3% (less than 2% in most cases). All results are summarized in Table I.

In the absence of TMEDA, **6** as well as **7c** gave somewhat larger rate constants than those obtained in the presence of TMEDA. Driftings in k_1 were also observed. For the evaluation of k_{7c}, it was assumed that the apparent k_1 was a sum of the two competing reactions, the fragmentation (k_{7c}) and the epimerization $k_{e,cis}\cdot$[TMEDA]). See the text for the estimation procedures.

Registry No. 1c, 73378-17-3; **1t**, 71155-82-3; **2c**, 73378-18-4; **2t**, 73378-19-5; **3c**, 73378-20-8; **3t**, 73378-21-9; **4**, 35947-70-7; **5**, 35947-66-1; **6**, 57015-11-9; **7c**, 16141-47-2; **7t**, 20432-17-1; **8**, 4287-98-3; **9**, 35202-08-5; *erythro*-3-hydroxy-2-methyl-3-phenylpropionic acid, 14366-86-0; *threo*-3-hydroxy-2-methyl-3-phenylpropionic acid, 14366-87-1; *threo*-3-hydroxy-2-isopropyl-3-phenylpropionic acid, 14664-78-9; *erythro*-3-hydroxy-2-isopropyl-3-phenylpropionic acid, 14929-06-7; *threo*-2-*tert*-butyl-3-hydroxy-3-phenylpropionic acid, 58113-93-2; *erythro*-2-*tert*-butyl-3-hydroxy-3-phenylpropionic acid, 58113-94-3; 3-hydroxy-2,2-dimethyl-3-phenylpropionic acid, 23985-59-3; 3-hydroxy-3-methyl-2-phenylbutyric acid, 6343-61-9; *threo*-3-hydroxy-2,3-diphenylpropionic acid, 4603-32-1; *erythro*-3-hydroxy-2,3-diphenylpropionic acid, 4603-33-2; 3-bromo-3-(*p*-nitrophenyl)propionic acid, 57999-52-7; 2,2-dimethyl-3,3-diphenyl-3-hydroxypropionic acid, 27925-29-7.

Arylation and Alkylation of Olefins by Arylamines or Hydrazines via Carbon-Nitrogen Bond Cleavage in the Presence of Palladium(II) Salts

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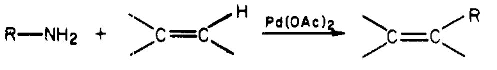
Arylamines ($ArNH_2$) have been found to function as arylating agents by way of C-N bond cleavage to give aryl-substituted olefins when treated with palladium salts and acetic acid. The reactivity of various amines and olefins has been investigated. Hydrazines such as phenylhydrazine and methylhydrazine are also able to act as arylating and alkylating agents, respectively. The addition of *tert*-butyl nitrite greatly increases the yields.

Aromatic substitution of olefins by palladium salts is a very convenient method for preparing aromatic-substituted olefins.[1] In subsequent related studies, we tried to react styrene with phenyl azide in the hope of obtaining nitrogen-containing products such as aminostilbenes and triazolines. However, no significant amounts of such products were obtained; instead (*E*)-stilbene was obtained in 2% yield together with (*E,E*)-1,4-diphenylbutadiene (4%) and acetanilide (29%). This suggested to us that aniline was formed from the decomposition of phenyl azide and that the aniline formed reacted with styrene to give (*E*)-stilbene via the C-N bond cleavage. We have found that various primary arylamines such as aniline and toluidine and also some phenyl- or methylhydrazines undergo the C-N bond cleavage and that the resulting organic moiety can be transferred to olefins to give substituted olefins.

