would appear reasonable that the enzyme is making general catalysis possible by enhancing the ease of C–O bond breaking.

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Aromatic Substitution of Olefins. VI. Arylation of Olefins with Palladium(II) Acetate

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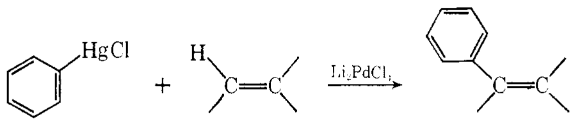
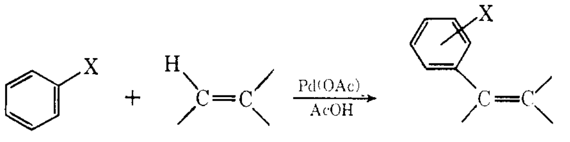
Abstract: Olefins react with benzene derivatives to produce aryl-substituted olefins *via* direct substitution of the aromatic compound for hydrogen on the double bond of the olefin in the presence of palladium salts and reduced palladium metal. The reaction may be made catalytic with respect to the palladium salts by using cupric acetate or silver acetate, and air as reoxidants. The reaction provides an extremely convenient method for the synthesis of a wide variety of olefinic compounds.

Extensive studies on reactions of olefins in the presence of transition metal compounds have been carried out. Much less is known about arylation of olefins with transition metal compounds.

Most recently, Heck described interesting arylation reactions of olefins with arylating agents such as arylmercuric halides in the presence of group VIII metal salts, and showed that palladium salts are the most generally useful, with rhodium and ruthenium salts next best.[2]



We have reported a novel method of synthesizing stilbene derivatives by substitution of aromatic compounds for hydrogen on the double bond of the styrene–palladium chloride complex.[3] In the course of our work, palladium acetate was found to be the most effective for the direct arylation of olefins with aromatic compounds in the presence of acetic acid. The present paper reports a study of substitution reaction of olefins with benzene derivatives by means of palladium salts, especially palladium acetate. A preliminary communication of a portion of this work has been given.[4]



Results and Discussion

In previous papers[3] we described our initial work on the reactions of the styrene–palladium(II) chloride complex with benzene derivatives to give stilbenes. It was noted that for this arylation on a β-carbon atom of styrene, the presence of a carboxylic acid such as acetic is essential because the reactants form a homogeneous solution and the reaction proceeds best in this solvent. Further, it was found that when sodium acetate was added, the yield was greatly increased.

Palladium(II) acetate has been found to be the most generally useful, with palladium(II) chloride–sodium acetate next best for the direct arylation of olefins with benzene derivatives.

The aromatic substitution of olefins takes place in homogeneous solutions of reactant olefin and palladium(II) acetate (equal mole equivalents to olefin) in a solution of the aromatic compound (large excess) and acetic acid. The solution is stirred in the presence of air for a few minutes to several hours (8 hr usually), to give from 10% to *ca.* 90% yield of arylated products, with reduced metallic palladium and a very small amount of acetates. Results are given in Table I.

With unsymmetrical olefins, the aryl group generally adds predominantly to the less substituted carbon atom of the double bond because of steric hindrance of the substituents. This is consistent with that observed in the Heck arylation.[2] Although *cis* and *trans* mixtures are formed, no mixtures resulting from arylation in both directions to unsymmetrical olefins have been found.

Increasing substitution on the olefinic carbons decreases the reactivity of the olefin in the palladium acetate arylation reaction. For example, the reaction of triphenylethylene with benzene and a palladium acetate catalyst gave tetraphenylethylene in low yield (13%),[5] while styrene reacts with benzene to afford *trans*-stilbene in almost quantitative yield.

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[2] (a) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968); (b) R .F. Heck, *ibid.*, **90**, 5526 (1968); (c) R. F. Heck, *ibid.*, **90**, 5531 (1968); (d) R. F. Heck, *ibid.*, **90**, 5535 (1968); (e) R. F. Heck, *ibid.*, **90**, 5542 (1968).

[3] (a) I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, 1119 (1967); (b) Y. Fujiwara, I. Moritani, and M. Matsuda, *Tetrahedron*, **24**, 4819 (1968).

[4] Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *Tetrahedron Lett.*, 633 (1968).

