with $Hg(OOCCF_3)_2$] was taken up in anhydrous ether (15 ml) and reduced with lithium aluminum hydride (0.100 g, 2.63 mmol) under the same conditions used for the mercuration reaction in acetic acid to give a residue which was analyzed by GLC. The ratios of 5 to 6 are reported in Table I. Reactions of 1 with each salt carried out for each solvent under the same conditions but stopping after relatively longer contact times (1 hr for the reactions with the trifluoroacetate and 4 hr for the reactions with the acetate) yielded the same product composition within the experimental error. However, much longer contact times showed changes in the ratios between 5 and 6.

Acknowledgment. This work was supported in part by a grant from the Consiglio Nazionale delle Ricerche. We thank Dr. M. Ferretti for the gas–liquid chromatography and Dr. V. Nuti for the elemental analyses.

Registry No.—**1**, 2415-82-9; **2**, 771-98-2; **4a**, 56437-51-5; **4b**, 56437-52-6; **5**, 30689-79-3; **6**, 30689-80-6; **7b**, 56437-53-7; mercuric acetate, 1600-27-7; mercuric trifluoroacetate, 13257-51-7.

References and Notes

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Mercury in Organic Chemistry. VI.[1] A Convenient Stereospecific Synthesis of α,β-Unsaturated Carboxylic Acids and Esters via Carbonylation of Vinylmercurials

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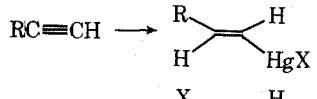
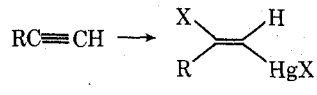
Vinylmercuric chlorides readily react with carbon monoxide (atmospheric pressure), lithium chloride, and palladium chloride in an alcohol solvent at low temperatures (<−20°) to give near-quantitative yields of α,β-unsaturated carboxylic esters in which the chloromercuri group is stereospecifically replaced by a carboalkoxy group. α,β-Unsaturated carboxylic acids may be obtained in an analogous fashion by employing 1–5% aqueous tetrahydrofuran as the solvent. The reaction accommodates a variety of functional groups and can also be effected using only catalytic amounts of palladium chloride or palladium on carbon if cupric chloride is used as a reoxidant. A mechanism involving vinyl- and acylpalladium intermediates is suggested.

The direct carbonylation of organomercurials is exceedingly difficult, requiring high temperatures and pressures and usually resulting in only very poor yields of carboxylic acids or their derivatives.[2,3] The addition of palladium salts generates organopalladium compounds[4] which are much more readily carbonylated.[5] Both the palladium exchange[6] and carbonylation[7] reactions have been determined to proceed with stereochemical retention of configuration. Unfortunately, the palladium-promoted carbonylation of alkyl-[6] and arylmercurials[8] gives poor yields of carboxylic acids or their derivatives and these reactions appear to be of rather limited synthetic utility. With the ready availability of a number of vinylmercurials through acetylene addition reactions (eq 1, 2)[9–11] and the ability of these reactions to accommodate a wide variety of functional groups, we were encouraged to examine some possible synthetic applications of these compounds. We wish to report now that the extremely facile palladium-promoted carbonylation of vinylmercurials provides an excellent new method for the preparation of α,β-unsaturated carboxylic acids and esters.

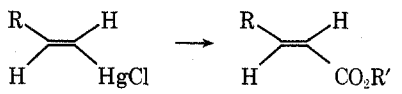

(1)


(2)

Results and Discussion

α,β-Unsaturated Esters. In order to determine the best conditions for converting vinylmercurials into α,β-unsaturated carboxylic esters, we have examined the stoichiometry of this reaction. Both styrylmercuric chloride (1 mmol) and *trans*-1-hexenylmercuric chloride (1 mmol) were treated with varying amounts of palladium chloride, lithium chloride, and methanol or ethanol under 1 atm of carbon monoxide at low temperatures, and the yield of ester determined by GLC analysis (eq 3). The results are indicated in Table I.

