Arylation of Styrene by Palladium Acetate-Phosphine Complexes

Young-ae Whang Park* and Seong Won Hwang

Department of Chemistry, College of Natural Science, Sang Myung University, 7 Hongji Dong, Chongno Ku, Seoul 110-743, Korea

Received December 10, 1996

When phenylation of styrene was carried out in the presence of $Pd(OAc)_2$ and PPh_3 in benzene, *trans*-stilbene was obtained in good yield (566%) with high selectivity (98%) under mild condition (55 °C, 50 psi O_2, 20 h). Since *trans*-stilbene could be produced not only from benzene but also from phenyl group of PPh_3 by migration of its phenyl group to Pd, the competitiveness of benzene and the migratory aptitude of aryl group of triarylphosphine toward styrene has been investigated with various phosphines (PR_3 : P(*p*-$C_6H_4CH_3)_3$, P(*p*-$C_6H_4OCH_3)_3$, P(*p*-$C_6H_4F)_3$, P(*p*-$C_6H_4Cl)_3$, P($C_6H_5)_3$, P($C_6H_{11})_3$, P($OC_4H_9^n)_3$, P($CH_2C_6H_5)_3$ and P($C_6F_5)_3$). The yield and selectivity toward *trans*-stilbene are increased as the basicity of the phosphines increases. The composition of arylated olefin from arylphosphine, in turn, increases as the electronegativity of the substituent on the aryl group of arylphosphines increases.

Introduction

Catalytic activation of carbon-hydrogen bond by transition metal complex has been an important subject for organometallic chemists.[1] Arylation reactions of olefins have been extensively studied with palladium complexes since Heck found the palladium salts as the most useful catalysts.[2-7] The mechanism presumably involves the formation of unstable aryl-palladium intermediates from palladium(II) salts (PdX_2) and arene solvents, followed by the insertion reaction of coordinated olefin into aryl-palladium bond, then rapid decomposition to arylated olefin and palladium metal.

The previously reported synthetic problems are arising from the fact that raising the reaction temperature and increasing the amount of olefins might improve the yield of the product, but would give poor selectivity toward *trans*-stilbene due to the dimerization of olefins. When Fujiwara *et al.* used $Pd(OAc)_2$ with acetic acid as a catalyst for the phenylation of styrene at 80 °C for 8 h in the air, the yield was only 90%.[8] They also tried the same reaction except using additional $Cu(OAc)_2$ as an oxidant under much severer condition. (80 °C, 8 h, 500 psi O_2), which resulted in 446% yield with 82% selectivity. The rest of the product (18%) was *trans,trans*-1,4-diphenylbutadiene formed from dimerization of styrenes. Oxidants were used for the oxidation of Pd^0 to Pd^{2+} to make the arylation reaction catalytic. Shue reported the olefin arylation reaction catalyzed by $Pd(OAc)_2$ and oxygen pressure alone (80 °C, 300 psi O_2, 5.5 h) with 238% yield and extremely low selectivity (14%).[7] Recently, Fuchita and his coworkers isolated the trimeric palladium-aryl complex, $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$, in the reaction of palladium(II) acetate with dialkyl sulfide in benzene.[9-11] They claimed that they performed the reaction under milder condition (70 °C for 5h) than the previously reported ones. However, the yield of trans-stilbene was only 113% under O_2 with the molar ratio of styrene to palladium salt to be 10 to 1. Besides, dimerization of excess amount of olefins gave 21% of *trans,trans*-$(PhCH{=}CH)_2$ as well.

When we reacted styrene with benzene using $Pd(OAc)_2$ and PPh_3, *trans*-stilbene was obtained in good yield (566%) with high selectivity (98%) under mild condition (55 °C, 50 psi O_2, 20 h). However, *trans*-stilbene could be produced not only from benzene but also from PPh_3 since the phenyl group of PPh_3 is known to migrate to Pd to form an intermediate, Pd-Ph complex, which reacts with styrene to give the product. However, so far there is no systematic work reported about the competitveness of benzene and the migratory aptitude of aryl groups of triarylphosphines by varying the substituents on the phosphines

Herein we wish to report the phenylation of styrene with benzene in the presence of $Pd(OAc)_2$-PPh_3 catalyst and the investigation about the competitiveness of benzene and aryl groups of triarylphosphines toward styrene.

