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Aromatic Substitution of Olefin. X. Formation of Biphenyl Derivatives by Means of Olefin-Palladium Chloride Complexes and Silver Nitrate[*1]

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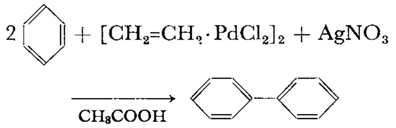
The system, olefin-palladium chloride complex-silver nitrate has been shown to cause the oxidative coupling reaction of the aromatic compounds to afford biphenyl derivatives. The mechanism was also discussed in connection with the aromatic substitution of olefins by palladium salts.

We have reported a novel method of arylation by substitution of aromatic compounds for hydrogen on the double bond of the olefin.[1)]

In the course of this work, it has been found that the system, olefin-palladium(II) chloride complex-silver(I) nitrate does cause the oxidative coupling reaction of aromatic compounds to give biaryl derivatives easily.



On the formation of biaryl derivatives by palla-

[*1] Presented at the Symposium on Homogeneous Catalytic Reactions Involving Palladium, American Chemical Society, Minneapolis, U. S. A., April 1969.

1) a) I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, **1967**, 1119; b) Y. Fujiwara, I. Moritani and M. Matsuda, *Tetrahedron*, **24**, 4819 (1968); c) Y. Fujiwara, I. Moritani, M. Matsuda and S. Teranishi, *Tetrahedron Lett.*, **1968**, 633; d) Y. Fujiwara, I. Moritani, M. Matsuda and S. Teranishi, *ibid.*, **1968**, 3868; e) Y. Fujiwara, I. Moritani, R. Asano and S. Teranishi, *ibid.*, **1968**, 6015; f) Y. Fujiwara, I. Moritani, S. Danno, R. Asano and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969); g) S. Danno, I. Moritani and Y. Fujiwara, *Tetrahedron*, **25**, 4809 (1969); h) Y. Fujiwara, I. Moritani, R. Asano, H. Tanaka and S. Teranishi, *ibid.*, **25**, 4815 (1969); i) S. Danno, Y. Fujiwara and I. Moritani, *ibid.*, **25**, 4819 (1969).

dium salts, van Helden and Verberg[2] have reported that benzene gives biphenyl in the presences of palladium(II) chloride and sodium acetate in an 82% yield, and Davidson and Trigg[3] have described a similar biphenyl formation by palladium(II) acetate and that when perchloric acid is used with palladium(II) acetate, the yield of biphenyl increases up to 55%.

We have investigated the biaryl derivative formation reaction involving palladium chloride complexes and silver nitrate. Interesting aspects of the present reaction are that the olefin palladium(II) chloride complex and silver(I) nitrate are employed together and that the yield of biphenyl is almost quantitative (99%) with respect to palladium(II) when the ethylene-palladium(II) chloride complex is used with silver(I) nitrate.

The present paper reports a study of the coupling reaction of benzene derivatives by means of the olefin-palladium(II) chloride complex and silver(I) nitrate.

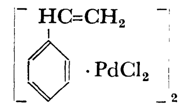
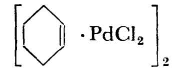
Results and Discussion

In the course of the study on the aromatic substitution of olefin, we have performed the reaction of the ethylene-palladium(II) chloride complex with benzene in the presence of silver(I) nitrate in a hope of preparing styrene directly.[4] Unexpectedly, no styrene was formed, but biphenyl was obtained in almost quantitative yield[5] with a very small amount of chlorobenzene. The result is reproducible on triplicate reactions. This higher yield of biphenyl comparing to van Helden (82%) and Davidson's results (55%) prompted us to investigate the oxidative coupling of benzene derivatives in the system, olefin-palladium(II) chloride complex-silver(I) nitrate in detail.

The oxidative coupling of benzene derivatives takes place in the homogeneous solution of olefin-palladium(II) chloride complexes, silver(I) nitrate (equal mol equivalent to Pd(II) in the olefin-palladium complex)[6] and the benzene derivatives (large excess) in acetic acid. The solution is stirred in the presence of air for 20 hr to give several per cent to 99% yield of biphenyl derivatives.

