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REACTION OF COORDINATED PHOSPHINES—II

ARYLATION OF SUBSTITUTED OLEFINS BY PALLADIUM(II) ACETATE AND TRIARYLPHOSPHINE[1]

T. YAMANE, K. KIKUKAWA, M. TAKAGI and T. MATSUDA*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812, Japan

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Abstract—Phenylation of 1-octene, cyclohexene, styrene, acrylonitrile, vinyl acetate, ethyl acrylate, and ethyl but-3-enoate with $Pd(PAr_3)_2(OAc)_2$ was carried out in acetic acid at 50°. *para* Substituted triphenylphosphine palladium acetate complex produced corresponding *para* substituted phenyl derivatives.

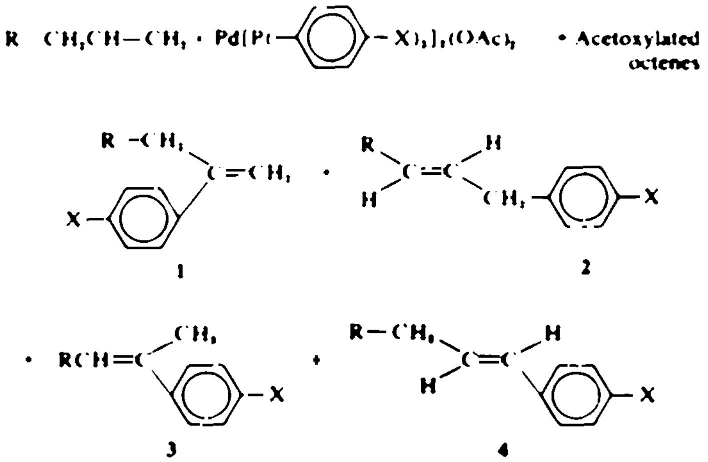
INTRODUCTION

In a previous communication we reported a novel arylation of olefin by $Pd(PAr_3)_2(OAc)_2$.[1] The reaction involves a facile cleavage of the P—C bond, which energetically is comparable to the C—C bond and chemically stable under ordinary conditions.

The present paper concerns the phenylation of 1-octene, cyclohexene, acrylonitrile, styrene, vinyl acetate, ethyl acrylate, and ethyl but-3-enoate with $Pd(PPh_3)_2(OAc)_2$ and presents a possible mechanism. In a series of papers,[2] Heck has described phenylpalladation of a variety of olefinic compounds by a phenyl palladium species, which were prepared by an exchange reaction between palladium salts and phenyl metal compounds such as phenyl-mercury, -tin, or -lead. These exchange reactions probably involve an electrophilic attack of palladium(II) on the aromatic nucleus. On the other hand, in the present arylation by $Pd(PAr_3)_2(OAc)_2$, it seems that an aryl palladium species is produced through migration of the aryl group from the phosphorus to palladium, which might be initiated by attack of a nucleophile on coordinated phosphorus.

RESULTS AND DISCUSSION

Arylation of 1-octene. In all these and subsequent reactions, olefin and $Pd(PAr_3)_2(OAc)_2$ were warmed to 50° or 60° in acetic acid until most of the complex reacted to produce metallic palladium. Results with 1-octene are summarized in Eq (1) and Table 1. In Eq (1) no description is given of the product which carries phosphorus, since little is known about the fate of dearylated triarylphosphine, except that a small amount of diphenylphosphinic acid can be recovered from the reaction. Most of the unreacted phosphine was trans-



$R = n\text{-}C_5H_{11}$, X = H–, or CH_3 (1)

