Aromatic Substitution of Olefins. 25.[1] Reactivity of Benzene, Naphthalene, Ferrocene, and Furan toward Styrene, and the Substituent Effect on the Reaction of Monosubstituted Benzenes with Styrene

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The relative reactivity of various aromatic compounds toward styrene in the presence of palladium(II) acetate has been examined by competitive reactions. The order of reactivity is benzene < naphthalene < ferrocene < furan. This result and the effect of substituents on the reactions of monosubstituted benzenes with the olefin are similar to those of electrophilic aromatic substitution, which suggests that the present reaction involves an electrophilic attack of Pd^{II} on the aromatic ring to form an aromatic palladium σ complex.

In 1967 we reported a novel class of reactions wherein the double bond of olefins undergoes substitution reactions with aromatic compounds in the presence of palladium(II) salts, and opened a new area of the palladium-promoted reactions between aromatic compounds and olefins.[2]

Heck reported the related arylation reaction of olefins with arylating agents such as arylmercuric halides in the presence of group 8 metal salts, especially those of palladium.[3] Most recently, Heck et al. also described that aryl halides could react as an arylating agent.[4] In our reaction, the aromatic compound itself reacts with the olefin. It has been found that benzenoid as well as nonbenzenoid aromatic compounds undergo this reaction.[5]

Although the addition–elimination mechanism has been proposed for this type of reaction,[3] the nature of the first step, forming an aryl–palladium σ complex, is not yet fully understood. To help to clarify this point, we have investigated the reactivity of the various aromatic compounds, and the substituent effect on the reactivity of monosubstituted benzenes in the aromatic substitution reaction occurring between aromatic compounds and olefins.[6]

The reactivities of benzene, naphthalene, ferrocene, and furan toward styrene and the substituent effect on the reactions of monosubstituted benzenes with the olefin are similar to those of the electrophilic aromatic substitution. Hence we conclude that this reaction involves electrophilic aromatic substitution as the first step to form an aromatic Pd σ complex, followed by its addition to the olefin and elimination of a Pd–H unit.

Results

Reactivity of Benzene, Naphthalene, Ferrocene, and Furan toward Styrene. The reactivity was investigated by competitive reaction using styrene, which is most reactive, as the standard olefin and equimolar amounts of the aromatic substrates. The results are summarized in Table I.

From the reaction of benzene and naphthalene, *trans*-2-styrylnaphthalene[7] (**2**) and *trans*-stilbene (**1**) were obtained in 20 and 5% yields, respectively, together with a 11% yield of *trans,trans*-1,4-diphenylbutadiene (**3**).[9]

From the competitive reaction of naphthalene and ferrocene toward styrene, we obtained a 19% yield of *trans*-styrylferrocene (**4**) and a trace amount of **2** with 8% yield of **3**.

Ferrocene and furan led to *trans*-2-styrylfuran (**5**) and *trans,trans*-2,5-distyrylfuran (**6**) in 15 and 40% yields,[10] respectively, and no product derived from ferrocene was detected indicating that furan is far more reactive than ferrocene.

From these results, we estimate the order of reactivity as benzene (1) < naphthalene (4) < ferrocene (100) < furan (1000).[11] The sequence of reactivity is similar to but its magnitude is greatly different from that of the usual electrophilic aromatic substitution.

Table I. Competitive Reaction of Benzene, Naphthalene, Ferrocene, and Furan toward Styrene in the Presence of Palladium Acetate

Aromatic compd	Product and yield,[a] %
Benzene vs. naphthalene[b]	**1**, 5; **2**, 20
Naphthalene vs. ferrocene[c]	**4**, 19; **2**, trace
Ferrocene vs. furan	**5**, 15; **6**, 40

[a] Yields are based on styrene. [b] An 11% yield of **3** was also formed. [c] An 8% yield of **3** was also formed.