Experimental

Materials. Palladium acetate and phosphines purchased from Aldrich and styrene from Sigma were all reagent-grade and were used without further purification. Benzene and hexane were distilled over sodium-benzophenone and sodium respectively, at reflux under N_2 just prior to use.

Measurements. The reactions were carried out using 0.45 mmol of $Pd(OAc)_2$, 0.45 mmol of phosphine and 0.5 mL of styrene (10 times excess) in 70 mL of benzene at 55 °C under 50 psi O_2 for 20 h in a PARR 4842 reactor. After decanting the solution and washing the residue with hexane to remove palladium metal, the solvent was evaporated to dryness. The mixture was then dissolved in hexane and filtered through a column packed with silica gel 60 (230-400 mesh ASTM, Ar. 9385, Merck) to remove any remaining palladium metal or was sometimes separated by column chromatography. The collected solution was dried and the solid mixture was analyzed and characterized by Varian GCMS-3400 instrument on a DB-5 column or Hewlett Packard 5890 3 Series II spectrometer on a HP-5 column: PhCH=CHPh m/e 180 (M^+), $(PhCH{=}CH)_2$ m/e 206 (M^+), $PhCH{=}CHC_6D_5$ m/e 185 (M^+), $PhCH{=}CH(C_6H_4CH_3)$ m/e 194 (M^+), $PhCH{=}CH(C_6H_4OCH_3)$ m/e 210 (M^+), $PhCH{=}CH(C_6H_4F)$ m/e 198 (M^+), $PhCH{=}CH(C_6H_4Cl)$ m/e 214 (M^+), $PhCH{=}CH(C_6F_5)$ m/e 270 (M^+), $PhCH{=}CPh_2$ m/e 257 (M^+). Melting points were obtained on a MEL-TEMP II by Mi-

Table 1. Effect of Molar Ratio of $Pd(OAc)_2$ to PPh_3 on the Yields of *trans*-Stilbene[a]

Ratio	Yield, %
2 : 1	498
3 : 2	566
1 : 1	521
1 : 2	466
1 : 3	351
1 : 5	205

[a] Yields are based on the $Pd(OAc)_2$ used. $Pd(OAc)_2$: 0.45 mmol, Styrene: 0.5 mL (10 times excess), Benzene: 70 mL.

Table 2. Yields (%) for trans-Stilbene

PR_3	PhCH=CHPh	PR_3	PhCH=CHPh
$P(p\text{-}C_6H_4CH_3)_3$	611	$P(p\text{-}C_6H_4Cl)_3$	216
$P(C_6H_5)_3$	566	$P(OC_4H_9{}^n)_3$	206
$P(p\text{-}C_6H_4OCH_3)_3$	363	$P(CH_2C_6H_5)_3$	160
$P(C_6H_{11})_3$	291	$P(C_6F_5)_3$	153
$P(p\text{-}C_6H_4F)_3$	218	$S(C_6H_5)_2$	37

tamura Riken Kogyo: mp (°C); PhCH=CHPh 122-123, PhCH=CH(C_6F_5) 132-133, (PhCH=CH)$_2$ 149-150. Elemental analysis was carried out at KIST: Anal. Calcd for $C_{14}H_7F_5$ [PhCH=CH(C_6F_5)] : C, 62.2; H, 2.59. Found: C, 62.1; H, 2.57.

Results and Discussion

The phenylation of styrene was carried out using palladium acetate with various phosphines, PR_3 (R=C_6H_5, *p*-C_6H_4F, *p*-C_6H_4Cl, *p*-$C_6H_4OCH_3$, *p*-$C_6H_4CH_3$, C_6F_5, C_6H_{11}, $CH_2C_6H_5$, $OC_4H_9{}^n$). The molar ratio of $Pd(OAc)_2$ to PPh_3 for maximum yield of trans-stilbene (566%) is 3/2 as shown in Table 1. As the ratio increases, the yield tends to decrease. It seems that the structure of the catalytic species is similar to the Fuchita's trimeric palladium sulfide complex[11] and excess phosphine inhibits the arylation reaction by blocking the empty coordination site.[12] In order to maintain the high efficiency and the identical reaction condition, the molar ratio of 3/2 has been kept for other phosphines. The products were identified by melting point, elemental analysis and the comparison of the retention time and mass number with those of authentic samples in GC/MS. The yield was determined either by GC using hexadecane as an internal standard or by the isolated weight of the products. Yields based on $Pd(OAc)_2$ are the average values of three or four trials and are summerized in Table 2.

