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THE MECHANISM OF REACTIONS OF ORGANOPALLADIUM SALTS WITH VINYLCYCLOPROPANES

WILLIAM FISCHETTI and RICHARD F. HECK
Department of Chemistry, University of Delaware, Newark, DE 19716 (U.S.A.)

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Summary

Cyclopropylmercuric chloride, lithium chloropalladite and methyl acrylate react at 0–25°C to give an 81% yield of methyl sorbate. A π-allylic palladium intermediate is proposed since vinylcyclopropane, carbomethoxymercuric acetate, and lithium chloropalladate give the same product. The corresponding reactions with styrene and cyclopropylmercuric chloride or vinylcyclopropane and phenylmercuric chloride also give the same, isolable π-allylic palladium complex. Deuterium labeling experiments support the occurrence of a common intermediate in the two reactions. 1,1-Dicarboethoxy-2-vinylcyclopropane reacts similarly with "phenylpalladium chloride" but the π-allylic product has the palladium attached at the benzyl carbon rather than the next carbon away. The reaction with "phenylpalladium acetate" in place of the chloride yields only dienes. Studies with the deuterated vinylcyclopropane diester suggest that the mode of elimination from the initial palladium adduct is strongly influenced by the anion present. The reaction of "cyclopropylpalladium chloride" with alkenes appears to be a general method for preparing, selectively, internal π-allylic palladium complexes.

Interactions of palladium salts with vinylcylopropanes have been studied by several groups in recent years [1–5]. π-Complexes of the olefinic double bond with the metal ion appear to form initially and these generally rearrange with opening of the cyclopropane ring. Various products are formed depending on the structure of the vinylcyclopropane derivative.

We were interested in preparing various substituted vinylcyclopropanes by either adding cyclopropylpalladium compounds to alkenes or by arylating or alkylating vinylcyclopropanes using methods employed by us previously in other systems [6]. While this work was in progress a study of the arylation of vinylcyclopropanes with arylmercuric halides and Li_2PdCl_4 was reported by Larock [7]. The synthetic aspects of the reaction for the preparation of π-allylic palladium complexes were emphasized in that study. A typical example is shown in eq. 1. We report here our

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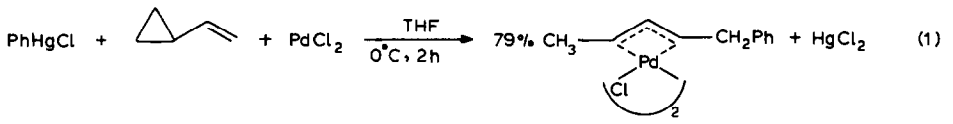
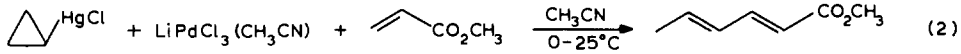


results pertaining to the mechanism of this and closely related reactions which are of special interest because they involve the breaking of carbon–carbon bonds at or below room temperature.

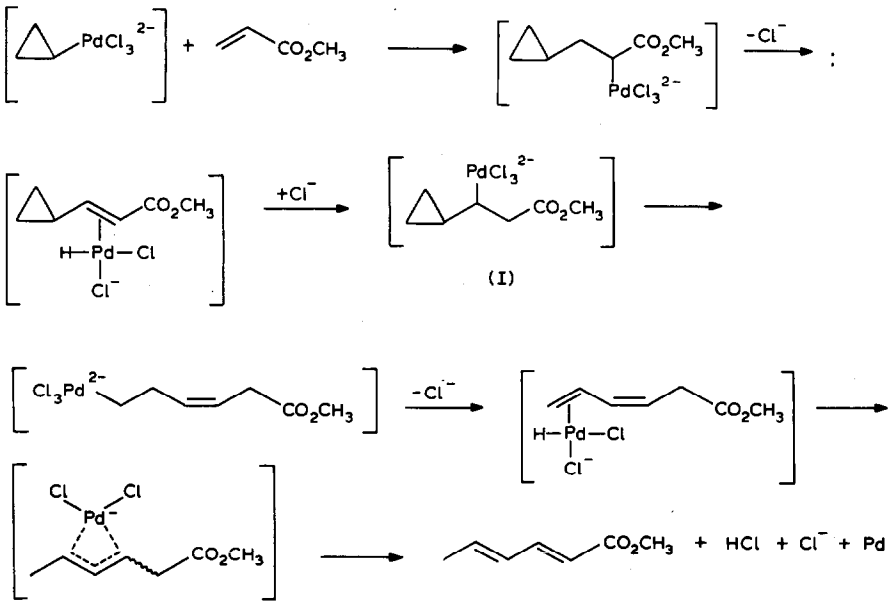
Results and discussion

We began our study by reacting "cyclopropylpalladium chloride" prepared in situ from cyclopropylmercuric chloride and lithium chloropalladite in acetonitrile solution with methyl acrylate at 0–25°C. An 81% yield of methyl sorbate was obtained (eq. 2). A likely mechanism for this reaction involves the addition of the cyclopro-

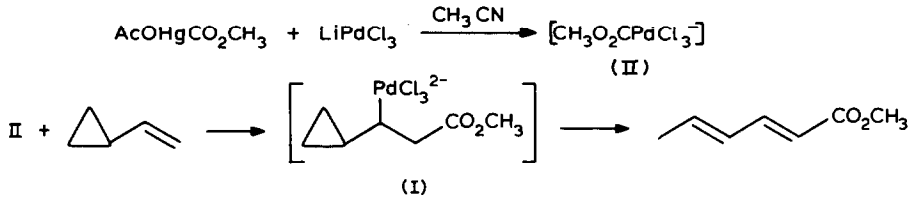


pylpalladium intermediate to the double bond of methyl acrylate followed by elimination to form the hydridopalladium-cyclopropylacrylate ester π-complex. A readdition of the metal hydride in the reverse direction to produce I (Scheme 1) followed by elimination with ring opening would form the terminal alkyl palladium. A final hydridopalladium elimination-readdition and reelimination of the hydrogen α to the ester group via a π-allylic intermediate would account for the product.