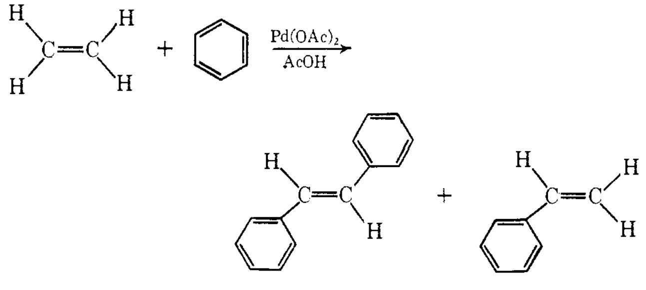
[5] Yields of arylation products given in this paper are based on the amount of palladium salt utilized.

Table I. Arylation of Olefins with Aromatic Compounds by Palladium(II) Acetate

Olefin[a]	Palladium salt, g	Aromatic compd, ml	AcOH, ml	Temp, °C	Product and yield
Ethylene[b]	$Pd(OAc)_2$, 11.2	Benzene, 340	80	Reflux	*trans*-Stilbene, 16%; styrene, *ca.* 4%[c]
Ethylene[b]	$Pd(OAc)_2$, 11.2	Toluene, 340	80	Reflux	*p*-Methylstyrene, 32%;[c] *trans-p,p'*-dimethylstilbene, 5%
1-Butene[d]	$Pd(OAc)_2$, 6.47	Benzene, 300	100	Reflux	*trans*-1-Phenyl-1-butene, 14%;[c] *cis*-1-phenyl-1-butene, 3%[c]
Styrene	$Pd(OAc)_2$, 7.21	Benzene, 340	80	Reflux	*trans*-Stilbene, 90%[e]
Styrene	$PdCl_2$,[f] 2.87	Benzene, 120	40	Reflux	*trans*-Stilbene, 79%[e]
Styrene	$PdCl_2$,[g] 5.74	Benzene, 340	80	Reflux	*trans*-Stilbene, 26%
Styrene	$Pd(OAc)_2$, 7.21	Toluene, 340	80	Reflux	*trans-p*-Methylstilbene, 58%;[e] *trans-o*-methylstilbene, 3%
Styrene	$Pd(OAc)_2$, 7.21	*p*-Xylene, 340	80	110	*trans*-2,5-Dimethylstilbene, 47%[e]
Styrene	$Pd(OAc)_2$, 4.34	Ethylbenzene, 185	43	110	*trans-p*-Ethylstilbene, 52%[e,h]
Styrene	$PdCl_2$,[f] 8.22	Ethylbenzene, 483	113	110	*trans-p*-Ethylstilbene, 22%[e,i]
Styrene	$Pd(OAc)_2$, 5.50	Anisole, 230	55	110	*trans-p*-Methoxystilbene, 61%[e]
Styrene	$Pd(OAc)_2$, 5.52	Nitrobenzene, 235	55	110	*trans-m*-Nitrostilbene, 60%[e]
Styrene	$PdCl_2$,[f] 8.02	Nitrobenzene, 470	110	110	*trans-m*-Nitrostilbene, 25%[e,j]
1,1-Diphenylethylene	$Pd(OAc)_2$, 3.59	Benzene, 170	40	Reflux	Triphenylethylene, 72%[k]
1,1-Diphenylethylene	$PdCl_2$,[f] 5.67	Benzene, 340	80	Reflux	Triphenylethylene, 45%[l]
trans-Stilbene	$Pd(OAc)_2$, 1.20	Benzene, 57	13	Reflux	Triphenylethylene, 28%
trans-Stilbene	$PdCl_2$,[f] 5.67	Benzene, 340	80	Reflux	Triphehylethylene, 20%[m]
Triphenylethylene	$Pd(OAc)_2$, 3.59	Benzene, 170	40	Reflux	Tetraphenylethylene, 13%
Triphenylethylene	$PdCl_2$,[f] 5.67	Benzene, 340	80	Reflux	Tetraphenylethylene, trace
p-Methylstyrene	$Pd(OAc)_2$, 7.21	Benzene, 340	80	Reflux	*trans-p*-Methylstilbene, 75%
p-Methylstyrene	$Pd(OAc)_2$, 7.21	Toluene, 340	80	110	*trans-p,p'*-Dimethylstilbene, 55%
Acrylonitrile	$Pd(OAc)_2$, 6.47	Benzene, 300	100	Reflux	*trans*-β-Cyanostyrene, 17%; *cis*-β-cyanostyrene, 8%

