

of a dianion from water into the micellar nonaqueous phase could therefore increase its reactivity.

These general explanations of the role of electrostatic effects upon the heterolysis of the phosphorus-oxygen bond are consistent with the observation that the cationic micelle decreases the activation energy of the reaction.

The reaction between hydroxide ion and the aryl phosphate dianion is not assisted to any appreciable extent by CTA micelles. This result is at first sight surprising, but we have observed that incorporation of one anion into the micelle strongly inhibits approach of another, as shown by the inhibition studies. Also the micellar catalysis itself shows that a dianion on the micelle tends to separate into two monoanions, and therefore the micelle should not encourage anions to come together, as would be required for reaction between hydroxide ion and either of the aryl phosphate dianions. In making this assessment of the inability of CTA micelles to catalyze the reaction between hy-

dride ion and the dinitrophenyl phosphate dianions we are assuming that sodium hydroxide, acting as an electrolyte, does not have a large inhibiting effect upon the CTA-catalyzed heterolysis of the aryl phosphate dianion to phenoxide and metaphosphate ions. The rate inhibition by added salts decreases markedly with increasing charge density of the anion, *e.g.*; chloride or mesylate is an ineffective inhibitor as compared with the bulkier anions. There are linear relations between the surface potential for monolayers of stearyltrimethylammonium ions and logarithm of the ionic strength of sodium chloride,²⁰ but the Stern equation takes into account not only ionic strength, but also the size of the ions located around the micelle and interactions such as van der Waal's forces and hydrophobic bonding,²¹ and our results suggest that simple ionic atmosphere effects are relatively unimportant for bulky anions.

(20) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press Inc., New York, N. Y., 1961, p 76.

(21) O. Stern, *Z. Elektrochem.*, **30**, 508 (1924); ref 20, p 85.

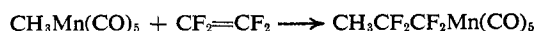
Arylation, Methylation, and Carboxyalkylation of Olefins by Group VIII Metal Derivatives

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Abstract: Aryl, methyl, and carboxyalkyl derivatives of group VIII metal salts, particularly palladium, rhodium, and ruthenium salts, react with olefins to produce aryl-, methyl-, or carboxyalkyl-substituted olefins, and reduced metal salt or metal. The reaction may be made catalytic with respect to the metal salt by employing cupric chloride or cupric chloride, air, and hydrogen chloride as reoxidants. The reaction is insensitive to oxygen and water and, therefore, provides an extremely convenient method for the synthesis of a wide variety of olefinic compounds.

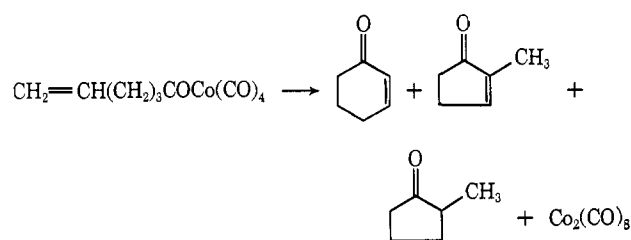
Addition reactions of nontransition metal alkyls and aryls to olefins are well known. Much less is known about the addition reactions of alkyl and aryl transition metal compounds. Presumably such reactions are responsible for the olefin polymerization reactions caused by combinations of alkylating or arylating agents and titanium, vanadium, or chromium salts. Only a few reasonably clear examples of the addition of transition metal alkyls to olefins without the formation of polymers have been reported. The addition of methylmanganese pentacarbonyl to tetrafluoroethylene¹ and the cyclization of 5-hex-



enoylcobalt tetracarbonyl to a mixture of cyclohexenone, 2-methylcyclopentenone, and 2-methylcyclopentanone² are two of the best examples. The present paper reports a study of the reaction of simple aryl and alkyl derivatives of group VIII metals with olefins.

(1) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 218 (1963).

(2) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3116 (1963).



Results and Discussion

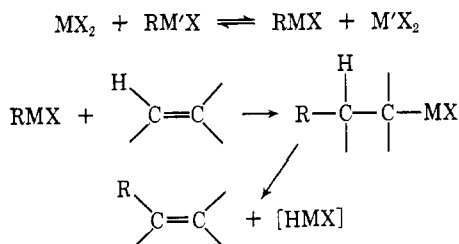
Group VIII metal alkyls and aryls have been prepared by reaction of the metal halides with Grignard reagents and alkali metal alkyls. Isolatable products have been obtained only from platinum halides³ or from phosphine-metal halide complexes⁴ and certain other complexes containing "stabilizing" ligands.

Even with these stabilizing ligands, saturated alkyl derivatives (with β -hydrogen substituents) of the group VIII metals are generally unstable with respect to the olefin and the metal hydride.⁴ We chose to prepare

(3) M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 299 (1951).

(4) For example, see J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959); G. Calvin and G. E. Coates, *ibid.*, 2008 (1960).

group VIII metal alkyls and aryls by exchange reactions from the less reactive alkylating or arylating agents to be able to have various functional groups present in the reaction components and to be able to use polar organic solvents for the reactions. Although Grignard reagents and the like can be used under very special conditions, lead, tin, and particularly mercury alkyls and aryls are preferred as alkylating or arylating agents. Homogeneous solutions of group VIII metal salts and the alkylating or arylating agents in polar solvents such as methanol, acetonitrile, or acetic acid react, probably reversibly, to form what are believed to be solvated alkyl or aryl group VIII metal salts. The latter species are unstable and generally decompose at room temperature to coupling product, or olefin if β hydrogens are present in the alkyl group. In the presence of olefins, however, alkyls without β hydrogen groups and aryls apparently add to the olefin-forming alkylethyl or arylethyl-metal salts which then rapidly decompose into metal hydride and alkylated or arylated olefin. Presumably, the metal hydride would be

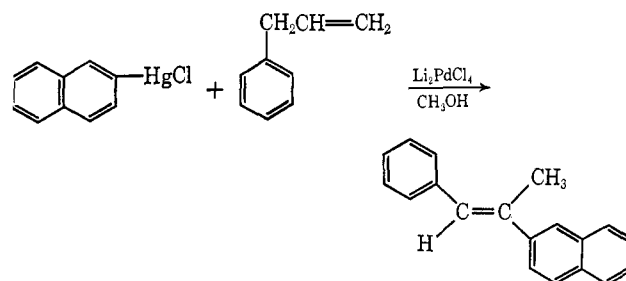


capable of reducing olefins in the reaction mixture. Since the reactant olefin is normally present in excess and would be generally more reactive than the product olefin, it would be the one reduced. Hydrogenated products corresponding to the alkylated or arylated olefin products have not been detected in any of our reactions. The major part of the metal hydride appears to decompose without further reaction into the free metal (or other reduced species) and an acid.

At least small amounts of arylated olefins seem to be obtained with all group VIII metal salts under some conditions. Results are given in Table I. In most examples, yields of highly purified products are reported and the actual yields are, no doubt, considerably higher.

Palladium salts have been found to be the most generally useful, with rhodium and ruthenium salts next best. The anion present in the catalyst appears to have little influence on the reaction provided the salt has some solubility in the reaction medium. Generally, chlorides were used because of their availability and solubility, most often lithium palladium chloride. The olefin arylation or alkylation reaction takes place at room temperature in the presence of air and moisture or even in aqueous organic solutions, in a few minutes to several hours, to give from a few per cent to near quantitative yields of products. With unsymmetrical olefins, the alkyl or aryl group is generally added exclusively to the less substituted carbon atom of the double bond. In no examples have we found mixtures resulting from addition two ways to unsymmetrical olefins, although *cis* and *trans* mixtures are found. Increasing substitution on the olefinic carbons decreases the reactivity of the olefin in the arylation reaction. Some tri- and tetrasubstituted

olefins react so slowly that decomposition of the aryl metal salt intermediate to biaryl is the major reaction. Olefin isomerization occurs with some olefins under the reaction conditions. For example, the reaction of 2-chloromercurinaphthylene with allylbenzene and a lithium palladium chloride catalyst gave large amounts of 2-(2-naphthyl)-1-phenyl-1-propene rather than only 1-(2-naphthyl)-3-phenyl-1-propene. Since recovered



starting olefin is largely isomerized, it appears that the isomerization and arylation or alkylation reaction are independent reactions. Isomerization may be largely avoided by using a reaction mixture containing only acetate as the anion. Thus, phenylmercuric acetate and allylbenzene, with palladium acetate, yield only 1,3-diphenylpropene (73% yield) while with a chloride system 20% 1,2-diphenyl-1-propene is formed along with only 7% of 1,3-diphenylpropene.