Among the series of phosphines, $P(p\text{-}C_6H_4CH_3)_3$ in which electron-donating group is on the *para*-position of phenyl group gives best efficiency and the best yield of 611%. Triphenylphosphine, $P(C_6H_5)_3$, afforded the second best yield (566%). However, in the case of $P(p\text{-}C_6H_4OCH_3)_3$ possessing the electron-donating methoxy group, the yield (363%) was much lower the the expected value, of which the reason is not certain. Tolman's substituent constant, χ, of $P(p\text{-}C_6H_4OCH_3)_3$ (χ=3.4) is same as that of $P(p\text{-}C_6H_4CH_3)_3$ (χ=3.4) and Tolman's cone angles of both phosphines are the same (θ=145°).[13] Phosphines with electron-withdrawing groups, such as $P(p\text{-}C_6H_4F)_3$, $P(p\text{-}C_6H_4Cl)_3$ and $P(OC_4H_9{}^n)_3$ give about the same yield (218%, 216%, 206% in sequence) and $P(C_6F_5)_3$ with highly electronegative substituent results in much lower yield (153%). In the cases of phosphines with aliphatic substituents, $P(C_6H_{11})_3$ (χ=0.1, θ=170°) and $P(CH_2C_6H_5)_3$ (χ=3.4, θ=165°), the yields are low (291%, 160% respectively) compared to their basicity, which might be due to the steric hindrance. When we tried the same type of reaction using diphenylsulfide instead of phosphine under the identical reaction condition (55 °C, 50 psi O_2, 20 h) as a reference, the yield was extremely low (37%) compared with PPh_3 case. Therefore, in general, the catalytic reaction involving $Pd(OAc)_2$ and PPh_3 affords better yield of *trans*-stilbene with higher selectivity than previously reported catalytic systems under reasonably mild condition and the yield tends to increase as the basicity of the substituents in phosphines increases; $P(p\text{-}C_6H_4CH_3)_3$>$P(C_6H_5)_3$>$P(p\text{-}C_6H_4OCH_3)_3$>$P(C_6H_{11})_3$>$P(p\text{-}C_6H_4F)_3 \approx P(p\text{-}C_6H_4Cl)_3 \approx P(OC_4H_9{}^n)_3$>$P(CH_2C_6H_5)_3$>$P(C_6F_5)_3$>>$S(C_6H_5)_2$.

In the arylation reaction of olefin catalyzed by palladium complex, the aryl-palladium forming step is considered to be the rate determining one. And the aryl-palladium intermediate might be formed more effectively with the phosphines containing electron-donating groups since the dissociation of anion (X^-) from palladium salt (PdX_2) might be accelerated with the help of more electron-rich phosphines to make aryl group coordinate to Pd more easily. It is known that the formation of the aryl-palladium intermediate should be preceeded by dissociation of an anion.[14] Actually $Pd(OAc)_2$ is considered to be more effective catalyst than $PdCl_2$ because acetate is more easily dissociated. Also, the coordinated styrene might be activated more effectively by these basic phosphines so that the insertion reaction of styrene to Pd-aryl bond might take place. Therefore, generally the phosphines with more basic substituents could afford higher yield.

On the other hand, *trans*-stilbene can be produced not only from benzene but also from PPh_3 by migration of the phenyl group of PPh_3 to Pd. Previously, Kikukawa *et al.* observed the formation of *trans*-stilbene in the reaction of Pd$(PPh_3)_2(OAc)_2$ with styrene in tetrahydrofuran and they proposed the mechanism of P-C bond cleavage as follows: the PPh_3 ligand coordinated to Pd is in effect phosphonium ion, which is attacked by acetate ion on P (nucleophilic attack), and concurrently the phenyl group on P migrates to the vacant coordination site on Pd (electrophilic substitution). Thus, the mechanism is an electrophilic substitution of phosphine by Pd promoted by nucleophilic assistance by acetate ion.[12,15,16]

When we used the aryl-substituted phosphines in the reaction of styrene with benzene, arylation reaction took place to form *trans*-PhCH=CHPh from benzene as well as *trans*-PhCH=CHR from triarylphosphine (PR_3).

