Carbonylation Reactions of Ortho-Palladation Products of α-Arylnitrogen Derivatives

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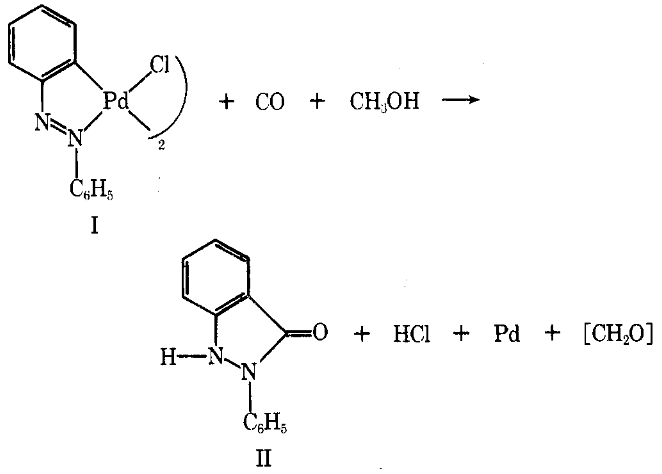
Ortho-palladation products of azobenzene, Schiff bases (two isomeric types), benzaldazine, acetophenone dimethylhydrazone, 1-methyl-1-phenylhydrazones, and tertiary benzylamines have been prepared and treated with carbon monoxide under mild conditions. A variety of unusual heterocyclic compounds have been obtained, often in good yields, from these reactions. Mechanistic patterns have appeared which should allow reaction products to be predicted from the carbonylations of the many other types of ortho-palladation products which probably can be prepared.

The formation of ortho-palladation products from numerous α-arylnitrogen derivatives and palladium salts is well known. For example, complexes with azobenzene,[1] Schiff bases,[2-5] tertiary benzylic amines,[6] oximes,[7-9] and appropriately substituted pyridines[10] and pyrazoles[11] are known. However, relatively little chemistry has been done with these readily obtainable, reactive complexes. The ortho-metalation reaction is ideally suited for use in the synthesis of heterocyclic compounds, since the metalated complexes can be made directly from monosubstituted aromatics. Previously, for example, in one of the few experiments carried out, the azobenzene–palladium chloride complex, I, was treated with carbon monoxide in methanol solution at 40 psi and room temperature and 2-phenyl-1*H*-indazolone (II) was formed, although only in 17% yield.[12] Much better yields were obtained at 100° under 150 atm pressure, however.[13]



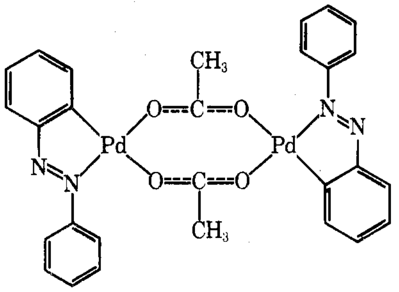
I

II

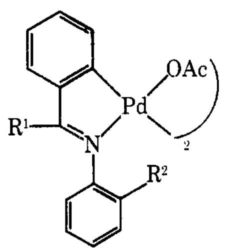
In the present paper we report the synthesis of several new ortho-palladated complexes and a study of the reactions of these and some previously known complexes with carbon monoxide.

Results and Discussion

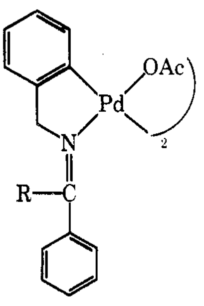
I. Palladium Complexes. Seven structurally different types of chelated, five membered ring, nitrogen-coordinated, ortho-palladated complexes were prepared for carbonylation by treating the parent aromatic compound with the appropriate palladium salt (chloride or acetate). The azobenzene–palladium chloride complex (I) was reinvestigated to determine the reason for the low yield of the carbonylation product found previously.[12] The related azobenzene–palladium acetate complex (III) was also prepared for comparison with the chloride. The higher reaction rates, better solubility, and higher yields of organic products obtained with the acetate derivative (results to be described) led us to investigate only the acetates of the other six structures. The known benzaldehyde–Schiff base-palladium acetate complexes, IV,[3] and the new type of complex from benzyl-



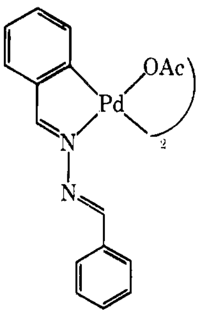
III



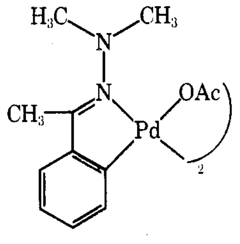
IVa, $R^1 = R^2 = H$
b, $R^1 = H$; $R^2 = CH_3$
c, $R^1 = CH_3$; $R^2 = H$