Support for this mechanism was obtained by treating "carbomethoxypalladium chloride" (II) with vinylcyclopropane (Scheme 2). The same intermediate, I, should



SCHEME 1

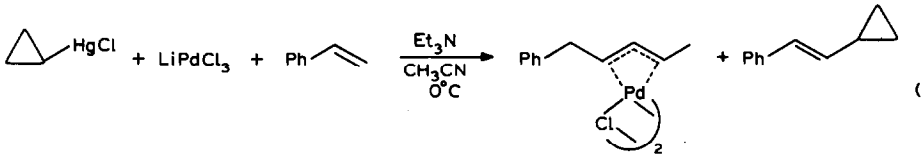


SCHEME 2

be formed in this reaction and the same product should result. As predicted the reaction gave methyl sorbate as the only product that could be identified. The low yield obtained, 42%, is characteristic of reactions of the unstable carbomethoxypalladium complexes [6].

A similar pair of reactions were then carried out with reactants containing a phenyl substituent in place of the carbomethoxy group where a more stable π-allylic palladium intermediate should be formed [7].

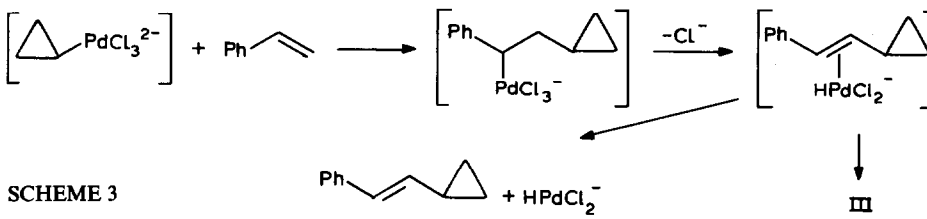
The reaction of "cyclopropylpalladium chloride" with styrene gave 55% of the expected *syn,syn*-π-allylic complex (dimer) along with 30% β-cyclopropylstyrene (eq. 3). The corresponding reaction of "phenylpalladium chloride" with vinylcyclopro-



(3)

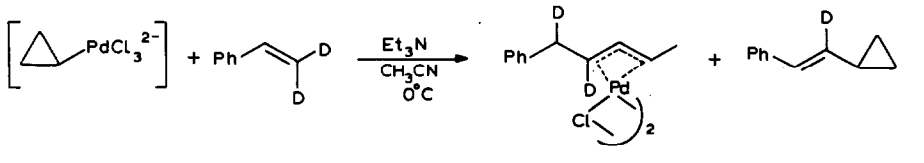
(III)

pane gave the same π-allylic complex, III, in 80% yield without forming a significant amount of the β-cyclopropylstyrene as reported, also by Larock [7]. The absence of the last product indicates that it is probably formed in the previous reaction by dissociation (displacement) of the hydridopalladium group from the initial elimination complex (Scheme 3).



SCHEME 3

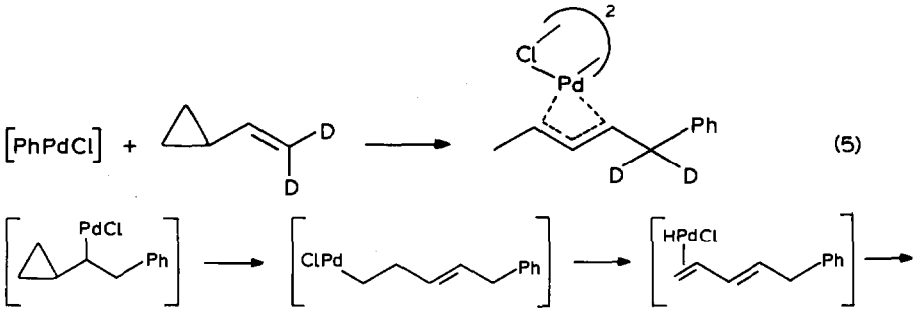
Additional evidence in favor of this mechanism was obtained by treating "cyclopropylpalladium chloride" with β,β-dideuteriostyrene. The cyclopropylstyrene product was monodeuterated at the β-position and the π-allylic complex (IV) was monodeuterated at both the benzyl carbon and the neighboring terminal carbon of the π-allylic system (eq. 4).

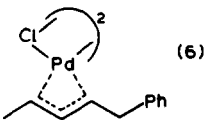


(4)

(IV)

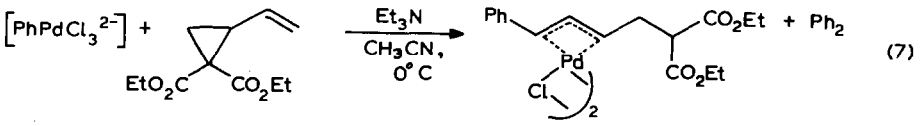
The reaction of (2',2'-dideuteriovinyl)cyclopropane with "phenylpalladium chloride" gave 76% of the π-allylic complex with both benzylic hydrogens replaced with deuterium (eq. 5). This result also is consistent with Scheme 1 where a complex of type I is formed initially and cyclopropane opening, palladium hydride (deuteride) elimination and reverse readdition occur to form the π-allylic product (eq. 6).

