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AROMATIC SUBSTITUTION OF OLEFIN—VIII

SUBSTITUENT EFFECTS ON THE REACTIONS OF STYRENE WITH MONOSUBSTITUTED BENZENES IN THE PRESENCE OF PALLADIUM(II) SALTS[1]

Y. FUJIWARA, I. MORITANI, R. ASANO, H. TANAKA and S. TERANISHI
Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama,
Toyonaka, Osaka, Japan

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Abstract—In the reactions of styrene with monosubstituted benzenes such as toluene, ethylbenzene, anisole or chlorobenzene in the presence of palladium(II) salts, the direction of substitution but not the reactivity is strongly influenced by the substituent on a benzene ring.

INTRODUCTION

ARYL substituted olefins are produced by substitution with aromatic compounds at the double bond of the olefin by means of palladium(II) salts.[2] When styrene and toluene react in the presence of palladium(II) acetate, *o*- and *p*-methylstilbene are formed, indicating *ortho* and *para* orientation.[2b] This result prompted us to investigate the reaction of styrene with monosubstituted benzenes and the mechanistic implications.

RESULTS AND DISCUSSION

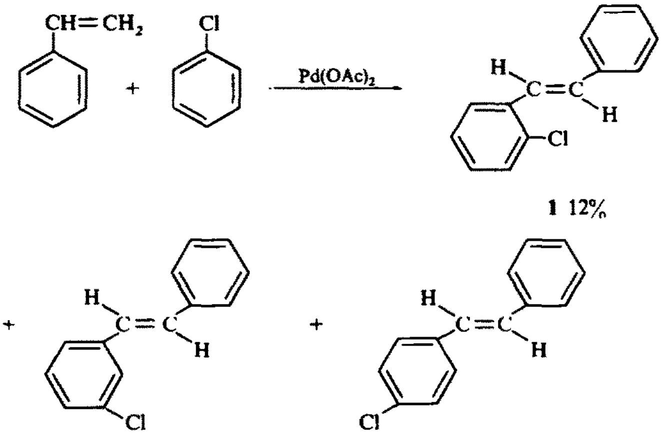
The reactions were performed in the presence of $PdCl_2$-NaOAc, or $Pd(OAc)_2$.[2b] The experimental results are summarized in Table 1 and show that the direction of the substitution is controlled by the *ortho-para* directing nature of the alkyl group, and by the *meta* directing nature of the nitro group.

TABLE 1. THE REACTION OF STYRENE WITH MONOSUBSTITUTED BENZENES

Monosubstituted benzene	*trans*-Stilbene	Yield, %[a]	
		$PdCl_2$-NaOAc[b]	$Pd(OAc)_2$
Toluene	*o*-Methylstilbene	—	3
	p-Methylstilbene	—	58
Ethylbenzene	*p*-Ethylstilbene	22	52
Anisole	*p*-Methoxystilbene	—	61
Nitrobenzene	*m*-Nitrostilbene	25	60
Chlorobenzene	*o*-Chlorostilbene	10	12
	m-Chlorostilbene	12	20
	p-Chlorostilbene	13	30

[a] Yields are based upon the starting styrene.
[b] 20 mol. equivalents to palladium chloride were used.

Contrary to this, chlorobenzene gave a mixture of considerable amounts of each isomer.



1 12%

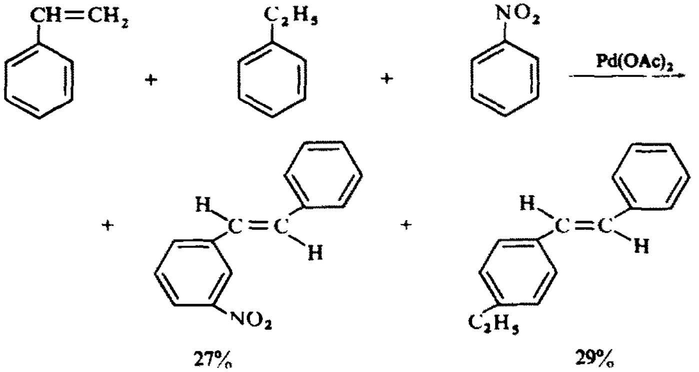
2 20%

3 30%

The formation of the *meta* isomer may be due to coordination of the Cl atom of chlorobenzene to the palladium(II) salt. In the reaction, the coordinated chlorine could not direct the reaction in an *ortho-para* manner because its lone pair electrons were held by the palladium. Therefore, the directive effect of the substituent in the present reaction is the same as in any typical aromatic substitution.