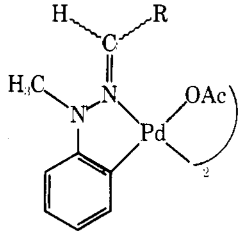
Va, R = H
b, R = CH_3



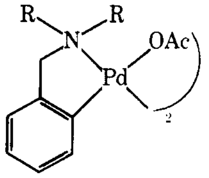
VI



VII

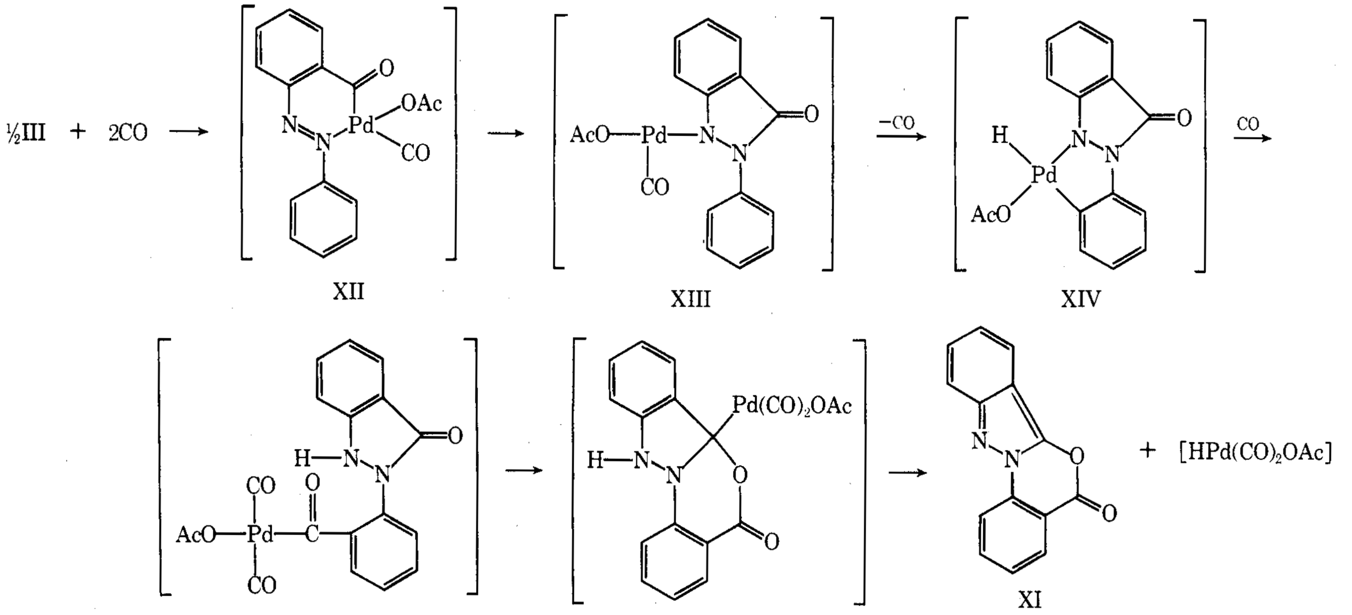


VIIIa, R = H
b, R = CH_3



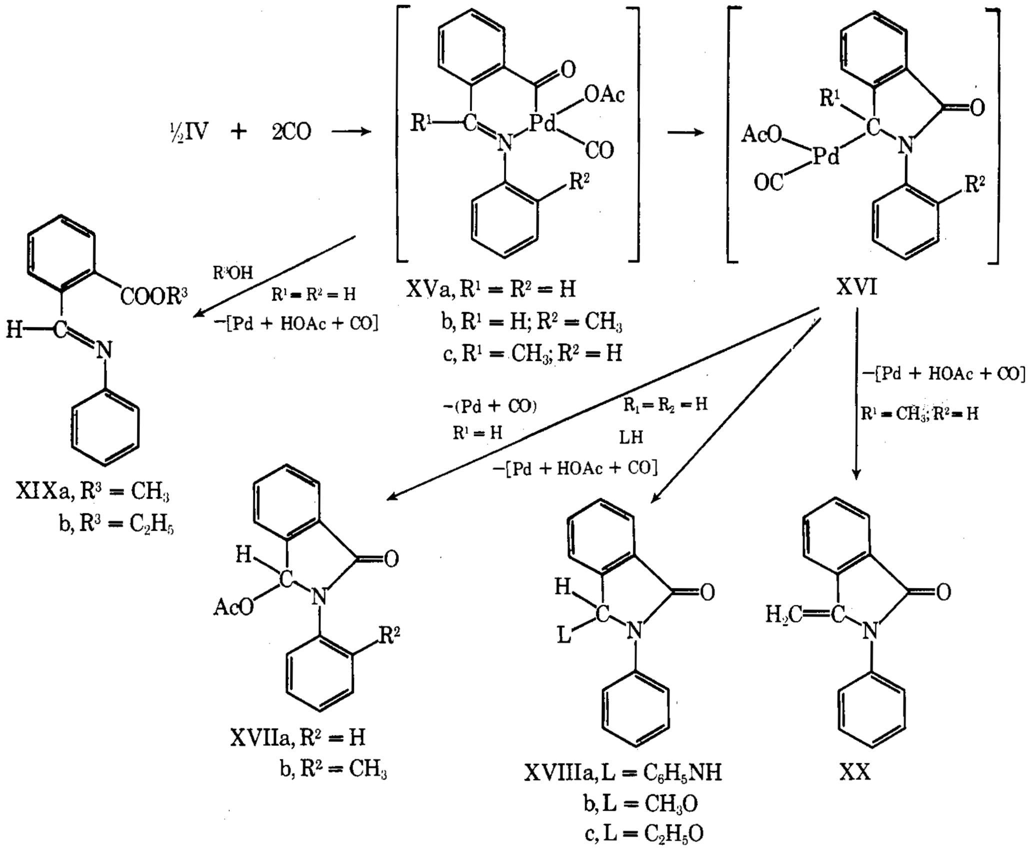
IXa, R = CH_3
b, R = C_2H_5
c, R-R = $(CH_2)_4$

Scheme I
Carbonylation of the Azobenzene–Palladium Acetate Complex



$[HPd(CO)_2OAc] \longrightarrow HOAc + Pd + 2CO \qquad XIII + HOAc \longrightarrow II + Pd(OAc)_2$