Several points are obvious from this study. Although excellent yields are obtained in almost all reactions, the combination of 1 equiv of palladium chloride and 2 equiv of

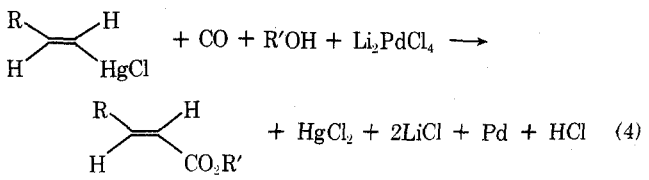


(3)

$R = C_6H_5, n\text{-}C_4H_9$
$R' = CH_3, C_2H_5$

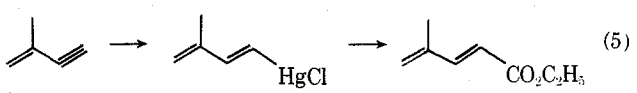
lithium chloride gives the best results. Styrylmercuric chloride gives higher yields than *trans*-1-hexenylmercuric chloride under comparable conditions and the yields in methanol are superior to those in ethanol. Use of a cosolvent resulted in sharply reduced yields of esters. The best yields are obtained by mixing the reagents at −78° where no reaction appears to occur and allowing the reaction mixture to slowly warm on its own to room temperature, at which time the reaction is complete.

Treatment of a wide variety of other vinylmercurials with carbon monoxide (1 atm), lithium chloride (2 equiv), and palladium chloride (1 equiv) in an alcohol solvent at low temperatures (−78° to room temperature) also results in near-quantitative yields of the corresponding α,β-unsaturated esters (eq 4) (see Table II). It should be noted that



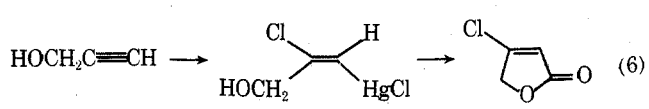
(4)

not only cyano and ester groups are readily accommodated by this reaction, but that the dienylmercurial derived from isopropenyl acetylene also gives an excellent yield of the α,β-γ,δ-unsaturated carboxylic ester (eq 5). Particularly in-



(5)

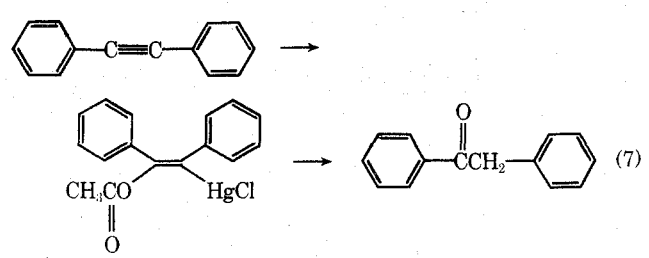
teresting is the last entry in Table II. Progargyl alcohol readily reacts with saturated aqueous solutions of mercuric chloride to give the *trans*-β-chlorovinylmercurial.[12] Subsequent carbonylation in diethyl ether provides the corresponding β-chlorobutenolide in 96% crude yield (eq 6). We



(6)

are currently extensively studying this novel new route to butenolides.

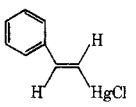
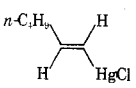
Several other β-substituted vinylmercurials were less successful, however. *trans*-3-Acetoxy-2-butenylmercuric chloride[13] gave several unidentified products in about equal amounts. On the other hand, *cis*-β-acetoxystilbenylmercuric chloride[14] gave a near-quantitative yield of deoxybenzoin characterized by comparison with an authentic sample (eq 7). We presently have no mechanistic explana-



(7)

tion for formation of this product other than simple protonolysis of the vinylmercurial or -palladium compound and subsequent hydrolysis of the enol acetate upon ammonium chloride work-up.

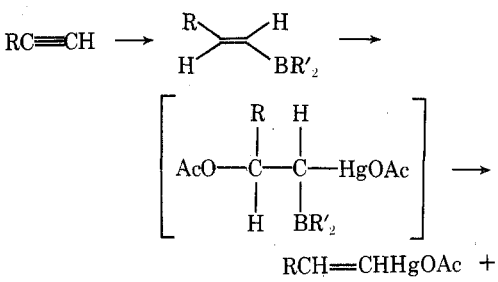
Table I
Stoichiometry of Vinylmercuric Chloride Carboalkoxylation

Vinylmercuric chloride	$PdCl_2$, mmol	LiCl, mmol	Alcohol	Temp, °C	Ester yield, %[a]
	0.5		CH_3OH	0	85
	0.5	1.0			95
	1.0				87
	1.0	2.0			100
			C_2H_5OH		88
			CH_3OH		88
				−20	95
				−78	99
			C_2H_5OH	0	67
				−20	95
				−78	95

[a] GLC analysis using an internal standard.

