quadrant of data out to $2\theta = 50°$; 2365 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed by using a standard programs;[7] all computations were carried out on the CDC Cyber 74 System. For structure factor calculations the scattering factors were taken from Cromer and Mann's tabulation.[8] The agreement factors are defined in the usual way as shown in eq 3 and 4.

$$R = (\sum||F_o| - |F_c||)/(\sum|F_o|) \qquad (3)$$

$$R_w = \frac{[\sum(|F_o| - |F_c|)(w^{0.5})]}{[\sum(|F_o|)(w^{0.5})]} \qquad (4)$$

In all least-squares refinement, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 3.05/[\sigma(F)^2 + 0.0003F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 147 for 2365 observations. Parameters varied included a scale factor, coordinates of all atoms except hydrogen, anisotropic thermal parameters for all O atoms and methyl group C atoms, and isotropic thermal parameters for all other atoms. The H atoms on the hydroxy group and the water molecule were located from a difference Fourier. The remaining H atom coordinates were determined by using the routine in SHELX-76 that fixes the C–H distance of 1.08 Å and orients the H atom positions to complete the appropriate coordination about each C atom. The full-matrix least-squares refinement converged at $R = 0.072$ and $R_w = 0.074$. The final atomic coordinates and thermal parameters are available as supplementary material in Table 2 and the bond distances and bond angles are in Table I. The list of calculated and observed structure factors is available from the authors as Table 3.

Registry No. 1, 5111-67-1; 2, 43025-83-8; 3, 1910-02-7; 9, 76480-23-4; 1-(diethylamino)-3-butanone, 3299-38-5.

Supplementary Material Available: Table 2 containing atomic coordinates and thermal parameters for hydroxy enone 9 (1 page). Ordering information is given on any current masthead page.

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[7] Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

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Communications

Palladium(II) Acetate Catalyzed Aromatic Substitution Reaction

Summary: Relative rate measurements indicate that the palladation reaction, although nonselective, adheres to the selectivity relationship for electrophilic aromatic substitution. Kinetic isotope effects and the dependence of the rate on oxidant concentration implicate arylpalladium(II) and arylpalladium(IV) compounds as intermediates in the reactions leading to biaryls and aryl acetates.

Sir: Palladium(II)-catalyzed aromatic substitution reactions have been widely studied.[1] Henry recently reviewed these contributions.[2] In brief, many substituents including the halogens[3,4] and the nitro,[1j,k,5] acetate,[1b,j,m] cyano,[1j,6,7] and phenyl groups[1l,8] can be introduced into the aromatic nucleus under the influence of this reagent. The reaction between benzene and palladium(II) acetate yields biphenyl in the absence of an added oxidant. In the presence of an oxidant, the reaction yields substitution products. Indeed, phenyl acetate and nitrobenzene are formed in efficient catalytic reactions in the presence of strong oxidants.[1f,j] Several different suggestions have been advanced concerning the role of the oxidant. Some attribute the influence of the oxidant to the conversion of Pd(II) compounds to more electrophilic Pd(IV) species, others to the conversion of arylpalladium(II) compounds to the observed oxidation products. The role of the oxidant in biaryl and aryl acetate formation remains puzzling. The isomer distributions obtained in these processes are rich in the meta isomer even when the substituent in the aromatic nucleus is an ortho,para directing group. Such observa-

Table I. Isomer Distributions for the Palladium(II) Acetate Catalyzed Oxidation of Benzene Derivatives in Acetic Acid at 90 °C for 16 h[a]

compd	aryl acetate, % 2-	3-	4-	% yield[b]
chlorobenzene	38	23	35	15
toluene	26	36	38	212
tert-butylbenzene	0	58	42	125

[a] A solution of the aromatic compound (33 mmol), palladium(II) acetate (0.5 mmol), methanesulfonic acid (3.1 mmol), and sodium dichromate dihydrate (15 mmol) in acetic acid (25 mL) with benzonitrile (3 mmol) used as a complexing reagent. [b] Based upon palladium(II) acetate.