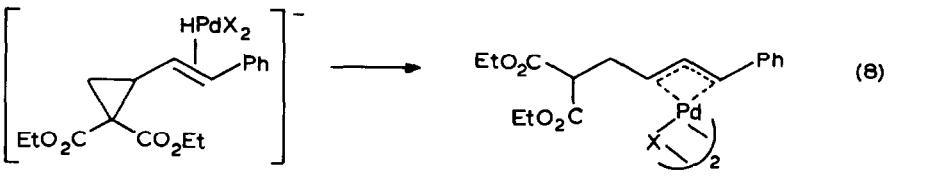




In agreement with the report of larock [7] and also consistent with the proposed mechanism was the formation of 1-benzyl-2,3-dimethyl-π-allylpalladium chloride dimer in 60% yield from 1-methyl-1-vinylcyclopropane and "phenylpalladium chloride".

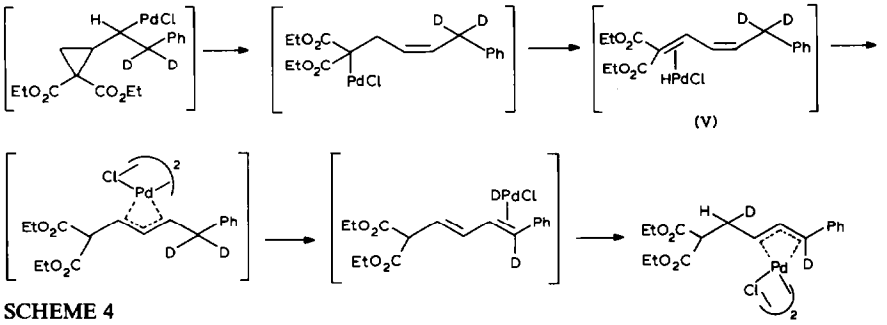
1,1-Dicarboethoxy-2-vinylcyclopropane and "phenylpalladium chloride", however, gave a rearranged π-allylic complex in 37% yield along with 42% of biphenyl. This cyclopropane is apparently less reactive for steric reasons than the cyclopropanes used above and the aryl coupling reaction competes with the addition to the double bond. The product π-allylic complex has a π-allylic system that includes the benzyl carbon and is the 1-phenyl-3-(2,2-dicarboethoxyethyl)-π-allylpalladium chloride dimer rather than the 1-benzyl-3-dicarboethoxymethyl derivative expected on the basis of the previous examples (eq. 7). Conceivably, this reaction could involve direct formation of the π-allylic product with proton transfer from the initial hydridopalladium elimination complex as shown in eq. 8.





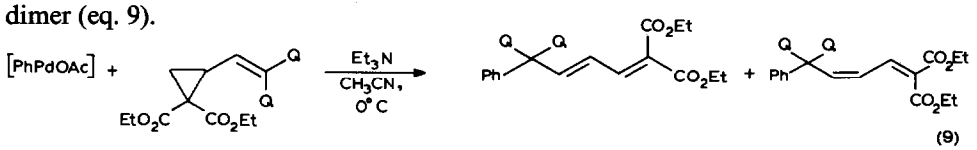
(X = Cl or OAc)

The reaction was carried out with the (2,2-dideuteriovinyl)cyclopropane diester and found to give only the π-complex monodeuterated at the benzyl-π-allylic carbon. The other deuterium was presumably on the carbon α to the ester groups and was lost by exchange with protons in the solution catalyzed by the triethylamine present and perhaps by palladium. The direct π-allylic complex mechanism would predict one deuterium would be found on the benzyl carbon and the other on the carbon bearing the two carboethoxy groups. The latter deuterium would be expected to be weakly acidic and exchange with protons (water?) in the solution. Thus, the results are consistent with the "direct" formation of the π-allylic intermediate. The alternative mechanism involving elimination to the alkenylpalladium derivative as in Scheme 1 followed by palladium hydride elimination-readdition, etc., would predict one deuterium on the benzyl carbon, carbon 6 and one on carbon 3 which should not be lost by exchange (Scheme 4).



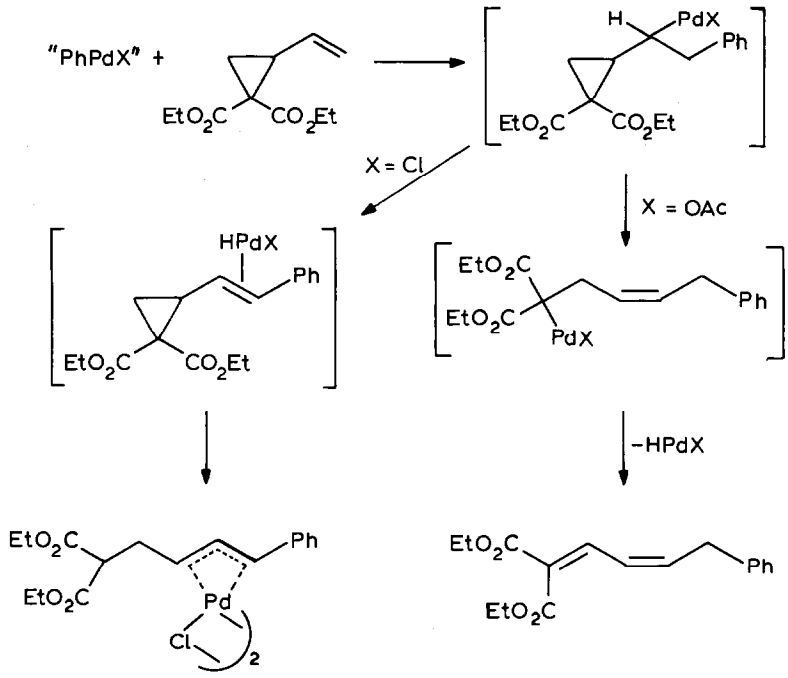
SCHEME 4

Additional information on this system was obtained when phenylmercuric acetate was used in place of the chloride in the stoichiometric reaction with the 2,2-dicarboethoxy-2-vinylcyclopropane. Presumably, the reacting species is now "phenylpalladium acetate" or a "phenylacetatochloropalladium anion" rather than a pure chloride. A 77% yield of a 2/1 mixture of *cis/trans* 2,4-dienoate esters was formed rather than the relatively less stable (compared to the chloride) π-allylic acetate dimer (eq. 9).