In most of these carbonylation reactions 1–2% yields of the stereochemically inverted product were obtained. However, 1-decenylmercuric chloride and methyl 11-chloromercuri-10-undecenoate give approximately 1:2 and 1:1.3 ratios of cis:trans mixtures, respectively. It was subsequently observed, however, that repeated recrystallization of the 1-decenylmercuric chloride eventually resulted in a mercurial which upon carbonylation gave pure (>99%) methyl *trans*-2-undecenoate in 98% isolated yield. However, the other vinylmercurial could not be as easily purified. These results suggest that the exchange and carbonylation reactions are highly stereospecific, but that the vinylmercurials themselves contain small amounts of the opposite isomer.

The low isomeric purity of the vinylmercurials obtained by the hydroboration–mercuration of 1-decyne and methyl 10-undecynoate is most unusual. We believe that stereospecificity is lost during mercuration of the intermediate vinylborane, possibly through a nonstereospecific addition–elimination sequence (eq 8). However, it is not at all clear

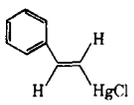
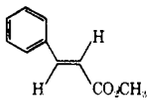
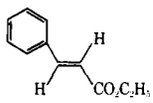
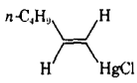
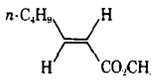
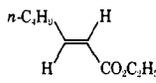
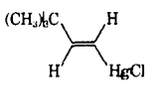
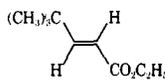
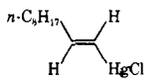
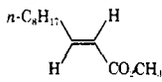
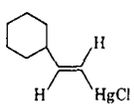
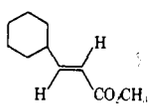
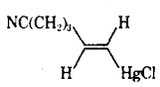
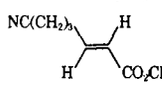
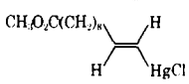
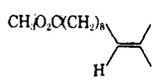
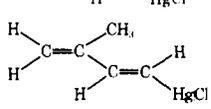
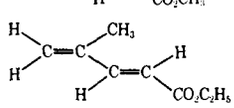
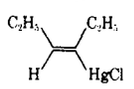
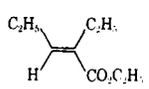
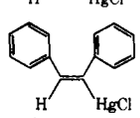
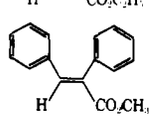
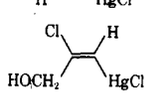
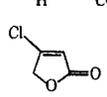


(8)

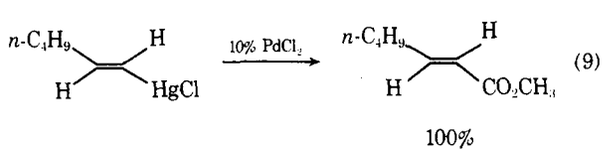
how the carbon chain length might affect the stereochemistry of such reactions. Side products in these mercuration reactions are also suggestive of attack upon the double bond of the vinylborane by mercuric acetate.[9] Furthermore, the halogenation of vinylboranes proceeds with exclusive attack upon the carbon–carbon double bond.[15,16] These results suggest that perhaps even the protonolysis of vinylboranes is proceeding by a highly stereospecific addition–elimination sequence and not direct electrophilic cleavage as previously assumed.[17]

The carbonylation reactions would achieve even greater synthetic utility if they could be carried out utilizing only catalytic amounts of palladium. This can indeed be accomplished very nicely by employing catalytic amounts of either palladium chloride or palladium on carbon and stoichiometric amounts of anhydrous cupric chloride (2 equiv) (eq 9–11).

Table II
Preparation of α,β-Unsaturated Carboxylic Esters

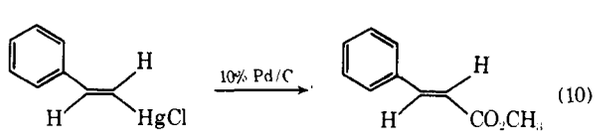
Vinylmercuric chloride	Registry no.	Carboxylic ester	Registry no.	% yield
	36525-03-8		1754-62-7	100[a]
			4192-77-2	99[a]
	50874-36-7		38693-91-3	98[a]
			54340-72-6	93[a]
	36525-02-7		22147-62-2	90[a]
	56453-77-1		56453-83-9	98
	36525-01-6		26429-99-2	96
	56453-78-2		56453-84-0	98
	56453-79-3 56453-80-6		13038-20-5 13038-18-1	98[b]
	56453-81-7		13369-24-9	93[a]
	36525-04-9		22147-74-6	85[a]
	16188-35-5		36854-27-0	99
	56453-82-8		56453-85-1	96[c]

[a] Yield by GLC analysis using an internal standard. [b] Vinylmercurial and ester are a mixture of cis and trans isomers. [c] Carbonylation in diethyl ether.



