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AROMATIC SUBSTITUTION OF OLEFIN—III

REACTION OF STYRENE-PALLADIUM(II) CHLORIDE COMPLEX[1]

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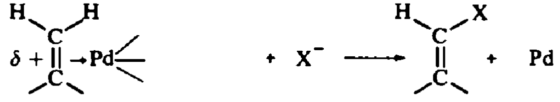
Abstract—*trans*-Stilbene derivatives have been obtained from a reaction of styrene-palladium (II) complex (**1**) with aromatic compounds in the presence of carboxylic acids. This novel method of synthesizing stilbene derivatives by substitution of an H atom on the double bond of the styrene of complex **1** is the first case of aromatic substitution of olefins.

In a typical reaction, the complex **1** with benzene and acetic acid afforded *trans*-stilbene in a 26 % yield and a saturated acetate (13 %), and when sodium acetate was added, the yield was surprisingly increased.

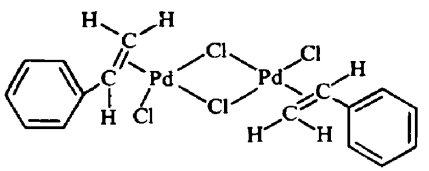
INTRODUCTION

ALDEHYDE derivatives,[2] enol acetate derivatives,[3] vinyl ethers,[4] amine derivatives[3c] and olefinic cyanides[5] have been obtained by the nucleophilic attack of water, acetate anion, alkoxy anion, amine and cyanide anion on olefins respectively.



In addition, olefins give carbonyl compounds, when treated with carbon monoxide and the palladium (II) chloride catalyst.[6] Substitution of aromatic compounds for hydrogen on the double bond of olefin–palladium (II) chloride complexes has not been observed.

As represented by the Ziegler-Natta catalysts, many reactions involving organometallic compounds proceed in a stereospecific manner. In order to study the stereochemistry of this nucleophilic substitution of olefins, styrene–palladium (II) chloride complex (**1**) was treated with acetic acid in benzene as the solvent.



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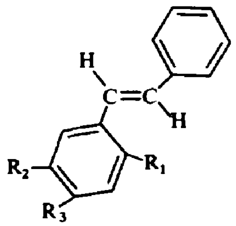
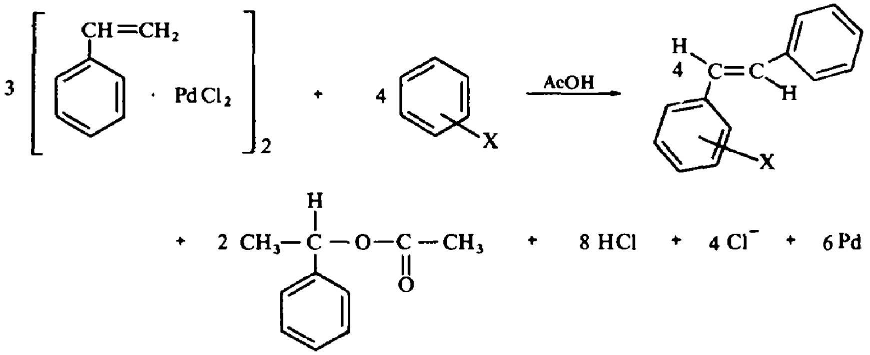


2a: $R_1 = R_2 = R_3 = H$
2b: $R_1 = R_2 = H, R_3 = CH_3$
2c: $R_1 = R_2 = CH_3, R_3 = H$

Complex **1** affords *trans*-stilbene (**2a**) by the substitution of the benzene for hydrogen on the double bond of complex **1** with the saturated acetate as by-product, and this acetate is not the expected β-acetoxystyrene (**4**; *cis* and/or *trans*), but α-phenyl-ethyl acetate (**3a**). Furthermore, complex **1** with toluene or *p*-xylene gives *trans-p*-methylstilbene (**2b**) and *trans*-2,5-dimethylstilbene (**2c**), respectively. These results show that a β-hydrogen of the styrene of **1** is substituted by the aromatic compound such as benzene, toluene or *p*-xylene.