Practically any arylmercuric salts (or lead or tin aryls as well) will function as the arylating agent in these reactions. In general, strong electron-supplying groups (*i.e.*, *p*-methoxyl, *o*-hydroxyl, *p*-diethylamino) decrease yields, while good coordinating groups such as amino very much retard or even completely stop the reaction, because the group VIII metal compound forms a stable, unreactive complex with the coordinating group. In the aliphatic series, methyl and carboalkoxy groups have been added to olefins in reasonable yields. Limited work with other aliphatic derivatives without β hydrogen groups indicated that additions do occur but yields have been very low. Examples of methylations and carboxyalkylations of olefins are given in Table II.

In the arylation of allylic ethers and esters, the use of chloride salts is best avoided. The problem is that the allylic ethers and acetates are converted, more or less completely, into allylic halides under the reaction conditions and the arylation of allylic halides produces allylaromatics rather than cinnamyl halides.⁵

The usefulness of the olefin arylation reaction is limited by the expense of the group VIII metal employed. Fortunately, metals such as palladium and rhodium are readily reoxidized under some reaction conditions and need be used in only catalytic amounts. At room temperature, cupric chloride, ferric salts, and mercuric salts (except halides) reoxidize palladium. Cupric chloride can be regenerated from cuprous chloride with oxygen (air) and hydrogen chloride also under olefin arylation conditions so that the reaction can be carried out catalytically with respect to both palladium and copper. In the catalytic reaction, when concentrated solutions of cupric chloride are employed (>0.5 M), 1-aryl-2-chloroethane derivatives are also

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

Table I. Arylation of Olefins by Group VIII Metal Aryls

Product	Arylating agent	Prepared from ^a		Olefin	Solvent	Yield, %
		Group VIII metal compd				
Styrene	Diphenylmercury	LiPdCl ₃	Ethylene ^b	CH ₃ CN	63 ^c	
Propenylbenzene	Diphenylmercury	LiPdCl ₃	Propylene ^d	CH ₃ CN	49 <i>trans</i> , ^e 10 <i>cis</i> ^e	
Anethole	<i>p</i> -Chloromercurianisole	LiPdCl ₃	Propylene ^e	CH ₃ CN	26 <i>trans</i> , ^e 6 <i>cis</i> ^e	
Cinnamaldehyde	Diphenylmercury	LiPdCl ₃	Acrolein	CH ₃ CN	60 ^e	
Benzalacetone	Diphenylmercury	LiPdCl ₃	1-Buten-3-one	CH ₃ CN	64 ^{e,f}	
Methyl cinnamate	Diphenylmercury	LiPdCl ₃	Methyl acrylate	CH ₃ CN	88 ^e	
Methyl cinnamate	Phenylmercuric chloride	LiPdCl ₃	Methyl acrylate	CH ₃ CN	53 ^e	
Methyl cinnamate	Phenylmercuric chloride	RuCl ₃	Methyl acrylate	CH ₃ OH	25 ^{e,g}	
Methyl cinnamate	Phenylmercuric chloride	RhCl ₃ · 3H ₂ O	Methyl acrylate	CH ₃ OH	60 ^e	
Methyl cinnamate	Phenylmercuric chloride	FeCl ₃	Methyl acrylate	CH ₃ OH	8 ^e	
Methyl cinnamate	Diphenylmercury	NiBr ₂	Methyl acrylate	CH ₃ CN	5 ^{e,h}	
Methyl cinnamate	Tetraphenyltin	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	100 ^e	
Methyl cinnamate	Tetraphenyllead	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	82 ^e	
Methyl cinnamate	Diphenylmercury	Pd(NO ₃) ₂	Methyl acrylate	CH ₃ OH	83 ^e	
Methyl cinnamate	Phenyltin trichloride	LiPdCl ₃	Methyl acrylate	CH ₃ OH	77 ^e	
Methyl cinnamate	Diphenyltin dichloride	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	75 ^e	
Methyl cinnamate	Phenylmagnesium bromide ^h	LiPdCl ₃	Methyl acrylate	THF-CH ₃ CN	8 ^e	
Ethyl cinnamate	Phenylmercuric chloride	Li ₂ PdCl ₄	Ethyl acrylate	C ₂ H ₅ OH	30 ^e	
3-(2-Naphthyl)acrylonitrile	2-Chloromercurinaphthylene	LiPdCl ₃	Acrylonitrile	CH ₃ CN	30 ⁱ	
Methyl 3-(2-naphthyl)acrylate	Di-2-naphthylmercury	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	35 ⁱ	
Methyl <i>p</i> -diethylaminocinnamate	<i>p</i> -Chloromercuridiethylaniline	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	22 ⁱ	
Methyl <i>m</i> -nitrocinnamate	<i>m</i> -Chloromercurinitrobenzene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	24 ⁱ	
Methyl <i>m</i> -methoxycarbonylcinnamate	<i>m</i> -Chloromercuribenzoic acid	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	54 ^{i,j}	
Methyl 3,4-dichlorocinnamate	1-Chloromercuri-3,4-dichlorobenzene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	45 ⁱ	
Methyl 3-(2-thienyl)acrylate	2-Chloromercurithiophene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	36 ⁱ	
Methyl <i>p</i> -acetamidocinnamate	<i>p</i> -Chloromercuriacetanilide	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	10 ⁱ	
Methyl <i>o</i> -hydroxycinnamate	<i>o</i> -Chloromercuriphenol	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	4 ⁱ	
Methyl <i>p</i> -phenylcinnamate	4-Chloromercuribiphenyl	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	2 ⁱ	
Methyl 5-chloro-2-hydroxycinnamate	4-Chloro-2-chloromercuriphenol	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	12.5 ⁱ	
Methyl 3,5-dichloro-2-hydroxycinnamate	2,4-Dichloro-5-chloromercuriphenol	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	11.4 ⁱ	
Methyl 3-nitro-4-methoxycinnamate	4-Chloromercuri-2-nitroanisole	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	40 ⁱ	
Methyl 3-nitro-4-chlorocinnamate	4-Chloromercuri-2-nitrochlorobenzene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	3 ⁱ	
Methyl 3-nitro-4,5-dichlorocinnamate	1-Chloromercuri-3-nitro-4,5-dichlorobenzene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	19 ⁱ	
Cinnamyl acetate	Phenylmercuric acetate	Pd(OAc) ₂	Allyl acetate	CH ₃ COCH ₃	63 ⁱ	
4-Methylstilbene	4-Chloromercuritoluene	Li ₂ PdCl ₄	Styrene	CH ₃ OH	47.5 ⁱ	
4-Isopropylstilbene	4-Chloromercuricumene	Li ₂ PdCl ₄	Styrene	CH ₃ OH	42.4 ⁱ	
4-Methoxycarbonylstilbene	4-Chloromercuribenzoic acid	Li ₂ PdCl ₄	Styrene	CH ₃ OH	26 ⁱ	
2-Styrylthiophene	2-Chloromercurithiophene	Li ₂ PdCl ₄	Styrene	CH ₃ OH	16 ⁱ	
4-Methoxy-3-nitrostilbene	4-Chloromercuri-2-nitroanisole	Li ₂ PdCl ₄	Styrene	CH ₃ OH	17.5 ⁱ	
3,5-Dichloro-2-hydroxystilbene	2,4-Dichloro-6-chloromercuriphenol	Li ₂ PdCl ₄	Styrene	CH ₃ OH	14.5 ⁱ	
2,3,4,5,6-Pentamethylstilbene	Pentamethylphenylmercuric chloride	LiPdCl ₃	Styrene	CH ₃ CN	42 ⁱ	
3-Formylstilbene	3-Chloromercuribenzaldehyde	Li ₂ PdCl ₄	Styrene	CH ₃ OH	38 ⁱ	
4-Methoxy-4'-phenylstilbene	4-Chloromercurianisole	Li ₂ PdCl ₄	4-Vinylbiphenyl	CH ₃ OH	11 ⁱ	
4-Methoxy-3-nitro-4'-phenylstilbene	4-Chloromercuri-2-nitroanisole	Li ₂ PdCl ₄	4-Vinylbiphenyl	CH ₃ OH	17 ⁱ	
2-(4-Methoxy-3-nitrophenyl)indene	4-Chloromercuri-2-nitroanisole	Li ₂ PdCl ₄	Indene	CH ₃ COOH	10 ⁱ	
1,2-Diphenyl-1-propene	Phenylmercuric chloride	Li ₂ PdCl ₄	1-Phenyl-1-propene	CH ₃ OH	21 ⁱ	
2- <i>p</i> -Anisyl-1-phenyl-1-propene	<i>p</i> -Chloromercurianisole	Li ₂ PdCl ₄	1-Phenyl-1-propene	CH ₃ OH	13 ⁱ	
1- <i>p</i> -Anisyl-2-(<i>m</i> -nitrophenyl)-1-propene	<i>m</i> -Chloromercurinitrobenzene	Li ₂ PdCl ₄	<i>trans</i> -Anethole	CH ₃ OH	7 ⁱ	
2-(2-Naphthyl)-1-phenyl-1-propene	2-Chloromercurinaphthylene	Li ₂ PdCl ₄	Allylbenzene	CH ₃ OH	18 ⁱ	
Dimethyl (1,3,5-trimethylbenzene)-2,4-bis(3-acrylate)	Bis(acetoxymercuri)mesitylene	LiPdCl ₃	Methyl acrylate	CH ₃ CN	17 ⁱ	
Dimethyl salicylaldehyde-3,5-bis(3-acrylate)	3,5-Bis(acetoxymercuri)-salicylaldehyde	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	13 ⁱ	
Dimethyl benzophenone-3,3'-bis(3-acrylate)	3,3'-Bis(chloromercuri)-benzophenone ^k	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	4 ⁱ	
Salicylaldehyde-3,5-bis(1-buten-3-one)	3,5-Bis(acetoxymercuri)salicylaldehyde	LiPdCl ₃	1-Buten-3-one	CH ₃ CN	1 ⁱ	
Dimethyl 3-nitrobenzene-1,5-bis(3-acrylate)	3,5-Bis(chloromercuri)nitrobenzene	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	18 ⁱ	