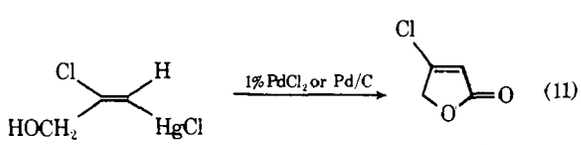
(9)

100%



(10)

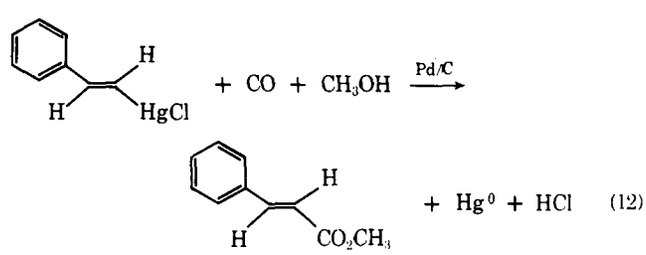
96%



(11)

96%

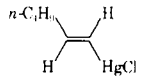
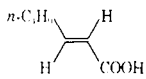
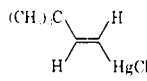
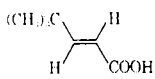
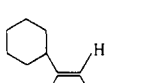
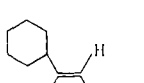
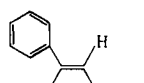
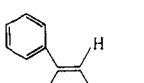
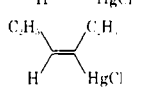
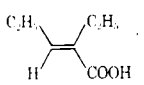
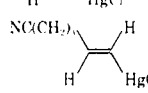
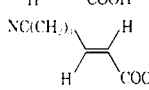
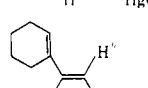
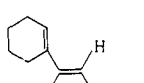
We have also examined possible palladium catalysis in the absence of added cupric chloride. Modest yields of ester can be obtained by employing 1 equiv of palladium on carbon (eq 12). Unfortunately, lesser amounts of palladium (10%) gave dismal yields (1–2%). In view of the hazardous nature of this reaction (two out of three caught fire!) and the low yields, Pd/C catalysis appears to be of little synthetic utility. Tetrakis(triphenylphosphine)palladium(0)



(12)

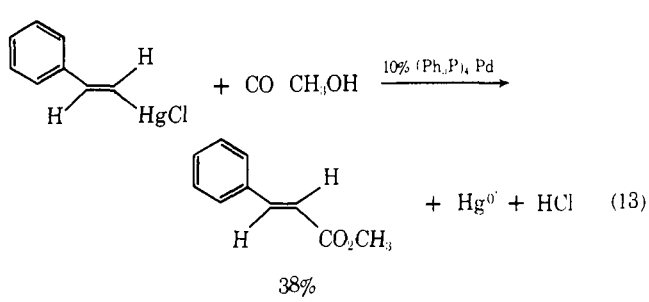
54%

Table III
Preparation of α,β-Unsaturated Carboxylic Acids

Vinylmercuric chloride	% aqueous THF	Carboxylic acid	Registry no.	% yield
	5		10352-88-2	98[a]
	2			99[a]
	5		16666-45-8	98
	5		56453-86-2	65
	2			82
	1			90
	0.5			77
	5		140-10-3	80
	1			30
	5		16403-07-9	85[a]
	2			60[a]
	5		56453-87-3	72
	2			65
	5		56453-88-4	45
	2			72
	1			57

[a] Yield by GLC analysis using an internal standard. [b] Registry no., 56453-89-5.

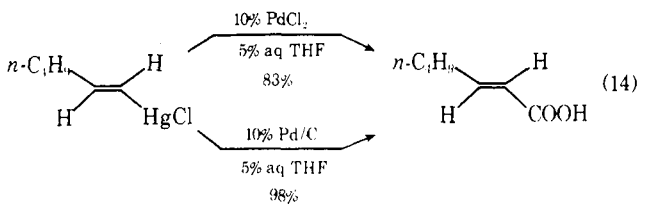
has also been examined as a possible catalyst, but was found wanting (eq 13). Thus, cupric chloride appears essential for high yields of ester.