Table II. Reaction of Monosubstituted Benzenes with Styrene in the Presence of Palladium Acetate

Monosubstituted benzene	*trans*-Stilbene	Yield, %[d]
Toluene	*o*-Methylstilbene	17
	m-Methylstilbene	24
	p-Methylstilbene	33
Ethylbenzene[a]	*o*-Ethylstilbene	11
	m-Ethylstilbene	23
	p-Ethylstilbene	48
Anisole	*o*-Methoxystilbene	30
	m-Methoxystilbene	5
	p-Methoxystilbene	48
Chlorobenzene[b]	*o*-Chlorostilbene	10
	m-Chlorostilbene	22
	p-Chlorostilbene	32
Nitrobenzene[c]	*o*-Nitrostilbene	4
	m-Nitrostilbene	29
	p-Nitrostilbene	4

[a] Trace amounts of **3** and β-acetoxystyrene were also formed. [b] A 3% yield of **3** was also formed. [c] A 7% yield of **3** was also formed. [d] Yields are based on styrene utilized.

Reactions of Monosubstituted Benzenes with Styrene. On the reactions of monosubstituted benzenes with olefins, we briefly reported that the position 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.[12] In connection with the study described above, we have reexamined the reactions of monosubstituted benzenes with styrene using gas chromatography equipped with FID since the earlier work was done using column chromatography for analysis of the products. Mixtures of palladium(II) acetate, styrene in equivalent amounts, acetic acid, and an excess of the monosubstituted benzenes were stirred for 8 h at 110 °C. The results are summarized in Table II. It was revealed that

Table III. Competitive Reaction of Benzene and Monosubstituted Benzenes toward Styrene in the Presence of Palladium Acetate

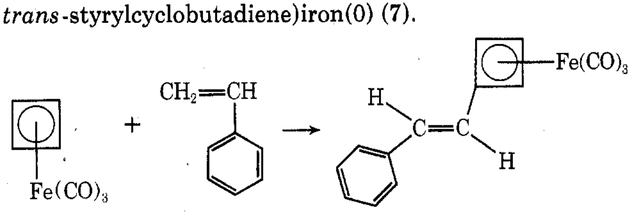
Monosubstituted benzene	Product[a]		
	trans-Stilbene, % yield	Trans-monosubstituted stilbene	% yield
		o-Methylstilbene	11.6
Toluene	24.4	*m*-Methylstilbene	15.3
		p-Methylstilbene	21.6
		o-Ethylstilbene	6.1
Ethylbenzene	26.3	*m*-Ethylstilbene	12.2
		p-Ethylstilbene	18.2
		o-Methoxystilbene	26.0
Anisole	13.8	*m*-Methoxystilbene	3.8
		p-Methoxystilbene	41.5
		o-Chlorostilbene	4.1
Chlorobenzene	42.2	*m*-Chlorostilbene	10.5
		p-Chlorostilbene	15.0
		o-Nitrostilbene	0.5
Nitrobenzene	23.9	*m*-Nitrostilbene	5.2
		p-Nitrostilbene	0.5

[a] Yields are based on styrene used.

in the cases of CH_3, C_2H_5, and Cl groups, considerable amounts of the meta-substituted stilbenes were also formed and no remarkable ortho-para directing nature of the groups was observed. However, OCH_3, a strong electron-releasing group, and NO_2, a strong electron-withdrawing group, have a tendency to show the ortho-para and meta orientation, respectively.

In order to clarify the reactivity of the monosubstituted benzenes, competitive reactions with benzene as a standard were carried out. The results, summarized in Table III, again show general trends similar to the case of the electrophilic aromatic substitution.

Since it became apparent that this reaction is an electrophilic aromatic substitution, it was expected that cyclobutadiene–metal complexes should also react with olefins. Reaction of tricarbonyl(η-cyclobutadiene)iron(0) with styrene and $Pd(OAc)_2$ in a mixture of dioxane and acetic acid under reflux for 8 h gave a 6% yield of light yellow oil, tricarbonyl(η-*trans*-styrylcyclobutadiene)iron(0) (7).