Scheme II
Carbonylation of Schiff Base–Palladium Acetate Complexes

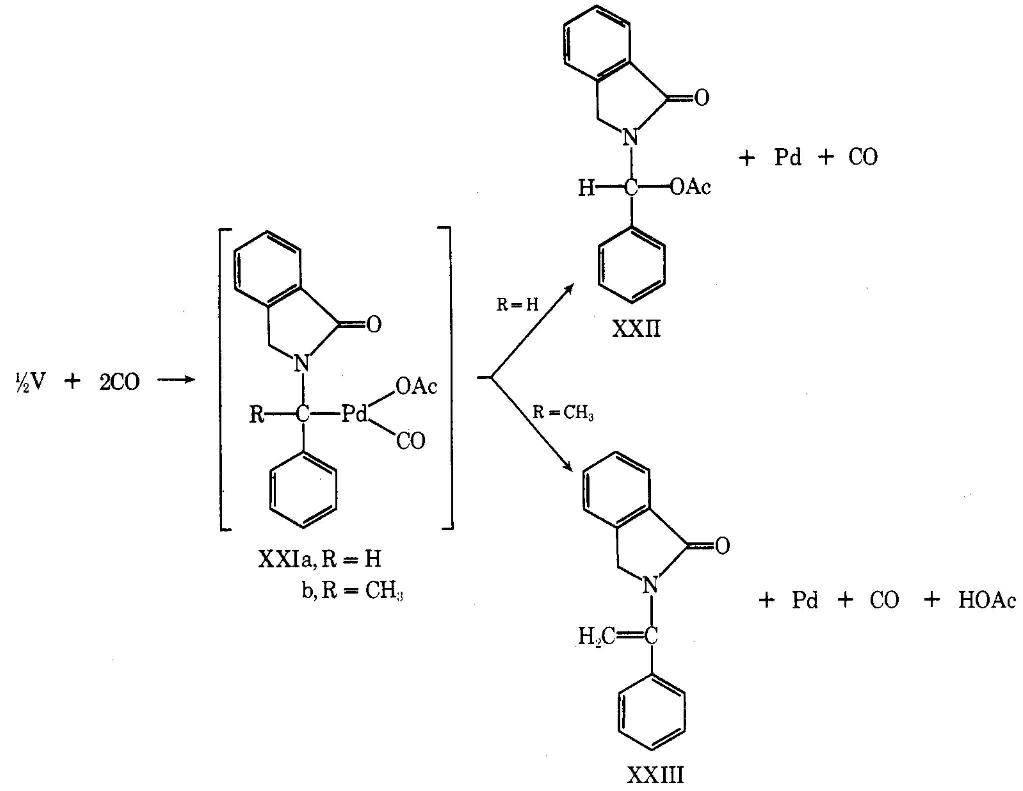


amine–Schiff bases, V, were similarly prepared by heating the Schiff bases with palladium acetate. While syn and anti isomers about the C–N double bond were possible, only one, presumably the anti isomer, was found in these complexes. Three varieties of hydrazone complexes were likewise prepared. Benzaldazine gave complex VI as bright red needles, acetophenone dimethylhydrazone gave complex VII, and 1-methyl-1-phenylhydrazones gave complexes of structure VIII.

Complex VIIIb was a mixture of syn and anti hydrazone complexes dimerized to both cis and trans isomers about the acetate bridges. The seventh type prepared was the palladium acetate complex with various *N,N*-dialkylbenzylamines. Palladium chloride derivatives of these ligands were already well known.[6] Three *N,N*-dialkylbenzylamines were used: the dimethyl, diethyl, and tetramethylene derivatives.

II. Carbonylation Reactions. A. Azobenzene Com-

Scheme III
Carbonylation of Benzylamine–Schiff Base–Palladium Acetate Complexes



plexes. The carbonylation of the azobenzene–palladium chloride complex (I) was examined in the inert solvent xylene at 100° under 1 atm of CO. About 4 equiv of CO per mole of dipalladium complex was absorbed and a dark purple precipitate formed (complex X). This material was insoluble in all solvents. It had ν_{CO} 1950 cm^{-1} indicative of terminal carbonyls. Analyses suggest the formula $C_7H_5NOClPd$, or more probably a polymer of this formula. The compound reacted with warm methanol with precipitation of palladium and formation of II in 77% yield. (See below.) If this formulation of X is correct, the material was obtained in 98% yield. Two other products were also formed in the carbonylation: the lactone XI, isolated in 25% yield, identical with the material obtained by the high-temperature carbonylation of azobenzene with nickel carbonyl,[14] and 9% of II.

The carbonylation of the azobenzene–palladium acetate complex (III) in chlorobenzene at 100° gave 15% II and 15% XI. The remainder of the material was insoluble and could not be separated from the palladium metal also formed.

Compounds XI and II probably are being formed in the azobenzene carbonylation as shown in Scheme I. An initial CO insertion, forming XII, and an addition of the acylpalladium group across the nitrogen–nitrogen double bond would give XIII. This complex could then either internally ortho palladate to give complex XIV or react with acetic acid (or water in the reaction of I) formed in subsequent reactions and produce II. Complex XIV would then undergo a hydrogen shift from palladium to nitrogen, insert CO, and cyclize by internal addition of the acylpalladium group to the amide carbonyl. A final 1,4-hydridopalladium acetate elimination would form XI. Apparently, the 6:5 ring closure observed is much more favorable than the symmetrical 5:5 closure which might have been expected.

Carbonylation of III in ethanol at 50° produces 44% of II, 21% of azobenzene, and 15% of a new compound, 2-ethoxycarbonylazobenzene. Apparently, the last compound is being formed by ethanolysis of XII. The origin of the azobenzene is not clear.

A catalytic synthesis of II from azobenzene using cobalt carbonyl as catalyst in an inert solvent at 190° and 150 atm pressure has been reported.[15] Cobalt[7] analogs of III, XII, and XIII with "$(CO)_3Co$" replacing "PdCl" are presumably involved in this reaction. The last complex could be reduced with $HCo(CO)_4$; the $Co_2(CO)_8$ formed would ortho metalate the azobenzene and the catalytic cycle would be complete.[12]

B. Schiff Base Complexes. The tendency for azobenzene to react at both aromatic rings complicated the carbonylation reaction. Carbonylations of the Schiff base complexes, IVa–c, were more straightforward. The benzalaniline–palladium acetate complex (IVa) carbonylated readily in xylene at 100° with 1 atm of CO, forming only one product, 3-acetoxy-3-phenylphthalimidine (XVIIa), in 65% yield. The *o*-methyl derivative IVb reacted analogously.