(13)

α,β-Unsaturated Acids. Several obvious difficulties arose in attempting to extend the carbonylation reaction to the preparation of α,β-unsaturated carboxylic acids. The carboalkoxylation reactions required low temperatures (<20°) and alcohol as the solvent. Obviously we could not obtain homogeneous aqueous solutions of organomercurials at such very low temperatures. Instead we examined a variety of aqueous organic solvent systems (acetone, ether, tetrahydrofuran, dimethoxyethane) at the lowest of possible temperatures. Although an occasional reaction gave high yields, most of the reactions gave only poor yields and were highly irreproducible. We observed, however, that the yields seemed to improve by reducing the amount of water present in the system. With less than 10% water in tetrahydrofuran (THF) we were able to lower the temperature of the reaction to −78° and obtain reproducible results. Some representative yields of α,β-unsaturated acids are included in Table III. In most cases the highest yields were obtained by using 5% aqueous THF. In two examples, however, we obtained higher yields with lesser amounts of water. The aqueous carbonylation of styrylmercuric chloride also proved considerably more difficult than the analogous alcohol reactions which produced excellent yields under almost all conditions. In fact, carbonylation with 50% aqueous acetone at −20° produced *trans,trans*-1,4-diphenylbutadiene as the major product. In general, the yields of α,β-unsaturated carboxylic acids are slightly less than the corresponding esters.

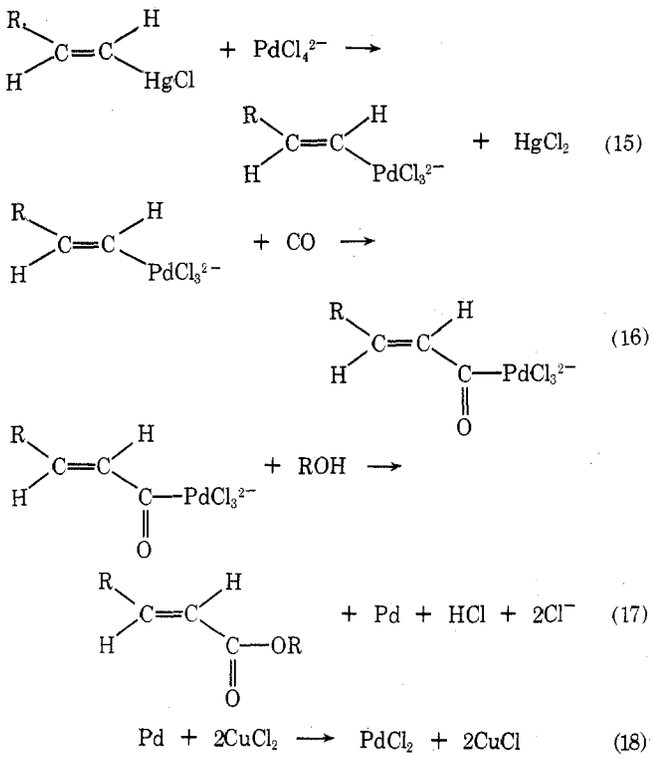
Once again we were able to effect these reactions using only catalytic amounts of either palladium chloride or palladium on carbon if cupric chloride (2 equiv) was employed (eq 14). Cupric acetate and 10% $PdCl_2$ under identical conditions gave only a 30% yield of *trans*-2-heptenoic acid.



(14)

α,β-Unsaturated Amides. We have attempted to extend the carbonylation of vinylmercurials to the synthesis of the corresponding amides. Carbonylation of styrylmercuric chloride in diethylamine under conditions identical with those used in the preparation of α,β-unsaturated esters resulted in 92% recovery of starting vinylmercurial. On the theory that the very basic diethylamine was coordinating too strongly with the palladium salt to allow exchange with the vinylmercurial, we examined the analogous reaction of much less basic pyrrole. Addition of pyrrole to the palladium salt resulted in a vigorous reaction, presumably electrophilic substitution on the aromatic ring. No further amidation reactions were attempted.

Mechanism. The palladium-promoted carbonylation of vinylmercurials undoubtedly proceeds by an initial mercury–palladium exchange reaction (eq 15), carbon monoxide insertion into the resultant vinylpalladium compound (eq 16), and subsequent solvolysis to give the α,β-unsaturated acid or ester and palladium metal (eq 17). In the catalytic reactions the palladium metal is reoxidized to palladium(II) by cupric chloride (eq 18). Support for this mech-



(15)

(16)

(17)

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl \quad (18)$$

anism is found in the many analogous reactions reported previously.[5] Presumably similar steps are involved in Heck's palladium-catalyzed carboalkoxylation of vinyl halides (eq 19).[18] The carbonylation reactions using palladi-

$$RCH{=}CHX \xrightarrow[CO/ROH/R_3N]{(Ph_3P)_2PdI_2} RCH{=}CHCO_2R \quad (19)$$

um on carbon or tetrakis(triphenylphosphine)palladium(0) in the absence of cupric chloride presumably involve initial mercury–palladium interchange via oxidation–reduction (eq 20). Alternatively, oxidative addition of the vinylmer-

$$RCH{=}CHHgCl + Pd^0 \longrightarrow RCH{=}CHPdCl + Hg^0 \quad (20)$$

curial to palladium(0) might provide a species capable of undergoing carbonylation.