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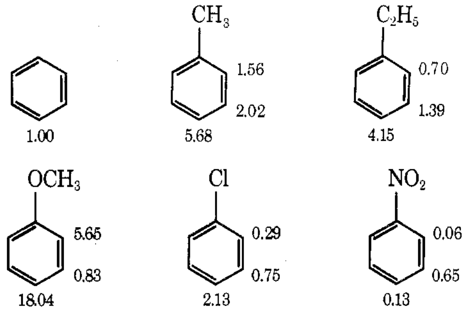
Discussion

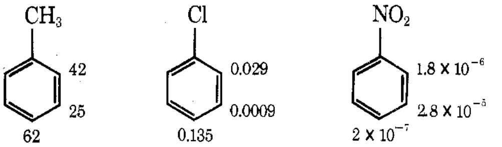
From the data in Table III, we have calculated the partial rate factors as shown in Chart I.[13] It is of interest that both direction of substitution and the reactivity are not so strongly influenced by the substitution on a benzene ring as in the usual electrophilic aromatic substitution. With respect to orientation, OCH_3 and NO_2 groups direct ortho-para and meta, respectively. The electron-releasing groups increase the reactivity, but the difference in the reactivity is very small compared to the usual aromatic substitution. For example, in the nitration of monosubstituted benzenes, toluene is 10^6 times as reactive as nitrobenzene[14] but in the present reaction, the relative rate of anisole and nitrobenzene is only 20:1.

In Figure 1, the Hammett plots of the logarithm of the partial rate factors and σ^+ are shown. With respect to the para position, a good straight line was obtained and one can see a tendency characteristic of the electrophilic aromatic substitution. It is noted that the absolute value of ρ (−1.4) is somewhat smaller than that of the usual aromatic substitution. For example, ρ values for bromination, chlorination, and Friedel–Crafts ethylation of monosubstituted benzenes are reported to be −12.1,[15] −8.1,[16] and −2.4,[17] respectively. Although the small absolute ρ value seems to suggest a radical process, this possibility might be ruled out by the following facts: (1) Pd^{II} is a diamagnetic species, (2) radical inhibitors such as benzoquinone, *tert*-butylcatechol, or oxygen did not have a predictable effect on the reaction, (3) no evidence was obtained that ortho substitution is favored over meta and para substitution, which is typical of the radical process,[18] (4) anisole is about 20 times as reactive as nitrobenzene, and both nitrobenzene and chlorobenzene are less reactive than benzene itself despite the fact that substituents on a benzene ring increase the substitution rate in the radical aromatic substitution,[18] (5) no by-products typical of the radical process were obtained.

Chart I. Partial Rate Factors in the Substitutions of Monosubstituted Benzenes with Styrene in the Presence of Palladium Acetate



cf. partial rate factors in nitration of some monosubstituted benzenes[a]



[a] J. D. Roberts and H. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, p 800.

These observed substituent effects and the similarity in the reactivity of various aromatic compounds show that the reaction represents an electrophilic aromatic substitution, and that the reaction would proceed via electrophilic attack of Pd^{II} to a benzene ring forming an aryl–palladium σ complex.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded by a Japan Spectroscopic IR-E spectrometer. The NMR spectra were obtained by a Japan Electron Optics JNM-4H-100 or JEOL C-60 HL spectrometer using Me_4Si as an internal standard.

Materials. Palladium acetate was prepared according to the procedure of Wilkinson and co-workers.[21] Benzene, toluene, ethylbenzene, and anisole were refluxed with sodium metal and distilled. Nitrobenzene and chlorobenzene were dried over anhydrous calcium chloride and distilled. Acetic acid was dried over phosphorus pentoxide for 1 week and distilled through a 45-cm Widmer distilling column. Styrene was dried over sodium sulfate and distilled under reduced pressure.

General Procedure for Competitive Reaction of Aromatic Compounds. Mixtures of palladium acetate (10 mmol), styrene in equivalent amount, two aromatic compounds (10 mmol each), dioxane (120 ml), and acetic acid (30 ml) were stirred for 8 h at reflux. The resulting mixture was treated as reported already[2] and the products were analyzed and isolated by GLC or column chromatography. Identities with the products formed were proven by mixture melting point, ir, or NMR comparison with authentic samples. The melting points of the styryl derivatives are listed in the following section.