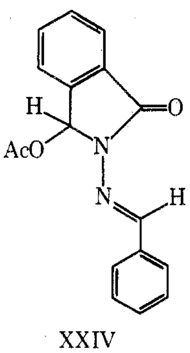
The carbonylation of IVa in the presence of nucleophiles led to incorporation of the nucleophile in the products. In the presence of aniline, 3-anilino-2-phthalimidine (XVIIIa) was formed in 63% yield rather than the acetate. The acetate was apparently not the initial product, since it did not react with aniline under these conditions. Similarly, in methanol solution 3-methoxy-2-phthalimidine (XVIIIb) was formed in 24% yield along with the uncyclized ester, XIXa, isolated in 55% yield. In ethanol the yields were reversed and 58% cyclization to XVIIIc occurred along with formation of 29% of "open chain" ester, XIXb.

The methyl derivative, IVc, carbonylated in xylene at 100° to form exclusively the olefinic product XX in 86% yield rather than the tertiary acetate. These reactions may be explained by the equations shown in Scheme II. Initially, CO insertion and bridge breaking likely occur forming intermediate XV, which then has two possible reaction paths in alcohol solvents. The alcohol may either attack the carbonyl group and form noncyclicized ester XIX or the compound may undergo an internal addition of the acylpalladium group to the nitrogen–carbon double bond to form XVI. The second path is the sole reaction course in xylene solvent. Complex XVI then has three possible reaction paths it may follow depending upon the substituents present and whether nucleophiles are in the reaction solution. A simple reductive elimination of product acetate, XVII from complex XVI, apparently occurs if R^1 is H. If R^1 is methyl (or presumably any other alkyl with an α-hydrogen substituent), metal hydride elimination is preferred and olefin XX is formed. When nucleophiles are present, at least when R^1 = H, the palladium group may also be replaced by the ligand minus a hydrogen.

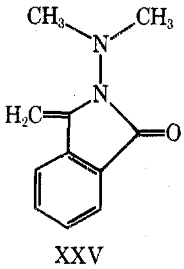
Schiff base–palladium acetate complexes of type V underwent carbonylation in xylene to form different cyclic products than type IV complexes because of the exocyclic double bond. See Scheme III. Carbon monoxide insertion followed by an internal addition of the acylpalladium group to the nitrogen–carbon double bond would produce complex XXI, which then may either reductively eliminate product acetate if R = H forming XXII (obtained in 48% yield at 100°), or eliminate metal hydride if R = CH_3 producing olefin XXIII (isolated in 49% yield after reaction in xylene at 130°. Complex XXIb did not carbonylate rapidly below 130°).

C. Azine and Hydrazone Complexes. The benzaldazine–palladium acetate complex (VI) carbonylated readily in xylene at 100°, producing a single product, isolated in 48% yield, 3-acetoxy-2-benzalimidophthalimidine (XXIV). This material is likely formed by a mechanism analogous to the one proposed for the carbonylation of IVa by Scheme II. The presence of the second carbon–nitrogen double bond apparently does not affect the reaction.

Carbonylation of the palladium acetate complex of the 1,1-dimethylhydrazone of acetophenone (VII) in xylene at 100° was similar to the corresponding reaction of IVc in Scheme II. A CO insertion, cyclization, and metal hydride elimination sequence was now followed forming XXV in 61% yield, since a tertiary palladium complex with β hydrogen substituents was the intermediate in the reaction.



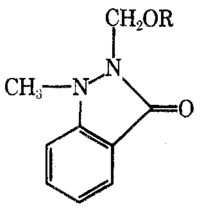
XXIV



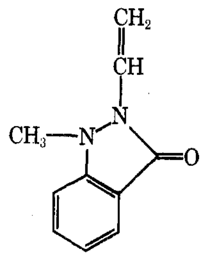
XXV

The above data led us to expect that the hydrazone–palladium acetate complexes VIIIa and VIIIb would behave analogously to complexes Va and Vb. Indeed this turned out to be correct. Complex VIIIa in xylene at 100° reacted readily with carbon monoxide, forming acetate XXVIa in 53% yield. Carbonylation in ethanol at room temperature formed 38% XXIXa, 28% formaldehyde 1-methyl-1-phenylhydrazone, and 13% XXVIb. Complex VIIIb carbonylated at room temperature in benzene, forming mainly olefin XXVII (68%) along with traces of what appeared to be the secondary acetate XXVIIIa.

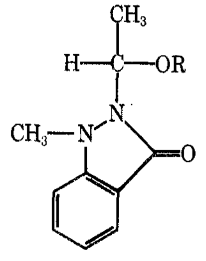
Carbonylation of VIIIb in methanol at room temperature gave mainly uncyclized methyl ester XXIXb (69%) and 20% of the cyclized methyl ether XXVIIIb. In ethanol, only the cyclized ethyl ether, XXVIIIc (68%), was obtained.



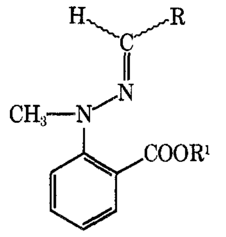
XXVIa, R = $COCH_3$
b, R = CH_2CH_3



XXVII



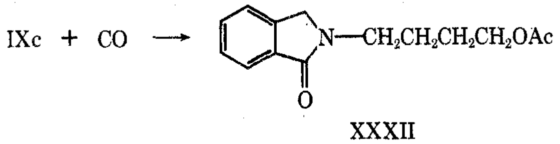
XXVIIIa, R = $COCH_3$
b, R = CH_3
c, R = C_2H_5