^a All reactions were carried out at room temperature for 15–24 hr. ^b At 45 psig. ^c Yield by gas chromatographic analyses. ^d At 40 psig. ^e At 30 psig. ^f 2,4-Dinitrophenylhydrazones, mp 221.5–222° (lit. mp 223°). ^g Yield after 24 hr at 40°. ^h Phenylmagnesium bromide in THF solution was added to the reaction mixture at Dry Ice temperature and the mixture was allowed to warm up to room temperature with stirring. ⁱ Yield of purified, isolated product. ^j Isolated as the methyl ester formed by heating the reaction mixture to boiling for 2 hr. ^k Crude mixture of mono- and bis(chloromercuri)benzophenones.

Table II. Methylation and Alkoxy carbonylation of Olefins by Palladium Salts

Product	Alkylating or alkoxy carbonylating agent	Prepared from Group VIII metal compd	Olefin	Solvent	Yield, ^a %
Methyl crotonate	CH ₃ HgCl	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	16
Methyl crotonate	(CH ₃) ₄ Sn	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	57
Methyl crotonate	(CH ₃) ₄ Pb	Li ₂ PdCl ₄	Methyl acrylate	CH ₃ OH	112
<i>trans</i> -1-Phenyl-1-propene	CH ₃ HgCl	Li ₂ PdCl ₄	Styrene	CH ₃ OH	75
<i>trans</i> -1-Phenyl-1-propene	(CH ₃) ₄ Sn	Li ₂ PdCl ₄	Styrene	CH ₃ OH	95
<i>trans</i> -1-Phenyl-1-propene	(CH ₃) ₄ Pb	Li ₂ PdCl ₄	Styrene	CH ₃ OH	108
Methyl acrylate	ClHgCOOCH ₃	Li ₂ PdCl ₄	Ethylene ^b	CH ₃ COOH	50
Methyl crotonate	ClHgCOOCH ₃	LiPdCl ₃	Propylene ^b	CH ₃ CN	16
Ethyl acrylate	CH ₃ COHgCOOC ₂ H ₅	LiPdCl ₃	Ethylene ^b	CH ₃ CN	50
Methyl cinnamate	CH ₃ COHgCOOCH ₃	Li ₂ PdCl ₄	Styrene	CH ₃ OH	33
Ethyl cinnamate	CH ₃ COHgCOOC ₂ H ₅	Li ₂ PdCl ₄	Styrene	C ₂ H ₅ OH	13

^a Yields determined by gas chromatography. ^b At 30 psig pressure.**Table III.** Catalytic Arylation of Olefins by Group VIII Metal Compounds

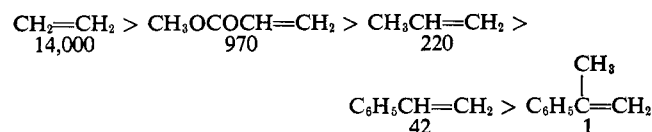
Product	Arylating agent	Prepared from Catalyst	Reoxidant	Olefin	Solvent	<i>t</i> , ^a °C	Time, hr	Yield, %
Methyl cinnamate	Phenylmercuric chloride	Li ₂ PdCl ₄	CuCl ₂	Methyl acrylate	CH ₃ OH	RT	2	57 ^b
Methyl cinnamate	Phenylmercuric chloride	Li ₂ PdCl ₄	CuCl ₂ , NaCl, O ₂ , HCl	Methyl acrylate	CH ₃ OH	RT	24	60 ^{b,c}
Methyl cinnamate	Diphenylmercury	Pd(NO ₃) ₂	Fe(NO ₃) ₃ ·9H ₂ O	Methyl acrylate	CH ₃ OH	RT	24	37 ^d
Methyl cinnamate	Diphenylmercury	Pd(NO ₃) ₂	Hg(NO ₃) ₂ ·H ₂ O	Methyl acrylate	CH ₃ OH	RT	24	37 ^d
Methyl 3-methyl-3-phenyl-acrylate	Phenylmercuric chloride	Li ₂ PdCl ₄	CuCl ₂	Methyl crotonate	CH ₃ OH	RT	24	24 ^{b,e}
Methyl 2-methyl-3-phenyl-acrylate	Phenylmercuric chloride	Li ₂ PdCl ₄	CuCl ₂	Methyl methacrylate	CH ₃ OH	RT	24	35 ^b
3-(2-Naphthyl)acrolein	Di-2-naphthylmercury	Li ₂ PdCl ₄	CuCl ₂	Acrolein	CH ₃ OH	RT	24	8 ^{b,f}
Methyl <i>p</i> -methoxycarbonyl-cinnamate	<i>p</i> -Chloromercuribenzoic acid	Li ₂ PdCl ₄	CuCl ₂	Methyl acrylate	CH ₃ OH	RT	24	20 ^b
Methyl <i>p</i> -methoxycinnamate	<i>p</i> -Acetoxymercurianisole	Pd(OAc) ₂	Hg(OAc) ₂	Methyl acrylate	CH ₃ COOH	60	2	27 ^d
<i>trans</i> -1,3-Diphenylpropene	Phenylmercuric acetate	Pd(OAc) ₂	Hg(OAc) ₂	Allylbenzene	CH ₃ COCH ₃	RT	24	8 ^b
3-Phenylbutenyl acetate	Phenylmercuric chloride	LiPdCl ₃ ^g	CuCl ₂ ^g	Crotyl acetate	CH ₃ CN	RT	4	15 ^b
Cinnamyl ethyl ether	Phenylmercuric acetate	Pd(OAc) ₂	Hg(OAc) ₂	Allyl ethyl ether	CH ₃ COCH ₃	RT	5	42 ^d (25)

^a RT = room temperature. ^b Yield of isolated product (100% basis). ^c There was also found a 10% yield of methyl 2-methoxy-2-phenylpropionate. ^d Yield determined by gas chromatography. ^e An 8% yield of methyl 2-chloro-3-phenylbutyrate was also obtained. ^f Isolated as the 2,4-dinitrophenylhydrazone. ^g Dicyclohexylethylamine added to remove HCl.

formed.⁶ Examples of catalytic olefin arylations are given in Table III.

Various complications arise with some vinylic and allylic derivatives such as the halides, esters, and ethers, in the arylation reaction. These will be described in the following publications.^{5,7}

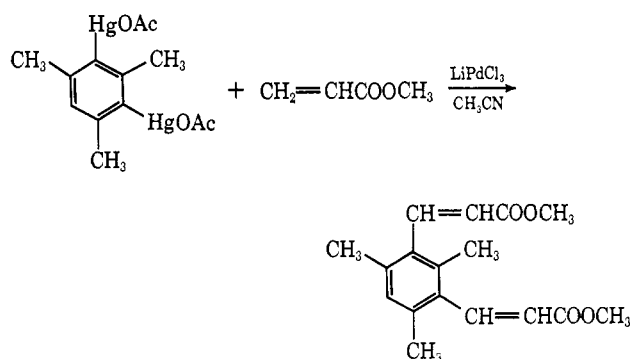
That the olefin arylation reaction is a true organometallic reaction and not a radical or ionic reaction is shown by the fact that ethylene is the most reactive olefin in the reaction. The following relative rates were determined by carrying out competitive reactions with limited amounts of the group VIII metal compound (lithium palladium chloride).