Table 1. Arylation of 1-octene

Run No.	Reactant, g (mole ratio, P:Pd)	1-Octene g	Solvent g	Temp °C	Time hr	Yield, %[a] Ac	Yield, %[a] Ph	Composition of phenylated products, % 1	2	3	4
1	$Pd(PPh_3)_2(OAc)_2$, 2.17 (2:1)	6	AcOH, 25	30 50	3 8	30	116	9	39	12	40
2	$Pd(PPh_3)_2(OAc)_2$, 1.08 (2:1)	3	AcOH, 13	r.t. 50	25 4	34	96	6	25	12	57
3	$Pd(PPh_3)_2(OAc)_2$, 4.34 (2:1)	12	AcOH, 50	50	9	3	97	9	33	19	39
4	$Pd[P(p\text{-tolyl})_3]_2(OAc)_2$, 2.37 (2:1)	6	AcOH, 25	50	30	23	56[b]	9[b]	30[b]	14[b]	47[b]
5	$Pd(OAc)_2$, 1.12, PPh_3, 3.94 (3:1)	6	AcOH, 25	50	530	156	0				
6	$Pd(OAc)_2$, 1.12, PPh_3, 2.62 (2:1)	6	AcOH, 25	50	312	56	88	8	38	15	39
7	$Pd(OAc)_2$, 1.12, PPh_3, 1.31 (1:1)	6	AcOH, 25	50	25	25	81	12	28	15	45
8	PPh_3, 3.9 (1:0)	6	AcOH, 25	50	48	0	0				
9	$Pd(PPh_3)_2Cl_2$, 3.51 (2:1)	6	AcOH, 25	50 120	24 30	0	0				
10	$Pd(PPh_3)_2Cl_2$, 3.51, AcONa, 0.82	5.1	AcOH, 25	50	45	3	74	8	30	19	43
11	$Pd(OAc)_2$, 2.24, PPh_3, 2.62 (1:1)	10.2	toluene, 90	60 in nitrogen 60 in air	84 1	4	53	19	22	8	51
12	$Pd(OAc)_2$, 1.12, PPh_3, 1.31 (1:1)	5.1	toluene, 40 AcOH, 20	60	28	23	112	23	26	2	49

[a] The yields of the products are on the assumption that one mole of Pd(II) is needed to produce one mole of arylated or acetoxylated olefins and calculated from the peak area of GLC. Ac, acetoxylated octenes; Ph, phenylated octenes.
[b] *para*-Tolyl derivatives corresponding to the products in Eq (1).

formed into triphenylphsophine oxide. The phenylation of olefins occurred similarly when a mixture of 1-octene and PPh_3 was added to $Pd(OAc)_2$ in acetic acid solution (Table 1, run 6 and 7). Excess PPh_3, however, inhibits the phenylation (run 5). Palladium chloride complex, which is only slightly soluble in acetic acid even at an elevated temperature, did not show any activity in arylation and could be recovered nearly quantitatively after the reaction (run 9). However, in combination with sodium acetate, the complex proved to be as effective an arylation system as palladium acetate (run 10). It may be argued that the limited concentration of the complex species in solution made the arylation virtually undetectable. However, the addition of sodium acetate did not increase the solubility of the chloride complex. The role of acetate ion in run 10 presumably resides not in the solubilization of the otherwise insoluble complex itself but in some direct participation in the arylation.

The nature of the product and the reaction conditions in the present study remind one of the known arylation reactions developed by Moritani *et al.*,[3] where olefins were arylated by palladium acetate in aromatic solvent such as benzene, toluene, or other substituted aromatics. To check the possibility of participation of this type of arylation under current reaction conditions, $Pd(PPh_3)_2(OAc)_2$ was allowed to react with 1-octene in (i) toluene and (ii) a mixture of toluene and acetic acid. Tolyl derivatives of octene were not detected in either case and phenylated products were obtained in yields similar to those in acetic acid solvent. Thus, the present reaction conditions are inadequate for aromatic electrophilic substitution involving a palladium (II) reagent as was shown by the foregoing authors.

When tris(*p*-tolyl)phosphine was used in place of triphenylphosphine, the arylation proceeded to give *p*-tolyl derivatives of octenes (run 4). Thus, the aromatic C atom, bound to phosphorus, becomes bonded to the olefinic carbon. Since a direct reaction of olefin with coordinated triphenylphosphine to produce phenylated olefin is unlikely, the overall reaction must involve at least two phases of reaction sequence, cleavage of the aryl-P bond to form an intermediate which carries an activated aryl group, possibly on palladium, and the reaction of the intermediate with olefin. Inspection of the product indicated that the latter phase is the phenylpalladation of olefin as described by Heck,[2] and thus, the intermediate is some aryl palladium species. A comparison between run 1 and 4 (or run 15 and 16 in Table 2) indicated that the yield of arylated product was lower for the phosphine with an electron-releasing *p*-substituted phenyl group. This fact may be important in understanding the mechanism of the first phase of the reaction, i.e., the cleavage of aryl-P bond.