XXIXa, R = H; R^1 = C_2H_5
b, R = CH_3; R^1 = CH_3
c, R = CH_3; R^1 = C_2H_5

D. Tertiary Benzylamine Complexes. The carbonylation of the palladium acetate–tertiary benzylamine complexes (IXa and IXb) might have been expected to produce only mixed anhydrides and ketones as observed in the carbonylation of simple arylpalladium acetate derivatives.[16,17] Ketones were not observed; hydrolysis products of the mixed anhydrides were, however. An unexpected third type of product was also formed. The third product, which was formed in both reactions, was a phthalimidine produced by cyclization and loss of one of the *N*-alkyl groups. Compound IXa, the *N,N*-dimethylbenzylamine complex, on carbonylation in xylene at 100° for 30 min gave 72% of the demethylated product, 2-methylphthalimidine (XXXa), along with 4.5% of acid (zwitterion) XXXIa, presumably formed by hydrolysis during isolation of an initially formed mixed anhydride with acetic acid. Similarly, complex IXb, the *N,N*-diethylbenzylamine complex, on carbonylation at 100° in xylene for 15 min gave 27% of 2-ethylphthalimidine (XXXb) and 36% of the acid XXXIb. There was also a trace of the ethyl ester of XXXIb formed. The last product was isolated in 24% yield when the reaction was carried out at 100° for 5 hr instead of for only 15 min. In this reaction 53% of XXXb was also formed. It is not clear how the ester was being produced, but obviously it was being formed in a secondary reaction since very little was formed in 15 min, by the time the palladium had all precipitated and the total amount of carbon monoxide had been absorbed. When the carbonylation of IXb was carried out at room temperature in benzene for 3 hr the only product formed was apparently the mixed anhydride, since a 63% yield of acid XXXIb was isolated after exposure to moist air.

We were not able to determine the fate of the second alkyl group in the reactions when esters of XXXI were not formed. We, therefore, investigated the carbonylation of IXc, the palladium acetate–*N*-benzylpyrrolidine complex, where the "second alkyl group" could not be lost as a low molecular weight fragment. The carbonylation of IXc gave only one significant product, 2-(4′-acetoxybutyl)phthalimi-

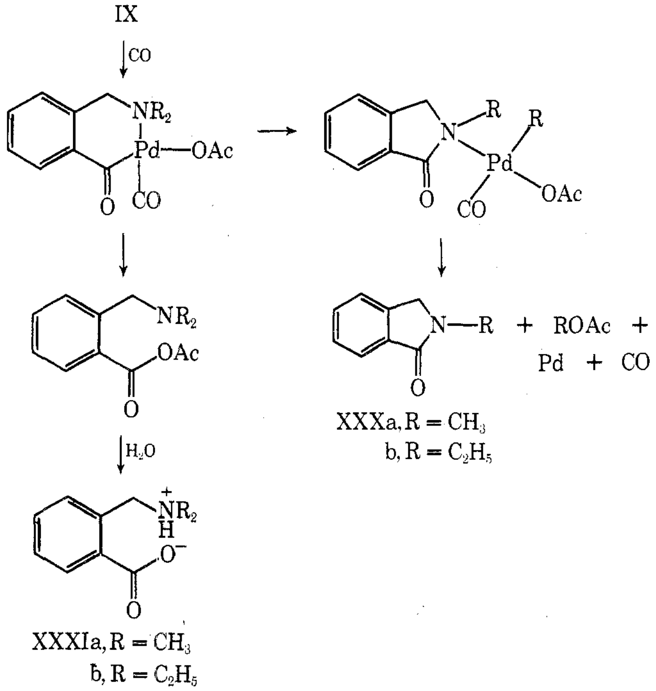


XXXII

dine (XXXII) showing that in this example, at least, the "alkyl group" was converted into the alkyl acetate.

The mechanism by which the carbon–nitrogen bond is cleaved is not certain, but it is probably a 1:2 shift of alkyl from nitrogen to palladium occurring with the ring closure. Plausible mechanisms for the ring closure and hydrolysis reaction are shown in Scheme IV.

Scheme IV
Carbonylation of *N,N*-Dialkylbenzylamine–Palladium Acetate Complexes



Conclusions

The carbonylation of isolable ortho-metalated palladium complexes has proved to be a general reaction capable of producing a variety of unusual five-membered ring heterocyclic and open-chain products. Mechanisms of reaction have been suggested which will allow prediction of products which can be obtained by carbonylation of the many related complexes which probably can be prepared.

Experimental Section

Reagents. Palladium chloride and palladium acetate were obtained from Engelhard Industries. They were generally used without further purification, although the purity of the palladium acetate varied significantly from batch to batch and particularly bad lots, as judged the amount of benzene-insoluble material (pure material is completely soluble), were recrystallized from acetic acid before use. Carbon monoxide (99.5%) was obtained from Matheson Gas Products. *N,N*-Dimethylbenzylamine was used as obtained from the Aldrich Chemical Co. *N,N*-Diethylbenzylamine and *N*-benzylpyrrolidine were prepared from benzyl chloride and the appropriate secondary amine.

Di-μ-chlorobis[*o*-(phenylazo)phenyl]dipalladium (I). This material was prepared by the method of Cope.[1]

Di-μ-acetatobis[*o*-(phenylazo)phenyl]dipalladium (III). A solution of 1.91 g (10.5 mmol) of azobenzene and 2.24 g (10.0 mmol) of powdered palladium acetate in 50 ml of anhydrous methyl alcohol was boiled for 1 hr. The mixture was concentrated under reduced pressure and cooled in Dry Ice. The crystals which formed were filtered and recrystallized from benzene–hexane. There was obtained 1.91 g (57%) of very dark red prisms, mp 208–210°.

Anal. Calcd for $C_{28}H_{24}N_4O_4Pd_2$: C, 48.51; H, 3.48; N, 8.08. Found: C, 48.82; H, 3.35; N, 7.99.

NMR ($CDCl_3$) τ 2.85 (multiplet, 18 aromatic protons), 7.96 (singlet, 6 acetate methyl protons), 7.77 and 8.82 (two singlet of low intensity, assigned to the nonequivalent acetate methyls of the cis dimer).