Another interesting feature of the olefin arylation reaction is the lack of serious steric effects. For example, bis(acetoxymercuri)mesitylene reacted with methyl acrylate and a lithium palladium chloride catalyst under normal conditions to form dimethyl 1,3,5-trimethylbenzene-2,4-bis(3-acrylate) in 20% yield.

(6) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5538 (1968).

(7) R. F. Heck, *ibid.*, **90**, 5535 (1968).



The olefin arylation reaction, therefore, provides a very convenient route to a wide variety of olefin derivatives.

Experimental Section

Materials. Anhydrous palladium chloride and rhodium trihydride were from Englehard Industries, Inc. Ruthenium trichloride, chloroplatinic acid, anhydrous cupric chloride, and palladium nitrate came from the Fisher Scientific Co. Palladium acetate was from the City Chemical Corp. Mercuric acetate, mercuric oxide, and lithium chloride were products of the J. T. Baker Co. Acetonitrile, obtained from Custom Service Chemicals, Inc., was purified by passage through molecular sieves before use. Other materials were commercially available samples which were used as received or were prepared as described below.

Lithium palladium chloride solutions (0.1 *M* usually) were prepared by stirring 2 equiv of anhydrous lithium chloride with 1 equiv of anhydrous palladium chloride overnight at room temperature in the solvent desired. Lithium chloride (1 mol) per mole of palladium chloride dissolves in acetonitrile, while 2 mol dissolve in methanol, ethanol, and acetic acid.

Mercurials. Phenylmercuric chloride was obtained from the Aldrich Chemical Co., Inc. Diphenylmercury was from Eastman Organic Chemicals. *p*-Tolylmercuric chloride was supplied by the City Chemical Corp. 2-Naphthylmercuric chloride and bis-2-naphthylmercury were products of the Metallomer Laboratories. 4-Chloromercuribenzoic acid was obtained from Columbia Organic Chemicals Co., Inc.

p-Chloromercurianisole was prepared by the method of Dimroth.⁸ The *o*- and *p*-chloromercuriphenols were prepared as described in ref 9. *m*-Chloromercurinitrobenzene was prepared as described by Kapproth and Westheimer.¹⁰ 1-Chloromercurithiophene was obtained by the procedure of Cherbuliez and Giddey.¹¹ 3,5-Bis(chloromercuri)salicylaldehyde was prepared as described by Whitmore.¹²

Carbomethoxy- and carbethoxymurcuric acetates and chlorides were prepared by the method of Schoeller, *et al.*¹³

Other mercurials were prepared as described below. Analyses of the mercurials were generally poor because they are very insoluble materials and difficult to purify. In all examples, subsequent arylation reactions with the crude mercurials showed that they contained at least substantial amounts of the expected products. The mercurations carried out in 72% perchloric acid are potentially explosive. We have had no problems but all operations were carried out behind a 12-in. concrete barricade until the reaction mixtures were diluted with water.

***p*-Chloromercuridiethylaniline.** To a stirred slurry of 32 g of mercuric acetate in 150 ml of alcohol was added 15 g of diethylaniline. The mixture was stirred overnight and the insoluble product was filtered from the solution, dissolved in warm acetone, filtered from a little insoluble material, and treated with a saturated aqueous solution containing 0.2 mol of lithium chloride. After the solution was stirred for a few minutes, the solid was filtered and air dried. There was obtained 36 g of colorless solid of mp 190° dec after recrystallization from toluene.

Anal. Calcd for $C_{16}H_{14}NClHg$: Hg, 52.20; Cl, 9.23. Found: Hg, 52.21; Cl, 9.03.

***p*-Chloromercuricumene.**¹⁴ A solution of 94 g of mercuric acetate, 400 ml of acetic acid, 10 ml of 70% perchloric acid, and 120 g of cumene was stirred at room temperature for 6 hr. The resulting mixture was poured into 500 ml of water containing 25 g of sodium chloride with stirring. The product was recrystallized from ethanol. There was obtained 60.57 g of colorless needles with mp 179–180°.

Anal. Calcd for $C_{9}H_{11}ClHg$: Hg, 56.47; Cl, 9.98. Found: Hg, 56.42; Cl, 10.3.

Chloromercurimesitylene. A solution of 32 g of mercuric acetate and 24 g of mesitylene in 200 ml of methanol was allowed to react at room temperature for about 17 hr and filtered. The filtrate was poured into a flask with 0.2 mol of calcium chloride and steam distilled until no more mesitylene came over. The solid remaining was filtered and recrystallized from ethanol. There was obtained 7.23 g of colorless solid, mp 202–203°.

Anal. Calcd for C_9H_7HgCl : Hg, 56.47; Cl, 9.98. Found: Hg, 57.8; Cl, 9.7.

2,4-Bis(acetoxymurcuri)mesitylene. A mixture of 20 ml of mesitylene, 64 g of mercuric acetate, 100 ml of methanol, and 1.0 ml of 70% perchloric acid was refluxed for 1 hr. The cooled solution was filtered and the filtrate was cooled in a Dry Ice-acetone bath. The crystals which separated were filtered, dissolved in 300 ml of hot chloroform, filtered, and the product precipitated with pentane. There was obtained 19 g of colorless powder, mp 224–227°.

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(10) C. Kapproth and F. Westheimer, *J. Amer. Chem. Soc.*, **72**, 4461 (1950).

(11) E. Cherbuliez and C. Giddey, *Helv. Chem. Acta*, **35**, 162 (1952).

(12) F. C. Whitmore and E. B. Middleton, *J. Amer. Chem. Soc.*, **45**, 1330 (1923).

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

(14) R. Josephson of these laboratories kindly furnished the details of this preparation.

Anal. Calcd for $C_{18}H_{16}O_4Hg_2$: Hg, 62.94. Found: Hg, 62.3, 62.1.

4-Chloromercuribiphenyl. A mixture of 77 g of biphenyl, 80 g of mercuric acetate, 300 ml of acetic acid, and 3 ml of 70% perchloric acid was stirred at room temperature overnight. The thick slush was then poured into 1 l. of water. The solid was dissolved in about 1 l. of hot acetone and filtered. About 1 mol of lithium chloride was added, and the mixture was stirred and diluted with water. The solid which separated was filtered, washed with acetone and warm benzene several times, and air dried. There was obtained 14 g of colorless product which did not melt below 360°. A sample was recrystallized from toluene for analyses.

Anal. Calcd for $C_{12}H_8HgCl$: Hg, 51.53; Cl, 9.11. Found: Hg, 53.2; Cl, 9.2.

4-Chloromercuri-2-nitroanisole. A solution of 310 g of *o*-nitroanisole and 310 g of mercuric acetate in 1 l. of acetic acid containing 5 ml of 70% perchloric acid was stirred at room temperature for 3 days. A solution of 1.2 mol of calcium chloride in methanol was then added. After stirring for a few minutes the solid present was separated by filtering, washed with aqueous methanol, and air dried. There was obtained 180 g of product, mp 245–247°. A sample after recrystallization from toluene melted at 282–284°.

Anal. Calcd for $C_7H_5O_3NClHg$: Hg, 51.67; Cl, 9.13. Found: Hg, 52.2; Cl, 9.1.

4-Chloro-2-chloromercuriphenol. A solution of 127.5 g of mercuric acetate in a minimum of warm methanol was mixed with a saturated solution of 51.4 g of *p*-chlorophenol in warm methanol and the resulting solution was stirred at room temperature overnight. The solid formed was filtered, washed with cold methanol, and air dried. There was obtained 103 g of colorless 4-chloro-2-acetoxymurcuriphenol.

Anal. Calcd for $C_6H_3O_2ClHg$: Hg, 51.81; Cl, 9.16. Found: Hg, 51.8; Cl, 8.9.

The corresponding chloromercuri derivative was obtained in quantitative yield by slurrying the acetate with alcoholic calcium chloride.

2,4-Dichloro-6-chloromercuriphenol. A solution of 33 g of 2,4-dichlorophenol and 64 g of mercuric acetate in 100 ml of warm methanol was stirred at room temperature for 3 days. The crystals were washed with hot methanol, then slurried with 100 ml of acetone and 0.4 mol of lithium chloride. After stirring for 30 min, water added, and the solid was filtered, washed well with water, and air dried. There was obtained 47 g of colorless product.

Anal. Calcd for $C_6H_3Cl_3OHg$: Hg, 50.39; Cl, 26.72. Found: Hg, 50.0; Cl, 20.6.

