Table IV. pK_a's and Hydrogen Bonding with Phenol in CCl_4 of Sulfoxides

	t-BuSOMe	DMSO	PhSOMe	Ph_2SO
$\Delta\nu_{OH}$[a]	393	366	330	305
pK_a	−1.62	−1.80	−2.27	−2.54

[a] Free. ν_{OH} = 3615 cm^{-1}.

thermodynamic ones. On the same basis the large ρ value (3.84) reported by Andersen might also be rationalized.

Relations between basicity and strength of hydrogen bond with a given hydrogen donor (as measured by the shift of X–H stretching frequencies) have been found for several classes of compounds.[9,22] Such a relation seems to hold also in the case of sulfoxides.

In fact, the pK_a's in water of DMSO, *t*-BuSOMe, PhSOMe, and Ph_2SO are found to correlate well (s = 91.01; r = 0.992) with the $\Delta\nu_{OH}$ (cm^{-1}) of phenol in CCl_4[23] due to hydrogen bonding with the sulfoxides above (Table IV).

The present study clearly shows that the protonation behavior of sulfoxides differs considerably from that of typical Hammett bases. This fact caused previous attempts to measure the pK_a's of sulfoxides to fail, since either Hammett primary amine bases or the H_0 function were employed as reference.

We also feel that many studies on acid-catalyzed reactions of sulfoxides[24–28] should be reconsidered on the basis of our findings.

Experimental Section

DMSO, trimethylamine, and sulfuric and perchloric acids were Analar grade commercial products, purified, where necessary, by standard methods.

The sulfoxides were synthetized by oxidation with iodobenzene dichloride[29] of the corresponding sulfides, in turn prepared by standard methods. All sulfoxides were carefully purified by column chromatography and by repeated crystallizations. The physical constants agreed with the best values reported in the literature.

Sulfuric and perchloric acids solutions were prepared by dilution and titrated with standard NaOH. The H_0 and H_A values were obtained by interpolation of published data.[14c,30,31]

The solutions of the sulfoxides (about 0.2 *M* for nmr spectra and 2 × 10^{-4} *M* for uv spectra) were made immediately before running the spectra.

The nmr spectra were recorded on a Varian DP 60 instrument operating at 56.4 MHz using $(CH_3)_3N$ (about 0.2 *M*) as internal standard. Calibration was performed by the side-band technique.

The uv spectra were recorded on a Cary 14 and/or a Zeiss M4Q instruments in 1-cm thermostated cells.

The ionization ratio [BH$^+$]/[B] were obtained by the usual relations.[12,14] The least square treatment of data was performed taking points from 5 to 95% protonation.

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(22) D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959.

(23) P. Biscarini, G. Galloni, and S. Ghersetti, *Boll. Sci. Fac. Chim. Ind. Bologna*, **21**, 154 (1963).

(24) S. Allenmark, *Acta Chem. Scand.*, **15**, 928 (1961), and other papers in this series.

(25) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

(26) S. Oae and N. Kunieda, *Bull. Chem. Soc. Japan*, **41**, 696 (1968); S. Oae, M. Yokoyama, and M. Kise, *ibid.*, **41**, 1221 (1968).

(27) D. Landini, F. Montanari, G. Modena, and G. Scorrano, *Chem. Commun.*, 86 (1968).

(28) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

(29) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc., C*, 659 (1968).

(30) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

(31) R. S. Ryabova, I. M. Medvetskaya, and M. I. Vinnik, *Russ. J. Phys. Chem.*, **40**, 182 (1966).

The Mechanism of Arylation and Carbomethoxylation of Olefins with Organopalladium Compounds

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Abstract: Phenylation and carbomethoxylation of olefins with "phenyl and carbomethoxylpalladium acetate," prepared *in situ* by the exchange reaction of the corresponding mercury compounds and palladium acetate, have been investigated under conditions where the initially formed products are stable. The reactions yield almost completely "anti-Markovnikov" products except with the least substituted (least hindered) olefins, such as propylene, where up to 30% "Markovnikov" addition may occur depending upon the reaction conditions. Substantial amounts of nonconjugated olefins are generally formed depending upon the substituents present. The reactions are quite stereospecific, yielding products expected from a *cis*-addition of the organopalladium acetate followed by a *cis*-elimination of hydridopalladium acetate. Minor amounts of unexpected olefin products are seen in some reactions, apparently arising from readdition of the eliminated palladium hydride species in the reverse direction followed by re-elimination of a hydride containing a different hydrogen atom.

Arylation, methylation, and carboalkoxylation of olefins with organomercury compounds and palladium salts have been shown to be useful reactions for the synthesis of a wide variety of vinyl-substituted olefinic compounds.[1] Little information was obtained about

(1) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

Table I. Phenylation of Propylene[a]

Phenylating agent	Palladium compound	Solvent	Total yield	Product composition[b]					
				% *trans*-1P1P	% *cis*-1P1P	% AB	% 2P1P	% *n*-PB	% *i*-PB
C_6H_5HgOAc	$Pd(OAc)_2$	CH_3OH	66	60	9	15	16	ND[c]	ND
C_6H_5HgCl	$PdCl_2$	CH_3OH	76	87	4	0.5	7	1	0.5
C_6H_5HgOAc	$Pd(OAc)_2$	CH_3OH	58[d]	60	9	15	16	ND	ND
C_6H_5HgOAc	$Pd(OAc)_2$	CH_3CN	102	57	5	12	26	ND	ND
C_6H_5HgOAc	$Pd(OAc)_2$	CH_3COOH	87	63	7	14	16	ND	ND
C_6H_5HgOAc	1:4, $Pd(OAc)_2$:NaOAc	CH_3COOH	68	57	7	16	20	ND	Trace
$(C_6H_5)_4Sn$	$Pd(OAc)_2$	CH_3OH	6	63	9	6	14	6	3
C_6H_5HgOAc	$CaPd(OAc)_4 \cdot 4HOAc$	CH_3CN	90	64	5	1	30	ND	ND
C_6H_5HgOAc	1:4, $Pd(OAc)_2$:NaOAc	CH_3CN	83	66	4	14	16	ND	ND
C_6H_5HgOAc	$Pd(OAc)_2$	9:1, CH_3CN:C_5H_5N	4	55	5	27	13	ND	ND