Conclusion

Although the palladium-promoted carbonylation of alkyl-[6] and arylmercurials[8] has been observed previously, the reaction appears to be of little synthetic value owing to the low yields of carboxylic acids and derivatives obtained. We report here the first carbonylation of vinylmercurials. The ready availability of a wide variety of functionally substituted vinylmercurials, the exceedingly mild reaction conditions, the high stereospecificity, and the excellent yields of α,β-unsaturated carboxylic acids and esters suggest considerable preparative utility for this reaction.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless indicated otherwise. *trans*-3-Acetoxy-2-butenylmercuric chloride,[13] *cis*-β-acetoxystilbenylmercuric chloride,[14] and (*E*)-2-chloro-3-hydroxy-1-propenylmercuric chloride[12] were prepared according to literature procedures. All other vinylmercuric chlorides were prepared by hydroboration–mercuration of the appropriate alkyne.[9,10]

The following vinylmercurials have apparently not previously been reported.

trans-1-Decenylmercuric chloride, mp 102.5–103°.

Anal. Calcd for $C_{10}H_{19}ClHg$: C, 32.00; H, 5.10; Hg, 53.45. Found: C, 31.98; H, 5.20; Hg, 53.43.

trans-5-Cyano-1-pentenylmercuric chloride, mp 89.5–90°.

Anal. Calcd for C_6H_8ClHgN: C, 19.17; H, 2.53; Hg, 62.82. Found: C, 19.06; H, 2.54; Hg, 62.72.

Methyl *cis*- and *trans*-11-chloromercuri-10-undecenoate, mp 54–?.

Anal. Calcd for $C_{12}H_{21}ClHgO_2$: C, 33.26; H, 4.88; Hg, 46.29. Found: C, 33.21; H, 4.96; Hg, 46.43.

trans-3-Methyl-1,3-butadienylmercuric chloride: pale yellow crystals unstable toward heat or light; melts with decomposition; ^1H NMR peaks at δ 1.83 (s, 3 H, CH_3), 5.06 (s, 2 H, $=CH_2$), 6.00 (d, J = 18 Hz, 1 H, vinyl), and 6.58 (d, J = 18 Hz, 1 H, vinyl).

Anal. Calcd for C_5H_7ClHg: C, 19.81; H, 2.33; Hg, 66.17. Found: C, 19.61; H, 2.48; Hg, 66.02.

trans-(1-Cyclohexenyl)ethenylmercuric chloride, mp 170.5–171°.

Anal. Calcd for $C_8H_{11}ClHg$: C, 28.00; H, 3.23; Hg, 58.44. Found: C, 27.95; H, 3.36; Hg, 58.58.

Stoichiometry of Carboalkoxylation. The appropriate alcohol (5 ml), lithium chloride, palladium chloride, and a suitable hydrocarbon GLC internal standard were placed in a 25-ml round-bottom flask containing a septum inlet. A pressure-equalizing addition funnel containing the vinylmercuric chloride (1 mmol) and 5 ml of alcohol was placed on top of the flask. After cooling the reaction mixture to the appropriate temperature and flushing the system with carbon monoxide (a balloon works fine), the vinylmercurial was slowly added to the reaction mixture. After 1 hr at the low temperature the reaction mixture was allowed to slowly warm to room temperature and maintained there overnight. GLC analysis using an appropriate hydrocarbon internal standard gave the yields indicated in Table I.