***m*-Chloromercuribenzoic acid** was prepared by the method used for *m*-chloromercurinitrobenzene.¹⁰ To 5.5 g of yellow mercuric oxide dissolved in 250 ml of 64% perchloric acid was added 10 g of powdered benzoic acid. The benzoic acid dissolved and the mercurated product soon began to crystallize. After being stirred at room temperature overnight, the mixture was added to 75 g of sodium chloride in 750 ml of water. The precipitate was separated by filtering, washed with water, and dissolved in warm acetone, filtered, and reprecipitated with water. There was obtained 6.0 g of colorless product, mp 256.5–257.5°.

Anal. Calcd for $C_7H_5O_2ClHg$: Hg, 56.16; Cl, 9.93. Found: Hg, 55.0; Cl, 11.1.

3,4-Dichloromercuribenzene. A solution of 86 g of yellow mercuric oxide in 2 l. of 72% perchloric acid was stirred with 100 ml of *o*-dichlorobenzene overnight at room temperature behind a heavy barricade. A solution of 0.6 mol of calcium chloride in 2 l. of water was slowly added, and the solid produced was separated by filtering and rinsed several times with water. The solid was dissolved in acetone containing 0.5 mol of LiCl, filtered, and precipitated with water. The colorless powder was separated by filtration, washed with water, and air dried giving 108 g of product, mp 204–205°. A sample was recrystallized from toluene for analyses, mp 206.0–207.5°.

Anal. Calcd for $C_6H_2Cl_2Hg$: Hg, 56.02; Cl, 27.84. Found: Hg, 55.9; Cl, 24.8.

3-Chloromercuribenzaldehyde. To a stirred solution of 86 g of yellow mercuric oxide in 2 l. of 72% perchloric acid was added remotely from behind a heavy barricade 120 ml of benzaldehyde, dropwise. The resulting clear brown solution was stirred at room temperature under nitrogen overnight. Then 0.5 mol of calcium chloride in 2 l. of water was added slowly (also remotely from behind a barricade) keeping the temperature below 40°. The resulting slurry was cooled in an ice bath. The tan solid which separated was washed with cold water. The product was then dissolved in warm acetone containing 0.5 mol of LiCl, filtered from a small

amount of solid and reprecipitated by adding water. The solid was filtered, washed with water, and dried under reduced pressure at room temperature. The tan solid obtained weighed 95.3 g, mp 228–229°.

Anal. Calcd for C_7H_5OClHg : Hg, 58.80; Cl, 10.39. Found: Hg, 59.3; Cl, 10.3.

4-Chloro-3-nitrochloromercuribenzene was prepared the same way as 3,4-dichlorochloromercuribenzene, employing 94 g of *o*-nitrochlorobenzene in place of *o*-dichlorobenzene. Precipitation from acetone containing LiCl gave a fine colorless powder. There was obtained 117.7 g of product, mp 211–213°. It may be further purified by extraction with methanol in a Soxhlet extractor. The product precipitated from the methanol, mp 228–229°.

Anal. Calcd for $C_6H_3Cl_2O_2NHg$: Hg, 51.09; Cl, 18.06. Found: Hg, 50.8; Cl, 17.8.

Mercuriation of Benzophenone. A solution of 11 g of mercuric oxide in 500 ml of 60% perchloric acid was stirred at room temperature with 20 g of benzophenone for 2 days. This mixture was then poured into 2 l. of cold water containing 50 g of sodium chloride. After stirring for 1 hr, the solvent was decanted and the pasty product was washed several times with water and dissolved in 100 ml of boiling acetone. The acetone solution was filtered, and water was added to the filtrate until it became cloudy. After cooling to -5° , the solid formed was filtered, and air dried. There was obtained 4.5 g of colorless product, mp 251–252°.

Anal. Calcd for $C_{13}H_9OClHg$: Hg, 48.07; Cl, 8.50. Found: Hg, 49.3, 48.9; Cl, 7.6, 7.7.

5-Chloromercuri-3-nitro-1,2-dichlorobenzene. To a mixture of 22 g of yellow mercuric oxide and 29 g of powdered 2,3-dichloronitrobenzene was added 500 ml of 72% perchloric acid remotely from behind a barricade. The mixture was stirred and heated in a thermostated water bath at 65° for 24 hr. The mixture was allowed to cool to room temperature and a solution of 0.25 mol of calcium chloride in 400 ml of water was added slowly, also remotely from behind a heavy barricade. The solid product was washed thoroughly with water, extracted several times with hot hexane to remove unreacted dichloronitrobenzene, and reprecipitated from acetone containing lithium chloride by diluting with water. The colorless solid obtained after water washing and air drying weighed 36 g, mp 285–286°.

Anal. Calcd for $C_6H_2Cl_3NO_2Hg$: Hg, 46.97; Cl, 24.91. Found: Hg, 44.9; Cl, 24.3.

3,5-Bis(chloromercuri)nitrobenzene. A mixture of 4.3 g of yellow mercuric oxide, 100 ml of 72% perchloric acid and 1 ml of nitrobenzene was stirred at 65° behind a heavy safety shield for about 20 hr. After cooling to room temperature, a solution of 25 mmol of calcium chloride in 200 ml of water was added slowly. After stirring for 10 min, the solid present was separated by filtration and dissolved in about 250 ml of warm acetone containing 20 mmol of LiCl. The solution was filtered from a small amount of insoluble material and the product was precipitated by adding water. The gelatinous solid formed was filtered, washed with water, and air dried. There was obtained 4.1 g of solid which had no melting point.

Anal. Calcd for $C_6H_3O_2NCl_2Hg_2$: Hg, 67.63; Cl, 11.95. Found: Hg, 65.8; Cl, 11.85.

Methyl 3-Chloromercuribenzoate. 3-Chloromercuribenzoic acid (50 g) was extracted in a Soxhlet apparatus with 300 ml of methanol containing 3 ml of concentrated sulfuric acid. About 1 week was required to extract most of the acid. The methanol slurry was cooled in ice water and the precipitated solid was washed several times with aqueous methanol and air dried. There was obtained 30.5 g of product, mp 207–208°.

Anal. Calcd for $C_8H_7O_2ClHg$: Hg, 54.04; Cl, 9.55. Found: Hg, 52.4; Cl, 9.8.

Methyl 4-chloromercuribenzoate was obtained in the same way as methyl 3-chloromercuribenzoate starting with 4-chloromercuribenzoic acid (Columbia Organic Chemicals Co.). The product did not melt below 300° .

Anal. Calcd for $C_8H_7O_2ClHg$: Hg, 54.04; Cl, 9.55. Found: Hg, 53.3; Cl, 8.9.

General Procedure for Alkylation or Arylation of Olefins with Organomercury, -lead and -tin Compounds. Mixtures of the organometallic compound, the olefin in equivalent amount (or better, twofold or more excess), and solvent were stirred and the group VIII metal compound was added as a solid or as a solution. Stirring was continued overnight at room temperature. Generally, enough organometallic reagent was added to produce a concentration between 0.1 and 1.0 *M*. A more concentrated solution could not be used, because the slurries obtained could not be stirred

effectively. Gaseous olefins were added under pressure, usually 30 psi was sufficient. Methanol, acetic acid, ethanol, or acetonitrile was usually the solvent. Generally, acetonitrile gave lower yields than the other solvents. The products (if soluble) are isolated by filtering to remove precipitate and distilling under reduced pressure to remove the solvent. The product may be distilled directly from the residue or taken up in a solvent which does not dissolve the salts, such as methylene chloride, filtered, and then distilled or recrystallized.

In catalytic reactions, a slight excess of the oxidizing salt was added initially, and the group VIII metal compound was generally added in an amount between 0.01 and 1.0% of the oxidizing salt. Analyses of products by gas chromatography were carried out on 6-ft Apiezon N or Carbowax 20M columns. Specific examples of the reaction are given in detail below.

3-(2-Naphthyl)acrylonitrile. A mixture of containing 1.81 g of 2-naphthylmercuric chloride, 5 ml of acrylonitrile, and 50 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. The solvent was then evaporated under vacuum and the product was dissolved in hot methanol and filtered; water was then added until the solution became cloudy. After cooling, the crystals which separated were recrystallized twice from aqueous methanol. There was obtained 0.32 g (30%) of off-white crystals, mp 144–145°. Analytical data and infrared bands for the compound are given in Table IV.

Dimethyl *m*-Carboxycinnamate. A mixture of 2.5 g of *m*-chloromercuribenzoic acid, 7.0 ml of methyl acrylate, and 70 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature for 2 hr and then heated in a closed container at 80° for 2 hr. The mixture was then filtered and the filtrate was evaporated at room temperature under vacuum. The residue was extracted with boiling hexane. Concentration and cooling of the hexane extracts gave colorless crystals of the product. Two further recrystallizations from hexane gave 0.83 g (54%) of methyl *m*-carboxymethoxycinnamate, mp 79–80°. Infrared bands and analytical data are given in Table IV.