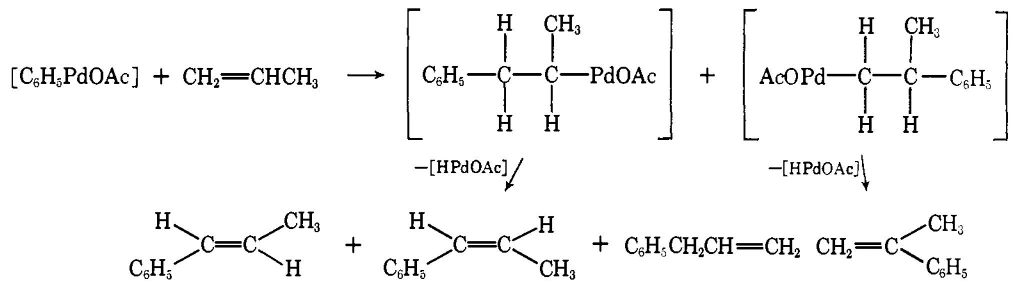
[a] Reaction mixtures consisted of 5 mmol of arylating agent, 5 mmol of palladium compound, and 10 ml of solvent which were allowed to react at 30° and under 30 psig of propylene for 1 hr. Analyses did not change significantly with longer reaction times with phenylmercuric acetate as the arylating agent. [b] *trans*-1P1P = *trans*-1-phenyl-1-propene; *cis*-1P1P = *cis*-1-phenyl-1-propene; AB = allylbenzene; 2P1P = 2-phenyl-1-propene; *n*-PB = *n*-propylbenzene; *i*-PB = isopropylbenzene. [c] ND = none detected. [d] At 0° instead of 30°.

the mechanism of the reaction, however. A study of relative rates of reaction of "phenylpalladium chloride" with various olefins showed ethylene to be more reactive than methyl acrylate, propylene, styrene, and α-methylstyrene, in that order, suggesting that a relatively nonpolar covalent addition of the organometallic reagent to the olefin was probably occurring, although conceivably this order could be a measure of relative stabilities of the π complexes rather than of relative rates of additions. The previous work was carried out mainly with chloride salts since they were generally more readily available and the reactions could be carried out catalytically in the palladium salt with cupric chloride present. It was noted, however, that the chloride ion-containing reaction mixtures promoted olefin isomerization causing both double bond migration and *cis–trans* isomerism, which greatly complicated the task of identifying the products initially formed. Reactions carried out with acetate as the only anion, on the other hand, generally produced products without appreciable accompanying isomerization. We have now made further studies on the arylation and carbomethoxylation reactions in acetate systems to determine more about the structures of the initial products formed and to deduce more information about the mechanism of the addition and elimination steps that are apparently involved.

Results and Discussion

The direction of addition of aryl-, methyl-, and carboalkoxy-palladium salts to unsymmetrical olefins was shown to be mainly, at least, of the non-Markovnikov type but we believed this was more the result of steric than electronic factors.[1] Information on the preferred direction of elimination has now been obtained by studying the addition of "phenylpalladium acetate," prepared from phenylmercuric acetate and palladium acetate, to propylene. The composition of "phenylpalladium acetate" is not known. Certainly it is solvated or made complex with other materials in the reaction mixtures but since these other coordinating groups are not known at present we have used quotation marks around this and similar names and brackets around their formulas to indicate that they are incompletely identified. In methanol solution at 30° propylene and "phenylpalladium acetate" gave a 66% yield of an olefin mixture, consisting of 60% *trans*-1-phenyl-1-propene, 9% *cis*-1-phenyl-1-propene, 15% allylbenzene, and 16% α-methylstyrene. The products were stable for several times the reaction period in the reaction mixture. The presence of significant amounts of the Markovnikov addition product, α-methylstyrene, was not noted previously because of the difficulty of separating *cis*-1-phenyl-1-propene from this material by glpc. The results of this and other related experiments are summarized in Table I. The reaction can be explained as shown.

$$C_6H_5HgOAc + Pd(OAc)_2 \longrightarrow [C_6H_5PdOAc] + Hg(OAc)_2$$

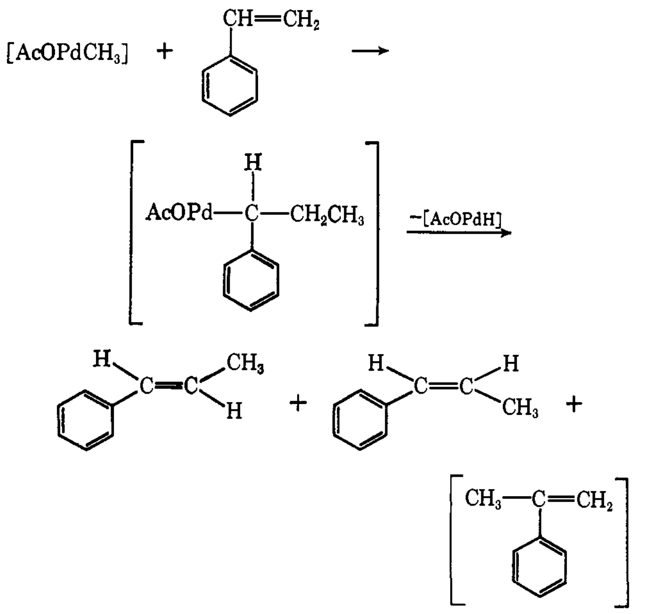


A similar result was obtained at 30° in acetic acid solvent and at 0° in methanol solvent. In acetonitrile solution at 30° relatively more α-methylstyrene was formed (26%). The differences observed probably are largely the result of different ligands, either solvent or anions, being attached to the palladium in the addition and elimination steps.

Control experiments have shown that allylbenzene and *cis*-1-phenyl-1-propene are not appreciably isomerized during the arylation reaction or subsequently to it, by the reaction products. Minor amounts of the allylbenzene are converted to 1,3-diphenylpropene and small amounts of product may be converted into mercuric acetate adducts by the mercuric acetate produced in the reaction. Reduced products, *n*-propyl- and isopropylbenzene are not observed in these examples. In an experiment using tetraphenyltin as the source of the phenyl group, and allowing it to react with propylene and palladium acetate, a similar product mixture was obtained although in much lower yield, suggesting that mercuric acetate does not significantly affect the product composition. Thus, elimination of the benzylic hydrogen in methanol solution is preferred 6:1 over the terminal hydrogen and formation of the *trans* olefin over the *cis* is favored by about 6:1. Anti-Markovnikov addition is preferred about 6:1 over Markovnikov addition.

A comparison of the phenylation of propylene with "phenylpalladium acetate" and phenylpalladium chloride" showed 15% allylbenzene formed in the former reaction and only 0.4% in the latter under the same conditions, presumably because [HPdCl] is isomerizing the allylbenzene in the latter case. The amount of *cis*-1-phenyl-1-propene decreased from 9% to 4% and α-methylstyrene decreased from 16% to 7%. Thus, the chloride system favors anti-Markovnikov addition more than the acetate system does.

The related reaction of "methylpalladium acetate" from methylmercuric acetate and palladium acetate with styrene is much more selective, producing in 40% yield a mixture containing 95% *trans*-1-phenyl-1-propene, about 3% of the *cis*-isomer and 2% of α-methylstyrene. No allylbenzene was detected.