Some comment should be made on a combined yield of acetoxylated and phenylated products in Table 1. Since the reaction was carried out in air, the reduced palladium was reoxidised to a divalent state. The over 100% yields are explained by considering such a catalytic cycle. Also in the present reaction the formation of a phenylated product did not parallel that of metallic palladium. The precipitation of zero valent palladium seemed to be inhibited by the presence of a phosphine ligand and became significant after the phosphine ligand had been destroyed by oxidation to phosphine oxide. Oxidation of triphenylphosphine in the presence of palladium to the phosphine oxide is known.[4] In most of the reactions in Table 1 the conditions (time and temp) were adopted in order to make the precipitation of metallic palladium complete and thus the subsequent work-up easy.

The time course of phenylation illustrated in Fig 1 and 2 shows that the phenylation was nearly complete in a much shorter time and under much milder conditions than the conditions in Table 1. In these figures, small aliquots which were taken from the mixture were analysed directly on GLC and the yields of phenylated products were plotted against reaction time. The mixture was initially heterogeneous because of the low solubility of the 1:1 complex, $Pd(PPh_3)(OAc)_2$, in acetic acid or acetonitrile at room temperature. Addition of a 10 fold excess olefin solubilized the complex to an appreciable extent to afford a deep orange solution and in ½ hr most of the solid dissolved. One hr after the addition of olefin, the mixture began to darken and the precipitation of metallic palladium became evident. As already mentioned it was a general observation that the precipitation of palladium is delayed as compared to the formation of phenylated product.

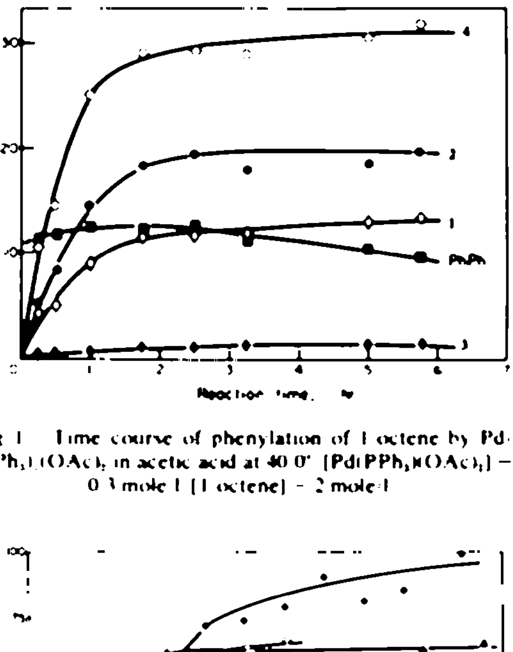


Fig 1. Time course of phenylation of 1-octene by $Pd(PPh_3)_2(OAc)_2$ in acetic acid at 40.0° $[Pd(PPh_3)_2(OAc)_2]$ = 0.3 mole/l [1-octene] = 2 mole/l

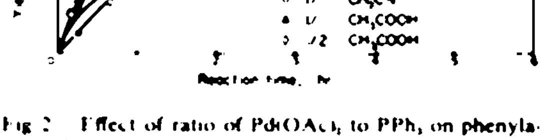


Fig 2. Effect of ratio of $Pd(OAc)_2$ to PPh_3 on phenylation of 1-octene at 40.0° $[Pd(OAc)_2]$ = 0.2 mole/l, [1-octene] = 2 mole/l