Methyl 3-(2-Thienyl)acrylate. A mixture containing 3.70 g of 2-chloromercurithiophene, 10 ml of methyl acrylate, and 100 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred 2 days at room temperature. The mixture was then filtered, the solvent was evaporated under vacuum, and the product was extracted with boiling hexane. The extracts were filtered, concentrated to about 50 ml, and cooled in Dry Ice. The crystalline solid which separated was recrystallized twice from hexane. There was obtained 0.85 g (36%) of yellow crystals, mp 40.0–40.2°, of methyl 3-(2-thienyl)acrylate. The analyses and infrared bands are reported in Table IV.

Methyl 3-Nitro-4,5-dichlorocinnamate. A mixture containing 4.27 g of 2,3-dichloro-5-chloromercurinitrobenzene, 5 ml of methyl acrylate, and 100 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. The solvent was evaporated under reduced pressure and the product extracted from the residue with boiling hexane. On cooling, the product crystallized from the hexane solution. Another crystallization from hexane containing a little benzene gave 0.53 g of off-white needles, mp 145–146°.

Dimethyl 3-Nitrobenzene-1,5-bis(3-acrylate). A mixture of 3.0 g of 3,5-bis(chloromercuri)nitrobenzene, 5 ml of methyl acrylate, and 110 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. The solvent was removed under reduced pressure and the product was extracted from the residue with hot chloroform. After evaporation of the chloroform and crystallization from benzene–hexane, there was obtained 0.27 g of colorless powder, mp 213.5–214.5°.

3-Formylstilbene. A mixture of 3.41 g of 3-chloromercuribenzenaldehyde, 5 ml of styrene, and 110 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. The reaction mixture was then concentrated under reduced pressure at room temperature. The product was extracted with boiling hexane. The hot hexane extracts were treated with decolorizing charcoal, filtered, concentrated, and cooled. The colorless solid obtained was recrystallized from hexane. There was obtained 0.78 g of product, mp 94.5–95.0°.

2,3,4,5,6-Pentamethylstilbene. A mixture of 3.83 g of pentamethylphenylmercuric chloride (prepared from pentamethylbenzene and mercuric acetate followed by reaction with chloride ion), 5 ml of styrene, and 110 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was extracted with boiling methylene chloride. The extracts were then chromatographed on alumina. Recrystallization of the solid, eluted with methylene chloride, from benzene–hexane gave 1.06 g of nearly colorless

Table IV. Properties and Analyses of Compounds Prepared by Olefin Arylation

Compound	Bp (mm) or mp (lit.), °C	Found, %			Calcd, %			Ir (cm ⁻¹) or uv spectrum, ^f mμ (ε) absorption spectrum
		C	H	Other	C	H	Other	
3-(2-Naphthyl)acrylonitrile	144–145	86.90	5.34	...	87.12	5.06	...	1612, 2015
Methyl 3-(2-naphthyl)acrylate	91–92	79.14	5.84	...	79.22	5.70	...	1640, 1710
Methyl <i>p</i> -diethylaminocinnamate	41.5–42.5	72.02	8.62	...	72.07	8.21	...	1635, 1700
Methyl <i>m</i> -nitrocinnamate	121–122 (123–124) ^a	57.85	4.73	6.52 (N)	57.97	4.38	6.76 (N)	1650, 1720
Methyl <i>m</i> -methoxycarbonyl- cinnamate	79–80 ^b	65.17	5.45	...	65.44	5.49	...	1645, 1725
Methyl <i>p</i> -methoxycarbonyl- cinnamate	125.5–126.5	65.71	5.91	...	65.44	5.49	...	1640, 1720
Methyl 3,4-dichlorocinnamate	117–118 ^c	51.95	3.82	31.04 (Cl)	51.98	3.49	30.69 (Cl)	1650, 1720
Methyl 3-(2-thienyl)acrylate	40.0–40.5	57.25	5.00	...	57.12	4.79	...	1640, 1710
Methyl <i>p</i> -acetamidocinnamate	193–194	65.41	6.20	...	65.74	5.98	...	1640, 1705, 3440
Methyl <i>o</i> -hydroxycinnamate	136–137 (137) ^d	1640, 1700
Methyl <i>p</i> -phenylcinnamate	147.0–147.5	80.50	6.19	...	80.65	5.92	...	1640, 1720
Methyl 3-chloro-6-hydroxy- cinnamate	211–212	56.58	4.56	...	56.48	4.27	...	1645, 1710
Methyl 3,5-dichloro-2-hydroxy- cinnamate	188–189	48.53	3.63	27.70 (Cl)	48.61	3.26	28.70 (Cl)	1645, 1715
Methyl 3-nitro-4-methoxy- cinnamate	130.0–130.5	55.75	5.18	...	55.69	4.68	...	1625, 1710
Methyl 3-nitro-4-chlorocinnamate	116.5–117.0	50.37	3.44	5.91 (N)	49.70	3.34	5.80 (N)	1650, 1725
Methyl <i>p</i> -methoxycinnamate	89–90 (90) ^e	68.25	6.39	...	68.73	6.30	...	1640, 1715
3-(2-Naphthyl)acrolein	2,4-DNP 268.0–268.5	62.57	3.94	...	62.98	3.89
4-Methylstilbene	123.5–124.5 (119.5) ^g	92.53	7.48	...	92.74	7.26	...	324 (sh) (16,700), 311 (27,800), (29,300), 238 (sh) (9700), 299 (15,300), 224 (14,700)
4-Isopropylstilbene	90.0–91.0	91.70	8.35	...	91.84	8.16	...	324 (sh) (18,000), 311 (30,500), 297 (31,200), 237 (sh) (10,450), 229 (16,400)
4-Methoxycarbonylstilbene	167.5–168.0	81.11	6.23	...	80.65	5.92	...	320 (38,100), 313 (sh) (22,900), 289 (37,400), 226 (13,800)
Methyl 3-nitro-4,5-dichloro- cinnamate	145–146	43.48	2.29	5.35 (N)	43.50	2.56	5.07 (N)	1620, 1715
2,3,4,5,6-Pentamethylstilbene	154–154.5	91.19	8.80	...	91.14	8.86	...	273 (16,200), 247 (14,800)
3-Formylstilbene	94.5–95.0	85.75	6.32	...	86.51	5.81	...	295 (26,200), 258 (16,800), 234 (sh) (14,600)
4-Methoxy-4'-phenylstilbene	236.0–236.5	88.30	6.34	...	88.08	6.33	...	321 (42,700)
4-Methoxy-3-nitro-4'-phenyl- stilbene	213.5–214.5	76.22	5.31	4.29 (N)	76.11	5.17	4.23 (N)	321 (55,000)
1,3-Diphenylpropene	145–147 (3 mm)	92.77	7.64 ^h	...	92.74	7.26	...	966
3-Phenylbutenyl acetate	100–140 (3 mm)	76.39	7.30 ^h	...	75.76	7.42	...	1240, 1630, 1745
Cinnamyl ethyl ether	89–93 (2 mm)	82.15	9.48	...	81.44	8.70	...	292 (890), 283 (1300), 250 (15,200)
2-Styrylthiophene	105.0–105.5	77.03	5.65	...	77.38	5.41	...	321 (18,600), 228 (10,800)
4-Methoxy-3-nitrostilbene	129.0–129.5	70.37	5.54	5.31 (N)	70.58	5.13	5.49	305 (sh) (31,900), 300 (32,100), 222 (19,600)
3,5-Dichloro-2-hydroxystilbene	89.5–90.0	63.54	4.03	26.5 (Cl)	65.65	3.80	26.75 (Cl)	345 (sh) (10,000), 331 (26,600), 321 (sh) (24,700), 308 (27,700), 295 (31,200), 227 (29,600)
2-(4-Methoxy-3-nitrophenyl)indene	147.5–148.0	71.91	5.33	...	71.90	4.90	...	312 (36,600), 246 (sh) (16,700), 238 (22,700), 232 (22,700)
1,2-Diphenyl-1-propene	88–89	92.75	7.46	...	92.74	7.26	...	272 (20,000)
2- <i>p</i> -Anisyl-1-phenyl-1-propene	107–108	85.35	7.49	...	85.67	7.19	...	272 (22,600)
1- <i>p</i> -Anisyl-2-(<i>m</i> -nitrophenyl)-1- propene	101.0–101.5	71.62	5.87	4.34 (N)	71.36	5.61	5.20 (N)	295 (sh) (20,500), 273 (22,300)
1-(2-Naphthyl)-2-phenyl-1-propene	147.5–148.0	93.39	6.90	...	93.60	6.60	...	297 (21,200), 264 (33,400), 224 (31,400)
Dimethyl (1,3,5-trimethylbenzene)- 2,4-bis(3-acrylate)	129.0–129.5	70.50	7.27	...	70.81	7.00	...	1640, 1720
Dimethyl salicylaldehyde-3,5-bis- (3-acrylate)	193–195	62.04	5.14	...	62.07	4.86	...	1640, 1665, 1715
Dimethyl benzophenone-3,3'- bis(3-acrylate)	113–114	71.71	5.36	...	71.99	5.18	...	1645, 1660, 1720
Salicylaldehyde-3,5-bis- (1-buten-3-one)	88.0–88.5	69.34	5.66	...	69.76	5.46	...	1640, 1660, 1700
Dimethyl 3-nitrobenzene- 1,5-bis(3-acrylate)	213.5–214.5	57.69	4.54	4.86 (N)	57.73	4.50	4.81 (N)	1650, 1715