Anisole and nitrobenzene gave almost equal amounts of stilbenes in the reactions with styrene under identical reaction conditions. These results indicate that the reactivity of various aromatic compounds is not influenced by the substituent, but the substituent on the olefin does influence its reactivity towards benzene and this will be described in the following paper.[3]

In order to clarify this point, the relative reactivity of some aromatic compounds was examined by competitive reactions. As a typical example, if ethylbenzene and nitrobenzene (very slow in the usual aromatic substitution) were allowed to react with styrene, both ethyl- and nitrostilbene were produced in the almost equal amounts.



Several competitive reactions were carried out in which benzene was employed as a standard. The results are summarized in Table 2.

TABLE 2. THE COMPETITIVE REACTIONS OF BENZENE AND MONOSUBSTITUTED BENZENES TOWARD STYRENE

Monosubstituted benzene	Product, %[a]		
	trans-Stilbene		*trans*-Monosubstituted stilbene
Toluene	36	*o*-Methylstilbene	1
		p-Methylstilbene	25
Ethylbenzene	35	*p*-Ethylstilbene	23
Chlorobenzene	34	*o*-Chlorostilbene	1
		m-Chlorostilbene	5
		p-Chlorostilbene	14
Nitrobenzene	38	*m*-Nitrostilbene	19

[a] Yields are based upon the starting styrene.

From the data in Table 2, we have calculated the partial rate factors as shown in Fig. 1.

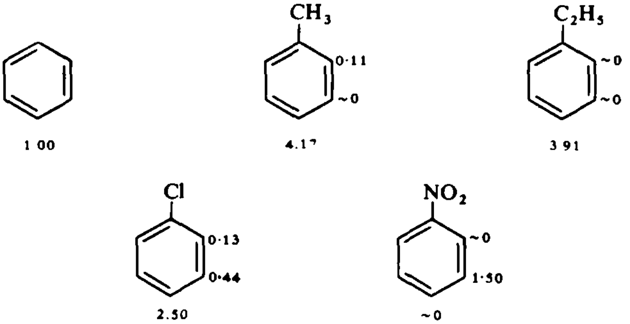


FIG. 1 Partial rate factors in the substitutions of some monosubstituted benzene with styrene.

In conclusion, the reaction may proceed through a *sigma* bonded benzene-palladium complex,[4] but as there is no effect on the reactivity, the rate determining step can not be the formation of a *sigma* bond between benzene and palladium.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer; NMR spectra were obtained by a Japan Electron JNM-4H-100 spectrometer. Chemical shifts are given in τ-scale together with splitting patterns and relative integrated area. The reactions of styrene with toluene, ethylbenzene, anisole and nitrobenzene, and assignment of the products formed have been described.[2a]