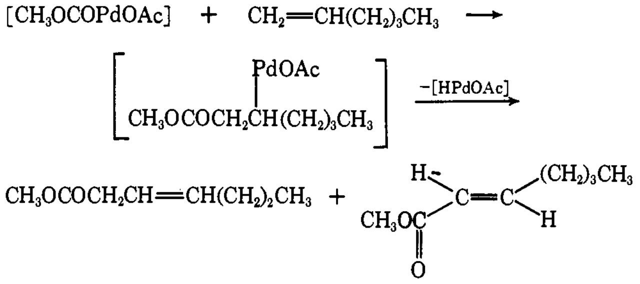
The arylation of propylene with "*p*-anisylpalladium acetate" was studied to determine the effect of the *p*-methoxyl group upon the reaction. A reaction carried out in methanol solution at 30°, as in the "phenylpalladium acetate" reaction, produced a 65% yield of an olefin mixture containing 10% estragole (*p*-allylanisole), 47% *trans*-, 16% *cis*-anethole (*p*-propenylanisole), and 27% of the Markovnikov product, 2-*p*-anisyl-1-propene. Thus, the *p*-methoxyl group had little effect upon the preference for elimination of benzylic *vs.* terminal hydrogen but appreciably increased the amount of *cis*-propenyl product formed relative to the *trans* isomer, and significantly increased the yield of the Markovnikov product. Similar results were noted in acetic acid solution while in acetonitrile a much larger amount (43%) of the Markovnikov product was found. The use of a chloride system in acetonitrile solution led to the formation of 54% *trans*- and 10% *cis*-anethole, no estragole, and 36% 2-*p*-anisyl-1-propene. The yield was only 7% under the conditions used. Again in the previous work a substantial amount of Markovnikov product was probably missed because of the great difficulty in separating this compound from *cis*-anethole by glpc. The results of the "*p*-anisylpalladium acetate" experiments are summarized in Table II.

Table II. Anisylation of Propylene

	Product composition				
Solvent	Total yield, %	% *trans*-anethole	% *cis*-anethole	% estragole	% 2-*p*-anisyl-1-propene
CH_3OH^a	65	47	16	10	27
CH_3CN^a	74	50	3	4	43
CH_3COOH^a	67	49	8	17	26
CH_3CN^b	7	54	10	0	36

[a] Reaction mixtures consisted of 5 mmol of *p*-anisylmercuric acetate, 5 mmol of palladium acetate, and 10 ml of solvent, allowed to react at 30° under 30 psig of propylene for 1 hr. [b] Reaction mixture as in *a* except *p*-anisylmercuric chloride and palladium chloride were used instead of the acetates.

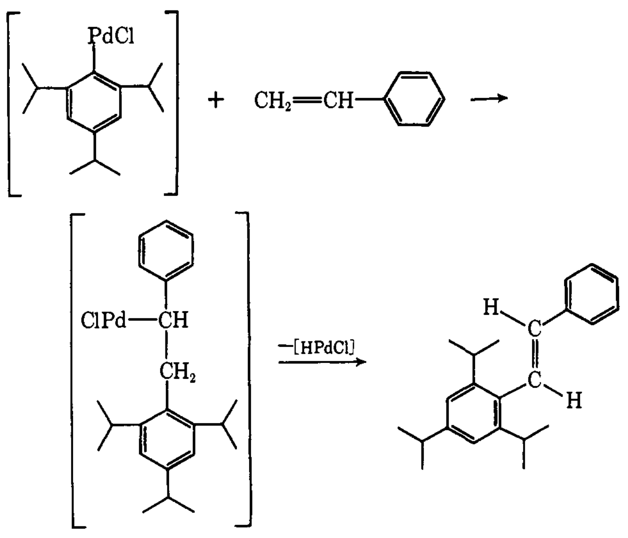
The addition of "carbomethoxypalladium acetate" from carbomethoxymercuric acetate and palladium acetate to 1-hexene was also investigated. In methanol solution a 73% yield of a mixture of esters consisting of 41.5% methyl *trans*-2-heptenoate and 58.5% of methyl 3-heptenoate (uncertain stereochemistry but probably *trans*) was obtained. The products were stable in the reaction mixture.



The results of these experiments suggest that the hydride elimination is not very specific but that the more hydridic hydrogen tends to be lost slightly more easily.

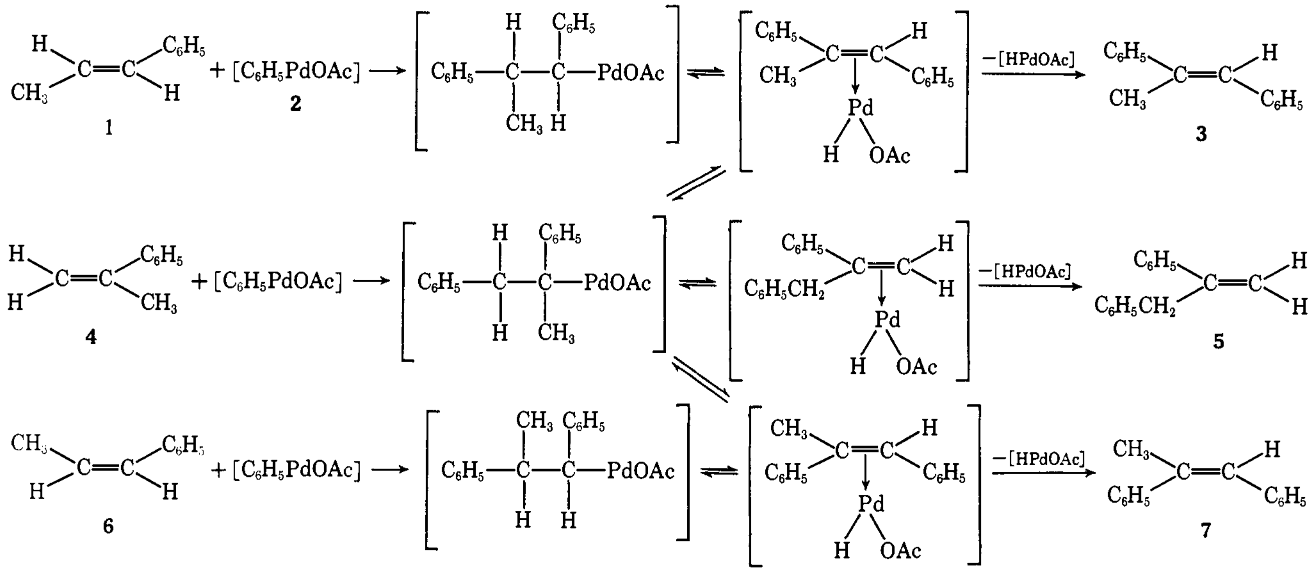
The elimination reaction is remarkably insensitive to steric effects. Even "2,4,6-triisopropylphenylpalladium chloride" and styrene reacted normally to form *trans*-2,4,6-triisopropylstilbene in better than 40% yield (yield of pure isolated product). Presumably, if the hindrance to elimination were significant a second addition to the styrene would have occurred to form ultimately 1,3-diphenyl-4-(2,4,6-triisopropylphenyl)-1-butene.