There is some discrepancy in isomer distribution of the product between Table 1 and Fig 1, especially in the relative abundance of 1 and 3. Since they are isomers in which only the location of the double bond is different, it could reasonably be interpreted that the increased content of 3 in Table 1 was derived from the isomerization of 1 due to a much longer reaction time. It seems that the results in Fig 1 reflect the isomer distribution directly derived from the reaction intermediate, since no significant isomerization of the arylated products was verified in the reaction and subsequent analytical procedure. In this direct GLC analysis a considerable amount of biphenyl was detected, but it decreased gradually with reaction time and finally diminished after about 20 hr. Biphenyl would be formed by thermal decomposition of PPh_3-$Pd(OAc)_2$ in the injection part of the GLC instrument. In Table 1 no biphenyl was obtained, but when the reaction was carried out without olefin, biphenyl became the predominant product. It is interesting to recall that phenyl palladium reagent decomposes to give biphenyl.[5]

In Fig 2 it is to be noted that the initial reaction rate decreased as the ratio of $Pd(OAc)_2$ to PPh_3 decreased. This is in accord with the experiment in Table 1, run 5. The observation is general irrespective of the solvent. This fact is further stressed by pointing out that 1:2 complex is usually much more soluble than 1:1 complex, $Pd(PPh_3)(OAc)_2$, in any ordinary solvent. In other words, the high reactivity of the 1:1 complex more than compensates for the low concentration in the reaction medium. From a mechanistic point of view the above observation seems to imply that some coordination vacancy or unsaturation is necessary for the initiation of the reaction. As to the effect of solvent on the reaction, not much difference has been observed in the reaction rate and product composition in solvents such as acetic acid, acetonitrile, acetone, benzene or nitromethane, though more work is needed in this respect.

Phenylation of other olefins. The results with some of other olefins are summarized in Table 2.

Phenylcyclohexane and biphenyl, the reaction products from cyclohexene, could be produced by a secondary reaction, i.e., through hydrogenation and dehydrogenation of phenylcyclohexenes, since the former product was not detected in the reaction under milder condition (Fig 3). The formation of 3- and 4-phenylcyclohexene, the main products from cyclohexene, is in contrast to the case of 1-octene which produced mainly styrene derivatives. The time course of phenylation of cyclohexene (Fig 3) further verified that the main products were 3- and 4-phenylcyclohexene, where 1-phenylcyclohexene was detected only in small amounts. A similar orientation of phenyl group has recently been reported for phenylpalladation of cyclohexene.[7]

The conversion curves of phenylation of 1-octene, cyclohexene, and ethyl acrylate in Fig 4 indicate a similar rate of reaction among these olefins. On the other hand, when the reaction was carried out with a mixture of two olefins, a significant difference in reactivity was observed between these olefins (Table 3). This could be attributed to the difference in coordination ability of olefins.* As the rate of phenylation was decreased by increasing the ratio of PPh_3 to $Pd(OAc)_2$, it is probable that there is an equilibrium in which PPh_3

Table 2. Arylation of substituted olefins by $Pd(PPh_3)_2(OAc)_2$ in acetic acid at 60°C

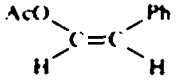
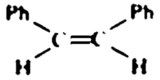
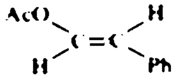
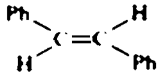
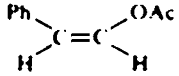
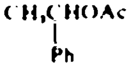
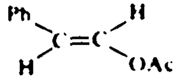
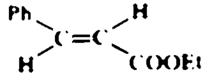
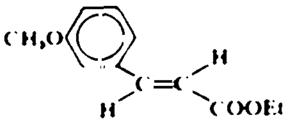
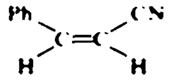
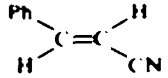
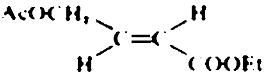
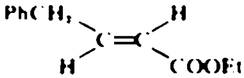
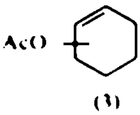
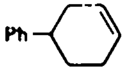
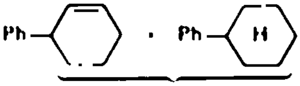
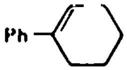
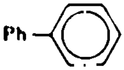
Run No	Olefin	Reaction time, hr	Products, %[a]	
13	styrene	123	 (63)	 (29)
			 (104)	 (82)
14	vinyl acetate	20	unknown[b] (11)	 (17)
			 $CH_3CH(OAc)Ph$ (2)	 (24)
15	ethyl acrylate	20	unknown[b] (3)	unknown[c] (11)  (115)
16	ethyl acrylate[d]	48	 (50)	
17	acrylonitrile	24	unknown[b] (trace)	 (19)
			$AcOCH_2CH_2CN$ (4)	 (36)