Therefore, we tried to investigate the competitiveness of benzene and the migratory aptitude of aryl groups of triarylphosphines toward styrene in the presence of $Pd(OAc)_2$ and triarylphosphines by varying the substituents on the phenyl groups of phosphines in this work. All the possible reaction products are indicated in equation (1).

Table 3. Composition of Arylation Products (%)

PR_3	1	2	3	4	χ^a	θ^b
$P(p\text{-}C_6H_4CH_3)_3$	98	1		trace	3.5	145
$P(p\text{-}C_6H_4OCH_3)_3$	87	11	trace	2	3.4	145
$P(C_6D_5)_3$	71	27	trace	2	4.3	145
$P(C_6H_{11})_3$	93		1	6	0.1	170
$P(p\text{-}C_6H_4F)_3$	72	27		1	5.0	145
$P(p\text{-}C_6H_4Cl)_3$	74	26			5.6	
$P(OC_4H_9{}^n)_3$	79			21	6.5	
$P(CH_2C_6H_5)_3$	93			6	3.4	165
$P(C_6F_5)_3$	65	32	1	4	11.2	184
$S(C_6H_5)_2$	79			21		
None	53			47		

[a] Tolman's substituent constant. [b] Tolman's cone angle.

$$\text{PhCH=CH}_2+\text{C}_6\text{H}_6 \xrightarrow[55\ ^\circ\text{C, 50 psi O}_2]{\text{Pd(OAc)}_2,\ \text{PR}_3}$$

$$\underset{\mathbf{1}}{\textit{trans}\text{-PhCH=CHPh}} + \underset{\mathbf{2}}{\textit{trans}\text{-PhCH=CHR}}$$

$$+ \underset{\mathbf{3}}{\textit{cis}\text{-PhCH=CHPh}} + \underset{\mathbf{4}}{\textit{trans,trans}\text{-(PhCH=CH)}_2} \qquad (1)$$

(PR_3: $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4OCH_3)_3$, $P(p\text{-}C_6H_4F)_3$, $P(p\text{-}C_6H_4Cl)_3$, $P(C_6H_5)_3$, $P(C_6H_{11})_3$, $P(OC_4H_9{}^n)_3$, $P(CH_2C_6H_5)_3$ and $P(C_6F_5)_3$)

Although many products are listed in equation (1), only two or three of them are produced in each case. The dimerization product of styrene, *trans,trans*-(PhCH=CH)$_2$ (**4**), may be formed by the coordination of two moles of styrene to Pd simultaneously and then the insertion reaction of one of the bonded styrenes to the other. The composition of the reaction products are shown in Table 3. Tolman's substituent constant, χ, and Tolman's cone angle, θ, are also indicated to correlate the electonic and steric effect of the substituent on the phosphine with the yield and selectivity for the formation of *trans*-stilbene (composition of *trans*-stilbene), respectively.[13] It is interesting to point out the major factor of the selectivity to *trans*-stilbene is the basicity of the phosphine ligand and the steric factor doesn't seem to matter very much. For the more basic phosphines, such as $P(p\text{-}C_6H_4CH_3)_3$, $P(C_6H_5)_3$, $P(C_6H_{11})_3$ and $P(CH_2C_6H_5)_3$, the selectivities are 98, 98, 93 and 93% respectively. In spite of the use of excess amount of styrene (10 times excess), dimerization product was found only a few % or trace. As stated above for the yield of *trans*-stilbene, the selectivity in case of $P(p\text{-}C_6H_4OCH_3)_3$ is low (87%) again and large portion of **2** (11%) has been obtained comparing with its basicity. The phosphines with halo-substituted aryl groups, $P(p\text{-}C_6H_4F)_3$ and $P(p\text{-}C_6H_4Cl)_3$, give the selectivity of 72 and 74% where 27% of $C_6H_5CH=CHC_6H_4F$ and 26% of $C_6H_5CH=CHC_6H_4Cl$ (**2**) have been formed, respectively. Maximum composition (32%) of $C_6H_5CH=CHC_6F_5$, **2**, is found for $P(C_6F_5)_3$, which has the most electronegative substituent in the series. Therefore, the phosphine ligands containing the more electronegative substituent on the aryl group yielded more composition of aryl(R)-substituted product, **2**, in other words, the selectivity for the formation of *trans*-stilbene is higher for the system containing more basic phosphine ligand in this work.