(Q = H or D) (9)

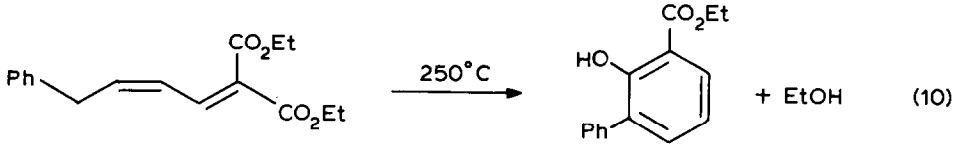
The dideuteriovinylcyclopropane diester in the same reaction gave only a *cis–trans* mixture of the 6,6-dideuteriodienoates. This result is not consistent with the direct π-allylic complex formation since this would require the loss or at least movement of one of the deuteriums. The results are in agreement with the previous alkenylpalladium mechanism, however, if loss of "HPdOAc" occurs from the first diene π-complex, V. In the absence of further information it appears that the initial "phenylpalladium salt" adduct with the vinylcyclopropane diester prefers to eliminate a benzylic proton (deuteron) first to form the olefinic palladium π-complex when only chloride anion is present while if acetate ion is present, elimination to the 4-alkenylpalladium salt is preferred. The difference between the chloride and acetate may be due to differences in the ionic character of the carbon–palladium bonds in the intermediates (Scheme 5).



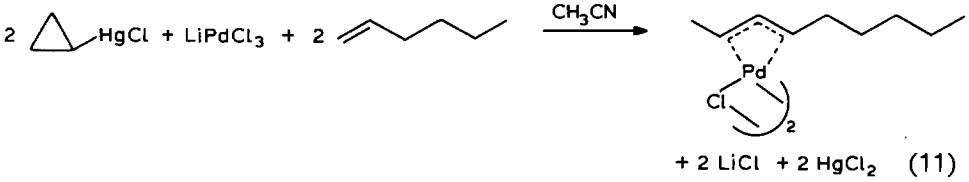
SCHEME 5

The *trans*-diene observed in the acetate reaction, at least, is mainly arising by isomerization of the presumably first formed *cis*-diene since its concentration increases with longer reaction time.

It is interesting and of possible synthetic value that the *cis*-diene undergoes a thermal cyclization in the gas chromatograph at 250°C (inlet temperature) to ethyl 3-phenylsalicylate while the *trans*-isomer is unreactive under the same conditions (eq. 10).



"Cyclopropylpalladium chloride" also reacts with unactivated alkenes forming the expected π-allylic complexes. 1-Hexene gave the 1-methyl-3-pentyl-π-allylpalladium chloride dimer in 56% yield (eq. 11). This method should be useful for preparing selectively, internal π-allylic palladium complexes.



Experimental

The properties and analytical data pertaining to the compounds prepared in this study are given in the Table 1.

Materials. Acetonitrile and triethylamine were dried with Linde 4A molecular sieves before use. Palladium chloride and palladium acetate were used as received from Johnson Matthey, Ltd. Carbomethoxymercuric chloride [8], 1-methyl-1-vinylcyclopropane [9], and diethyl 2-vinylcyclopropanedicarboxylate [10] were prepared by literature methods. Other materials were either prepared as described below or were commercial products which were used as received.

Cyclopropylmercuric chloride. Cyclopropylbromide [11] (18.0 g, 0.15 mol) was dissolved in 50 ml of THF (distilled from sodium benzophenone) and added dropwise to 3.9 g (0.16 mol) of magnesium turnings in 50 ml of dry THF under nitrogen. The reaction began during the addition and was controlled by the rate of addition of the bromide. After the addition, the solution was heated under a reflux condenser for 1 h. The resulting solution of the cyclopropylmagnesium bromide was transferred under nitrogen to a dropping funnel and added to a stirred slurry of 40.6 g (0.15 mol) of mercuric chloride in 100 ml of dry THF. A colorless precipitate appeared during the addition. After the addition, the mixture was stirred at room temperature for 3 h. Then 200 ml of saturated aqueous ammonium chloride was added and the product was extracted with chloroform. After washing the organic phase with water, it was dried with magnesium sulfate and the solvent was removed in a Rotary Evaporator at room temperature. The resulting crude product was recrystallized from ether to give 16.3 g (40%) of colorless mercurial, m.p. 184–185°C (Reported, 186–187°C [12]).

Reaction of "cyclopropylpalladium chloride" with methyl acrylate. A solution of 0.64 g (3.6 mmol) of palladium chloride, 0.15 g (3.5 mmol) of lithium chloride, 0.5 g triethylamine, 0.86 g (10 mmol) methyl acrylate, 1.0 g (3.6 mmol) cyclopropylmercuric chloride and 10 ml of acetonitrile was stirred at room temperature for 12 h. Then 20 ml of ether was added and the mixture was filtered through Celite to remove the precipitate of palladium metal. The filtrate was washed with 3% hydrochloric acid, water, and dried with magnesium sulfate. Filtration, evaporation of the solvent, and distillation gave 0.30 g (66%) of colorless methyl sorbate, b.p. 55°C (20 mmHg). The NMR spectrum was identical with an authentic spectrum. The yield of methyl sorbate as determined by GLC was 81% (n-dodecane internal standard).