The present reaction can be expressed in the following scheme:



In addition to styrene other olefins such as ethylene undergo this substitution yielding phenyl-substituted olefins which will be reported in a separate paper. A preliminary communication of this work has been given.[7]

RESULTS AND DISCUSSION

trans-Stilbene (**2a**) was obtained from the reaction of complex **1** and acetic acid in dry benzene, suggests that a β-hydrogen of styrene was substituted by the solvent benzene, although a Ph group of stilbene may be derived from the decomposition of styrene and not from benzene itself. In order to clarify this point, toluene was used instead of benzene. If the reaction involves a substitution of the solvent molecule, Me-substituted stilbene should be obtained, and if the decomposition of styrene is involved, *trans*-stilbene (**2a**) should be produced.

On treating the reaction mixture as usual, *trans-p*-methylstilbene (**2b**) and **3a** were obtained in 25% and 14% yields respectively. This result shows that the toluene reacted with styrene. As benzene adds to styrene initially to form diphenylethane, which is followed by the dehydrogenation with Pd(O) or $Pd^{II}Cl_2$ (path A), diphenylethane was treated under similar conditions, the starting material was recovered quantitatively.

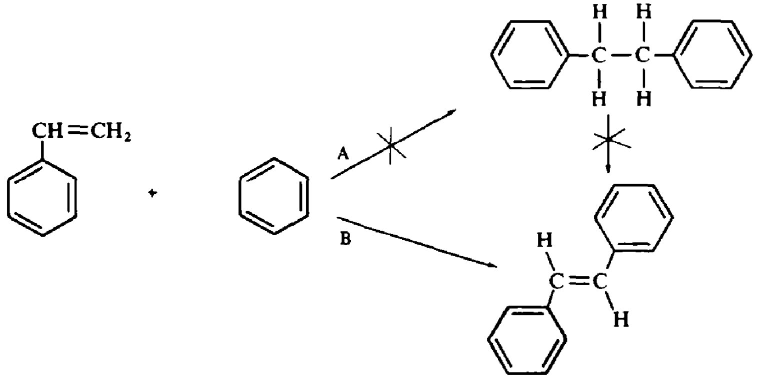


TABLE 1. THE REACTION OF COMPLEX 1 WITH AROMATIC COMPOUNDS

Expt. No.	Complex **1** (mole)	Aromatic compounds (ml)	Carboxylic acid (ml)	Reaction temp and time (°C)	(hr)	Products (%) Stilbene	Acetate
1	0·016	benzene, 340	acetic acid, 80	reflux	8	**2a**, 26	**3a**, 13
2	0·059	toluene, 1000	acetic acid, 300	110°	74·5	**2b**, 25	**3a**, 14
3	0·050	*p*-xylene, 1000	acetic acid, 250	110°	74·5	**2c**, 25	**3a**, 15
4	0·047	mesitylene, 500	acetic acid, 100	110°	44·5	—	**3a**, 15
5	0·018	benzene, 350	monochloroacetic acid, 80[a]	110°	8	**2a**, 18	**3b**, 7
6[b]	0·0071	benzene, 150	acetic acid, 36	reflux	8	**2a**, 86	**3a**, 1·8 **4**, 4·7
7	0·017	benzene, 300	HCl gas[c]	reflux	8	—	—

[a] Presented in grams.

[b] 2 mole equivalents of sodium acetate to $PdCl_2$ of **1** were used.

[c] Dry HCl gas was bubbled into the reaction mixture.

Moreover, when **3a**, a by-product in the reaction, was treated with benzene, acetic acid and $Pd^{II}Cl_2$ (and Pd(O)), it was also recovered quantitatively. Thus it becomes clear that *trans*-stilbene (**2a**) is formed by the direct substitution of a β-hydrogen of styrene with benzene (Path B). Furthermore, in case of *p*-xylene, *trans*-2,5-dimethylstilbene (**2c**) was obtained in 25% yield. However in case of mesitylene, no stilbene derivatives were obtained. This can be attributed to steric hindrance of three Me groups on benzene These results are summarized in Table 1.

Effect of co-solvent. When a solution of complex **1** in benzene was heated under reflux without acetic acid, styrene was recovered almost quantitatively. Similarly, no stilbene derivative was obtained, if complex **1** was treated with benzene in the presence of dry hydrogen chloride (Expt. 7).

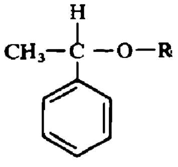
On the other hand, if monochloroacetic acid was used, *trans*-stilbene (**2a**; 18% yield) and α-phenylethyl monochloroacetate (**3b**; 7% yield) were obtained. Finally if acetone, ethanol (protic solvent) or ether (aprotic solvent) were used as the solvent, no stilbene was obtained. These results are summarized in Table 2.