Identification of the products obtained from the reaction of "phenylpalladium acetate" with *trans*- and *cis*-1-phenyl-1-propene has provided definitive information on the stereochemistry of the reaction. The results ob-



tained are explicable on the basis of the equations in Scheme I.

Scheme I



trans-1-Phenyl-1-propene (**1**) and "phenylpalladium acetate" (**2**) in methanol solution react at 30° to form a mixture of olefins in near-quantitative yield. The mixture of products, which was stable in the reaction mixture, contained 98% *trans*-1,2-diphenyl-1-propene (**3**), 0.5% 2,3-diphenyl-1-propene (**5**) and only a trace of *cis*-1,2-diphenyl-1-propene (**7**). Only a trace of the Markovnikov product, 1,1-diphenyl-1-propene was observed. We did not look for 1,1-diphenyl-2-propene but since no unknowns were found by glpc there could not have been much of this compound formed. Analyses of the unreacted starting olefin after completion of the reaction showed that less than 2% of the *trans*-1-phenyl-1-propene had isomerized to the *cis* isomer.

The corresponding reaction with *cis*-1-phenyl-1-propene (**6**) produced, in 85% yield, a mixture of products consisting of 65% *cis*-1,2-diphenyl-1-propene (**7**), 10% 2,3-diphenyl-1-propene (**5**), 22% *trans*-1,2-diphenyl-1-propene (**3**), and about 3% 1,1-diphenyl-1-propene. Again the composition of the reaction mixture did not change significantly with time. About 10% of the excess starting olefin, *cis*-1-phenyl-1-propene was isomerized to the *trans* isomer at the end of the reaction time.

The major products in both of the above reactions are the ones expected from a *cis*-addition–*cis*-elimination mechanism. A *trans*-addition–*trans*-elimination would also be consistent but this possibility seems unlikely in view of the anti-Markovnikov addition observed and the relative rates of reaction of various olefins mentioned above which indicate that the addition is probably not ionic or radical in character. Termolecular mechanisms should be considered also but reasonable possibilities are not apparent. Thus, a covalent *cis*-addition of the "phenylpalladium acetate" to the olefin followed by a covalent (four-centered) *cis*-elimination of "hydridopalladium acetate" seems to best explain the results.

The formation of significant amounts of the *trans* isomer of 1,2-diphenyl-1-propene (**3**) in the *cis*-1-phenyl-1-propene phenylation probably is partly the result of the reaction of some of the isomerized starting olefin. Measurement of the relative rates of reaction of *cis*-1-phenyl-1-propene and the *trans*-isomer in a competitive experiment showed the *cis*-isomer to be about 1.3 times more reactive. Therefore, a few per cent of the *trans*-1,2-diphenyl-1-propene could have come from the isomerized starting material depending upon how fast isomerization was compared with phenylation. Most of this product, however, must have been formed in some other way or ways. One other possibility is suggested.

The mechanism of formation of the 2,3-diphenyl-1-propene (**5**) is not immediately obvious since it cannot arise from direct elimination of "hydridopalladium acetate" from the initial adduct. Possibly this material arises from isomerization of one or both of the 1,2-diphenyl-1-propene isomer products. This possibility seems unlikely, however, because the presumably much more reactive and concentrated *cis*-1-phenyl-1-propene (**6**) is relatively little isomerized under the same conditions. A more probable explanation is that the intermediate organopalladium complex undergoes a rearrangement *via* a π complex to "1,2-diphenyl-2-acetatopalladopropane" which then decomposes partly into 2-3-diphenyl-1-propene. Support for this possibility is found in a study of the reaction of "phenylpalladium acetate" with 2-phenyl-1-propene (**4**). This reaction should produce directly the rearranged intermediate

Table III. Phenylation of Phenylpropenes[a]

						Products %			
Phenylating agent	Phenylpropene	Solvent	Pd compd	Time, hr	Total yield	1,1-Diphenyl-1-propene	*cis*-1,2-Diphenyl-1-propene	*trans*-1,2-Diphenyl-1-propene	2,3-Diphenyl-1-propene
C_6H_5HgOAc	*trans*-1-Phenyl-1-propene[b]	CH_3CN	$Pd(OAc)_2$	2	86	Trace	0	99.5	0.5
C_6H_5HgOAc	*trans*-1-Phenyl-1-propene[b]	CH_3OH	$Pd(OAc)_2$	2	~100	1	Trace	98.5	0.5
C_6H_5HgOAc	*trans*-1-Phenyl-1-propene[b]	CH_3COOH	$Pd(OAc)_2$	2	88	2	0.5	95	2.5
C_6H_5HgOAc	*cis*-1-Phenyl-1-propene[c]	CH_3CN	$Pd(OAc)_2$	6	89	Trace	90	2	8
C_6H_5HgOAc	*cis*-1-Phenyl-1-propene	CH_3CN	$Pd(OAc)_2$	2	~100	Trace	88.5	4	7.5
C_6H_5HgOAc	*cis*-1-Phenyl-1-propene[d]	CH_3OH	$Pd(OAc)_2$	2	85	3	65	22	10
C_6H_5HgOAc	*cis*-1-Phenyl-1-propene[e]	CH_3COOH	$Pd(OAc)_2$	2	61	4	72	18	6
C_6H_5HgCl	*cis*-1-Phenyl-1-propene[f]	CH_3CN	$PdCl_2$	2	~100	6	14	77	3
C_6H_5HgOAc	2-Phenyl-1-propene	CH_3CN	$Pd(OAc)_2$	2	73	0	Trace	42	58
C_6H_5HgCl	2-Phenyl-1-propene	CH_3CN	$PdCl_2$	2	59	0	10	80	10
C_6H_5HgOAc	2-Phenyl-1-propene	CH_3OH	$Pd(OAc)_2$	2	96	0	0	57	43
C_6H_5HgOAc	2-Phenyl-1-propene	CH_3CN	$Pd(OAc)_2$	6	49	0	0	36	64
C_6H_5HgOAc	2-Phenyl-1-propene	CH_3COOH	$Pd(OAc)_2$	2	53	0	0	45	55
C_6H_5HgOAc	1:1, *cis* and *trans*-1-Phenyl-1-propene	CH_3OH	$Pd(OAc)_2$	1	73		42	52	6
$(C_6H_5)_4Pb$	*cis*-1-Phenyl-1-propene[d]	CH_3OH	$Pd(OAc)_2$	1	79	1	68	24	7
$(C_6H_5)_4Sn$	*cis*-1-Phenyl-1-propene[c]	CH_3OH	$Pd(OAc)_2$	1	70	2	42	41	15

[a] Reaction mixture consisted of 5 mmol of phenylating agent, 5 mmol of palladium compound, 2 ml of the phenylpropene, and 10 ml of solvent. All reactions were carried out at 30°. [b] Less than about 2% of the excess *trans*-1-phenyl-1-propene was isomerized during 2 hr reaction time. [c] 18% of the *cis*-1-phenyl-1-propene was isomerized to the *trans* isomer during the 2 hr reaction time. Reaction was carried out at 20°. [d] 10% of the *cis*-1-phenyl-1-propene was isomerized to the *trans* isomer during the 2 hr reaction time. [e] 13% of the *cis*-1-phenyl-1-propene was isomerized to the *trans* isomer during the 2 hr reaction time. [f] 96% of the *cis*-1-phenyl-1-propene was isomerized to the *trans* isomer during the 2 hr reaction time.