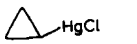
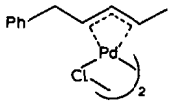
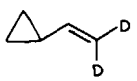
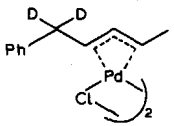
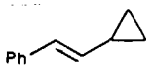
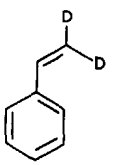
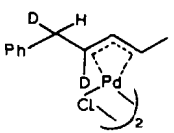
Vinylcyclopropane. Cyclopropylcarbinol (Aldrich) (6.0 g, 0.083 mol) dissolved in 20 ml of anhydrous methylene chloride was added rapidly to a stirred solution of 26.4 g (0.124 mol) of pyridinium chlorochromate in 100 ml of methylene chloride at room temperature according to the procedure of Corey [13]. After stirring for 3 h the mixture was passed through a short column of Florisil. The black residue was rinsed with ether and the washings also were put through the column. The combined eluates were concentrated under reduced pressure to leave 3.5 g (60%) of cyclopropylcarboxaldehyde.

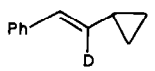
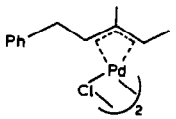
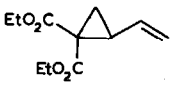
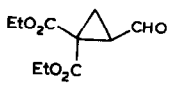
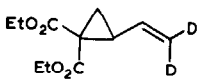
In a 100 ml 3-necked flask under nitrogen was placed 1.48 g (0.03 mol) of a 50% dispersion of sodium hydride in mineral oil. Dry dimethylsulfoxide (36 ml) was added and the mixture was warmed to about 70°C to dissolve the sodium hydride. The solution was then cooled to room temperature and 12.12 g (0.03 mol) of

(Continued on p. 402)

TABLE 1

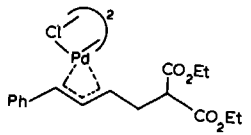
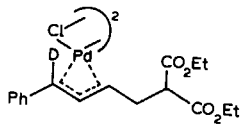
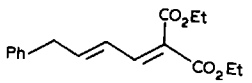
PHYSICAL PROPERTIES AND ANALYSES OF COMPOUNDS PREPARED

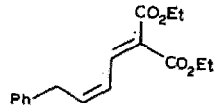
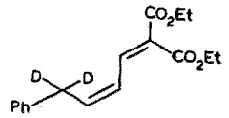
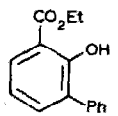
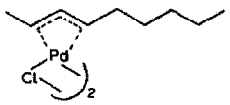
Compound	m.p. or b.p. (°C) or (°C/mmHg)	Analyses (%) or Mol. Wt. [a]	^{1}H NMR, δ (ppm)	^{13}C NMR, δ (ppm)
	184–185		0.61(m, 3H); 0.70(m, 2H).	2.84 q, 18.7 d.
	164–165 dec.	C, 45.94 (Calcd. 46.03) H, 4.37 (Calcd. 4.56)	1.30(d, *J* 6.4 Hz, 3H); 2.98(m, 2H); 3.80(dq, *J* 6.4, 10.9 Hz, 2H); 5.12(bt, *J* 10.9 Hz, 1H); 7.30(m, 5H).	17.61 q, 37.84 t, 78.52 d, 79.61 d, 111.47 d, 125.41 d, 127.50 d, 129.75 d,
			0.44(m, 2H); 0.73(m, 2H); 1.45(m, 1H); 5.36(m, 1H).	
	166–168 dec.		1.30(d, *J* 6.4 Hz, 3H); 3.80(m, 2H); 5.12(bt, *J* 10.9 Hz, 1H); 7.30(m, 5H).	
		Mol. Wt. 144.093 (Calcd. 144.093)	0.48(m, 2H); 0.79(m, 2H); 1.55(m, 1H); 5.70(dd, *J* 8.9, 15.7 Hz, 1H); 6.44(d, *J* 15.7 Hz, 1H); 7.27(m, 5H).	7.19 t, 14.40 d, 125.86 d, 14.40 d, 128.02 d, 134.20, 135.37 s, 137.71.
	34/10	Mol. Wt. 106.74 (Calcd. 106.75)	6.68(bs, 1H); 7.2–7.4(m, 5H).	
	166–167 dec.		1.30(d, *J* 6.4 Hz, 3H); 2.98(d, *J* 9.3 Hz, 1H); 3.80(dq, *J* 6.4, 10.9 Hz, 1H); 5.12(d, *J* 10.9 Hz, 1H). ^{2}H NMR: 2.85(1D); 3.73(1D).	

		Mol. Wt. 145.100 (Calcd. 145.100)	0.48(m, 2H); 0.79(m, 2H); 1.55(m, 1H); 6.45(s, 1H); 7.27(m, 5H).	
	167–168 dec.	C, 47.93 (Calcd. 47.90) H, 5.06 (Calcd. 5.02) Cl, 11.88 (Calcd. 11.80) Pd, 35.11 (Calcd. 35.30)	1.26(d, *J* 6.4, 3H); 2.10(s, 3H); 3.12(m, 2H); 3.60(m, 2H); 7.24–7.28(m, 5H).	
	73–75/0.9		1.26(t, *J* 7.1 Hz, 3H); 1.27(t, *J* 7.1 Hz, 3H); 1.54(dd, *J* 4.8, 8.9 Hz, 1H); 1.68(dd, *J* 4.8, 7.5 Hz, 1H); 2.57(dd, *J* 7.6, 16.5 Hz, 1H); 4.20(m, 1H); 5.14(dd, *J* 2.1, 9.6 Hz, 1H); 5.32(dt, *J* 2.1, 17.0 Hz, 1H); 5.4–5.5(m, 1H).	13.7 q, 13.8 q, 19.9 t, 30.6 d, 35.6 s, 61.0 t, 61.1 t, 117.9 t, 132.9 d, 166.9 s, 169.2 s.
	115/5	Mol. Wt. 214.106 (Calcd. 214.105)	1.28(t, *J* 7.1 Hz, 6H); 1.82(dd, *J* 7.25, 11.5 Hz, 1H); 2.09(dd, *J* 7.25, 11.5 Hz, 1H); 2.76(m, 1H); 4.25(q, *J* 7.1 Hz, 4H); 9.30(d, *J* 7.2 Hz, 1H).	
		Mol. Wt. 214.117 (Calcd. 214.117)	1.26(t, *J* 7.1 Hz, 3H); 1.27(t, *J* 7.1 Hz, 3H); 1.54(dd, *J* 4.8, 8.9 Hz, 1H); 1.68(dd, *J* 4.8, 7.5 Hz, 1H);	