TABLE 2. EFFECT OF CO-SOLVENT

Solvent	Formation of *trans*-stilbene
None	No
CH_3COOH	Yes
$CH_2ClCOOH$	Yes
HCl gas	No
CH_3COCH_3	No
C_2H_5OH	No
$C_2H_5OC_2H_5$	No

These results clearly show that an acid such as acetic, plays a key role in the reaction Although most olefin–palladium chloride complexes are insoluble in the common organic solvents,[8] the reaction proceeds homogeneously in a mixture of benzene–acetic acid. Another role of acetic acid, especially that of the acetate anion will be discussed in a separate paper.

Acetates. Saturated acetates **3a**, and **3b**, by-products in the reactions, are formed by the addition of acetic acid and monochloroacetic acid respectively to styrene. As **3a** is only formed when styrene is treated with acetic acid in the presence of $PdCl_2$ and not in the absence of the mineral acid catalysts such as hydrochloric acid and sulphuric acid, $PdCl_2$ must be an active catalyst for the addition of acetic acid to styrene. Since carboxylic acids add to olefins easily to give saturated acetates in the presence of acid catalyst,[9] the hydrochloric acid evolved from the $PdCl_2$



3a: R = CH_3CO
3b: R = CH_2ClCO

may act as a catalyst for the addition reaction. But if the hydrochloric acid formed from $PdCl_2$, was neutralized with sodium acetate, **3a** was also obtained in 1·8% yield with *trans*-stilbene (**2a**; 86%) and β-acetoxystyrene (**4**; *cis* and *trans*, 4·7%) (Expt. 6), thus proving that $PdCl_2$ is an active catalyst in the reaction.

Therefore, the reaction of styrene complex **1** with aromatic compounds gives aromatic-substituted olefin products by direct substitution in the presence of carboxylic acids and that α-phenylethyl acetate formed is a by-product formed by addition of carboxylic acid to styrene.

This aromatic substitution of styrene is a new reaction and should be useful in the field of synthetic chemistry.

EXPERIMENTAL

All temps were uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer; UV spectra were obtained by a Hitachi EPS-2U spectrophotometer; NMR spectra were recorded by a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in tau-scale together with splitting patterns and relative integrated area. VPC analyses were made by a Yanagimoto GCG-3 gas chromatograph. Benzene, toluene, *p*-xylene and mesitylene were refluxed with Na metal and distilled. AcOH was dried over P_2O_5 for a week and distilled through a 45-cm Widmer distilling column.

Reaction of styrene-palladium (II) *chloride complex* (**1**) *with benzene*

(a) *Reaction in acetic acid* (*Expt.* 1). In a soln of dry benzene (340 ml) and AcOH (80 ml), 9·10 g (0·016 mole as a dimer) of styrene complex **1**[10] was dissolved, and the mixture was refluxed with continued stirring for 8 hr. After separation of the precipitated palladium, the reaction mixture was poured into water. The organic layer was separated, the aqueous layer extracted twice with benzene and the combined the organic layers washed and dried over Na_2SO_4.

Distillation under reduced press gave 1·87 g of styrene (56% yield based on styrene of **1**), 0·73 g of distillate **3a**, b.p. 65–68° (5 mmHg), and the residual material crystallized (1·67 g). Recrystallization of the crude substance from pet. ether gave the white crystals of **2a** (1·50 g, 26%) m.p. 122–123°, (reported[11] m.p. 122–123°), which was assigned as *trans*-stilbene by comparing IR spectrum and mixed m.p. with an authentic sample. The crude liquid substance was purified by VPC (5 mm × 2 m, Apiezon L, 140°) to give 0·67 g of **3a**, (13%), b.p. 105–107° (15 mmHg), (reported[12] b.p. 105–108° (15 mmHg)), which was assigned as α-phenylethyl acetate through comparison of the IR spectrum and retention time with those of an authentic material. IR spectrum: 699, 760 cm^{-1} (mono-sub. benzene), 1235 cm^{-1} ($\nu_{C—O—C}$), 1730 cm^{-1} ($\nu_{C=O}$); NMR spectrum: 2·76 (s, 5); 4·19 (qu, 1); 8·00 (s, 3) and 8·49 (d, *J* = 6 c/s, 3). (Found: C, 73·24; H, 7·47. $C_{10}H_{10}O_2$ requires: C, 73·14; H, 7·37%).