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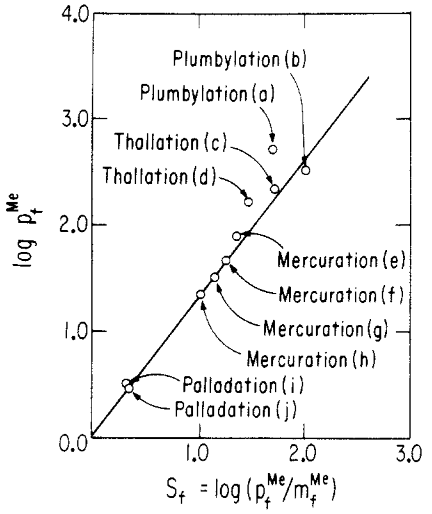
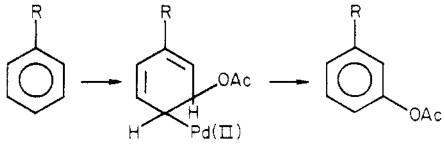


Figure 1. Selectivity relationship for electrophilic aromatic substitution reactions of toluene ($r = 0.995$).[12] The line is based on the statistical analysis of data for more than 100 reactions of toluene. The data for the 10 metalation reactions are identified: (a) $Pb(O_2CCF_3)_4$, CF_3CO_2H, 25 °C, ref 9; (b) $Pb(O_2CCH_3)_4$, Cl_2CHCO_2H, 25 °C, ref 9; (c) $Tl(O_2CCF_3)_3$, CF_3CO_2H, 25 °C, ref 9; (d) $Tl(O_2CCF_3)_3$, CF_3CO_2H, 25 °C, ref 10; (e) $Hg(O_2CCF_3)_2$, CF_3CO_2H, 0 °C, ref 10; (f) $Hg(O_2CCF_3)_2$, CF_3CO_2H, 25 °C, ref 11; (g) $Hg(O_2CCH_3)_2$, CH_3CO_2H, $HClO_4$, 25 °C, ref 11; (h) $Hg(O_2CCH_3)_2$, CH_3CO_2H, 90 °C, ref 11; (i) $Pd(O_2CCH_3)_2$, CH_3CO_2H, 90 °C, this study; (j) $Pd(O_2CCH_3)_2$, $ClCH_2CO_2H$, 100 °C, ref 1k.

tions have prompted several workers to consider the involvement of addition products such as I in the reaction.[1e,l]



I

We have examined these suggestions by a study of the relative rates of reaction of aromatic compounds, the dependence of the reaction rates on the concentration of the oxidizing agent, and the primary kinetic isotope effects. Sodium dichromate was chosen as the oxidizing agent because the acetoxylation could be carried out homogeneously and because the uncertainties associated with one-electron oxidants, e.g., copper(II) or peroxydisulfate, could be avoided. The product distributions for several aromatic compounds are presented in Table I.

The intermolecular selectivity was determined by competition experiments. Replicate experiments established that the toluene to benzene rate ratio was 1.4 ± 0.1. The partial rate factors calculated from this datum and the isomer distribution, Table I, are $o_f^{Me} = 1.09$, $m_f^{Me} = 1.51$, and $p_f^{Me} = 3.19$. These results are very similar to the rate factors determined by Norman and his associates for the palladium(II)-catalyzed nitration of toluene under related conditions.[1k] The similar rate factors for these two reactions suggest that palladation is the rate-controlling and product-controlling process in each case. The relationship between the intermolecular and intramolecular selectivity in palladation is compared with the selectivity in other aromatic substitution reactions in Figure 1.

The relative rate data for palladation conform to the empirical relationship established for the other reactions of toluene. Inasmuch as the expected relationship between inter- and intramolecular selectivity is realized for this reagent, there is no need to postulate that the initial benzenonium ion is captured by the nucleophile to yield an adduct, I, which subsequently undergoes reductive elimination.[13] Rather, the palladation is well described as a nonselective aromatic substitution reaction.

Table II. Product Distributions for the Palladium(II) Acetate Catalyzed Oxidation of Benzene in Acetic Acid at 90 °C after 16 h[a]

sodium dichromate dihydrate, mmol	% yield[b] phenyl acetate	biphenyl
0	<1	22
1	99	23
3	190	33
7.5	353	19
15	403	<1
30[c]	203	<1

[a] Each reaction solution contained benzene (56 mmol) and palladium(II) acetate (1 mmol) in acetic acid (25 mL). [b] Calculated on the basis of palladium(II) acetate. [c] Heterogeneous.