In case of triphenylphosphine, competition between $P(C_6H_5)_3$ and the solvent, benzene, for the arylation is expected. To clarify the mode of reaction, the arylation reaction has been carried out with $P(C_6D_5)_3$ to differentiate the migratory aptitude of phenyl group from triphenylphosphine and that from benzene, which results in the formation of 71% of $C_6H_5CH=CHC_6H_5$ and 27% of $C_6H_5CH=CHC_6D_5$.

For the phosphines with non-aromatic groups such as $P(C_6H_{11})_3$, $P(CH_2C_6H_5)_3$ and $P(OC_4H_9{}^n)_3$, **2** is not formed, but dimerization product is found in higher ratio (6, 6, 21% in sequence). Especially, in case of $P(OC_4H_9{}^n)_3$, there might be some more chances for the simultaneous coordiantion of two styrene molecules to Pd to form the dimerization product compared with aryl-phosphines, since aryl-phosphines occupy one more coordination site by aryl group migration and thereby the coordination of other ligand is blocked. In case of $S(C_6H_5)_2$, the phenyl group of sulfide did not migrate, but the selectivity was low down to 79% due to the formation of dimerization product of styrene. Thus, the selectivity is quite low compared with $P(C_6H_5)_3$ of same substituent not to speak of the yield. When phosphine was not added, selectivity was even lower, 53%.

In conclusion, 1) the catalytic arylation reaction of styrene using $Pd(OAc)_2$-PPh_3 system yields trans-stilbene in good yield with high selectivity under mild condition compared with previously reported systems, 2) aryl-substituted phosphines also produce arylated olefin, and its composition increases as the electronegativity of the arylsubstituent increases, therfore, 3) the more basic phosphines afford the better yield and better selectivity for the formation of *trans*-stilbene.

Acknowledgment. Authors thank to Korea Science and Engineering Foundation for the financial support in 1995 and Dr. Jae Sung Lee at KIST for his assistance for collecting GC/MS data.

References

1. Tsuji, J. *Acc. Chem. Res.* **1973**, *2*, 8.
2. (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518. (b) Heck, R. F. *ibid.* **1968**, *90*, 5526. (c) Heck, R. F. *ibid.* **1968**, *90*, 5531. (d) Heck, R. F. *ibid.* **1968**, *90*, 5542.
3. Moritani, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, 1119.
4. Fujiwara, Y.; Moritani, I.; Matsuda, M. *Tetrahedron* **1968**, *24*, 4819.
5. Fujiwara, Y.; Moritani, I.; Matsuda, M.; Teranishi, S. *Tetrahedron Lett.* **1968**, 633.
6. Stern, E. W.; Spector, M. L.; Leftin, M. P. *J. Catalysis* **1966**, *6*, 152.
7. (a) Shue, R. S. *J. Am. Chem. Soc.* **1971**, *27*, 279-282. (b) Shue, R. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1510. (c) Shue, R. S. *J. Catalysis* **1972**, *26*, 112.
8. Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166.
9. Fuchita, Y.; Hiraki, K.; Kamogawa, Y.; Suenaga, M. *J. Chem. Soc., Chem. Commun.* **1987**, 941.
10. Fuchita, Y.; Kawakami, M.; Shimoke, K. *Polyhedron* **1991**, *10*, 2037.

11. Fuchita, Y.; Takeda, Y.; Taga, M. *Inorg. Chim. Acta* **1994**, *216*, 253.
12. Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron* **1973**, *29*, 955.
13. Tolmaan, C. A. *Chem. Rev.* **1977**, *77*, 313.
14. Danno, S. *J. Chem. Soc., Chem. Commun.* **1970**, 610.
15. Kawamura, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Jpn. Chem. Soc.* **1977**, *50*, 2021.
16. Kikukawa, K.; Matsuda, T. *J. Organomet. Chem.* **1982**, *235*, 243.