[a] An equal amount to palladium salts was used, and reactions were all carried out for 8 hr. [b] Ethylene was bubbled into the reaction mixtures at a rate of 40 ml/min. [c] Yields were determined by vpc. [d] 1-Butene was passed through the reaction mixtures at a rate of 30 ml/min. [e] A mixture of *cis*- and *trans*-β-acetoxystyrene was also formed in *ca.* 1% yield. [f] 20 mol equiv to palladium chloride of sodium acetate was employed. [g] 7.2 mol equiv to palladium chloride of potassium acetate was also used. [h] A trace amount of *trans,trans*-1,4-diphenylbutadiene was also formed. [i] A 2% yield of *trans,trans*-1,4-diphenylbutadiene was also obtained. [j] An 8% yield of *trans,trans*-1,4-diphenylbutadiene was also formed. [k] There was also found a 6% yield of 1,1,4,4-tetraphenylbutadiene. [l] A 1% yield of 1,1,4,4-tetraphenylbutadiene was also formed. [m] An unidentified acetate was also obtained (0.1 g).

Interestingly, in the case of the reaction of ethylene with benzene, *trans*-stilbene is formed as a major product, suggesting that the styrene derived from the arylation of ethylene undergoes a further arylation reaction with benzene. This may be due to the higher reactivity of styrene[6] in the present reaction. Other two-step arylation reactions have not been found in our limited work with olefins.



In general, it appears that electron-supplying groups on olefinic carbon atoms decrease yields.[2]

Another interesting feature of the olefin arylation reaction is the reaction of styrene with monosubstituted benzenes. When electron-supplying groups (methyl, ethyl, methoxyl) are attached to the benzene ring, they appear to be *ortho–para* directing, whereas nitro, an electron-withdrawing group, appears to be *meta* directing. These effects will be discussed in the following publication.

Palladium(II) chloride can also catalyze the arylation reaction in the presence of metal acetates such as those of sodium or potassium, although palladium(II) chloride has no function as an arylation catalyst without metal acetate. These results show that the metal acetates play an important role in the reaction. As suggested in a preliminary publication,[4] it may be that after the chloride anion is abstracted from the palladium(II) chloride by the metal cation (Na^+, K^+),[8] the palladium metal coordinates with the acetate anion which is a weaker ligand than the chloride anion, thus increasing the ability of the metal to coordinate with olefins. Therefore, it becomes possible for the olefin arylation to take place. Therefore, palladium(II) acetate which needs no such a halide anion abstraction step is more reactive than palladium(II) chloride toward the substitution reaction between olefins and benzene derivatives.

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[6] This high reactivity of styrene presumably arises from the ease with which styrene coordinates with palladium salts to form styrene–palladium complex.[7]

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

[8] As one of the referees has pointed out, there is no direct evidence for this point, but the fact that palladium(II) chloride without metal acetates cannot cause the present reaction seems to suggest that acetate anion or olefins can not easily coordinate with palladium(II) chloride since chloride anions are strongly fixed to palladium(II).

Table II. Catalytic Arylation of Olefins

Olefin,[a] mmol	Catalyst, mmol	Reoxidant, mmol	Benzene, ml	AcOH, ml	Product, %[b]
Styrene,[c] 5.0	Pd(OAc)$_2$, 0.5	Cu(OAc)$_2$, 0.5	20	5	*trans*-Stilbene, 446[d,e]
Styrene,[c] 5.0	Pd(OAc)$_2$, 0.5	AgOAc, 0.5	20	5	*trans*-Stilbene, 245[d,f]
Ethylene[g,h]	Pd(OAc)$_2$, 10.0	AgOAc, 100	100	24	*trans*-Stilbene, 75; styrene, 59[i]
Styrene,[h] 12.5	Pd(OAc)$_2$, 5.0	AgOAc, 25	50	12	*trans*-Stilbene, 138[d,j]
Styrene,[h] 16.1	Pd,[k] 16.1	AgOAc, 32.1	170	40	*trans*-Stilbene, 21

[a] Reactions were carried out at reflux temperature with stirring for 8 hr in the presence of oxygen (or air). [b] Yields are based upon the catalyst used. [c] Reaction was performed with oxygen gas (50 atm) in an autoclave at 80°, and no palladium or copper (or silver) precipitates were formed after the reaction. [d] A trace amount of β-acetoxystyrene was also obtained. [e] An 18% yield of *trans,trans*-diphenylbutadiene was also formed. [f] A 12% yield of *trans,trans*-diphenylbutadiene was also formed. [g] Ethylene was bubbled through at a rate of 40 ml/min. [h] Air was also added by bubbling through during the reaction. [i] Yield was determined by gas chromatography. [j] A 6% yield of *trans,trans*-diphenylbutadiene was also formed. [k] Metallic palladium was prepared from the reduction of palladium chloride with sodium formate.