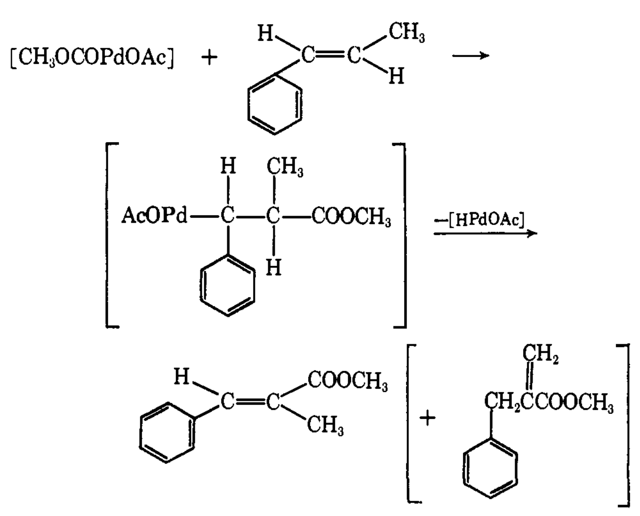
palladium complex suggested above. The observed reaction product in methanol solution (obtained in 96% yield) consisted of 43% of 2,3-diphenyl-1-propene (**5**) and 57% *trans*-1,2-diphenyl-1-propene (**3**). Thus, all of the 2,3-diphenyl-1-propene (**5**) and much of the observed, "unexpected" *trans*-1,2-diphenyl-1-propene (**3**) from the *cis*-1-phenyl-1-propene phenylation should have been formed from the rearranged intermediate. Qualitatively similar results were obtained using acetonitrile and acetic acid instead of methanol as solvent for the phenylations. Since more than the expected amount of the *trans*-olefin (**3**) was formed in the above reactions and considering the amount of starting olefin isomerized, some other mechanism of isomerization must also be operating. The results of these experiments are summarized in Table III.

The use of tetraphenyltin in place of phenylmercuric acetate in the reaction with *cis*-1-phenyl-1-propene and palladium acetate in methanol led to a significantly different mixture of reaction products. *cis*-1,2-Diphenyl-1-propene was obtained in 23% lower yield and *trans*-1,2-diphenyl-1-propene in 19% higher yield, indicating that different intermediates were involved. Since tetraphenyllead and phenylmercuric acetate gave similar reaction products, the tetraphenyltin reaction is unusual. Probably, the acetoxytin exchange products remains attached to the palladium in some way (either by coordination or addition to form a Pd(IV) species) during the addition and elimination reaction with the *cis*-1-phenyl-1-propene.

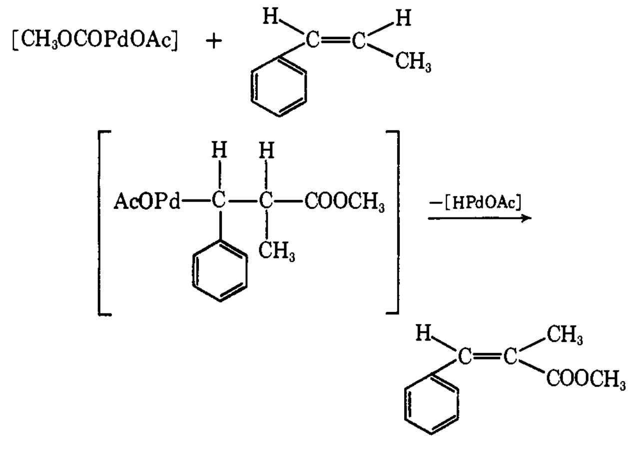
Attempts were made to determine the stereochemistry of the addition of "methylpalladium acetate" to *cis*- and *trans*-stilbenes but the yields of methylated products were so small that the results were probably not significant. Large substituents on the olefinic carbons were previously observed to decrease greatly the yields in the arylation reaction.[1] Methylation appears to be particularly sensitive to the size and number of substituents on the double-bond carbons.

Confirmation of the stereochemistry of phenylation and determination of the stereochemistry of carbomethoxylation was obtained in a study of related reactions producing isomeric methyl phenylbutenoates or phenylbutenoic acids. The carbomethoxylation of *trans*- and *cis*-1-phenyl-1-propene and of 2-phenyl-1-propene gave results analogous to those of the phenylation described above.

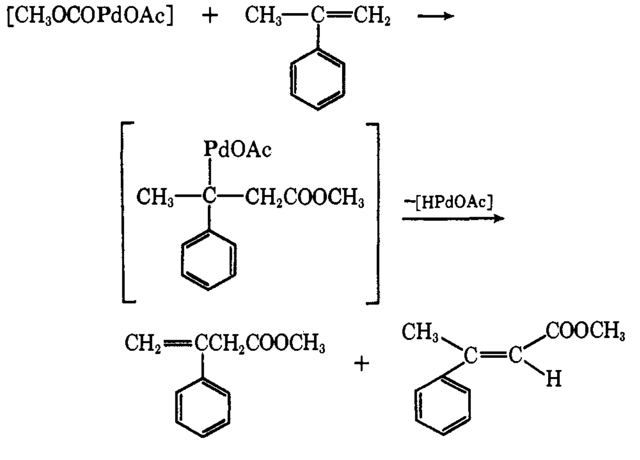
trans-1-Phenyl-1-propene and "carbomethoxypalladium acetate" reacted at 30° in acetonitrile to form, in 85% yield, a mixture of products containing about 94% methyl *trans*-2-methylcinnamate and 6% of a mixture of two or three unknown materials one of which is probably methyl 2-benzylacrylate judging by its nmr spectrum and glpc retention time.