Effect of Olefin-$PdCl_2$ Complex. As the ethylene complex-silver nitrate system affords biphenyl from benzene quantitatively, the effect of the similar olefin complexes such as styrene or cyclohexene has been investigated under the same condition. Table 1 shows the yields of biphenyl.

TABLE 1. BIPHENYL FORMATION BY OLEFIN-PALLADIUM CHLORIDE COMPLEX-SILVER NITRATE SYSTEM

Olefin-complex	Biphenyl yield, %[a]
$[CH_2{=}CH_2\cdot PdCl_2]_2$	99[b]
	68[c]
	3[d]
$PdCl_2$	40

a) Yields are based on palladium(II) of the complex.
b) A trace amount of chlorobenzene was also obtained.
c) A 22% yield of 1-phenylethyl acetate and a 7% yield of tetraphenylethylene were also formed.
d) A 9% yield of isomeric terphenlys was also obtained.

It can be seen that the yield of biphenyl decreases in the following sequence:

ethylene > styrene > cyclohexene

That this sequence is consistent with the stability of the olefin-complex[7] suggests that the reactivity depends upon the ease with which the olefin ligand on Pd(II) exchanges with benzene. Table 1 also shows that biphenyl can be formed in the presence of $PdCl_2$ and $AgNO_3$, but the yield is low indicating

TABLE 2. EFFECT OF METAL SALTS[a]

$PdCl_2$	Metal slat	Biphenyl yield, %[b]
○	$AgNO_3$	40
○	×	×
×	$AgNO_3$	×
○	AgOAc	45
○	Ag_2O	24
○	HgOAc	23
○	$Cu(OAc)_2$	22

a) Reactions were carried out at 80°C with stirring for 20 hr, charging 25 mmol of $PdCl_2$, an equal mole amount of $AgNO_3$, 280 m*l* of benzene, and 40 m*l* of acetic acid.
b) Yields are based on palladium (II) chloride.

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[2] R. van Helden and G. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

[3] J. M. Davidson and C. Trigg, *Chem. Ind.* (London), **1966**, 457.

[4] It has been known that styrene can be prepared directly from ethylene and benzene by palladium acetate.[1f]

[5] Interestingly, in the absence of siliver nitrate, no biaryl derivatives are formed except the arylated products in the aromatic substitution of olefins by means of palladium salts.[1]

[6] When 1/2 mol equivalent of $AgNO_3$ to Pd(II) was used, a greenish black complex was obtained after the reaction. As it has a function to cause the coupling of benzene, it can be considered to be one of the reaction intermediates. Owing to the insolubility, purification is not practical, but approximate composition is $Ag_2Pd_2(OAc)_2Cl_4$.

[7] M. S. Kharasch, R. C. Seiler and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

that the ethylene-$PdCl_2$ complex is the most effective for the oxidative coupling of benzene.

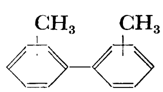
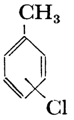
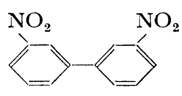
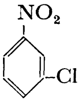
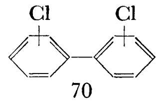
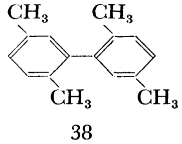
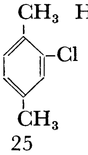
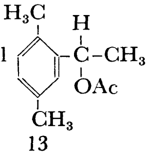
Effect of Metal Salts. Further, the effect of metal salts was studied. The results are shown in Table 2.

It can be seen that $PdCl_2$ alone or $AgNO_3$ alone can not effect the coupling of benzene, indicating that coexistence of $PdCl_2$ and $AgNO_3$ is necessary for the present reaction.[8] Of metal salts, mercuric or copper salts, rather than $AgNO_3$ can also act as cocatalysts but silver salts are the most effective. From these results, it becomes clear that the system, ethylene-$PdCl_2$ complex-$AgNO_3$ is the most useful one for the oxidative coupling of benzene.