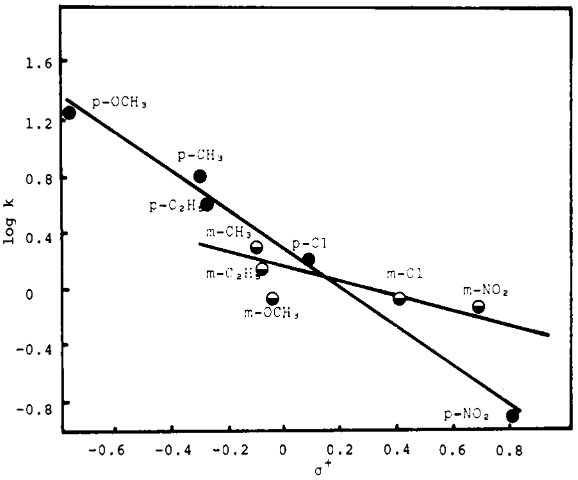


Figure 1. Plots of the logarithm of the partial rate factors *k* vs. σ^+ for substitution of para- (●) and meta- (⊖) substituted benzenes with styrene in the presence of palladium acetate.

Styryl-Substituted Aromatic Compounds. *trans*-2-Styrylnaphthalene (**2**), mp 143 °C,[22] *trans*-styrylferrocene (**4**), mp 119–119.5 °C,[23] *trans*-2-styrylfuran (**5**), mp 52.5–54 °C,[24] *trans,trans*-2,5-distyrylfuran (**6**), mp 144–145.5 °C.[24]

General Procedure for Reaction of Monosubstituted Benzenes with Styrene. Mixtures of palladium acetate (6 mmol), styrene (6 mmol), monosubstituted benzene (60 ml), and acetic acid (14 ml) were stirred for 8 h at 110 °C. The resulting mixture was treated as described already[2] and the products were analyzed and isolated by GLC and column chromatography. The products were identified by the same procedure described above. Properties of stilbenes have been reported.[2]

General Procedure for Competitive Reaction of Styrene with Monosubstituted Benzenes. Mixtures of styrene (6 mmol), palladium acetate (6 mmol), benzene (400 mmol), monosubstituted benzene (400 mmol), and acetic acid (15 ml) were stirred at 90 °C for 8 h. The products were analyzed by GLC. The results are listed in Table III.

Reaction of Tricarbonyl(η-cyclobutadiene)iron(0) with Styrene. A solution of tricarbonyl(η-cyclobutadiene)iron(0) (10 mmol),[25] styrene (10 mmol), and palladium acetate (20 mmol) in a mixture of dioxane (160 ml) and acetic acid (40 ml) was refluxed for 8 h. After workup, the residue was chromatographed on a column of alumina. Elution with petroleum ether gave the starting cyclobutadiene complex and the subsequent elution gave a light yellow oil. This was assigned to be tricarbonyl(η-*trans*-styrylcyclobutadiene)iron(0) (**7**),[8] 6% yield: ir (Nujol) 2080, 1970, 960, 934, 831, 759, and 701 cm^{-1}; NMR (CCl_4) τ 2.81 (m, 5 H), 3.55 (d, J = 16 Hz, 1 H), 3.85 (d, J = 16 Hz, 1 H), 5.73 (s, 2 H), and 5.96 (s, 1 H). Further elution with ether gave **3** in 16% yield. Finally elution with MeOH gave a tarry substance.

Registry No.—**2**, 2840-89-3; **4**, 1272-54-4; **5**, 21676-00-6; **6**, 41082-14-8; **7**, 58117-30-9; benzene, 71-43-2; naphthalene, 91-20-3; ferrocene, 102-54-5; furan, 110-00-9; toluene, 108-88-3; ethylbenzene, 100-41-4; anisole, 100-66-3; chlorobenzene, 108-90-7; nitrobenzene, 98-95-3; tricarbonyl(η-cyclobutadiene)iron(0), 12078-17-0; styrene, 100-42-8.

References and Notes

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(9) Yields given in this paper are based on the amount of the olefin utilized.
(10) It has been confirmed that compound (**6**) is derived from further styrylation of the monostyryl derivative **5.**[5]
(11) Number in parenthesis shows the approximate relative rate.
(12) Y. Fujiwara, I. Moritani, R. Asano, H. Tanaka, and S. Teranishi, *Tetrahedron*, **25,** 4815 (1969).
(13) Calculation was done using a general procedure analogous to the reported procedure.[12]
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(19) Since arylpalladium(II) σ complexes are very unstable and react rapidly with olefins, they are unlikely to be present in large amount. Therefore, the rate-determining step could be the palladation reaction.[20]
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