In this paper we describe the results of reactions of amines with olefins in the presence of palladium salts.[2]



Results

A mixture of equimolar amounts of palladium acetate, aniline, and styrene in dioxane-acetic acid was heated at reflux for 8 h in air to give a 19% yield of (*E*)-stilbene together with (*E,E*)-1,4-diphenylbutadiene (11%), acetanilide (65%), biphenyl (trace), (*E*)-*p*-aminostilbene (trace), ammonia, and metallic palladium. Of particular interest is that a considerable amount of (*E*)-stilbene is formed while essentially no aminostilbene, the usual aro-

Table I. Reactions of Amines with Styrene

amine	product	yield, %[a] condn A[b]	yield, %[a] condn B[c]
aniline	(*E*)-stilbene	19[d]	52
p-toluidine	(*E*)-*p*-methylstilbene	28[e]	74
p-anisidine	(*E*)-*p*-methoxystilbene	30[e]	62
p-nitroaniline	(*E*)-*p*-nitrostilbene	17[e]	51
p-chloroaniline	(*E*)-*p*-chlorostilbene	40[e]	
α-naphthylamine	(*E*)-α-styrylnaphthalene		48
β-naphthylamine	(*E*)-β-styrylnaphthalene		38
phenylhydrazine	(*E*)-stilbene	29	30
methylhydrazine	(*E*)-β-methylstyrene	4	9
hydrazobenzene	(*E*)-stilbene	1	

[a] Based on the starting amine by VPC. [b] Reactions were carried out with amine, styrene, and $Pd(OAc)_2$ (1 mmol each), dioxane (11 mL), and acetic acid (2.2 mL) under reflux with stirring for 8 h. [c] Reactions were carried out with amine, styrene, $Pd(OAc)_2$, and *tert*-butyl nitrite (1 mmol each) and acetonitrile (10 mL) at 60 °C with stirring for 8 h. [d] Acetanilide (65%), 1,4-diphenylbutadiene (11%), and biphenyl (trace) also were formed. [e] Considerable amounts of the corresponding acetanilide derivatives were formed via condensation of anilines and acetic acid.

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(1) (a) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969); (b) I. Moritani and Y. Fujiwara, *Synthesis*, 524 (1973); (c) Y. Fujiwara, R. Asano, I. Moritani, and S. Teranishi, *J. Org. Chem.*, **41**, 1681 (1976); (d) O. Maruyama, M. Yoshidomi, Y. Fujiwara, and H. Taniguchi, *Chem. Lett.*, 1229 (1979).

(2) A preliminary account of a portion of this study has been published: F. Akiyama, S. Teranishi, Y. Fujiwara, and H. Taniguchi, *J. Organomet. Chem.*, **140**, C7 (1977).

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Table II. Reactions of Aniline with Olefins Using the $Pd(OAc)_2$-Acetic Acid-Dioxane System[a]

olefin	product	yield, %[b]
styrene	(*E*)-stilbene	19
(*Z*)-stilbene	triphenylethylene	11
(*E*)-stilbene	triphenylethylene	12
1,1-diphenylethylene	triphenylethylene	16
propylene	(*E*)-β-methylstyrene	4
acrolein	cinnamaldehyde	6
methyl vinyl ketone	(*E*)-β-acetylstyrene	15
methyl acrylate	methyl cinnamate	11

[a] Reactions were carried out with aniline, the olefin, and $Pd(OAc)_2$ (1 mmol each), dioxane (11 mL), and acetic acid (2.2 mL) under reflux with stirring for 8 h. [b] VPC yield based on aniline.

matic substitution product, is produced. In order to confirm that one phenyl group of the stilbene formed was derived from aniline, we reacted *p*-toluidine with styrene in place of aniline. From this reaction, (*E*)-*p*-methylstilbene was obtained in 28% yield, showing clearly that the C–N bond of the aromatic amine undergoes rupture by palladium(II) acetate. It was also confirmed by control experiments that the reaction of styrene and acetanilide, which was formed via condensation of acetic acid and aniline, did not afford (*E*)-stilbene. Further the C–N bond cleavage of aniline by palladium was also confirmed by the following experiment. Bubbling of carbon monoxide at atmospheric pressure into a refluxing mixture of aniline, palladium acetate, acetic acid, and acetonitrile with stirring for 8 h and subsequent addition of bromine at −78 °C and methanolysis furnished methyl benzoate in 16% yield.[3]

Since it was made apparent that the C–N bond of anilines undergoes cleavage by palladium, the solvent effect was studied to optimize the yield. In acetonitrile slightly better yields were realized while poorer yields were obtained in the other solvents such as nitromethane, carbon tetrachloride, tetrahydrofuran, methyl sulfoxide, *n*-hexane, methanol, ethyl ether, and acetone.