As by-products, this reaction also gave enol acetates and sometimes, butadienes, the dimerized products under the reaction condition, but yields of those have been very low. Enol acetates have been known to be obtained by the nucleophilic attack of acetate anion on olefins.[9]

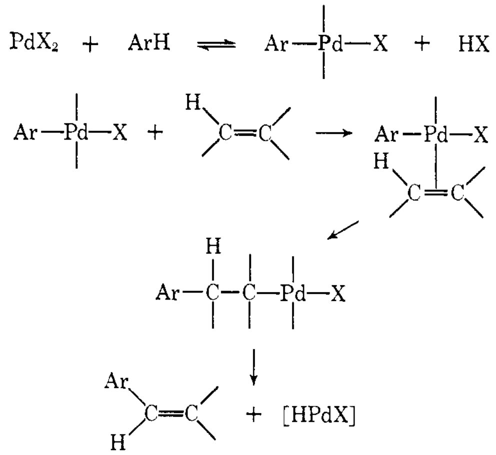
It is well known that olefins undergo oxidative coupling to give butadiene derivatives in the presence of palladium salts.[10] In addition, biaryl formation reactions by palladium salts have also reported.[11] Therefore it is of particularly interest that reaction mixtures of palladium(II) acetate, olefins, benzene derivatives, and acetic acid gives arylation products almost exclusively under the reaction condition mentioned.[12] That the reactivity of aromatic compounds toward olefins is far higher than that of acetate anion suggests that aromatics are highly activated by palladium(II) salts forming arylpalladium salts.[13]

In the arylation, the use of excess olefin relative to palladium(II) acetate is best avoided. The problem is that when more than 15 mol equiv of olefins to palladium(II) acetate was used, the major product varies from aryl-substituted olefins to butadiene derivatives, the coupling products. Thus, in general, an equivalent amount of palladium(II) acetate to olefins is necessary to direct the reaction toward arylation products, and not coupling products.[14]

The usefulness of the olefin arylation is limited by the expense of the palladium(II) acetate used. However, a noble metal such as palladium is readily reoxidized under some conditions and needs to be used in only catalytic amounts. We have found that when cupric(II) acetate or silver(I) acetate is employed together with oxygen (or air), the palladium acetate arylation reaction proceeds catalytically with respect to both palladium and copper (or silver) in which no palladium or copper (silver) precipitates were formed, and that even palladium metal can afford aryl-substituted olefins if these metals and air are introduced together.[15]

Some examples of catalytic olefin arylation are illustrated in Table II.

Finally, the mechanism of the olefin arylation reaction appears to be closely related to the Heck arylation reaction, although the present olefin arylation reaction does not employ such arylating agent as arylmercuric compounds. Presumably solvated arylpalladium salts are formed, probably reversibly, from a homogeneous solution of palladium(II) salts and benzene derivatives in polar solvent such as acetic acid.[13] The olefin presumably coordinates to the unstable arylpalladium salts followed by an insertion reaction into an aryl–palladium bond, forming arylethyl–palladium salts which then rapidly decompose into arylated olefin and palladium hydride. The latter species presumably decompose without further reaction into free palladium metal and an acid.



It is worthy of metntion that according to Davidson, *et al.*,[13] the transition metal ions which react with aromatic compounds, belong to "class b" [16] such as palladium(II), rhodium(III), or mercury(II), but palladium(II) salts do cause best the direct arylation reaction.[17]

The results reported here provide a very convenient route to a wide variety of olefin derivatives and open a new and interesting area of palladium chemistry concerned with substitution reactions of olefins with aromatic compounds.

(9) See, for example, A. Aguilo in "Advances in Organometallic Chemistry," Vol. 5, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1967, p 321.