Continued

TABLE 1 (continued)

Compound	m.p. or b.p. (°C) or (°C/mmHg)	Analyses (%) or Mol. Wt. [a]	^{1}H NMR, δ (ppm)	^{13}C NMR, δ (ppm)
			2.57(dd, *J* 7.6, 16.5 Hz, 1H); 4.13–4.30(m, 2H); 5.45(bd, 1H).	
	157–178 dec.	C, 47.22 (Calcd. 47.30) H, 4.87 (Calcd. 4.90) Cl, 8.45 (Calcd. 8.20)	1.24(t, *J* 7.1 Hz, 3H); 1.25(t, *J* 7.1 Hz, 3H); 2.27(t, *J* 6.5 Hz, 2H); 3.61(t, *J* 6.5 Hz, 1H); 3.71(m, 1H); 4.17(q, *J* 11.7 Hz, 2H); 4.18(q, *J* 7.1 Hz, 2H); 4.61(d, *J* 11.7 Hz, 1H); 5.70(dd, *J* 11.7, 10.6 Hz, 1H), 7.27(m, 3H); 7.46(m, 2H).	13.96 q, 14.00 q, 31.14 t, 50.78 d, 61.52 t, 61.60 t, 78.54 d, 80.72 d, 107.60 d, 127.94 d, 128.29 d, 128.94 d, 136.99 s, 168.31 s, 168.49 s.
			1.24(t, *J* 7.1 Hz, 3H); 1.25(t, *J* 7.1 Hz, 3H); 2.27(t, *J* 6.5 Hz, 2H); 3.61(t, *J* 6.5 Hz, 1H); 3.71(m, 1H); 4.17(q, *J* 7.1 Hz, 2H); 4.18(q, *J* 7.1 Hz, 2H); 5.70(d, *J* 10.8 Hz, 1H); 7.25–7.45(m, 5H).	
		Mol. Wt. 288.136 (Calcd. 288.136)	1.19(t, *J* 7.0 Hz, 3H); 1.20(t, *J* 7.0 Hz, 3H); 3.52(d, *J* 5.9 Hz, 2H); 4.21(q, *J* 7.0 Hz, 2H); 4.23(q, *J* 7.0 Hz, 2H); 6.34(dd, *J* 11.1, 15.8 Hz, 1H); 6.45(dd, *J* 15.8, 5.9 Hz, 1H); 7.06–7.27(m, 6H).	

		Mol. Wt. 288.136 (Calcd. 288.136)	1.30(t, *J* 7.0 Hz, 3H); 1.31(t, *J* 7.0 Hz, 3H); 3.67(d, *J* 7.05 Hz, 2H); 4.22(q, *J* 7.0 Hz, 2H); 4.24(q, *J* 7.0 Hz, 2H); 6.20(dd, *J* 7.05, 10.6 Hz, 1H); 6.52(dd, *J* 12.3, 10.6 Hz, 1H); 7.13–7.40(m, 5H); 7.70(d, *J* 12.3 Hz, 1H).	
		Mol. Wt. 290.148 (Calcd. 290.148)	1.30(t, *J* 7.0 Hz, 3H); 1.31(t, *J* 7.0 Hz, 3H); 4.22(q, *J* 7.0 Hz, 2H); 4.24(q, *J* 7.0 Hz, 2H); 6.20(d, *J* 10.6 Hz, 1H); 6.52(dd, *J* 12.3, 10.6 Hz, 1H); 7.13–7.40(m, 5H); 7.70(d, *J* 12.3 Hz, 1H).	
	[b]	Mol. Wt. 242.094 (Calcd. 242.095)	1.43(t, *J* 7.1 Hz, 3H); 4.43(q, *J* 7.1 Hz, 2H); 6.95(t, *J* 7.7 Hz, 1H); 7.25–7.60(m, 6H); 7.70(d, *J* 8.0 Hz, 1H); 11.38(s, 1H).	14.18 q, 61.56 t, 112.79 s, 125.10 d, 127.35 d, 128.13 d, 128.50 d, 129.32 d, 130.40 s, 136.48 d, 137.25 s, 158.97 s, 170.59 s.
	95–96	C, 40.42 (Calcd. 40.45) H, 6.25 (Calcd. 6.36)	0.88(t, *J* 6.7 Hz, 3H); 1.28(d, *J* 6.2 Hz, 3H); 1.3–1.4(m, 4H); 1.4–1.7(m, 4H); 3.68(m, 2H); 5.15(t, *J* 10.9 Hz, 1H).	13.90 q, 17.76 q, 22.37 t, 28.59 t, 31.32 t, 31.94 t, 76.88 d, 81.76 d, 111.37 d.

[a] Molecular weight determined by high resolution mass spectrometry. [b] UV ($CHCl_3$): λ_{max} 265 ($\epsilon = 10{,}500$) and 338 nm ($\epsilon = 5000$).

methyltriphenylphosphonium iodide was added. The resulting bright yellow solution was stirred for 1.5 h cooled to 0°C, and 1.4 g (0.02 mol) of cyclopropanecarboxaldehyde was added dropwise. Stirring was continued overnight at room temperature. The product was distilled directly from the reaction mixture. Vinylcyclopropane (1.09 g, 80%) was obtained, b.p. 41°C. The ^{1}H NMR spectrum was the same as the spectrum of an authentic sample.