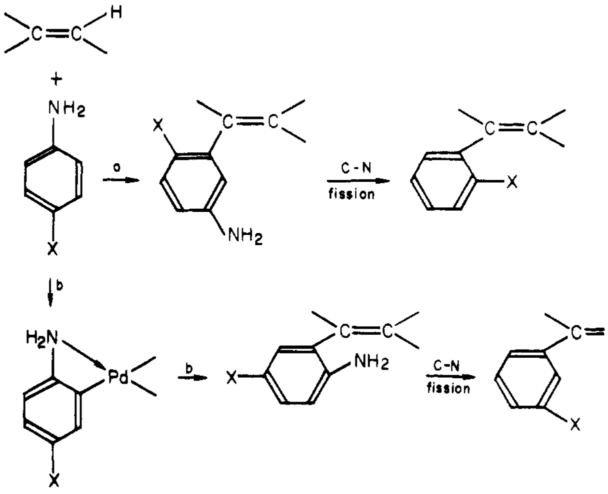
This reaction needs acetic acid as an additive, as no stibene is formed when the reaction is carried out in its absence. The effect of using various acids was studied and revealed that carboxylic acids such as acetic or propionic acid are good whereas mineral acids do not work.

$Pd(NO_3)_2$ and $Pd(OAc)_2$ are effective agents for the reaction. Substitution of other palladium compounds such as $PdCl_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, Pd sponge, Pd/charcoal (5%), $Pd(PPh_3)_4$, $PdCO(PPh_3)_3$, $Pd(PEt_3)_4$, and $Pd(dba)_3$ gave no stilbene.

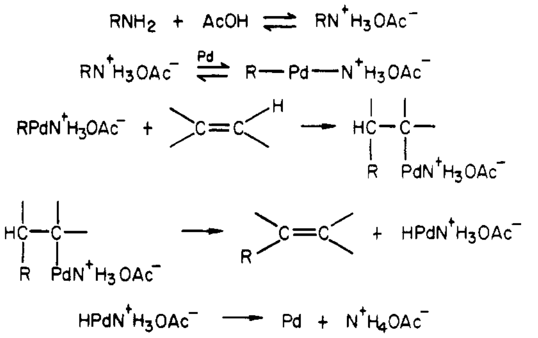
Using the $Pd(OAc)_2$–AcOH–dioxane system, we carried out reactions of styrene with various amines. The results are listed in Table I. From Table I, it can be seen that aniline derivatives can function as the arylating agent through C–N bond cleavage and that if appropriate hydrazines are used, not only arylation but also alkylation can occur, although the yield is low. Table II summarizes reactions of aniline with various olefins using the $Pd(OAc)_2$–AcOH–dioxane system, and the data in Table II show that the reaction is applicable to various olefins.

The present reaction is the first example of arylation and alkylation of olefins by amines by way of C–N bond cleavage by palladium salts, and the yield is low. The problem is to prevent the formation of acetanilide which is formed predominantly from the condensation reaction of aniline with acetic acid although the acetanilide formed can be removed from the reaction mixtures by treatment with concentrated hydrochloric acid. We investigated the effect of additives rather than acetic acid on the yield of the reaction of aniline and styrene using dioxane as a solvent. It was found that additives such as tertiary phosphines, $AlCl_3$, NaOAc, $NaNO_3$, $LiNO_3$, EtBr, Cu, and $Cu(OAc)_2$ had no appreciable effect on the reaction. However, addition of an equimolar amount of alkyl nitrites, especially *tert*-butyl nitrite to palladium acetate, resulted in a remarkable increase of the yield.

Scheme I



Scheme II



Reaction was carried out at 60 °C with stirring by using equimolar amounts of $Pd(OAc)_2$, styrene, amine, and *tert*-butyl nitrite in acetonitrile. The results of reaction of amines with styrene are also summarized in Table I.