Table III. Isotopic Composition of the Reagents and Products in Biaryl Formation in Acetic Acid at 90 °C

expt.	reagents $C_6H_6:C_6D_6$	products $C_6D_5C_6D_5:C_6D_5C_6H_5:C_6H_5C_6H_5$
1[a]	1.00:1.00	1.00:8.55:19.1
2[b]	1.00:1.00	1.00:9.47:22.0

[a] The solution contained benzene (28 mmol), benzene-d_6 (28 mmol) and palladium(II) acetate (1 mmol) in acetic acid (25 mL). [b] The solution contained benzene (28 mmol), benzene-d_6 (28 mmol), palladium(II) acetate (1 mmol) and sodium dichromate dihydrate (3 mmol) in acetic acid (25 mL).

The dependence of the product distribution on the concentration of the oxidizing agent is shown in Table II. Similar results were obtained for the reactions of toluene. These observations strongly suggest that the oxidant intercepts a reactive intermediate and diverts it virtually entirely to phenyl acetate. The primary kinetic isotope effects for biphenyl formation and for phenyl acetate formation were examined to gain further information on the nature of the intermediate. Benzene-d_6, toluene-*4-d* and *tert*-butylbenzene-*4-d* do not undergo exchange with the solvent in the presence of sodium dichromate. The primary kinetic isotope effects observed for the acetoxylation of benzene, toluene, and *tert*-butylbenzene are 4.5, 3.5, and 3.5, respectively. The isotope effect for the formation of biphenyl was determined by a competitive reaction of benzene and benzene-d_6. The results are presented in Table III.

Inasmuch as the palladodeprotonation reaction is not reversible under these experimental conditions, proton removal from the intermediate benzenonium ion is the rate-determining step in the reaction. The results presented in Table III indicate that two primary kinetic isotope effects occur in the reactions leading to the formation of biphenyl. The data are well satisfied by k_H/k_D values of 4.5 ± 0.2 for each step. The observation that the isotope effects for the arylation and acetoxylation reactions are the same strongly suggests that phenylpalladium(II) acetate is a common intermediate and that this intermediate reacts with benzene in a second electrophilic substitution reaction to yield diphenylpalladium(II). Thermal decom-

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(13) This conclusion is supported by the fact that (4-methylphenyl)mercury(II) compounds react with palladium(II) acetate in acetic acid to yield 4-methylphenyl acetate.[14]

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position would yield biphenyl and palladium(0).[15] The pattern of reactivity observed in these experiments also suggests that phenylpalladium(II) acetate is oxidized to an unstable phenylpalladium(IV) compound in the presence of dichromate ion. The thermal decomposition of this intermediate provides phenyl acetate and regenerates the electrophilic catalyst. The reaction path shown in eq 1 well accommodates the observations obtained under the conditions of these experiments.

$$(C_6H_5)_2Pd(II) \xleftarrow{C_6H_6} C_6H_5Pd(II)OAc \xrightarrow{[OX]} C_6H_5Pd(IV)OAc_3 \rightarrow C_6H_5OAc + Pd(II)OAc_2 \quad (1)$$

Registry No. Palladium(II) acetate, 3375-31-3; 2-chlorophenyl acetate, 4525-75-1; 2-methylphenyl acetate, 533-18-6; 3-chlorophenyl acetate, 13031-39-5; 3-methylphenyl acetate, 122-46-3; 3-*tert*-butylphenyl acetate, 13189-51-0; 4-chlorophenyl acetate, 876-27-7; 4-methylphenyl acetate, 140-39-6; 4-*tert*-butylphenyl acetate, 3056-64-2; chlorobenzene, 108-90-7; toluene, 108-88-3; *tert*-butylbenzene, 98-06-6; benzene, 71-43-2; phenyl acetate, 122-79-2; biphenyl, 92-52-4; benzene-d_6, 1076-43-3; 1,1′-biphenyl-*2,2′,3,3′,4,4′,5,5′,6,6′*-d_{10}, 1486-01-7; biphenyl-*2,3,4,5,6*-d_5, 20637-23-4.