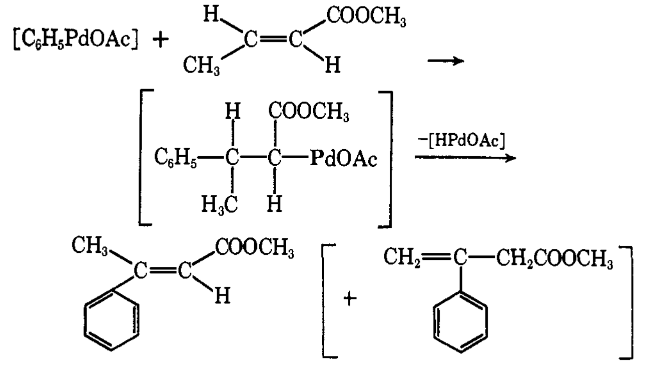
cis-1-Phenyl-1-propene and "carbomethoxypalladium acetate" reacted under the same conditions to give a 44% yield of the expected methyl *cis*-2-methylcinnamate along with about half as much unidentified higher boiling materials not containing ester groups. At the end of the reaction, 7% of the starting olefin had been isomerized to the *trans* isomer.



The reaction of "carbomethoxypalladium acetate" with α-methylstyrene gave, in 86% yield, a product containing about 96% of methyl 3-phenyl-3-lutenoate and 4% methyl *trans*-2-methylcinnamate. Thus, the carbomethoxylation reaction appears to be quite stereospecific also, probably involving a *cis*-addition and *cis*-elimination mechanism.

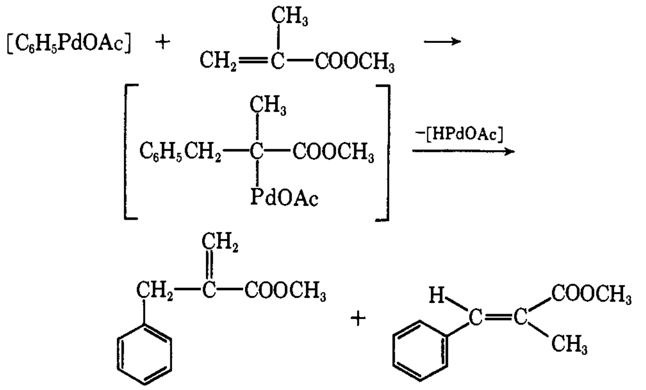


Several related reactions were carried out to help establish the generality of the stereospecific addition and elimination reactions. Methyl *trans*-crotonate and "phenylpalladium acetate" at 30° produced, in nearly quantitative yield by glpc, a mixture of esters containing about 95% methyl *trans*-3-methylcinnamate and (probably) about 5% of methyl 3-phenyl-3-butenoate.



The same reaction employing *trans*-crotonic acid in place of the ester led to the formation of *trans*-3-methylcinnamic acid but apparently only in low yield since the product could be isolated in only 6% yield. The use of 85% pure *cis*-crotonic acid instead of the *trans* isomer in this reaction gave *cis*-3-methylcinnamic acid in 24% isolated yield.

Methyl methacrylate and "phenylpalladium acetate" reacted in nearly quantitative yield to form a mixture of esters containing 72% methyl 2-benzylacrylate and 28% methyl *trans*-2-methylcinnamate. Conformational effects are probably responsible for the formation of large amounts of the thermodynamically less stable terminal olefin in this and other examples mentioned above.



The above experiments demonstrate the utility of the arylation and carboxyalkylation reaction in stereospecific syntheses. These results illustrate further the extraordinary usefulness of organopalladium compounds in organic syntheses.

Experimental Section

Reagents. Palladium acetate and chloride were purchased from Engelhard Industries, Inc. Phenylmercuric acetate and chloride were obtained from the Aldrich Chemical Co., Inc. *cis*- and *trans*-propenylbenzene were obtained from Chemical Samples Co. *p*-Anisylmercuric acetate was prepared by heating mercuric acetate with excess anisole at 100° for 1 hour and recrystallizing from alcohol. The chloride was obtained from the acetate by treating it with alcoholic lithium chloride.[2] Carbomethoxymercuric acetate was prepared by the method of Schoeller, *et al.*[3] Other materials were commercially available and were used without further purification.

Arylation of Propylene. All reactions listed in Tables I and II were carried out by the following procedure. A mixture of 5 mmol of the arylating agent and 5 mmol of the palladium compound was placed in a 180-ml heavy-walled Pyrex bottle. A magnetic stirring bar was added, the bottle was capped with a self-sealing butyl rubber-lined cap with two holes through the metal cap so that "hypodermic" injections could be made. The air inside the bottle was replaced through a "hypodermic" needle, first with nitrogen and then with propylene. The bottle was placed in a thermostat-controlled bath at the desired temperature and the propylene pressure was raised to 30 psig. The stirrer was started and 10 ml of the desired solvent, previously saturated with propylene at the same temperature under 30 psig, was added by means of a syringe. The reaction was then allowed to proceed for the desired time, keeping the propylene pressure at 30 psig by adding more as necessary. At the end of the reaction, the propylene was vented and a sample of the reaction mixture was removed and centrifuged to separate palladium metal. The clear solution obtained was removed and analyzed by glpc as soon as possible, although changes occurred relatively slowly in all cases. Analyses for the phenylpropenes were made at 85° on a 12 ft × 4 mm glass column packed with 5% polyphenyl ether (5P4E) and 5% Bentone 34 on 80–100 mesh Chromosorb Q (14 g packing). The anisylpropenes were analyzed on a similar column but at 150°.

Methylation of Styrene. A mixture of 1.12 g (5 mmol) of palladium acetate, 1.37 g (5 mmol) of methylmercuric acetate, 2 ml of styrene, and 8 ml of methanol was stirred at 30° for 1 hr and analyses were carried out as described above.

Carbomethoxylation of 1-Hexene. A mixture of 3.2 g (10 mmol) of carbomethoxymercuric acetate,[3] 20 ml of methanol, and 2 ml of 1-hexene was stirred magnetically in an ice bath and 2.3 g (10 mmol) of palladium acetate was added. The solution became black and it was allowed to stir without cooling at room temperature, for 2 hr. Analyses by glpc on a 6-ft Apiezon N on Chromosorb W column at 125° showed the solution to be 0.19 *M* in methyl 3-heptenoate and 0.14 *M* in methyl *trans*-2-heptenoate. There were at least three minor unknowns present also. Heating the reaction mixture to 100° for 1 hr had very little effect upon the yield or composition of the product mixture found. The products were identified by carbon-hydrogen analyses and by the nmr spectra of the pure components isolated by preparative glpc. The first compound eluted was methyl 3-heptenoate. *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.17; H, 9.76. The nmr spectrum in deuteriochloroform solution had bands at 0.87 (triplet of relative area 3), 1.45 (multiplet of area 2), 1.98 (multiplet of area 2), 2.98 (doublet of area 2), 3.64 (singlet of area 3), and at 5.50 ppm (complex groups of area 2). The vinyl protons at 5.5 ppm were poorly resolved and it was not possible to measure the coupling constant to determine stereochemistry.