Di-μ-acetatobis[*o*-(*N*-phenylformimidoyl)phenyl]dipalladium (IVa). This complex was prepared by the procedure of Onoue and Moritani.[3]

Di-μ-acetatobis[*o*-(*N*-*o*-tolylformimidoyl)phenyl]dipalladium (IVb). The preparation of this complex has also been described by Onoue and Moritani.[3]

Di-μ-acetatobis[*o*-(*N*-phenylacetimidoyl)phenyl]dipalladium (IVc). Onoue and Moritani have previously prepared this compound.[3] We obtained the product in 85% yield after recrystallization from benzene–hexane.

Di-μ-acetatobis[α-(benzylideneamino)-*o*-tolyl]dipalladium (Va). A mixture of 2.24 g (10 mmol) of $Pd(OAc)_2$ and 2.05 g (10.5 mmol) of *N*-benzylbenzaldehyde imine in 50 ml of acetic acid was boiled for 50 min. After cooling, water was added and the solid formed was separated by filtration. After washing with water and air drying, the product was crystallized from benzene to give 3.00 g (80%) of golden yellow crystals; mp 194° dec; NMR ($DCCl_3$) τ 2.7 (m, 18 aromatic protons and 2 methine protons), 5.50 (AB quartet, 4 methylene protons), 7.8 (s, 6 acetate protons).

Anal. Calcd for $C_{32}H_{30}N_2O_4Pd_2$: C, 53.44; H, 4.20; N, 3.89. Found: C, 53.49; H, 4.18; N, 3.78.

Di-μ-acetatobis[α-[(α-methylbenzylidene)amino]-*o*-tolyl]dipalladium (Vb). This complex was prepared by heating 2.09 g (10 mmol) of *N*-benzylacetophenone imine with 2.24 g (10 mmol) of palladium acetate in 30 ml of acetic acid at reflux temperature for 1 hr. After cooling, water was added and the solid formed was separated by filtration. After air drying, the crude material was dissolved in methylene chloride and chromatographed on silica gel. The yellow eluate was concentrated and pentane was added. Yellow crystals, 1.63 g (44%), of the product were obtained: mp 245–249° dec; NMR ($DCCl_3$) τ 2.77 (m, 18 aromatic protons), 6.5 and 5.5 (AB doublets, methylene protons, J = 14.4 Hz), 7.82 (s, methyl protons), 8.2 (s, 6 acetate protons).

Anal. Calcd for $C_{34}H_{34}N_2O_4Pd_2$: C, 54.63; H, 4.58; N, 3.75. Found: C, 54.81; H, 4.62; N, 3.66.

Di-μ-acetatobis[α-(benzylidenehydrazono)-*o*-tolyl]dipalladium (VI). A mixture of 2.18 g (10.5 mmol) of benzaldazine and 2.24 g (10 mmol) of $Pd(OAc)_2$ in 50 ml of acetic acid was boiled for 45 min. After cooling, water was added and the solid formed was separated by filtration, washed thoroughly with water, and air dried. Recrystallization from benzene–hexane gave 2.86 g (77%) of bright red needles, mp 218–222° dec.

Anal. Calcd for $C_{32}H_{28}O_4N_4Pd_2$: C, 51.56; H, 3.78; N, 7.51. Found: C, 51.55; H, 3.61; N, 7.67.

NMR ($DCCl_3$) τ 1.25, 1.35, 1.95, and 2.20 (all s, 4 protons, methine protons, τ 1.25 and 1.95 signals were from the cis dimer and τ 1.35 and 2.20 from the trans dimer), 2.5 (m, 18 aromatic protons), 7.68, 7.70, and 7.90 (all s, 6 protons, τ 7.68 and 7.90 signals were from the nonequivalent acetate methyls in the cis dimer, and the τ 7.70 signal was from the trans dimer; from the relative intensities the solution was calculated to contain 66% of the trans isomer). Addition of a few drops of pyridine to the NMR solution removed the multiple peaks due to cis and trans dimers by converting the compounds to mononuclear species.

Di-μ-acetatobis[*o*-[1-(dimethylhydrazono)ethyl]phenyl]dipalladium (VII). A mixture of 1.70 g (10.5 mmol) of acetophenone dimethylhydrazone and 2.24 g (10 mmol) of palladium acetate in 50 ml of acetic acid was heated on the steam bath for 1 hr. After cooling and diluting with water, the product which precipitated was washed and air dried. Purification was achieved by chromatography over silica gel, elution with benzene, and recrystallization from benzene–hexane. There was obtained 2.08 g (61%) of pale yellow crystals, mp 230–235° dec. The material was dried at 90° to remove occluded benzene.

Anal. Calcd for $C_{24}H_{32}N_4O_4Pd_2$: C, 44.12; H, 4.94; N, 8.57. Found: C, 44.28; H, 4.79; N, 8.19.

NMR (C_6D_6) τ 3.10 (m, 8 aromatic protons), 7.65 (s, 12 *N*-methyl protons), 7.82 (s, 6 methyl protons), 8.30 (s, 6 acetate protons).

Di-μ-acetatobis[*o*-(1-methyl-2-methylenehydrazino)phenyl]dipalladium (VIIIa). A mixture of 0.85 g (6.3 mmol) of the 1-methyl-1-phenylhydrazone of formaldehyde and 1.42 g (6.3 mmol) of $Pd(OAc)_2$ with 50 ml of methylene chloride was heated to boiling for 45 min. A little decolorizing carbon was added and the reaction mixture was filtered. Evaporation of the solvent under reduced pressure and recrystallization from benzene by adding hexane three times below 35° gave 1.11 g (58%) of yellow crystals of the product, mp 193° dec.

Anal. Calcd for $C_{20}H_{24}N_4O_4Pd_2$: C, 40.22; H, 4.05; N, 9.38. Found: C, 39.98; H, 3.99; N, 9.22.

NMR ($DCCl_3$) τ 3.30 (m, 8 aromatic protons), 3.80, 4.60 (2 d, 4 methylene protons, $J = 8$ Hz), 7.40 (s, 6 *N*-methyl protons), 7.85 (6 acetate protons).