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Received October 23, 1980

Cyclization of α,ω Aliphatic Diamines and Conversion of Primary Amines to Symmetrical Tertiary Amines by a Homogeneous Ruthenium Catalyst

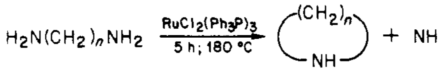
Summary: α,ω Aliphatic diamines were cyclized to heterocyclic amines by being heated at 180 °C for 5 h with $RuCl_2(Ph_3P)_3$ in diphenyl ether. Primary amines having an α-hydrogen atom are converted to symmetrical tertiary amines by being heated at 185 or 235 °C for 8 h with $RuCl_3 \cdot 3H_2O$ and Ph_3P in THF solution.

Sir: In a previous paper[1] we reported a convenient method of obtaining secondary amines by heating primary amines in the presence of the homogeneous catalyst $RuCl_2(Ph_3P)_3$.

As a development of this method we tried to synthetize some heterocyclic amines starting from α,ω aliphatic diamines. The best yields were achieved by heating the α,ω-diamines in a sealed, glass tube at 180 °C for 5 h in the presence of the catalyst $RuCl_2(Ph_3P)_3$ and using diphenyl ether as solvent (see the Table I).

We further developed experimental conditions to obtain tertiary amines from aliphatic primary amines. For this purpose primary amines having an α-hydrogen atom were reacted under an inert atmosphere in a sealed, glass tube at 185 or 235 °C for 8 h in presence of a catalytic amount of $RuCl_2(Ph_3P)_3$ or, more simply, with $RuCl_3 \cdot 3H_2O$ in THF solution. Preliminary experiments, performed on benzylamine and employing other solvents, gave poorer results. In fact, in dioxane (distilled from sodium) a mixture of dibenzylamine (20%) and tribenzylamine (75%) resulted, while in benzene solution dibenzylamine (65%), tribenzylamine (10%), and benzylidenebenzylamine (25%) were obtained. In acetic acid a quantitative formation of benzylacetamide was observed, while in a basic solvent such as pyridine only a poor conversion to benzylidenebenzylamine (25%) was obtained. We remark that there is no need to prepare the Ru catalyst in advance and that 2 mol of Ph_3P/mol of $RuCl_3 \cdot 3H_2O$ is sufficient to produce a good catalytic effect.

Table I. Conversion of α,ω Aliphatic Diamines to Heterocyclic Amines



n for diamine	mol % of catalyst	solvent	% yield[a]	bp, °C (torr)	
				found	lit.[6]
4	2		62	89	88.5–89
4	2	*b*	81		
5	2		79	106	106
5	2	*b*	90		
6	2.5		68	142 (760)	138 (749)
6	2.5	*b*	78		

[a] Yield of isolated product. [b] The solvent was $(C_6H_5)_2O$.

Tertiary amines were obtained as the main product (GLC yields ranging from 51% to 98%) along with secondary amines; the amount of unreacted primary amines was negligible. The low yields obtained from octyl-, dodecyl-, and cyclohexylamine were improved either by using a larger amount of the catalyst or by raising the reaction temperature to 235 °C (see Table II). The reaction therefore appears more sensitive to the steric bulk around the nitrogen atom than we found in the synthesis of secondary amines.[1] This feature is also reported for the addition of secondary amines to ethylene in the presence of $RhCl_3 \cdot 3H_2O$.[2]

In the absence of other evidence, it is reasonable to suppose that the secondary amine formed during the reaction adds to an intermediate imine through a reaction path similar to that already proposed for the secondary amines synthesis (ref 1 and references therein) or for the Pd[3] or the copper–chromium oxide[4] catalyzed alkylation of secondary amines by alcohols:

$$(RCH_2)_2NH + RCH{=}NH \rightleftharpoons RC(N(CH_2R)_2)HNH_2 \xrightarrow{\text{catalyst (H)}} (RCH_2)_3N + NH_3$$

The ammonia formation was ascertained in an experiment performed with benzylamine: 93% of the stoichiometric amount of gaseous ammonia was found at the end of the reaction by titration with 0.1 N HCl according to the equation $3RNH_2 \rightarrow R_3N + 2NH_3$.

The general procedure for heterocyclic amine synthesis was as follows. A mixture of α,ω aliphatic diamine (6

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