Discussion

First of all, it is clear that reaction does not proceed via the usual aromatic substitution[1] (path a, Scheme I) or via ortho metallation[4] (path b) since no meta- or ortho-substituted stilbenes were obtained when para-substituted anilines were allowed to react with styrene (Table I). The alternative mechanism involves oxidative addition of RNH_2 to Pd to form an R-Pd-N species (Scheme II). The Pd-N-type species has not been isolated yet, but it is thought to be an intermediate of isocyanide synthesis.[5] Attempted experiments to isolate both the Ph-Pd-NH_2-type intermediate and aniline from bromobenzene as outlined in eq 1 were unsuccessful. However, formation

$$PhBr \rightarrow PhPdBr \xrightarrow{NaNH_2} PhPdNH_2 \xrightarrow{PPh_3} PhNH_2 \quad (1)$$

of methyl benzoate can be best explained in terms of the

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[3] K. S. Y. Lau, P. K. Wong, and J. K. Stille, *J. Am. Chem. Soc.*, **98**, 5832 (1976).

[4] M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, **16**, 73 (1977).

[5] E. W. Stern, *J. Org. Chem.*, **31**, 596 (1966).

PhPdNH$_2$-type intermediate as shown in eq 2.[6]

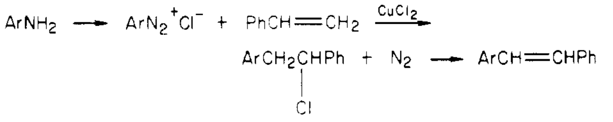
$$\mathrm{PhNH_2} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{Pd(OAc)_2}} \mathrm{PhPdNH_2} \xrightarrow{\mathrm{CO}} \mathrm{PhC(O)PdNH_2} \xrightarrow[\text{2. } \mathrm{CH_3OH}]{\text{1. } \mathrm{Br_2}} \mathrm{PhC(O)OCH_3} \quad (2)$$

The mechanism of the arylation in the presence of nitrites may involve an aryldiazonium salt, ArN$_2^+$OR$^-$, which undergoes oxidative addition to palladium to give Ar–Pd species.[7]

As can be seen from Table I, characteristic features of the arylation in the presence of nitrites are as follows. Anilines can behave as a regioselective arylating agents to give aryl-substituted olefins in good yield and in one step. For example, reaction of *p*-toluidine with styrene gives (*E*)-*p*-methylstilbene, and no ortho and meta isomers are obtained. The reaction is not influenced by the substituent on the benzene ring of the anilines: both the electron-withdrawing and -releasing groups give similar yields. The reaction does not give byproducts other than *tert*-butyl alcohol which can be easily eliminated from the products by simple distillation.

Reaction of naphthalene with styrene by Pd(OAc)$_2$ gives (*E*)-2-styrylnaphthalene in 40% yield, and none of the 1-styryl isomer was obtained.[1c] In contrast, when α- and β-naphthylamines were reacted with styrene, α- and β-styrylnaphthalenes were obtained, respectively (Table I), indicating that by the present reaction, α- or β-alkenyl-substituted naphthalene derivatives can be prepared regioselectively in just one step. Therefore, this provides a very convenient synthetic route for aryl-substituted olefins. Furthermore, hydrazines such as phenyl and methyl also react with styrene to give the corresponding styrene derivatives.

The present reaction has the advantage over alternate preparations of aryl-substituted olefins from arylamines.[8] Doyle et al. have reacted arylamines and olefins in the presence of alkyl nitrites and copper(II) halides.[9] In this case, the products are saturated β-aryl-α-halo derivatives and not the unsaturated ones. Aryl-substituted olefins are also obtained both in the Meerwein reaction[10] (eq 3) and in the Pd-catalyzed reaction with arenediazonium salts.[7] However, these methods need two steps.



$$\mathrm{ArNH_2} \longrightarrow \mathrm{ArN_2^+Cl^-} + \mathrm{PhCH{=}CH_2} \xrightarrow{\mathrm{CuCl_2}} \underset{\displaystyle\mathrm{Cl}}{\mathrm{ArCH_2CHPh}} + \mathrm{N_2} \longrightarrow \mathrm{ArCH{=}CHPh} \quad (3)$$

In conclusion, we have demonstrated that various arylamines undergo the C–N bond fission and that the organic moiety thus formed can be introduced into the olefinic carbon atom. This constitutes the first example for the arylation and alkylation of olefins by amines and hydrazines by way of the C–N bond cleavage by palladium salts. These reactions will open a new synthetic field with amines as arylating or alkylating agents.