Now, we have investigated the coupling reactions of benzene derivatives using the present system.

Reaction of Benzene Derivatives. The coupling reactions of toluene, chlorobenzene, nitrobenzene, and *p*-xylene are carried out using the ethylene-$PdCl_2$-$AgNO_3$ system at 80°C. Table 3 summarizes the results.

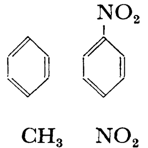
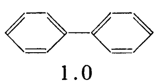
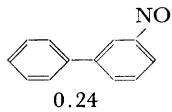
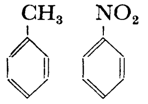
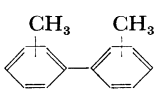
Table 3. Coupling reaction of benzene derivatives

Benzene derivative	Product, %[a]
Toluene	 61  10  8
Nitrobenzene	 60  21
Chlorobenzene	 70
p-Xylene	 38  25  13

a) Yields are based on palladium (II) of the complex.

In the cases of toluene and chlorobenzene, five isomeric dimethylbiphenyls[9] and dichlorobiphenyls are formed in 61% and 70% yields respectively. Contrary to this, nitrobenzene gives only *m,m'*-dinitrobiphenyl as the coupling product. *p*-Xylene also undergoes a coupling reaction in lower yield (38%) due to the steric hindrance of methyl groups. From the data in Table 3, it seems that the reactivity of benzene derivatives such as toluene or nitrobenzene will not be influenced by the substituent. In order to clarify this point, the relative reactivities were examined by competitive reactions. The typical examples are shown in Table 4.

Table 4. Competitive reactions of some benzenes[a]

Benzene derivative	Product ratio (mole)
	 1.0  0.24
	 1.0

a) Reactions were performed at 80°C with stirring for 20 hr, charging an equal amount (1.5 mol) of two benzene derivatives, the ethylene-$PdCl_2$ complex (25 mmol as a monomer), $AgNO_3$ (25 mmol), and acetic acid (40 m*l*).

It can be seen that the yield of mononitrobiphenyl decreases sharply and none of the dinitro derivative was detected in the reaction mixture. This result shows that the substituent on a benzene ring excerts an effect, that is, a methyl group (electron donating) increases the reactivity, and a nitro group (electron attracting) decreases it.[2] This is marked contrast to the fact that the substituent on a benzene ring does not influence on the reactivity in the aromatic substitution of olefins by palladium salts.[1h]

Finally, the mechanism of the present coupling reaction appears to be closely related to the aromatic substitution of olefins proposed in a previous paper.[1i] The reaction may proceed through a sigma bonded benzene-palladium complex.[10] This benzene-palladium sigma bond formation step is fast in the aromatic substitution of olefins and hence the substituent did not influence the reactivity.[1h] However, in the present case, this must be included in the rate determining step, and therefore, the reactivity becomes a function of the substituent.

The present reaction provides a convenient method for the synthesis of biphenyl derivatives.

Experimental

All melting points and boiling points are uncorrected.

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8) That $PdCl_2$ without $AgNO_3$ or NaOAc can not cause both the oxidative coupling and the aromatic substitution of olefins shows the role of $AgNO_3$ or NaOAc to be that Ag^+ or Na^+ abstracts the Cl^- ligand from the Pd(II) and then, it becomes possible for benzene to coordinate with Pd(II).[1f]

9) M. O. Unger and R. A. Fouty, *J. Org. Chem.*, **34**, 18 (1969).

10) J. M. Davidson and C. Trigg, *J. Chem. Soc., A*, **1968**, 1324.