Preparation of α,β-Unsaturated Carboxylic Esters. The following procedure for the preparation of methyl *trans*-β-cyclohexylacrylate is representative. Anhydrous lithium chloride (20 mmol), palladium chloride (10 mmol), and 100 ml of methanol were added to a well-dried 250-ml round-bottom flask containing a septum inlet and carbon monoxide inlet tube. The flask was cooled to −78° and *trans*-cyclohexylethenylmercuric chloride (10 mmol) was added. The flask was flushed thoroughly with carbon monoxide and the well-stirred reaction mixture was then allowed to slowly warm to room temperature over a 4-hr period and stirred overnight while maintaining a slight positive pressure of carbon monoxide. Ether and activated carbon were added to the reaction mixture, which was filtered, washed with saturated ammonium chloride, and dried over anhydrous sodium sulfate. Removal of the solvent provided 1.61 g (96%) of ester (essentially pure by GLC and ^1H NMR): ir max (neat) 2920, 2850, 1730, 1655, 1275, and 1170 cm^{-1}; ^1H NMR peaks (CCl_4) at δ 1.0–2.3 (br, 11 H, cyclohexyl), 3.63 (s, 3 H, OCH_3), 5.66 (d, J = 16 Hz, 1 H, vinyl), and 6.82 (dd, J = 9 and 16 Hz, 1 H, vinyl); *m/e* 168.1152 ± 0.0009 (calcd for $C_{10}H_{16}O_2$, 168.1150).

The following compounds were prepared in a similar fashion. Methyl *trans*-2-undecenoate: ir max (neat) 2915, 2840, 1730, 1660, 1270, and 1195 cm^{-1}; ^1H NMR peaks (CCl_4) at δ 0.89 (t, J = 5 Hz, 3 H, CCH_3), 1.30 (br, 12 H, CH_2), 2.13 (m, 2 H, allyl), 3.65 (s, 3 H, OCH_3), 5.69 (dt, J = 1 and 16 Hz, 1 H, vinyl), and 6.86 (dt, J = 7 and 16 Hz, 1 H, vinyl); *m/e* 198.1623 ± 0.0010 (calcd for $C_{12}H_{22}O_2$, 198.1620). Methyl *trans*-6-cyano-2-hexenoate: ir max (neat) 2940, 2240, 1750, 1660, 1275, and 1205 cm^{-1}; ^1H NMR peaks (CCl_4) at δ 1.5–2.0 (m, 2 H, CCH_2C), 2.0–2.5 (m, 4 H, CH_2CN and allyl), 3.58 (s, 3 H, OCH_3), 5.75 (dt, J = 1 and 16 Hz, 1 H, vinyl), and 6.78 (dt, J = 7 and 16 Hz, 1 H, vinyl); *m/e* 153.0799 ± 0.0015 (calcd for $C_8H_{11}NO_2$, 153.0790). Methyl 2-dodecenedioate, cis and trans mixture. Methyl α-phenylcinnamate, mp 77° (lit.[19] mp 77°). β-Chloro-$\Delta^{\alpha,\beta}$-butenolide, mp 52.5–53.0° (lit.[20] mp 52–53°).

All GLC yields were determined on reactions run on one-tenth the scale of the above preparative reactions using hydrocarbon internal standards. All retention times were identical with those of authentic samples.

Catalytic Esterification Reactions. β-Chloro-$\Delta^{\alpha,\beta}$-butenolide was prepared by modifying the above preparative procedure. The $PdCl_2$ was replaced by anhydrous $CuCl_2$ (20 mmol) and either 10% Pd/C (0.1 mmol) or $PdCl_2$ (0.1 mmol). Anhydrous diethyl ether replaced the alcohol solvent.

The methyl cinnamate and methyl *trans*-2-heptenoate yields were determined by GLC analysis using an appropriate hydrocarbon internal standard, carbon monoxide, the vinylmercuric chloride (1 mmol), methanol (10 ml), anhydrous cupric chloride (2 mmol), anhydrous lithium chloride (2 mmol), and either 10% Pd/C (0.1 mmol) or palladium chloride (0.1 mmol). Methyl cinnamate was prepared at 0°, methyl *trans*-2-heptenoate at −78°.

The stoichiometric Pd/C reaction was run just as above except

that the amount of Pd/C was increased to 1 mmol and the cupric chloride was omitted. Caution—fire hazard!

The yield of methyl cinnamate prepared by tetrakis(triphenylphosphine)palladium(0) catalysis was determined by GLC analysis on a reaction run at −78° employing methanol (10 ml), styrylmercuric chloride (1 mmol), carbon monoxide, and catalyst (0.1 mmol). No lithium chloride was added. The reaction was allowed to slowly warm on its own to room temperature and stirred overnight before analysis.

Preparation of α,β-Unsaturated Acids. Both preparative and GLC reactions were run in a manner identical with the above ester reactions except that 0.5–5% aqueous THF replaced the alcohol solvent.