Reactions of styrene with chlorobenzene

(*a*) ***With palladium chloride and sodium acetate.*** In a 2-liter 3-necked, round-bottomed flask fitted with a reflux condenser carrying a $CaCl_2$ tube and a stirrer, was placed a mixture of $PdCl_2$ (7·97 g; 0·045 mole), NaOAc (74·0 g; 20 mole equiv to $PdCl_2$), styrene (4·70 g; 0·045 mole), AcOH (110 ml) and chlorobenzene (470 ml). The soln was stirred at 110° for 8 hr. After separation of the precipitated Pd, the mixture was poured into water. The organic layer was separated, the aqueous layer extracted twice with $CHCl_3$ and the combined the organic layers washed and dried over Na_2SO_4. After the evaporation of the solvent, the residual material was chromatographed on a colum of alumina (100 g). Elution with pet ether (400 ml) yielded **1** and **2**. Compound **1** (0·96 g, 10%), m.p. 39–40° (EtOH), (reported[5] m.p. 39–40°) was *trans-o*-chlorostilbene, and the compound **2** (1·13 g, 12%), m.p. 72–73° (EtOH), (reported[5] m.p. 73–74°), *trans-m*-chlorostilbene. These compounds were proved identical by comparing IR spectrum and mixed m.p. with authentic samples. IR spectrum of **1**: ν_{Nujol} 690, 710, 750, 755 and 960 cm^{-1}; IR spectrum of **2**: ν_{Nujol} 680, 691, 752, 780, 881 and 960 cm^{-1}; NMR spectrum of **2** (in CCl_4): 3·00–3·10 (d, 2), 2·55–2·90 (m, 9).

Further elution with ether (160 ml) afforded **3** and **4**. Compound **3** (1·26 g, 13%), m.p. 128–128·8° (EtOH), (reported[6] m.p. 129°), was *trans-p*-chlorostilbene by comparison of the IR spectrum and mixed m.p. with an authentic specimen. IR spectrum of **3**: ν_{Nujol} 690, 705 and 961 cm^{-1}; NMR spectrum of **3** (in CCl_4): 3·05–3·10 (s, 2) and 2·55–2·90 (m, 9). Compound **4** (0·14 g, 3%), m.p. 148–149° (EtOH), (reported[7] m.p. 149°) was *trans,trans*-1,4-diphenylbutadiene by comparison of the IR spectrum and mixed m.p. with an authentic sample.

Finally, elution with MeOH gave a tarry material (2·22 g) which was not further examined. After evaporation of the solvent, styrene (1·13 g) was also detected by VPC.

(*b*) *With palladium acetate.* A mixture containing palladium acetate (5·50 g; 0·023 mole), styrene (2·34 g; 0·023 mole), AcOH (55 ml), and chlorobenzene (235 ml) was heated at 110° with stirring for 8 hr. After a similar work-up, *trans-o*-chlorostilbene (0·59 g, 12%), *trans-m*-chlorostilbene (0·95 g, 20%), and its *p*-isomer (1·45 g, 30%) were obtained with 1,4-diphenylbutadiene (4%) as a by-product.

Competitive reactions of styrene with aromatic compounds

(*a*) *Reaction with ethylbenzene and nitrobenzene.* A soln of palladium acetate (5·50 g; 0·023 mole) and styrene (2·34 g; 0·023 mole) in a mixture of ethylbenzene (1·0 mole) and nitrobenzene (1·0 mole) was heated at 110° with stirring for 8 hr. The resulting mixture was worked up as described and the residue was chromatographed on a column of alumina (120 g). Elution with pet ether (1100 ml) gave *trans-p*-ethylstilbene (1·35 g, 29%). Further elution with ether (450 ml) afforded *trans-m*-nitrostilbene (1·37 g, 27%). Finally elution with MeOH gave a tarry material (0·23 g).

(*b*) *Reaction with benzene and monosubstituted benzene—general procedure.* Mixtures of palladium acetate (0·023 mole), styrene (equiv amount), AcOH (55 ml), benzene (1·0 mole) and monosubstituted benzene (1·0 mole) were stirred at 90° for 8 hr. After work-up as described, the products were isolated by column chromatography. The results of toluene, ethylbenzene, chlorobenzene and nitrobenzene with benzene are listed in Table 2. Assignment of the products formed was confirmed by comparison of the IR spectrum and mixed m.p. with authentic samples. Their properties have been described in previous papers.[2]

From the data in Table 2, we calculated the partial rate factors[8] using the following equation:

$$\frac{d(\text{stilbene})}{dt} = k(\text{styrene})(\text{benzene})(\text{Pd(OAc)}_2)$$

where, the rate of stilbene formation is 1st order with respect to both styrene and aromatic compounds was confirmed by kinetic experiment. The results are shown in Fig. 1.

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