Table 2 *continued*

Run No	Olefin	Reaction time, hr	Products, %[a]	
18	ethyl but-3-enoate	52	unknown[b] (15)  (166)	unknown[c] (32)  (36)
19	cyclohexene[d]	29	 (3)  (12.0) unknown (2.2)	 (8.2)[f]  (trace)  (7.0)

[a] Based on Pd used

[b] Acetoxylated olefins by IR

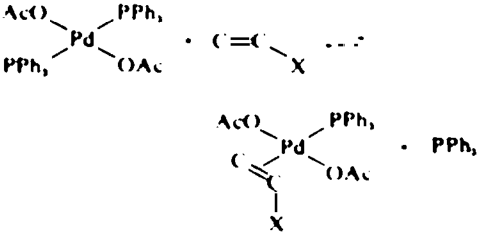
[c] Phenylated olefins by IR

[d] Pd[P( OCH$_3$)$_3$]$_2$(OAc)$_2$ was used in place of Pd(PPh$_3$)$_2$(OAc)$_2$

[e] Reaction temp 50°

[f] This fraction is largely composed of 3-phenylcyclohexene

competes with olefin in coordination (Eq 2) Even though two olefins exist in equimolar amounts in the system, one of them might be preferentially


(2)

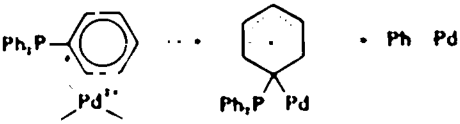
coordinated to palladium and react to give the corresponding phenylated product

Mechanism As suggested the phenylation product can most reasonably be interpreted in terms of the reaction of olefins with the phenyl palladium species formed during the reaction Allowing for the possible minor variance which might be introduced by the presence of a phosphine ligand, the present phenylation reaction has the following characteristics which are the essential features of the phenylpalladation reaction as developed by Heck (i) Phenylation of olefins under mild conditions, (ii) relatively low sensitivity to the change in reaction medium, (iii) stereochemistry formation of 3- and 4-phenylcyclohexene from cyclohexene, and preferred formation of terminally phenylated product from a terminal olefin

The most intriguing problem is the mechanism by which the phenyl palladium species is formed. Two possible ways are considered for the cleavage of the P—C bond (Eq 3 and 4)


(3)

Nu nucleophile


(4)

Equation (3) contains an initiation involving nucleophilic attack on phosphorus by a nucleophile, while Eq (4) represents electrophilic attack of a palladium species on the aromatic nucleus Electron-releasing groups (for example, Me or OMe) in tri-*p*-substituted triphenylphosphine proved to lower the reactivity of arylation[8] Thus, this arylation may involve a nucleophilic attack on phosphorus in the rate determining step, i.e., Eq (3) seems to be more reasonable The nature of the

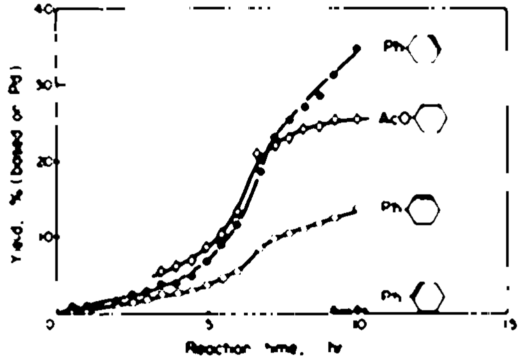


Fig. 3. Time course of phenylation of cyclohexene by $Pd(PPh_3)_2(OAc)_2$ in acetic acid at 30.0° $[Pd(PPh_3)_2(OAc)_2]$ = 0.1 mole/l [cyclohexene] = 1 mole/l