^a J. J. Sudborough and L. L. Lloyd, *J. Chem. Soc.*, **73**, 85 (1934). ^b Alkaline hydrolysis gave an acid of mp 275–276°. Calcd for C₁₀H₈O₄: C, 62.50; H, 4.19. Found: C, 62.39; H, 4.59. The melting point of *m*-carboxycinnamic acid is reported to be 275° by A. F. Titley, *J. Chem. Soc.*, **131**, 2581 (1928). ^c Alkaline hydrolysis gave an acid of mp 220–221°. The melting point of 3,4-dichlorocinnamic acid is reported to be 217–218° by C. Walling and K. B. Wolfstirn, *J. Amer. Chem. Soc.*, **69**, 852 (1947). ^d B. B. Dey, R. H. R. Rao, and T. R. Seshadri, *J. Ind. Chem. Soc.*, **11**, 743 (1934). ^e I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, London, 1953. ^f Isooctane was the solvent. ^g H. Meerwein, *et al.*, *J. Prakt. Chem.*, **152**, 237 (1939). ^h Analytical sample purified by preparative gc.

prisms, mp 153–154°. Another crystallization gave 0.80 g of colorless needles, mp 154–155°.

4-Methoxy-4'-phenylstilbene. A mixture of 10 mmol of 4-vinylbiphenyl (Aldrich Chemical Co.), 10 mmol of 4-chloromercurianisole, and 110 ml of 0.1 M Li_2PdCl_4 in methanol was stirred overnight at room temperature. The solvent was removed under reduced pressure and the product was extracted from the residue with boiling benzene. On cooling, the benzene extracts deposited crystals of the product. A recrystallization from benzene gave 0.25 g of colorless fluorescent plates, mp 236.0–236.5°.

4-Methoxy-3-nitro-4'-phenylstilbene. A reaction was carried out as in the above example employing 2.7 g of 4-vinylbiphenyl and 3.88 g of 4-chloromercuri-2-nitroanisole. Isolation of the product in the same manner gave 0.56 g of yellow crystals, mp 213.5–214.5°.

Cinnamyl Ethyl Ether. A mixture of 31.8 g of phenylmercuric acetate, 20 ml of allyl ethyl ether, 15.9 g of mercuric acetate, 100 ml of acetone and 2.24 g of palladium acetate was stirred at room temperature. After about 4 hr, gas chromatographic analyses indicated that the solution was 0.35 M in cinnamyl ethyl ether. The mixture was then diluted with water and pentane and filtered through Celite. The solids were extracted thoroughly with pentane and combined with the original filtrate. The pentane layer was separated and the aqueous phase was extracted four more times with pentane. The combined pentane extracts were washed with water, aqueous sodium bicarbonate, and water again. After drying over anhydrous magnesium sulfate, the product was distilled under reduced pressure. There was obtained 4.51 g of colorless liquid, bp 84–95° (2 mm), which was about 90% cinnamyl ethyl ether by gas chromatographic analyses. Redistillation gave a purer product, bp 89–93° (2 mm). The nmr spectrum and the uv spectrum confirmed that the compound was the cinnamyl rather than the propenyl ethyl ether.

Cinnamyl Acetate. A mixture of 31.8 g of phenylmercuric acetate, 100 ml of 1.0 M allyl acetate, and 0.10 mol of palladium(II) acetate was stirred at room temperature overnight and then at 40–50° for 1 hr. The solution was then diluted with water and pentane and the product was isolated as in the preparation of cinnamyl ethyl ether. There was obtained 11.0 g of cinnamyl acetate, bp 104–110° (3 mm), which was about 95% pure by gas chromatographic analysis. The nmr spectrum confirmed the structure of the product.

3-Phenylbutenyl Acetate. A mixture containing 0.10 mol of phenylmercuric chloride, 0.10 mol of CuCl_2 , 20 ml of dicyclohexylethylamine, 10 ml of crotyl acetate and 100 ml of 0.1 M Li_2PdCl_4 in acetonitrile was stirred and cooled initially to about 25°. After 3 or 4 hr of stirring at room temperature, the product was isolated as cinnamyl ethyl ether above except the pentane extracts were washed with dilute sulfuric acid before the aqueous bicarbonate wash to remove dicyclohexylethylamine. Distillation under reduced pressure gave two fractions: (1) bp 59–100° (3 mm), 0.8 g which was about 25% 3-phenylbutenyl acetate by gas chromatographic analyses and (2) bp 104–140° (3 mm), 3.6 g which was about 75% pure. A purer sample was isolated by preparative scale gas chromatography, n_D^{25} 1.5251.

1,3-Diphenylpropene. A mixture of 0.10 mol of phenylmercuric acetate, 50 mmol of mercuric acetate, 100 ml of acetone, 20 ml of allylbenzene and 10 mmol of palladium acetate, was stirred at room temperature overnight. The mixture was then diluted with water and the product was extracted with pentane as was cinnamyl ethyl ether. Distillation under reduced pressure gave 1.8 g of colorless liquid, bp 145–147° (3 mm), which was about 90% pure *trans*-1,3-diphenylpropene. The compound was further purified by preparative scale gas chromatography. It solidified on cooling and had a strong band at 966 cm^{-1} indicating the *trans* form was present. The *cis* bands at 772 and 920 cm^{-1} were absent.¹⁵ The nmr spectrum of the product confirmed the structure.

4-Isopropylstilbene. A mixture of 3.42 g of *p*-chloromercuricume, 4 ml of styrene, and 110 ml of 0.1 M Li_2PdCl_4 in methanol was stirred at room temperature for 3 days. It was then filtered and concentrated under reduced pressure at room temperature. The product was extracted with boiling hexane. The extracts were concentrated and cooled to yield colorless crystals. Two further crystallizations from methanol gave 1.14 g (42.4%) of 4-isopropylstilbene, mp 90–91°. The analyses and ultraviolet absorption spectrum for this compound are given in Table IV.

Dimethyl (1,3,5-Trimethylbenzene)2,4-bis(3-acrylate). A mixture containing 3.26 g of 2,4-bis(chloromercuri)mesitylene, 5 ml of methyl acrylate, and 100 ml of 0.1 M Li_2PdCl_4 in acetonitrile was stirred at room temperature overnight. Precipitated palladium was filtered off and the filtrate concentrated under reduced pressure to a viscous oil. A few milliliters of methanol were added and the solution was cooled in Dry Ice. The solid which separated was recrystallized three times from aqueous methanol. There was obtained 0.20 g of colorless plates, mp 129.0–129.5°. Another 0.05 g of product was isolated by chromatographing the material remaining in the mother liquors.

The nmr spectrum of this product at 60 Mc in deuteriochloroform showed bands at –146 cps (singlet of relative area 9 from the three methyl groups on the benzene ring), –228 cps (singlet of relative area 6 from the two ester methyl groups), –356 cps (doublet with $J = 17$ cps, relative area 2 from the two protons of the vinyl group α to the ester group), –414 cps (broad singlet of relative area 1 from the aromatic proton), and at –465 cps (doublet with $J = 17$ cps, relative area 2 from the vinyl protons β to the ester group) with respect to tetramethylsilane as an internal standard. Analyses and infrared bands for this product are given in Table IV.

Salicylaldehyde-3,5-bis[1-(1-buten-3-one)]. A mixture of 3.19 g of 3,5-bis(acetoxymethyl)salicylaldehyde, 2 ml of vinyl methyl ketone, and 100 ml of 0.1 M Li_2PdCl_4 in acetonitrile solution was stirred at room temperature overnight. Three such mixtures were combined, diluted with water and methylene chloride, filtered, and extracted several times with methylene chloride. The combined extracts were washed twice with water and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was evaporated under reduced pressure. The residue was recrystallized twice from hexane. There was obtained 0.050 g of pale yellow crystals, mp 86–87°. Three further recrystallizations from hexane raised the melting point to 88.0–88.5°.