(10) (a) R. Hüttel, J. Kratzen, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961); (b) C. F. Kohl and R. van Helden, *Rec. Trav. Chim.*, **86**, 193 (1967).

(11) (a) R. van Helden and G. Verberg, *ibid.*, **84**, 1263 (1965); (b) J. M. Davidson and C. Trigg, *Chem. Ind.* (London), 457 (1966); (c) M. O. Unger and R. A. Fouty, *J. Org. Chem.*, **34**, 18 (1969).

(12) No biaryls were detected in our arylation reaction.

(13) J. M. Davidson and C. Trigg have recently reported reactions between aryl compounds and palladium(II) salts to give arylpalladium complexes, in *J. Chem. Soc., A*, 1324 , 1331 (1968).

(14) Yields of enol acetate were very small and independent of the amount of olefin utilized under the reaction condition.

(15) Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *Tetrahedron Lett.*, 3863 (1968).

(16) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(17) Rhodium(III) chloride can also cause the present reaction although it is far less effective than palladium(II) salts as will be reported in a separate paper.

Table III. Properties and Analyses of Olefins Formed by Olefin Arylation

Compound	Mp or bp (mm) [lit.], °C	Found, %			Calcd, %			Ir, cm^{-1}; uv (EtOH), mμ (log ε); or nmr (τ) spectrum (CCl_4)
		C	H	N	C	H	N	
trans-2,5-Dimethylstilbene	43–44	92.00	7.77		92.26	7.74		ν(Nujol) 960, 805, 750, 686; λ 224 (4.30), 297 (4.32); 2.55–3.00 (m, 8), 3.10 (s, 2), 7.67 (s, 3), 7.70 (s, 3)
trans-*p*-Ethylstilbene	89–90 [90][a]	92.20	7.78		92.25	7.74		ν(Nujol) 958, 815, 756, 690; 2.55–3.05 (m, 9), 3.07 (s, 2), 7.40 (q, 3), 8.77 (t, 3)
trans-*p*-Methoxystilbene	134–135 [136][b]	85.25	6.78		85.68	6.71		ν(Nujol) 1258, 967, 813, 748, 686; 2.50–3.00 (m, 9), 3.10 (s, 2), 6.23 (s, 3)[c]
trans-*p*-Methylstilbene	119–120 [120][d]	92.68	7.36		92.74	7.26		ν(Nujol) 965, 805, 743, 703, 685; 2.55–3.00 (m, 9), 3.05 (s, 2), 7.65 (s, 3)
trans-*m*-Nitrostilbene	110.8–111.8 [112][e]	73.72	5.01	5.98	74.65	4.92	6.22	ν(Nujol) 1510, 1340, 965, 900, 810, 755, 695; 2.90–2.95 (d, 2), 1.67–2.75 (m, 9)
trans-1-Phenyl-1-butene	70–71[f] (8)	91.00	9.00		90.85	9.15		ν(neat) 1595, 965, 740, 690; 2.50–3.10 (m, 5), 3.60–4.05 (m, 2), 7.65–8.10 (m, 2), 8.82–9.03 (t, 3)
cis-1-Phenyl-1-butene	70–71[f] (8)	90.72	8.92		90.85	9.15		ν(neat) 1595, 745, 695
trans-β-Cyanostyrene	50–70[g] (6–9)	83.80	5.52	10.74	83.69	5.46	10.69	ν(neat) 2220, 1620, 965, 750, 690; 3.76 (s, 5), 3.95–4.67 (m, 2)[h]
cis-β-Cyanostyrene	50–70[g] (6–9)	83.36	5.52	10.69	83.69	5.46	10.69	ν(neat) 2220, 1615, 950, 690

[a] C. Sollscher, *Chem. Ber.*, **15**, 1681 (1882). [b] G. A. R. Kon and G. W. Spickett, *J. Chem. Soc.*, 2724 (1949). [c] $CDCl_3$ was the solvent. [d] H. Meerwein and E. Bucher, *J. Prakt. Chem.*, **152**, 237 (1939). [e] F. Bergman and D. Schapiro, *J. Org. Chem.*, **12**, 57 (1947). [f] Mixture of 18% *cis* and 82% *trans* isomer. [g] Mixture of 32% *cis* and 68% *trans* isomer. [h] Taken with a Japan Electron Optics JNH-MH-60 spectrometer.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded by a Hitachi EPI-S2 ir spectrometer and uv spectra were obtained on a Hitachi EPS-2U spectrophotometer. The nmr spectra were obtained by a Japan Electron Optics JNM-4H-100 spectrometer using trimethylsilane as an internal standard unless otherwise noted. Chemical shifts are given in τ units together with splitting patterns and relative integrated area. The letter designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quadruplet; m, unresolved multiplet.