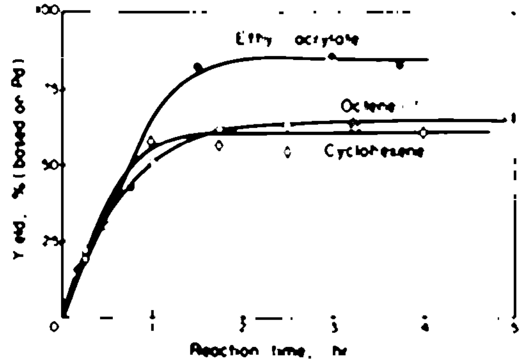


Fig. 4. Time course of phenylation of 1-octene, ethyl acrylate, and cyclohexene by $Pd(PPh_3)(OAc)_2$ in AcOH at 40.0° $[Pd(PPh_3)(OAc)_2]$ = 0.2 mole/l [olefin] = 2 mole/l

Table 3. Arylation of equimolar mixture of olefins in acetonitrile at 40.0°

Olefins	Ratio of arylated products
1-Octene, Cyclohexene	100 : 1
1-Octene, Ethyl acrylate	1.7 : 1

nucleophile in Eq (3) is not specified, but in the present reaction the acetate ion is probably the reagent which attacks the phosphorus. Whether the attack occurs by external ion or via coordination to palladium is not clear. This process converts triphenylphosphine to acetoxydiphenylphosphine, which, after oxidation and hydrolysis, should give diphenylphosphinic acid. Finally, two separate communications appeared recently which describe the facile cleavage of the phenyl-phosphorus bond in a transition metal complex.[9] Details of the reaction are not reported, and it is not yet clear whether they have something in common with the mechanism reported in this paper.

EXPERIMENTAL

Preparation of olefins. 1-Octene was prepared by thermal decomposition of *n*-octylacetate. Cyclohexene was prepared by dehydration of cyclohexanol. Other olefins were of commercial origin.

Preparation of palladium complexes. Palladium acetate, bis(triphenylphosphine)palladium acetate, bis(tris(*p*-tolyl)phosphine)palladium acetate and bis(tris(*p*-methoxyphenyl)phosphine)palladium acetate were prepared by the method of Wilkinson, *et al.*[11] $Pd(PPh_3)(OAc)_2$, 1:1 complex, was prepared similarly using equimolar amount of triphenylphosphine and palladium acetate and is an amorphous yellow powder. (Found: C, 52.05; H, 4.72. Calcd. for $Pd(PPh_3)(OAc)_2$: C, 54.28; H, 4.35%.) The product was used for reaction without further purification.