Dimethyl Salicylaldehyde-3,5-bis(3-acrylate). A mixture containing 4.90 g of 3,5-bis(acetoxymethyl)salicylaldehyde, 15 ml of methyl acrylate, and 160 ml of 0.1 M Li_2PdCl_4 in methanol was stirred at room temperature overnight. Precipitated palladium was filtered and the solvent was evaporated under reduced pressure at room temperature. The product was extracted with methylene chloride. The extract was then evaporated and the residue was recrystallized twice from absolute alcohol. There was obtained 0.274 g (13%) of pale yellow-green crystals of mp 193–195°. The nmr spectrum of the product in deuteriochloroform solution at 60 Mc had bands at –235 cps (two singlets of relative area 6 from the methyl groups), at –416, –432, –488, –506 cps (all doublets of relative area 1 each, from the four vinyl protons), at –517 and –524 cps (both doublets of total reactive area 2 from the aromatic protons), and at –648 cps (singlet of relative area 1 from the aldehyde proton) with respect to tetramethylsilane as an internal standard. The hydroxyl proton was not observed, probably because of line broadening from hydrogen bonding. Other properties of the product are given in Table IV.

Methyl *p*-Carbomethoxycinnamate. A mixture containing 3.6 g of *p*-chloromercuribenzoic acid, 1.6 g of cupric chloride, 1.0 ml of methyl acrylate, 8.0 ml of methanol, and 1.0 ml of 0.1 M Li_2PdCl_4 in methanol was stirred for 2 days at room temperature and then heated for 30 min in a closed container at 75°. The mixture was then filtered and the solvent was evaporated under vacuum. The residue was recrystallized twice from hexane and twice from crystals of mp 125.5–126.5°. Other properties are given in Table IV.

Methyl Cinnamate. In a 500-ml, three-necked flask provided with a condenser with a mercury-sealed gas outlet tube at the top, a stirrer, and a gas inlet tube which reached nearly to the bottom of the flask, was placed 62 g of phenylmercuric chloride, 20 g of sodium chloride, 2.0 g of cupric chloride, 120 ml of methanol, 20 ml of methyl acrylate, and 40 ml of 0.1 M Li_2PdCl_4 in methanol. The solution was stirred and kept at 40° in a thermostated bath, and a slow stream of oxygen was bubbled through. At 15-min intervals, 10-ml portions of freshly prepared 3 M hydrogen chloride in methanol were added. After five additions (50 ml), two more were made at 1-hr intervals. After being stirred at room temperature overnight, about three-fourths of the solvent was evaporated under reduced pressure at room temperature. The residue was diluted with water and the product was extracted with five portions of pentane. The extracts were washed once with water, dried over anhydrous magnesium sulfate, filtered, and distilled under reduced pressure. There was obtained 22.4 g of colorless product, bp 110–113° (6 mm). Gas chromatographic analyses showed that the product was 86% methyl cinnamate (60% yield),

(15) E. Raunio and W. A. Bonner, *J. Org. Chem.*, **31**, 396 (1966).

and 14% methyl 2-methoxy-3-phenylpropionate. A sample of the latter was isolated by preparative-scale gas chromatography.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.38; H, 7.34.

The nmr spectrum of this compound in deuteriochloroform at 60 Mc had bands at -150 cps (multiplet of relative area 2 from the benzylic protons), -185 cps (singlet of relative area 3 from the methoxyl group), -210 cps (singlet of relative area 3 from the ester group), and at -266 cps (four lines, $J_1 = 5.3$, $J_2 = 7.9$, of relative area 1 from the tertiary proton).

Measurements of Relative Rates of Reaction of Various Olefins with Phenylmercuric Chloride. 1. *Ethylene vs. Propylene.* In a 200-ml Pyrex pressure bottle containing a magnetic stirring bar was placed 1.0 mmol of phenylmercuric chloride. The bottle was closed, evacuated, and pressured to 5 psig with propylene and 25 psig with ethylene. The mixture was stirred and thermostated at 25.0° , and 10 ml of 0.1 M $LiPdCl_3$ in acetonitrile solution was injected by hypodermic syringe through the rubber-lined bottle cap. After 1 hr, reaction was complete. Gas chromatographic analyses showed that the solution contained 22 times as much styrene as 1-phenyl-1-propene and the concentration of styrene was very near 0.1 M. At 25.0° and 750 mm pressure 10 ml of acetonitrile dissolves 24.3 ml of ethylene and 69.3 ml of propylene. Thus, ethylene is about 60 times more reactive than propylene under these conditions.

2. *Styrene vs. Propylene.* In a 200-ml Pyrex pressure bottle containing a stirring bar was placed 1.0 mmol of phenylmercuric chloride. The bottle was closed, flushed with propylene, and pres-

sured to 25 psig with propylene. Then 0.5 ml of styrene was added at 25.0° , followed by 10 ml of 0.1 M $LiPdCl_3$ in acetonitrile solution. After 1 hr of stirring at 25.0° , analyses by gas chromatography showed that the solution was 0.063 M in 1-phenyl-1-propene (*trans*) and 0.0086 M in stilbene (*trans*). In a blank run under the same conditions, without the palladium or mercury compounds, the solution was found to be 0.60 M in propylene as determined by pressure drop. Since the styrene was initially present as a 0.41 M solution, propylene is about five times more reactive than styrene.

3. *Methyl Acrylate vs. Styrene.* A reaction was carried out as in the example above using 0.5 ml of methyl acrylate instead of propylene. After overnight stirring, gas chromatographic analyses showed that the solution was 0.050 M in methyl cinnamate and 0.017 M in stilbene (*trans*). Since the solution contained 5.55 mmol of methyl acrylate and 4.36 mmol of styrene initially, the relative rates of reaction are 2.3:1, respectively.

4. *α -Methylstyrene vs. Styrene.* A reaction was carried out as in the preceding example with 0.5 ml of α -methylstyrene in place of methyl acrylate. The reaction mixture was analyzed by gas chromatography and found to be 0.078 M in stilbene (*trans*) and 0.0017 M in 1,2-diphenyl-1-propene. Since the solution initially contained 3.87 mmol of α -methylstyrene and 4.36 mmol of styrene, the relative rates of reaction are 1:42, respectively.

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The Arylation of Allylic Alcohols with Organopalladium Compounds. A New Synthesis of 3-Aryl Aldehydes and Ketones

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Abstract: Arylpalladium salts, prepared *in situ* from arylmercuric salts and a palladium salt, react with primary or secondary allylic alcohols to produce 3-aryl aldehydes or ketones in low to high yields depending upon the mercurial and allylic alcohol used. Since the reaction is tolerant of most substituents, it provides a very convenient and useful new method for preparing a wide variety of 3-aryl aldehydes and ketones.

The arylation of olefins with aryl derivatives of the group VIII metals is a general reaction. Certain allylic compounds undergo reactions different from those of simple olefins because of the allylic substituent. Allylic ethers and esters react normally, producing cinnamyl ethers and esters, respectively,¹ but allylic halides lose halogen, forming allylaromatic compounds.² In this paper is reported another example of an unusual arylation reaction, the arylation of allylic alcohols.

Results

The arylation of primary and secondary allylic alcohols leads to the formation of 3-aryl aldehydes or ketones in low to high yields. Arylpalladium salts were found to be the most useful arylating agents. They were most conveniently prepared from arylmercuric salts, and palladium salts in the presence of the allylic alcohol. Various solvents, such as acetone, acetic acid, methanol, and ethanol, could be used but

the preferred solvent was acetonitrile. A variety of allylic alcohols have been arylated with various arylmercuric compounds and palladium salts. The results are summarized in Table I. Yields determined by gas chromatography were considerably higher than those found by isolation. Separation of the products from insoluble inorganic salts was probably not complete in most examples. As in the allyl ether arylations with chloride-containing systems,¹ dicyclohexylethylamine favored the reaction. It appears to prevent formation of halides from the allylic alcohol and by-product hydrogen chloride. These allylic halides react with the arylpalladium compounds to form allylic aromatics.² The amine also probably minimizes condensation of the product aldehyde because it neutralizes hydrogen chloride.

Little can be concluded about the effects of structure of the arylating group or of the allylic alcohol upon the reaction because of the limited amount of work done, but presumably the effects are similar to those found in the simple olefin arylation.¹ The reaction variables have by no means been exhaustively studied

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

(2) R. F. Heck, *ibid.*, **90**, 5531 (1968).