Experimental Section

Materials. Dioxane was refluxed with sodium metal and distilled. Other solvents were purified by the usual methods.[1] Pd(OAc)$_2$,[11] PdCl$_2$(PhCN)$_2$,[12] Pd(PPh$_3$)$_4$,[13] Pd(PEt$_3$)$_4$,[14] Pd(dba)$_3$,[15] and PdCO(PPh$_3$)$_3$[16] were prepared according to the literature.

General Procedure for Reaction of Amines with Olefins with Pd(OAc)$_2$–AcOH–Dioxane. Into a 10-mL flask equipped with a condenser with a calcium chloride tube at the top and a magnetic stirring bar were added palladium acetate (1 mmol), the amine (1 mmol), the olefin (1 mmol), acetic acid (2.2 mL), and dioxane (11 mL). The solution was stirred at reflux for 8 h. The resulting mixture was filtered to remove palladium metal, and the filtrate was poured into water. After the addition of ether, 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. From the combined aqueous solution, ammonia was detected with the Nessler reagent. After evaporation of the solvent, the products were isolated by column chromatography. The identities of the products formed were proven by mixture melting point, IR, or NMR comparison with authentic samples.[1] Physical properties of the products are already reported.[1]

General Procedure for Reaction of Amines with Styrene in the Presence of *tert*-Butyl Nitrite. Into a flask similar to that described above were added styrene (1 mmol), the amine (1 mmol), palladium acetate (1 mmol), and acetonitrile (10 mL), and then freshly prepared *tert*-butyl nitrite[17] (1 mmol) was added by a syringe. The mixture was stirred at 60 °C for 8 h. The resulting mixture was worked up as described above. The results are listed in Table I.

Reaction of Aniline with Carbon Monoxide in the Presence of Pd(OAc)$_2$. Into a refluxing mixture of Pd(OAc)$_2$ (0.70 g), aniline (0.30 g), acetic acid (5.2 mL), and acetonitrile (32 mL) was bubbled carbon monoxide under atmospheric pressure for 8 h. Then the reaction mixture was cooled to −78 °C, bromine (1.0 g) was added by a syringe, and the mixture was stirred for 30 min at −40 °C. The mixture was then allowed to warm slowly to room temperature, 10 mL of methanol was added, and the mixture was stirred for 2 h. After the workup as described above, the residue was analyzed by VPC (column: OV-17, 1.5 m) to detect the formation of methyl benzoate in 16% yield.

Acknowledgment. We thank Professor Peter M. Maitlis of the Department of Chemistry, The University, Sheffield, England, for helpful discussions and correspondences.

Registry No. Styrene, 100-42-5; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-nitroaniline, 100-01-6; *p*-chloroaniline, 106-47-8; α-naphthylamine, 134-32-7; β-naphthylamine, 91-59-8; phenylhydrazine, 100-63-0; methylhydrazine, 60-34-4; hydrazobenzene, 122-66-7; (*Z*)-stilbene, 645-49-8; (*E*)-stilbene, 103-30-0; 1,1-diphenylethylene, 530-48-3; propylene, 115-07-1; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; (*E*)-*p*-methylstilbene, 1860-17-9; (*E*)-*p*-methoxystilbene, 1694-19-5; (*E*)-*p*-nitrostilbene, 1694-20-8; (*E*)-*p*-chlorostilbene, 1657-50-7; (*E*)-α-styrylnaphthalene, 2840-87-1; (*E*)-β-styrylnaphthalene, 2840-89-3; (*E*)-β-methylstyrene, 873-66-5; triphenylethylene, 58-72-0; cinnamaldehyde, 104-55-2; (*E*)-β-acetylstyrene, 1896-62-4; methyl cinnamate, 103-26-4; Pd(OAc)$_2$, 3375-31-3; *tert*-butyl nitrite, 540-80-7.

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