The following procedure for the preparation of 4,4-dimethyl-*trans*-2-pentenoic acid is representative. Anhydrous lithium chloride (20 mmol), palladium chloride (10 mmol), 5 ml of water, and 95 ml of THF were added to a 250-ml round-bottom flask containing a septum inlet and carbon monoxide inlet tube (a balloon will suffice). The flask was cooled to −78° and 3,3-dimethyl-*trans*-1-butenylmercuric chloride (10 mmol) was added. The flask was thoroughly flushed with carbon monoxide. The well-stirred reaction mixture was then allowed to slowly warm to room temperature over a 4-hr period and stirred overnight while maintaining a slight positive pressure of carbon monoxide. Ether and activated carbon were added to the reaction mixture, which was filtered, washed with saturated ammonium chloride, and finally extracted several times with saturated sodium bicarbonate solution. The bicarbonate solution was acidified with cold hydrochloric acid and extracted several times with ether. After drying over anhydrous Na_2SO_4 and removal of the solvent, one obtains 1.25 g (98%) of acid (essentially pure by GLC and ^1H NMR), mp 62–62.5° (hexane) (lit.[21] mp 61–62°).

The following α,β-unsaturated carboxylic acids were obtained in a similar manner. *trans*-β-Cyclohexylacrylic acid, mp 57° (hexane) (lit.[22] mp 57–58°). Cinnamic acid, mp 132° (H_2O) (lit.[23] mp 132.6–132.8°). *trans*-6-Cyano-2-hexenoic acid: mp 69.5–70°; ir max (neat) 3600–2000, 2240, 1705, 1640, 1310, 1295, and 1210 cm^{-1}; ^1H NMR peaks ($DCCl_3$) at δ 1.90 (m, 2 H, CCH_2C), 2.1–2.7 (m, 4 H, $NCCH_2$ and allyl), 5.88 (dt, J = 1 and 16 Hz, 1 H, vinyl), 7.03 (dt, J = 7 and 16 Hz, 1 H, vinyl), and 11.06 (s, 1 H, COOH); *m/e* 121.0524 ± 0.0006 (calcd for $C_7H_9NO_2$, 121.0528). *trans*-β-(1-Cyclohexenyl)acrylic acid: mp 116.5–117.5° (hexane); ir max (KBr) 3300–2000, 1675, 1600, 1410, 1305, and 1275 cm^{-1}; ^1H NMR peaks ($DCCl_3$) at δ 1.66 (m, 4 H, CH_2CH_2), 2.18 (m, 4 H, allyl), 5.73 (d, J = 16 Hz, 1 H, CHCO), 6.20 (m, 1 H, vinyl), 7.35 (d, J = 16 Hz, 1 H, vinyl), and 11.28 (br, 1 H, COOH); *m/e* 152.0838 ± 0.0008 (calcd for $C_9H_{12}O_2$, 152.0837).

The catalytic carboxylic acid reactions were run exactly as those of the esters except that 5% aqueous THF was employed as the solvent and saturated ammonium chloride and ether were added to the reaction before GLC analysis.

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The Palladium Dichloride Complex of 4-Vinylcyclohexene

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In our hands the reported rearrangement of 4-vinylcyclohexene to 1,5-cyclooctadiene upon reaction with bisbenzonitrilepalladium dichloride does not occur. A variety of conditions were explored to try to induce rearrangement. NMR analysis of the product and its reactions with nucleophiles indicate that the product is the unrearranged π,π complex of 4-vinylcyclohexene. The reaction of related alkyl-substituted dienes with bisbenzonitrilepalladium dichloride is discussed.

The ability of transition metals to effect skeletal rearrangements of olefins is well documented.[1b] Wilkinson et al. reported the conversion of 4-vinylcyclohexene to 1,5-cyclooctadiene using an iridium salt.[2] This same conversion was reported using $(PhCN)_2PdCl_2$,[3] but an analogous reaction with Na_2PtCl_4 gave no rearranged product.[4a] In addition, no rearrangement occurred with 4-substituted 4-vinylcyclohexenes via the palladium complex.[4b]

In connection with our studies on the effect of diene structure on nucleophilic additions to palladium complexes, we investigated the reaction of 4-vinylcyclohexene with $(PhCN)_2PdCl_2$ and now report that the palladium complex remains unrearranged, in contrast to earlier reports.[3] We also report on the tendency of some related dienes to complex with palladium.

Results

The reaction between 4-vinylcyclohexene and bisbenzonitrilepalladium dichloride [$(PhCn)_2PdCl_2$] in benzene immediately produces a dark brown solid, which on standing