(2',2'-Dideuteriovinyl)cyclopropane. Cyclopropanecarboxaldehyde was treated with the Wittig reagent from trideuteriomethyltriphenylphosphonium iodide exactly as described above for the nondeuterated compound using DMSO-d_6 as solvent.

Reaction of vinylcyclopropane with carbomethoxypalladium chloride. A solution of 0.88 g (5 mmol) of palladium chloride, 0.21 g (5 mmol) of lithium chloride, 0.35 g (5 mmol) of vinylcyclopropane, 0.5 g of triethylamine, and 1.59 g (5 mmol) of carbomethoxymercuric acetate was prepared in 10 ml of acetonitrile at 0°C. The reaction mixture was stirred at 0°C for 2–3 h at which time black metallic palladium precipitated from solution. The reaction mixture was allowed to stir an additional 12 h at room temperature and then was filtered through Celite. The black metal precipitate was washed with two 10 ml portions of ethyl acetate and the combined filtrates were concentrated under reduced pressure at room temperature. The residue was chromatographed on silica gel (2.5 × 25 cm). Elution with methylene chloride afforded 0.27 g of a colorless oil after evaporation of the solvent. NMR analysis of the oil proved it to be methyl 2,4-hexadienoate (42%). No other identifiable products could be removed from the column.

Reaction of "cyclopropylpalladium chloride" with styrene. A solution of 0.88 g (5 mmol) of palladium chloride, 0.21 g of lithium chloride, 1.04 g (10 mmol) of styrene, 0.5 g of triethylamine, and 1.38 g (5 mmol) of cyclopropylmercuric chloride in 10 ml of acetonitrile was stirred at 0°C for 12 h and then for 12 h at room temperature. The reaction mixture was filtered through Celite and the black precipitate washed twice with 10 ml portions of methylene chloride. The combined filtrates were concentrated under reduced pressure at room temperature. The dark residue obtained was extracted with hexane to remove traces of biphenyl. The remaining oil was chromatographed on silica gel (2.5 × 25.0 cm). Elutions with pentane/CH_2Cl_2 (70/30) and evaporation of the solvent yielded 0.35 g of a colorless oil. Gas chromatography of this oil showed it to be a mixture (62/38) of excess styrene and (*E*)-1-cyclopropyl-2-phenyl ethylene (yield 30%). Elution with 100% methylene chloride gave 0.45 g (55%) of yellow crystalline π-allylpalladium complex, m.p. 167–168°C dec.

β,β-Dideuteriostyrene. A solution of 2.24 g (0.02 mol) of potassium t-butoxide in 50 ml of THF (distilled from sodium and benzophenone) was prepared under nitrogen and 8.14 g (0.02 mol) of trideuteriomethyltriphenylphosphonium iodide was added with stirring. After stirring for 2 h the solution was cooled in a dry ice/acetone bath and 2.12 g (0.02 mmol) of freshly distilled benzaldehyde was added. The cooling bath was removed and stirring was continued overnight. The resulting mixture was filtered through Celite and distilled under reduced pressure. There was obtained 1.6 g (75%) of styrene-d_2, b.p. 34°C (10 mmHg).

Reaction of β,β-dideuteriostyrene with "cyclopropylpalladium chloride". This reaction was carried out exactly as described above with the undeuterated styrene and the yields of products were identical. The ^{1}H NMR spectrum of the monodeuterated cyclopropylstyrene lacked the double doublet at 5.70 ppm as expected for the

1-cyclopropyl-1-deuterio isomer. The ^1H NMR spectrum of the π-allylic palladium complex lacked one allylic absorption at 3.80 ppm and one benzylic proton at 2.98 ppm. The ^2H NMR spectrum showed two peaks, one at 2.85 ppm and the other at 3.73 ppm of equal areas.

Reaction of "phenylpalladium chloride" with vinylcyclopropane. A mixture of 0.88 g (5 mmol) palladium chloride, 0.21 g (5 mmol) lithium chloride, 0.35 g (5 mmol) of vinylcyclopropane, 0.5 g (5 mmol) triethylamine and 1.56 g (5 mmol) phenylmercuric chloride was stirred in 10 ml acetonitrile at 0°C for 2 h. Then stirring was continued overnight at room temperature. The black reaction mixture was filtered through Celite and the residue was washed with 10 ml methylene chloride and filtered again. The combined filtrates were concentrated and extracted with hexane. The hexane solution yielded 0.10 g (12%) biphenyl on evaporation. The hexane insoluble fraction was dissolved in methylene chloride and chromatographed on silica gel. Concentration of the yellow eluate and addition of hexane gave 1.10 g (77%) of 1-benzyl-3-methyl-π-allylpalladium dimer, m.p. 166–168°C dec.

The reaction with the deuterated vinylcyclopropane was carried out exactly the same way. The yields were the same.

syn,syn-1-Benzyl-2,3-dimethyl-π-allylpalladium chloride dimer. To a stirred solution of 0.21 g (5 mmol) of lithium chloride, 0.88 g (5 mmol) palladium chloride, 0.5 g (5 mmol) triethylamine, and 20 ml of acetonitrile at 0°C was added 0.83 g (10 mmol) 1-methyl-1-vinylcylopropane [9] and 1.56 g (5 mmol) of phenylmercuric chloride. After stirring at 0°C for 1 h, stirring was continued at room temperature 24 h more. The resulting reaction mixture was filtered through Celite to remove palladium metal. The residue was washed twice with 10 ml portions of methylene chloride and the combined solutions were concentrated under reduced pressure. Chromatography of the residue of alumina gave 0.08 g (20%) of biphenyl in the pentane eluate. The yellow π-allylic complex was eluted with methylene chloride. Recrystallization from hexane/methylene chloride gave 0.90 g (60%) of the palladium complex, m.p. 139–140°C dec.