The second compound eluted was methyl *trans*-2-heptenoate. *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.09; H, 9.79. The nmr spectrum had peaks at 0.90 (triplet of relative area 3), ~1.4 (two overlapping complex groups of area 4), 2.16 (complex group of area 2), 3.70 (singlet of area 3), 5.77 (pair of triplets of area 1), and at 6.95 ppm (pair of triplets of area 1). The vinyl-methylene coupling constants were 7 and 1 Hz and the vinyl coupling constant was 16.5 Hz indicating it was the *trans* isomer.

2,4,6-Triisopropylphenylmercuric Chloride. A mixture of 20 g of 1,3,5-triisopropylbenzene, 200 ml of acetic acid, 1 ml of 72% perchloric acid, and 16 g of mercuric acetate was stirred at room temperature overnight after initially warming the solution slightly to dissolve all of the mercuric acetate. The reaction mixture was then diluted with ice-water and pentane and 10 g of lithium chloride was added. The colorless precipitate which formed was filtered, washed well with water, and crystallized from 95% ethanol. There was obtained 9.1 g of long, shiny colorless needles, mp 136°. *Anal.* Calcd for $C_{15}H_{23}ClHg$: Hg, 45.65; Cl, 8.07. Found: Hg, 46.3; Cl, 8.16. The nmr spectrum in deuteriochloroform showed two doublet methyl absorptions at 1.33 and 1.23 ppm (area ratio 2:1), with coupling constants of 6.5 Hz and 7.1 Hz. The tertiary isopropyl hydrogens were at 2.9 ppm and they consisted of two overlapping septuplets while the aromatic protons (singlet) were at 7.01 ppm.

***trans*-2,4,6-Triisopropylstilbene.** A mixture of 0.88 g (2 mmol) of 1,4,6-triisopropylphenylmercuric chloride, 2 ml of styrene, and 20 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution[1] was stirred at room temperature overnight. The reaction mixture was then filtered to remove precipitated palladium and the solvent was evaporated at 30° under reduced pressure. The residue was purified by chromatography on alumina using pentane as solvent. The product was then recrystallized twice from methanol. There was obtained 0.25 g of colorless product, mp 83–84°.

Anal. Calcd for $C_{23}H_{30}$: C, 90.14; H, 9.86. Found: C, 90.09; H, 10.23. The nmr spectrum in deuteriochloroform had bands at 1.19 (12 protons, doublet with $J = 7.0$ Hz from methyls of *ortho*-isopropyl groups), 1.25 (6 protons, doublet with $J = 7.0$ Hz from methyls of *para*-isopropyl group), ~2.9, and 3.25 (3 protons, overlapping septuplets, tertiary isopropyl hydrogens), 6.4 and ~7.1 (vinyl hydrogens of an AB quartet, each of area 1 with $J = 16.7$ Hz), 6.96 (singlet from 2 aromatic protons), and 7.1–7.5 ppm (complex multiplet from unsubstituted phenyl ring protons).

Phenylation of Phenylpropenes. The experiments listed in Table III were carried out in 180-ml Pyrex bottles with magnetic stirring as in the phenylation of propene above. A mixture of 5 mmol of the phenylating agent, 10 ml of solvent, and 2 ml of the phenylpropene were placed in the bottle. The mixture was stirred in a thermostated bath at the desired temperature for at least 10 min and then 5 mmol of the palladium compound was added and the bottle was capped and stirred for the desired time. A sample was then removed by syringe, centrifuged, and analyzed immediately by glpc on a 6 ft × $^1/_4$ in. stainless steel column packed with Apiezon "N" on Chromosorb W. The diphenylpropenes eluted at 225° and the propenylbenzenes at 150°. *cis*- and *trans*-1,2-diphenyl-1-propenes were prepared as described for use as standards in the analyses. 1,1-Diphenyl-1-propene was obtained by the reaction of phenyllithium with propiophenone followed by distillation from sodium bisulfate and crystallization from methanol, mp 48–49° (lit.[4] mp 52°). 2,3-Diphenyl-1-propene could only be isolated by preparative glpc since larger quantities always rearranged on distillation. Samples of the compound isolated from the concentrated reaction mixture of 2-phenyl-1-propene with "phenylpalladium acetate" gave the expected analysis, uv spectrum and nmr spectrum. *Anal.* Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.84; H, 7.27. The ultraviolet spectrum in isooctane solution had λ_{max} at 242 mμ (ε 10,200). The nmr spectrum in deuteriochloroform had bands at 3.73 (broad singlet, 2 protons from methylene group), 4.95 (broad singlet, from *cis*-vinyl hydrogen), 5.40 (sharp singlet from *trans*-vinyl hydrogen), and 7.1 ppm (complex group from 10 aromatic protons).

***cis*-1,2-Diphenyl-1-propene.** A mixture of 6.7 g (20 mmol) of phenylmercuric acetate, 40 ml of acetonitrile, 8 ml of 98% *cis*-1-phenyl-1-propene, and 4.5 g (20 mmol) of palladium acetate was stirred at room temperature for 2 hr. The reaction mixture was then diluted with ether and filtered. The filtrate was washed with water twice, then with dilute aqueous potassium cyanide solution (5 g in 100 ml) to remove soluble palladium compounds, and then with water again. After drying over anhydrous magnesium sulfate the solution was distilled. There was obtained about 3.5 g of distillate, bp 100–110° (1.5 mm). The crude material was recrystallized from pentane and from methanol twice. The colorless product, mp 47° (lit.[5] 48°), weighed 0.90 g (23%). The uv spectrum of this material in isooctane solution had λ_{max} at 263 mμ (ε 10,700).

***trans*-1,2-Diphenyl-1-propene.** The preparation of this compound was carried out as in the preceding experiment employing *trans*-1-phenyl-1-propene instead of the *cis* isomer. There was obtained a slightly higher yield of pure *trans* product, mp 81–82° (lit.[5] 82°). The uv spectrum of this compound in isooctane showed λ_{max} 272 mμ (ε 20,500).

Carbomethoxylation of *trans*-1-Phenyl-1-propene. A mixture of 1.6 g (5 mmol) of carbomethoxymercuric acetate,[3] 10 ml of acetonitrile, and 2 ml of 99% *trans*-1-phenyl-1-propene was stirred in a Pyrex bottle in a 30° thermostated bath for 10 min and 1.15 g (5 mmol) of palladium acetate was added. After stirring for 2 hr a sample was removed, centrifuged, and analyzed by glpc on a 6 ft × $^1/_8$-in. Apiezon N on Chromosorb W column at 175°. A sample of the major product obtained was isolated from a reaction

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[2] O. Dimroth, *Ber.*, **35**, 2867 (1902).