Infrared spectra were recorded by a Hitachi EPI-S2 IR spectrometer and UV spectra were recorded on a Hitachi EPS-2U spectrophotometer. The NMR spectra were obtained by a Japan Electron Optics JNM-4H-100 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are given in τ units together with splitting patterns and relative integrated area. Analyses of products were carried out by a column chromatograph or a Yanagimoto GCG-3 gas chromatograph using an Apiezon L column. Identities with the products formed were proved by mixture melting point, IR and NMR comparison with authentic samples. Olefin-$PdCl_2$ complexes used were prepared according to the method described by Kharasch *et al.*[7] Benzene, toluene, *p*-xylene were refluxed with sodium metal and distilled. Chlorobenzene and nitrobenzene were dried over Na_2SO_4 and distilled. Acetic acid was dried over P_2O_5 and distilled.

Coupling of Benzene with Ethylene-$PdCl_2$ Complex and $AgNO_3$. In a 500-m*l*, three necked flask provided with a condenser and a stirrer, was placed a solution of 4.13 g (25 mmol as a monomer) of the ethylene-complex, 4.25 g (25 mmol) of $AgNO_3$, 280 m*l* of benzene, and 40 m*l* of acetic acid. The solution was stirred for 20 hr at 80°C. During the reaction, ethylene gas, hydrogen chloride gas, and nitrogen dioxide gas evolved. The resulting mixture was filtered to remove palladium metal and AgCl, and the filtrate was poured into water and then the organic layer was separated. The organic layer was treated with aqueous sodium bicarbonate solution, washed with water to free it from acetic acid and then dried over Na_2SO_4. After evaporation of the benzene, the residue was chromatographed on a column of alumina. Elution with petroleum ether and recrystallization yielded 3.81 g, mp 69—70°C (lit,[11] 70°C) (99%, based on Pd(II) in the complex) of a colorless crystalline material which was assigned as biphenyl by comparison of the IR spectra and mixture melting point. IR (Nujol): 2995, 1575, 1480, 900, 728, and 695 cm^{-1}. Found: C, 93.38; H, 6.62%. Calcd for $C_{12}H_{10}$: C, 93.50; H, 6.52%.

From the benzene evaporated, a trace amount of chlorobenzene was also detected by glpc.

Coupling of Benzene with Styrene-$PdCl_2$ Complex and $AgNO_3$. The same procedure was followed as above, charging 25 mmol (as a monomer) of the syrene-complex, 25 mmol of $AgNO_3$, 280 m*l* of benzene, and 40 m*l* of acetic acid. After work-up as described above there were obtained biphenyl (68%), tetraphenylethylene (7%),[1f] mp 219.5—221°C (lit,[12] 223—224°C) and 1-phenylethyl acetate (22%).[1b]

Coupling of Toluene with Ethylene-$PdCl_2$ Complex and $AgNO_3$. The same procedure was followed as above. After evaporation of toluene, the residue was distilled under reduced pressure (10 mmHg), to give 0.45 g (10%) of the colorless liquid, bp 120—121°C (10 mmHg) which was assigned as *p*-(1-acetoxylethyl)toluene. IR (neat): 3015, 1750, 1240, 1085, 890, 820, and 745 cm^{-1}. NMR (CCl_4): 2.9 (multiplet, 4), 4.3 (quadruplet, 1), 7.8 (singlet, 3), 8.1 (singlet, 3), 8.6 (doublet, 3). Found: C, 74.28; H, 7.91%. Calcd for $C_{11}H_{14}O_2$: C, 74.15; H, 7.86%.

The distillation residue was chromatographed on a column of alumina. Elution with *n*-hexane yielded a colorless substance which crystallized partly. Recrystallization from ether gave 0.86 g (19%) of *p,p'*-dimethylbiphenyl, mp 123—124°C (lit,[13] 121°C). IR (Nujol): 3020, 1500, 1210, 810 cm^{-1}. Found: C, 92.51; H, 7.63%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

The oil part (1.91 g, 42%) was subjected to gas chromatograph (Apiezon L, 2m, 190°C) to detect four components. The four components were separated into A and B by preparative glpc.