Di-μ-acetatobis[*o*-(2-ethylidene-1-methylhydrazino)phenyl]dipalladium (VIIIb). This complex was prepared by stirring a mixture of 0.81 g (5.5 mmol) of the 1-methyl-1-phenylhydrazone of acetaldehyde (ca. 55% anti:45% syn) and 1.12 g (5 mmol) of $Pd(OAc)_2$ with 50 ml of acetone at room temperature for 3 hr. The solution was treated with decolorizing carbon and filtered, and the solvent was removed under reduced pressure at room temperature. The crude product was then crystallized from benzene by adding hexane slowly at room temperature. There was obtained 0.77 g (45%) of greenish-yellow crystals, mp 138° dec.

Anal. Calcd for $C_{22}H_{28}N_4O_4Pd_2$: C, 42.26; H, 4.51; N, 8.96. Found: C, 42.12; H, 4.45; N, 8.76.

The spectrum in $CDCl_3$ was very complex because of the presence of at least three isomeric forms, presumably isomers, at the carbon–nitrogen double bond and cis–trans isomers about the acetate bridges. The spectrum was considerably simplified by the addition of a few drops of deuterated pyridine to the $CDCl_3$ solution. The pyridine breaks the dimeric bridges and reduces the number of isomers present to only two: the syn and anti isomers of the carbon–nitrogen double bond. NMR τ 3.5 (m, 4 aromatic protons and an olefinic proton), 7.5 (s, 3 *N*-methyl protons), 7.8 and 8.4 (2 d, 3 protons of the syn and anti methyl group, $J = 5$ Hz, for both isomers, 55% anti and 45% syn), 2.1 (s, 3 acetate protons).

Di-μ-acetatobis[α-(dimethylamino)-*o*-tolyl]dipalladium (IXa). To 150 ml of methanol was added with stirring 5.40 g (40 mmol) of *N,N*-dimethylbenzylamine and 4.48 g (20 mmol) of palladium acetate. After stirring for 3 hr at room temperature, the solution was filtered and the solvent was removed under reduced pressure at room temperature. The solid residue was dissolved in benzene and purified by chromatography over silica gel. Evaporation of the yellow eluate and recrystallization from benzene–hexane gave 2.86 g (47%) of yellow crystals of the product, mp 210–211°.

Anal. Calcd for $C_{22}H_{30}N_2O_4Pd_2$: C, 44.09; H, 5.04; N, 4.67. Found: C, 44.13; H, 5.09; N, 4.71.

NMR (C_6D_6) τ 3.00 (m, 8 aromatic protons), 6.80 (AB quartet, 4 methylene protons, $J = 21.5$ Hz), 7.61 and 8.02 (s, 12 *N*-methyl protons), and 7.94 (s, 6 acetate protons).

Di-μ-acetatobis[α-(diethylamino)-*o*-tolyl]dipalladium (IXb). This complex was prepared from *N,N*-diethylbenzylamine and palladium acetate as described for the *N,N*-dimethylbenzylamine reaction above. Recrystallization of the product from hexane gave a 66% yield of pale yellow crystals, mp 189–192° dec.

Anal. Calcd for $C_{26}H_{38}N_2O_4Pd_2$: C, 47.65; H, 5.84; N, 4.27. Found: C, 47.73; H, 5.90; N, 4.31.

NMR ($CDCl_3$) τ 3.15 (m, 8 aromatic protons), 6.27 (AB quartet, $J = 13$ Hz, 4 methylene protons), 7.30 (m, 8 methylene protons in ethyl groups), 8.30 (s, 6 acetate protons), and 9.40 (t, 12 methyl protons).

Di-μ-acetatobis(α-1-pyrrolidinyl-*o*-tolyl)dipalladium (IXc). A mixture of 0.40 g (2.24 mmol) of *N*-benzylpyrrolidine, 0.56 g (2.24 mmol) of $Pd(OAc)_2$, and 30 ml of benzene was stirred at room temperature for 48 hr. The benzene solution was concentrated under reduced pressure and chromatographed on silica gel. The yellow eluate was concentrated and the solid residue was crystallized from hexane to give 0.36 g (45%) of pale yellow crystals of product, mp 164° dec.

Anal. Calcd for $C_{26}H_{34}O_4N_2Pd_2$: C, 47.94; H, 5.26; N, 4.30. Found: C, 47.78; H, 5.18; N, 4.14.

NMR ($CDCl_3$–C_6D_6) τ 2.90 (m, 4 aromatic protons), 6.70 (m, AB quartet, 2 methylene protons, $J = 14$ Hz), 6.3, 7.2, and 8.5 (m, 8 methylene protons), 8.00 (s, acetate protons).

Carbonylation of the Azobenzene–Palladium Chloride Complex (I) in Xylene. In the previously described gasometric apparatus[18] was placed 0.50 g (0.77 mmol) of I, the apparatus was flushed with CO at 100°, and 10 ml of xylene was injected with magnetic stirring. In 2 hr, 3–4 equiv per mole of I had been absorbed and the reaction mixture was filtered hot to remove the purple solid present. The solid was rinsed several times with methylene chloride and the rinsings were added to the original filtrate. The insoluble purple product, 0.395 g (98%), complex X, did not have a sharp melting point, but decomposition began at about 120°. The complex in a Nujol mull showed a strong carbonyl absorption at 1950 cm^{-1}.

Anal. Calcd for $(C_7H_5NOClPd)_n$: C, 32.46; H, 1.95; N, 5.41. Found: C, 32.15; H, 1.67; N, 5.25.

On reaction with hot methanol, complex X decomposed, producing a precipitate of palladium metal and a solution from which a 77% yield of compound II was obtained by sublimation, mp 206–207° (reported mp 203–204°).[12] The molecular weight by mass spectroscopy was 210.079 (calcd 210.0793).