Table 4. Spectral data of phenylated and acetoxylated products

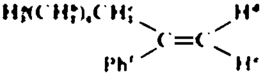
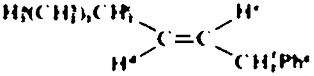
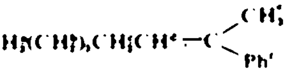
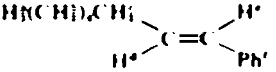
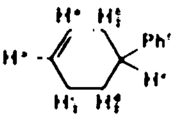
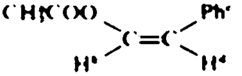
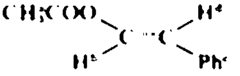
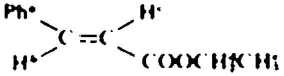
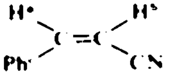
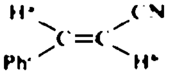
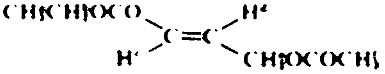
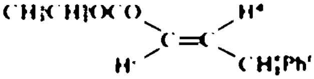
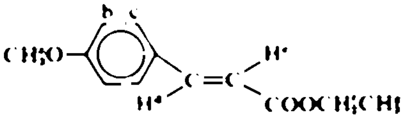
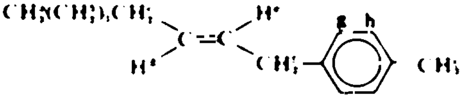
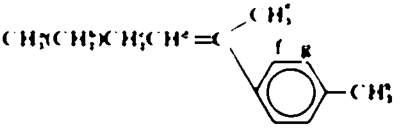
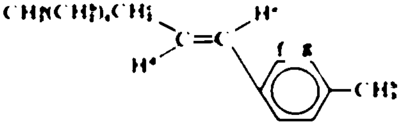
Compounds	NMR*, δ(ppm)	IR†, cm⁻¹
 $CH_3^a(CH_2^b)_4CH_2^c(Ph^f)C{=}CH^dH^e$	0.88(t,a), 1.30m(b), 2.44m(c) 4.98, 5.17(d,e) J_{ed} = 1c/s 7.12, 7.27(f)	893 δ_{CH} (>C=CH₂) 775 δ_{CH} (mono subst. benzene)
 $CH_3^a(CH_2^b)_3CH_2^cCH^d{=}CH^eCH_2^fPh^g$	0.90(t,a), 1.28m(b), 2.0m(c) 3.28d(f), 5.5m(d, e, ABX₂) 7.13s(g), J_{ef} = 4.5c/s	966 δ_{CH} (*trans* –CH=CH–) 746 δ_{CH} (mono subst. benzene)
 $CH_3^a(CH_2^b)_3CH_2^cCH^d{=}C(CH_3^e)Ph^f$	0.93(t,a), 1.30m(b), 1.99d(e) 2.14d(c), 5.70m(d), 7.2m(f) J_{cd} = 7, J_{de} = 1c/s	840 δ_{CH} (>C=CH–) 760 δ_{CH} (mono subst. benzene)
 $CH_3^a(CH_2^b)_4CH_2^cCH^d{=}CH^ePh^f$	0.90(t,a), 1.33m(b), 2.18q(c) 6.17m(d), 6.30d(e), 7.20m(f) J_{cd} = 5.0, J_{de} = 16.0c/s	964 δ_{CH} (*trans* –CH=CH–) 748 δ_{CH} (mono subst. benzene)
	1.90m(d), 2.10(c), 2.25(b) 2.8m(e), 5.70s(a), 7.17s(f)	