Materials. Anhydrous palladium chloride was a commercial grade. Palladium acetate was prepared from palladium sponge and glacial acetic acid in the presence of concentrated nitric acid according to the procedure of Wilkinson and coworkers.[18] 1,1-Diphenylethylene[19a] and triphenylethylene[19b] were prepared as described in ref 19. *trans*-Stilbene was prepared by our method.[3,4] *p*-Methylstyrene was prepared according to the method described by Mowry, *et al.*[19c] Other starting olefins were commercial grade and purified before use. Benzene, toluene, ethylbenzene, and *p*-xylene were refluxed with sodium metal and distilled. Nitrobenzene was 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. Petroleum ether refers to a fraction of bp 40–60°.

General Procedure for Arylation of Olefins with Aromatic Compounds. Mixtures of the palladium salts, the olefin in equivalent amount, acetic acid, and the aromatic compound were stirred for 8 hr (usually) at reflux (or at 110°). A larger excess of olefin should not be used in order to avoid the oxidative coupling reaction of the olefin producing butadiene derivatives. The reactions were carried out with excess aromatic compound which behaved as both a reactant and a solvent. Gaseous olefins were added by bubbling into the reaction mixture under atmospheric pressure. The resulting mixture was filtered to remove palladium metal and the filtrate was poured into water and 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 anhydrous sodium sulfate. After evaporation of the solvent, the products were isolated by column or gas chromatography. The results were extremely reproducible on duplicate or triplicate reactions. Analyses of products were carried out by a Yanagimoto GCG-3 gas chromatograph using an Apiezon L column. Identities with the products formed were proved by mixture melting point, ir, or nmr comparison with authentic samples.

Analyses and properties of the olefins formed by olefin arylation are listed in Table III. Specific examples of the reaction are given in detail below.

Reaction of Styrene with Ethylbenzene. In a 500-ml, three-necked, round-bottomed flask provided with a condenser with a calcium chloride tube at the top, and a stirrer, was placed a solution of 1.85 g (18 mmol) of styrene, 185 ml of ethylbenzene, 43 ml of acetic acid, and 4.34 g of palladium acetate. The solution was stirred for 8 hr at 110°. After work-up as described above, the residue was chromatographed on a column of alumina (200 g). Elution with petroleum ether (900 ml) and recrystallization yielded 1.93 g (52%) of colorless leaflets which were assigned as *trans*-*p*-ethylstilbene by comparison of the ir spectrum and mixture melting point. Further elution with ether (600 ml) gave *trans*,*trans*-diphenylbutadiene (0.06 g), mp 148.5–149.5° (lit.[20] mp 149°), the identity of which was confirmed by all the usual criteria. Finally elution with methanol gave a tarry material (0.22 g) which was not further examined. From the solvent after evaporation, styrene (0.13 g) and a trace amount of β-acetoxystyrene (*cis* and *trans* mixture)[21] were also detected by vpc.

Catalytic Phenylation of Stryene. In a 150-ml autoclave was placed a mixture of 20 ml of benzene, 5 ml of acetic acid, 5 mmol of styrene, 0.5 mmol of palladium acetate, and 0.5 mmol of cupric acetate. The autoclave was closed, flushed with oxygen, and pressured to 50 atm. The mixture was heated at 80° for 8 hr. No palladium or copper precipitates were found in the resulting solution. After treatment in the manner desdribed, there were obtained 0.40 g (446%) of *trans*-stilbene, and 0.019 g of *trans*,*trans*-diphenylbutadiene.[20] A trace amount of β-acetoxystyrene was also found by vpc.

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(18) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(19) (a) H. Gilman, Ed., "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 226; (b) A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1941, p 606; (c) D. T. Mowry, M. Renoll, and W. F. Huber, *J. Amer. Chem. Soc.*, **68**, 1105 (1946).

(20) A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1941, p 229.

(21) F. W. Semmler, *Chem. Ber.*, **42**, 584 (1909).