[3] W. Schoeller, W. Schrauth, and W. Essers, *ibid.*, **46**, 2864 (1913).

[4] A. Klages, *Ber.*, **35**, 2647 (1902).

[5] E. Ellingboe and R. C. Fuson, *J. Amer. Chem. Soc.*, **55**, 2964 (1933).

mixture as above but with four times the quantities. The crude reaction mixture was diluted with ether, filtered, washed with water and aqueous potassium cyanide and finally with water again as in the 1,2-diphenylpropene preparations. The ether solution was dried over anhydrous magnesium sulfate and distilled. There was obtained 2.25 g of crude product of bp 80–100° (1.5 mm). Recrystallization twice from methanol at Dry Ice temperature gave 0.80 g (23%) of methyl *trans*-2-methylcinnamate, mp 38–39° (lit.[6] 37–38°). The nmr spectrum of this product was identical with the reported spectrum.[6] *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.16; H, 7.00.

Carbomethoxylations of *cis*-1-Phenyl-1-propene. The reaction was carried out as in the preceding example using *cis*-1-phenyl-1-propene instead of the *trans* isomer. The major component in the product mixture was isolated by filtering and concentrating the reaction mixture under reduced pressure and separating the compound by preparative glpc. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.66; H, 6.91. The nmr spectrum of this material in deuteriochloroform had bands at 2.03 (three protons, doublet with $J = 1.4$ Hz from C-methyl group); 3.55 (sharp singlet, three protons from ester methyl group), 6.58 (one proton, quartet from vinyl hydrogen), and 7.16 ppm (single peak of relative area 5 from aromatic protons). Thus, the product is methyl *cis*-2-methylcinnamate. Isolation and nmr analyses of the minor product from the reaction mixture in the same manner showed it to be a mixture of olefinic compounds not containing an appreciable amount of methyl *trans*-2-methylcinnamate, since methyl ester absorption at around 3.7 ppm was absent from the spectrum. About 7% of the unreacted excess *cis*-1-phenyl-1-propene had isomerized to the *trans* isomer at the end of the reaction time.

Carbomethoxylation of 2-Phenyl-1-propene. This reaction was carried out as in the carbomethoxylation of *cis*-1-phenyl-1-propene using 2-phenyl-1-propene instead of the *cis* olefin. Analysis of the products and isolation as above showed the major product to be methyl 3-phenyl-3-butenoate. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.58; H, 7.09. The nmr spectrum in deuteriochloroform had bands at 3.45 (doublet, two protons of the methylene group), 3.57 (singlet, three protons from the methyl ester group), 5.16 (doublet, one proton, $J = 1.5$ Hz from a vinyl hydrogen), 5.46 (singlet, one proton on vinyl carbon), and 7.20 ppm (complex multiplet of relative area 5 from aromatic protons). The minor product in the reaction mixture was methyl *trans*-3-methylcinnamate judging by a comparison of its nmr spectrum with that reported for the known compound.[6]

Phenylation of Methyl *trans*-Crotonate. A mixture of 1.7 g (5 mmol) of phenylmercuric acetate, 10 ml of acetonitrile, and 2 ml of methyl *trans*-crotonate was stirred magnetically in a thermostated bath at 30° and 1.15 g (5 mmol) of palladium acetate was added. Stirring was continued for 2 hr and a sample was removed, centrifuged, and analyzed by glpc at 175° on a 6-ft Apiezon N on Chromosorb W column. The major product was shown to be methyl *trans*-3-methylcinnamate by comparison of its nmr spectrum, obtained by isolating a small sample by preparative glpc with that of the known compound.[6] *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.59; H, 7.14. This material had the mp 33–35° while 27° has been reported.[5] The minor product was probably methyl 3-phenyl-3-butenoate judging by its retention time.

***trans*-3-Methylcinnamic Acid.** A mixture of 2.0 g of *trans*-crotonic acid, 3.4 g (10 mmol) of phenylmercuric acetate, 20 ml of acetonitrile, and 2.3 g (10 mmol) of palladium acetate was stirred at room temperature overnight. The reaction mixture was then filtered through Celite and the filtrate was evaporated at 30° under reduced pressure to a dark oil. The residue was taken up in ether and the solution was extracted twice with 50-ml portions of saturated sodium bicarbonate. Acidification of the bicarbonate solution gave the crude acid. After recrystallization from aqueous methanol, there was obtained 0.10 g (6%) of colorless solid, mp 96–97° (lit.[7] mp 98.5°). *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.08; H, 6.17. The nmr spectrum in deuteriochloroform had bands at 2.58 (doublet, three protons of methyl group, $J = 1.5$ Hz), 6.08 (multiplet, one from vinyl hydrogen), 7.30 (multiplet, five protons from the phenyl group), and 11.80 ppm (broad singlet of carboxyl hydrogen).

***cis*-3-Methylcinnamic Acid.** A reaction was carried out as above but using 2.9 g of 85% *cis*-crotonic acid[8] in place of 2 g of the *trans* acid. The product was isolated in the same manner also except that after acidification of the bicarbonate extracts the acid was extracted with methylene chloride. After drying and evaporating the methylene chloride, the crude product was crystallized twice from hexane. There was obtained 0.20 g (24%) of colorless needles, mp 131° (lit.[7] mp 131.5°). *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.85; H, 6.05. The nmr spectrum in deuteriochloroform had bands at 2.20 (doublet, $J = 1.8$ Hz, three protons of c-methyl group), 5.86 (quartet, $J = 1.8$ Hz, one proton of the vinyl group), 7.22 (five aromatic protons), and 10.45 ppm (broad singlet from the carboxyl proton).

Phenylation of Methyl Methacrylate. A reaction was carried out as described above for the phenylation of methyl *trans*-crotonate using methyl methacrylate instead of the crotonate ester. After 2 hr reaction time analyses were made as before by glpc. The major product was isolated by preparative glpc and shown to be methyl α-benzylacrylate by carbon–hydrogen analyses and its nmr spectrum. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.00; H, 6.66. The nmr spectrum in deuteriochloroform had bands at 3.61 (doublet, $J = 1$ Hz, methylene group), 3.69 (singlet from ester methyl group), 5.41 (narrow multiplet, one vinyl proton), 6.18 (narrow multiplet, one vinyl proton) and at 7.18 ppm (broad singlet from five aromatic protons). The minor product from this reaction was similarly shown to be methyl *trans*-2-methylcinnamate. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.44; H, 6.93. The nmr spectrum was the same as that reported for the compound in the literature[6] and as found above.

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(6) H. Kasiwagi, N. Nakagawa, and J. Niwa, *Bull. Chem. Soc. Jap.*, **36**, 410 (1963).

(7) R. Stoermer, F. Grimm, and E. Laage, *Ber.*, **50**, 959 (1917).

(8) C. Rappe, *Acta Chem. Scand.*, **17**, 2766 (1963).