Reaction of 1,1-dicarboethoxy-2-vinylcyclopropane with "phenylpalladium chloride". A mixture of 0.88 g (5 mmol) of palladium chloride, 0.21 g (5 mmol) of lithium chloride, 2.12 g (10 mmol) of 1,1-dicarboethoxy-2-vinylcyclopropane [10], 0.5 g (5 mmol) triethylamine, and 1.56 g (5 mmol) of phenylmercuric chloride in 20 ml of acetonitrile was stirred at 0°C for 2 h and at room temperature for 12 h. The reaction mixture was filtered through Celite to remove precipitated palladium metal and the residue was washed twice with 10 ml portions of methylene chloride. After concentrating, the dark oil obtained was chromatographed on silica gel. Pentane eluted 0.16 g (42%) of biphenyl, 1/4 ethyl acetate to pentane eluted about 1.0 g of unreacted cyclopropane ester and 3/2 ethyl acetate to pentane eluted the π-allylic complex. Recrystallization from methylene chloride/hexane gave 0.8 g (37%) of the complex, m.p. 157–158°C dec.

1,1-Dicarboethoxy-2-(2,2-dideuteriovinyl)cyclopropane. 1,1-Dicarboethoxy-2-vinylcyclopropane (5.0 g, 23 mmol) was dissolved in 100 ml of dry methylene chloride, 4.0 g of methanol and 0.5 g of pyridine. The solution was cooled in dry ice/acetone and a stream of ozone was bubbled through the magnetically stirred solution. After 30 min the solution became blue and the ozone was replaced by a stream of nitrogen. After flushing with nitrogen, 3 ml of dimethyl sulfide was added and the solution was concentrated under reduced pressure and distilled. There was obtained

4.3 g (85%) of 1,1-dicarboethoxy-2-methanoylcyclopropane, b.p. 115°C (5 mmHg).

To a stirred solution of 2.24 g (20 mmol) potassium t-butoxide in 50 ml of dry THF was added 8.14 (20 mmol) trideuteriomethyltriphenylphosphonium iodide. The bright yellow solution was stirred for 2 h, cooled in a dry ice/acetone bath and 4.3 g (20 mmol) of the above aldehyde was added. The solution was allowed to come to room temperature and stirring was continued overnight. The reaction mixture was filtered through Celite, concentrated and chromatographed on silica gel. Elution with 1/4 ethyl acetate to pentane and concentration gave 2.90 g (68%) of the dideuteriovinyl product.

Reaction of 1,1-dicarboethoxy-2-(2',2'-dideuteriovinyl)cyclopropane with "phenylpalladium chloride". The reaction was carried out exactly as with the undeuterated compound but with one half of the quantities. The ^1H NMR spectrum of the π-allylic complex produced showed the loss of the allylic proton on the benzylic carbon at 4.61 ppm with the neighboring allylic proton becoming a doublet rather than the triplet seen in the all proton complex. We were unable to obtain meaningful ^2H spectra of this product because of its instability in solution over the time needed to obtain the spectrum.

Reaction of 1,1-dicarboethoxy-2-vinylcyclopropane with "phenylpalladium acetate". A solution of 0.88 g (5 mmol) palladium chloride, 1.06 g (5 mmol) 1,1-dicarboethoxy-2-vinylcyclopropane and 1.68 g (5 mmol) phenylmercuric acetate was prepared in 10 ml deuterochloroform at 0°C and then stirred at room temperature for 12 h. The solution was then centrifuged to remove precipitated salts and palladium. The ^1H NMR spectrum of the solution indicated all of the vinylcyclopropane ester had reacted and that the only products present were the *cis*- and *trans*-ethyl 2-carboethoxy-6-phenyl-2,4-hexadienoates in a ratio of 2/1, respectively. Gas chromatographic analysis of the solution also showed only two products present. Collection of the products from the gas chromatograph (5' SE30 at 250°C inlet temperature and 250°C column temperature) led to the isolation of the *trans*-dienoate ester and a new compound which proved to be ethyl 3-phenylsalicylate judging by its ^1H NMR, MS, and UV spectra. The original reaction mixture was allowed to stir for 3 days at room temperature at which time the ^1H NMR spectrum of the solution showed a 1/2 ratio of *cis* to *trans* dienoate esters. The reaction mixture was filtered and the residue was rinsed twice with 10 ml portions of methylene chloride. Addition of hexane to the washings precipitated 1.09 g of mercuric salts. Evaporation of the solvents from the washings and chloroform solution under reduced pressure at room temperature followed by chromatography on silica gel with ethyl acetate led to the isolation of 1.1 g (77%) of the 1/2 *cis/trans* dienoate ester mixture.

The same results were obtained employing acetonitrile in place of deuterochloroform as solvent. The use of the 1,1-dicarboethoxy-2-(2',2'-dideuteriovinyl)cyclopropane in acetonitrile in the reaction led to the formation of a mixture of *cis*- and *trans*-6,6-dideuteriodienoate esters in comparable yields to the reaction with the undeuterated reactant.

Reaction of 1-hexene with cyclopropylpalladium chloride. A mixture of 1.38 g (5 mmol) cyclopropylmercuric chloride 1.00 g (10 mmol) 1-hexene, 1.13 g (4.3 mmol) lithium tetrachloropalladite, 0.5 g (5 mmol) triethylamine, and 10 ml of acetonitrile was prepared at 0°C and then stirred at room temperature for 24 h. The resulting reaction mixture was filtered through Celite, rinsing the residue with methylene

chloride, and the filtrates were combined and concentrated at room temperature under reduced pressure. The crude product remaining was purified by chromatography on silica gel. Elution with 95/5 hexane/ethyl acetate gave 0.77 g of yellow π-allyl complex. Recrystallization from methylene chloride/hexane yielded 0.75 g (65%) 1-methyl-3-pentyl-π-allylpalladium chloride dimer, m.p. 95–96°C.

Acknowledgment

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