The component A: IR (neat): 3040, 1600, 1480, 1100, 820, 755, 726, 708 cm^{-1}. Found: C, 92.32; H, 7.68%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

The component B: IR (neat): 3040, 1610, 1480, 1092, 880, 820, 775, 700 cm^{-1}. Found: C, 92.40; H, 7.78%. Calcd for $C_{14}H_{14}$: C, 92.26: H, 7.74%. From these results, the oil part (A and B) can be considered to be a mixture of four isomeric dimethylbiphenyls. Further elution with benzene afforded 0.25 g (8%) of isomeric chlorotoluenes, mp 153—158°C. IR (Nujol): 3020, 1600, 1475, 1080, 885, 810, 750, 715 cm^{-1}. Found: C, 66.30; H, 5.51; Cl, 28.20%. Calcd for C_7H_7Cl: C, 66.41; H, 5.53; Cl, 28.06%.

Coupling of Chlorobenzene with Ethylene-$PdCl_2$ Complex and $AgNO_3$. The same procedure was followed as above. After evaporation of the chlorobenzene, the residue was chromatographed on a column of alumina. Elution with petroleum ether gave 0.78 g (14%) of a crystalline material which was assigned as *p,p'*-dichlorobiphenyl by comparison with an authentic sample. Mp 147—148°C (EtOH) (lit,[14] 148—149°C), IR (Nujol): 3050, 1590, 1090, 1000, 810, 700 cm^{-1}. Found: C, 64.65; H, 3.70; Cl, 32.12%. Calcd for $C_{12}H_8Cl_2$: C, 64.57; H, 3.60; Cl, 31.84%. Further elution with petroleum ether resulted 3.12 g (56%) of a liquid substance which was gas chromatographed to detect four components. The four components were separated into C and D by preparative glpc.

The component C: IR (neat): 3000, 1575, 1030, 825, 785, 750, 700 cm^{-1}. Found: C, 64.77; H, 3.48; Cl, 32.02%. Calcd for $C_{12}H_8Cl_2$: C, 64.57; H, 3.60; Cl, 31.84%.

The component D: IR (neat): 3000, 1580, 1555, 1450, 1085, 1055, 750, 700 cm^{-1}. Found: C, 65.00; H, 3.64; Cl, 32.16%. Calcd for $C_{12}H_8Cl_2$: C, 64.57; H, 3.60; Cl, 31.84%. From these results, the liquid substance (C and D) can be considered to be a mixture of four isomeric dichlorobiphenyls.

Coupling of Nitrobenzene with Ethylene-$PdCl_2$ Complex and $AgNO_3$. The products were *m,m'*-dinitrobiphenyl (60%) and *m*-chloronitrobenzene (21%): *m,m'*-Dinitrobiphenyl: mp 201—202°C (*n*-hexane-benzene) (lit,[14] 198.5—199°C). IR (Nujol): 2950, 1515, 1340, 1260, 1100, 855, 800, 726, 700 cm^{-1}. Found: C, 59.08; H, 3.28; N, 11.49%. Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.28; N, 11.48%.

Coupling of *p*-Xylene with Ethylene-$PdCl_2$ Complex and $AgNO_3$. The products were 2,5,2',5'-tetramethylbiphenyl (38%), 2-chloro-*p*-xylene (25%) and

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11) M. Gomberg and W. E. Bachman, *J. Amer. Chem. Soc.*, **46**, 2343 (1924).

12) N. Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, p. 914 (1941).

13) Th. Zincke, *Ber.*, **4**, 397 (1871).

14) B. Williamson and W. H. Rodebush, *J. Amer. Chem. Soc.*, **63**, 3018 (1941).

2-(1-acetoxyethyl)-1,4-dimethylbenzene (13%).

2,5,2′,5′-Tetramethylbiphenyl: mp 50.5—52°C (*n*-hexane) (lit,[15] 52°C). UV :λ_{max}^{EtOH} 270 (log ε 3.20), 277 (3.18). Found: C, 91.28; H, 8.52%. Calcd for $C_{16}H_{16}$: C, 91.37; H, 8.63%.

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15) G. H. Beaven and E. A. Johnson, *Spectrochim. Acta*, **14**, 67 (1957).