Table 4 *continued*

Compounds	NMR[a], δ(ppm)	IR[b], cm⁻¹
	2.18s(a), 5.59d(b) 7.3m(c), 7.38d(d) J_{bd} = 8.0c/s	1740 $\nu_{C=O}$ 1235 ν_{C-O} 704 δ_{CH} (mono subst. benzene)
	2.07s(a), 6.30d(b) 7.22s(c), 7.82d(d) J_{bd} = 12.5c/s	1735 $\nu_{C=O}$ 933 δ_{CH} (*trans* CH—CH) 752 δ_{CH} (mono subst. benzene)
	1.31t(e), 4.22q(d), 6.33d(c) 7.60d(b), 7.4m(a) J_{bc} = 16.0c/s	1710 $\nu_{C=O}$ 980 δ_{CH} (*trans* CH—CH) 718 δ_{CH} (mono subst. benzene)
$CH_3^aCOOCH_2^bCH_2^cCN$	2.10s(a), 2.65t(c) 4.24t(b) J_{bc} = 6.5c/s	2240 $\nu_{C\equiv N}$ 1745 $\nu_{C=O}$ 1230 ν_{C-O}
	5.38d(a), 7.05d(b) 7.38m(c, *m*-, *p*-), 7.77m(c, *o*-) J_{ab} = 12.0c/s	2240 $\nu_{C\equiv N}$ 1405 δ_{CH} (*cis* CH—CH) 780 δ_{CH} (mono subst. benzene)
	5.83d(a), 7.30d(b) 7.39s(c) J_{ab} = 17.0c/s	2240 $\nu_{C\equiv N}$ 965 δ_{CH} (*trans* CH—CH) 750 δ_{CH} (mono subst. benzene)
	1.28t(a), 2.07s(f), 4.16q(b) 4.70q(e), 5.92m(c), 6.90m(c) J_{cd} = 16.0, J_{de} = 5.0, J_{ce} = 2.0c/s	1740 $\nu_{C=O}$ 1720 $\nu_{C=O}$ 970 δ_{CH} (*trans* CH—CH)
	1.27t(a), 3.15d(e), 4.15q(b) 6.24m(d), 6.43d(c), 7.25s(f) J_{de} = 6.0, J_{cd} = 15.5c/s	1720 $\nu_{C=O}$ 970 δ_{CH} (*trans* CH- CH) 700 δ_{CH} (mono subst. benzene)
	1.29t(g), 3.78s(a), 4.20q(f) 6.20d(e), 7.55d(d), 6.81d(c) 7.42d(b) J_{de} = 16.0, J_{bc} = 9.0c/s	1710 $\nu_{C=O}$ 1240 ν_{C-O} 990 δ_{CH} (*trans* CH—CH) 830 δ_{CH} (*para* disubst. benzene)
	0.89t(a), 1.30m(b), 2.0m(c) 2.28s(i), 3.23d(f), 6.99s(g, h) 5.47m(d, e, ABX$_2$), J_{ef} = 4.5c/s	965 δ_{CH} (*trans* CH—CH) 805 δ_{CH} (*para* disubst. benzene)
	0.90t(a), 1.33m(b), 1.97d(e) 2.29s(h), 2.2m(c), 5.67m(d) 7.15d(f), 7.01d(g), J_{cd} = 7.0 J_{de} = 1.0, J_{fg} = 8.0c/s	818 δ_{CH} (*para* disubst. benzene)
	0.89t(a), 1.31m(b), 2.16q(c) 2.28s(h), 6.07m(d), 6.28d(e) 6.99d(g), 7.13d(f), J_{cd} = 5.5 J_{de} = 16.0, J_{fg} = 8.5c/s	970 δ_{CH} (*trans* CH—CH) 815 δ_{CH} (*para* disubst. benzene)

[a] These were examined as 5–10 vol% solution in carbon tetrachloride and the chemical shifts were measured from tetramethylsilane internal reference. s singlet, d doublet, t triplet, q quartet, m multiplet

[b] These were measured as neat

Table 5. Analytical data of products

Compounds		Found	Calcd
1-Phenyloctene-1	C	88.94	89.29
	H	10.61	10.71
cis-Cinnamonitrile	C	83.04	83.69
	H	5.68	5.46
	N	10.64	10.84
trans-Cinnamonitrile	C	83.23	83.69
	H	5.72	5.46
	N	10.55	10.84
4-Acetoxy crotonic acid ethyl ester	C	55.92	55.81
	H	7.19	7.03
4-Phenyl crotonic acid ethyl ester	C	68.17	75.76
	H	7.12	7.42

General procedure of the arylation of olefins. To a soln of Pd complex (5 mmole) in a solvent (25 g), olefin (50 mmole) was added. The mixture was stirred in an oil bath until the Pd metal deposited. The metal and soln were separated by centrifugation. To the soln, 100 ml of ether was added and washed twice with water. The ethereal extract was then washed with 10% $NaHCO_3$aq followed by sat. NaClaq, dried over $MgSO_4$ and distilled. Each component of the product was separated by GLC and identified by IR, NMR, and elementary analysis. Spectral and analytical data of the products are shown in Tables 4 and 5. 3-Phenylcyclohexene, *cis*- and *trans*-cinnamonitrile, ethyl 4-phenylcrotonate, and ethyl cinnamate were also assigned by comparison of the IR spectra and the retention times on GLC with those of authentic samples (Tables 4 and 5).

Determination of time course of phenylation. To a soln (or suspension) of Pd complex (0.5 mmole) in a solvent (5.0 ml) containing an appropriate internal standard (bibenzyl or diethyleneglycol dibutyl ether) olefin (5.0 mmole) or a mixture of olefins (5.0 mmole) were added and stirred in a thermostatted cell. Samples were withdrawn at appropriate time intervals by a microsyringe and directly analyzed on GLC equipped with flame ionization detector.

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