by nitrogen, by alternately evacuating and pressuring several times through a 20-gauge needle, and then by propylene. The bottle was thermostated at 30° and the propylene pressure was raised to 30 psig. A previously prepared, saturated solution (at 30 psig) of propylene in acetonitrile at 30°, 10 ml, was transferred by syringe to the above bottle and the stirrer was started. The propylene pressure was kept at 20 psig and stirring was continued for 1 hr. The pressure was then released and a sample was removed and centrifuged to remove palladium metal. Analyses of the clear reaction mixture by glc on a 12-ft 10% UCON 75H on Anakrom ABS column programmed from 100 to 240° at 7.9°/min showed the solution to be 0.187 *M* in allyl acetate, 0.016 *M* in methyl-3-butenoate, and 0.070 *M* in *trans*-methyl crotonate. The remainder of the product was probably a mixture of propenyl acetates which eluted before the allyl acetate.

(9) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5531 (1968).

(10) W. Schoeller, W. Schrauth, and W. Essers, *Ber.*, **46**, 2864 (1913).