(b) *Reaction in chloroacetic acid* (*Expt.* 5). A soln of **1** (10·0 g, 0·0178 mole), and chloroacetic acid (80·0 g, 0·845 mole) in dry benzene (350 ml) was heated at 110° with continued stirring for 8 hr. The precipitated Pd was removed and the filtrate washed with water and dried. Benzene was evaporated and the residue vacuum distilled to give **2a**, (1·13 g, 18%), m.p. 122–123° (EtOH), and acetate **3b** (0·050 g, 7%), b.p. 135–138° (16 mmHg), (reported[13] b.p. 135–140° (16 mmHg)), which was assigned as α-phenylethyl monochloroacetate by comparison of the IR spectrum and retention time with those of an authentic sample. IR spectrum: 690, 750, 1170, 1750 cm^{-1}; NMR spectrum: 2·74 (s, 5); 4·15 (qu, 1); 6·10 (s, 2), and 8·45 (d, *J* = 6 c/s, 3).

(c) *Reaction with sodium acetate in acetic acid* (*Expt.* 6). Complex **1** (4·00 g, 0·0071 mole) and NaOAc (2·29 g, 0·028 mole) were added to a mixture of dry benzene (150 ml) and AcOH (36 ml). The resulting soln was refluxed with continued stirring for 8 hr. The reaction mixture was treated as described in (a) yielding 2·20 g of **2a** (86%) and 0·17 g of a mixture, which was separated by preparative VPC. One component was identified as **3a**, (0·043 g, 1·8%) and the other as β-acetoxystyrene (0·107 g, 4·7%), b.p. 119–121° (10 mmHg), n_D^{20} 1·5482, (reported[14] b.p. 119–121° (10 mmHg), n_D^{20} 1·5483) by IR spectra and retention time with authentic β-acetoxystyrene.

Reaction of styrene-palladium (II) *chloride complex* (**1**) *with toluene in the presence of acetic acid* (*Expt.* 2)

A mixture of **1** (33·1 g, 0·059 mole), dry toluene (1000 ml) and AcOH (300 ml) was heated at 110° (gentle reflux) with continued stirring for 74·5 hr. After work-up as described above, **3a**, (2·66 g, 14%) and **2b**, (5·70 g, 25%), m.p. 119–120° (EtOH), (reported[15] m.p. 120°) were obtained. NMR spectrum of **2b**: 2·55–3·00 (m, 9); 3·05 (s, 2) and 7·65 (s, 3). (Found: C, 92·68; H, 7·36. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%). These compounds were identified by comparison of the IR spectrum and mixed m.p. with authentic samples. No *ortho*-, and *metha*- substituted stilbene was detected by VPC analysis.

Reaction of styrene-palladium (II) *chloride complex* (1) *with* p-*xylene in the presence of acetic acid* (*Expt.* 3)

A mixture of **1** (28·0 g, 0·050 mole), dry *p*-xylene (100 ml) and AcOH (250 ml) was stirred at 110° for 74·5 hr and treated in usual manner, yielding **3a**, (2·42 g, 15%), and **2c** (5·11 g, 25%), b.p. 113–114° (5×10^{-2} mmHg), m.p. 43–44° (EtOH), $n_D^{21\cdot 5}$ 1·6360, which was identical in all respects (IR, UV, NMR, and mixed m.p.) with authentic *trans*-2,5-dimethylstilbene. IR spectrum of **2c**; ν_{Nujol} 960, 805, 750 and 686 cm^{-1}. UV spectrum: $\lambda_{\max}$ (EtOH) 224 mμ (log ε 4·30), 297 mμ (4·32). NMR spectrum: 2·55–3·00 (m, 8), 3·10 (s, 2), 7·67 (s, 3), and 7·70 (s, 3). (Found: C, 92·00; H, 7·77. $C_{16}H_{16}$ requires: C, 92·26; H, 7·74%).

Authentic *trans*-2,5-dimethylstilbene with m.p. 43–44° (EtOH), was prepared in 11% yield from *p*-xylidine and cinnamic acid according to Meerwein's method.[16]

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