The soluble portion of the carbonylation reaction product was isolated by evaporation of the original filtrate. The mixture was separated by dissolving it in methylene chloride and chromatographing on silica gel. Methylene chloride eluted 0.029 g (9%) of compound II, mp 205–206° and ir spectrum identical with that of a known sample,[12] and methanol eluted 0.091 g (25%) of bright yellow lactone XI, mp 293–297° (reported mp 296°,[14] 300°[19]). The molecular weight by mass spectroscopy was 236.056 (calcd 236.0586).

Carbonylation of the Azobenzene–Palladium Acetate Complex (III). A. In Chlorobenzene Solution. Carbonylation of 1.70 g of complex III (2.45 mmol) in 15 ml of chlorobenzene at 100° under 1 atm of carbon monoxide was carried out as in the preceding experiment. In 3 hr, 169 ml of CO was absorbed and the reaction was complete. The precipitated palladium was separated by filtration and the solvent was evaporated from the filtrate under reduced pressure. The residue was separated by chromatography as in the preceding example. There was obtained 0.150 g of II (15%), mp 207–208°, ν_{CO} 1680 cm^{-1}, and 0.171 g (15%) of lactone XI, mp 293–297°.

B. In Ethanol Solution. The carbonylation of 0.300 g (0.43 mmol) of III in 10 ml of absolute ethanol was carried out at 50° as described in the preceding experiments. A total of 12.4 ml of CO was absorbed in 3 hr. The reaction mixture was then cooled and filtered, and the solvent was removed under reduced pressure. Hexane was added to the residue and the colorless crystals which formed were separated and recrystallized from aqueous ethanol. There was obtained in this manner 0.080 g (44%) of II, mp 203–205. The hexane solution obtained after filtration of II was concentrated and chromatographed on silica gel eluting with hexane. The first fraction eluted was azobenzene, 0.035 g (21%). This was followed by 0.032 g of red oil identified as 2-ethoxycarbonylazobenzene (15%): molecular weight by mass spectroscopy, 254.106 (calcd 254.1054); NMR ($CDCl_3$) τ 2.50 (m, 9 aromatic protons), 5.70 (q, 2 methylene protons), and 8.80 (t, 3 methyl protons).

Carbonylation of the Benzalaniline–Palladium Acetate Complex (IVa). A. In Xylene. Carbonylation of 1.0 g (1.45 mmol) of complex IVa in 10 ml of xylene at 100° was complete in 2.5 hr. Evaporation of the solvent and chromatography of the crude product on silica gel, eluting the product with benzene–ether, gave 0.50 g (65%) of colorless crystals of XVIIa, mp 84–85°, after crystallization from heptane. The ir spectrum showed a strong carbonyl absorption at 1730 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.87; H, 5.01; N, 5.28.

NMR ($CDCl_3$) τ 2.50 (m, 9 aromatic and 1 tertiary proton) and 7.95 (s, 3 acetate protons).

The product was readily hydrolyzed by boiling with aqueous alkali to give 2-phenyl-3-hydroxyphthalimidine: mp 170–171° (reported mp 171–172°);[20] molecular weight found by mass spectroscopy 225.081 (calcd 225.0790).

B. In Xylene with Aniline. Carbonylation of 3.0 g (4.3 mmol) of IVa in 20 ml of xylene containing 1.62 g (17.4 mmol) of aniline at 100° as above was complete in 2 hr. Evaporation of the solvent from the filtered reaction mixture and recrystallization of the residue from benzene–heptane gave 1.6 g (63%) of colorless crystals of XVIIIa: mp 166–167° (reported mp 162°);[21] molecular weight found by mass spectroscopy 300.127 (calcd 300.1263). There is a strong carbonyl absorption in the ir spectrum of the product at 1670 cm^{-1}; NMR ($CDCl_3$) τ 2.10 (m, 14 aromatic and 1 tertiary proton) and 5.00 (broad m, 1 amine proton).

C. In Methanol Solution. A solution of 0.50 g (0.71 mmol) of IVa in 10 ml of methanol was carbonylated at 50° in the usual manner. After 3.5 hr, 50 ml of CO had been taken up and the reaction stopped. The reaction mixture was filtered, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. A small amount of benzaldehyde was apparently present judging by the odor of the first fractions eluted. Benzene–hexane eluted a pale yellow oil, 0.203 g (55%) of ester XIXa: molecular weight found by mass spectroscopy 239.096 (calcd 239.0946); NMR ($CDCl_3$) τ 0.81 (s, 1 tertiary proton), 2.50 (m, 9 aromatic protons), and 6.20 (s, 3 methyl protons).

The benzene eluate from the chromatography contained 0.087 g (24%) of XVIIIb, mp 77–79°. The molecular weight found by mass spectroscopy was 239.092 (calcd 239.095); NMR ($CDCl_3$) τ 2.70 (m, 9 aromatic protons), 3.70 (s, 1 tertiary proton), 7.20 (s, 3 methyl protons).

D. In Ethanol Solution. This carbonylation was carried out at 50° exactly as described for the reaction in methanol employing anhydrous ethanol in place of methanol. Chromatography separated a 29% yield of the yellow liquid ester, XIXb, and a 58% yield of 2-phenyl-3-ethoxyphthalimidine (XVIIIc), mp 74–76° after crystallization from aqueous ethanol.

The ester product, XIXb, had a strong carbonyl bond at 1715 cm^{-1}. The molecular weight found by mass spectroscopy was 253.112 (calcd 253.110); NMR ($CDCl_3$) τ 0.75 (s, methine proton), 2.50 (m, 9 aromatic protons), 5.60 (q, methylene protons, J = 8 Hz), 8.60 (t, methyl protons).

The phthalimidine product XVIIIc had a molecular weight of 253.113 by mass spectroscopy (calcd 253.110); NMR ($CDCl_3$) τ 2.50 (m, 9 aromatic protons), 3.52 (s, tertiary hydrogen), 6.85 (m, methylene group), 8.95 (t, methyl protons).

Carbonylation of IVb in Xylene. The carbonylation of IVb, 0.690 g (0.94 mmol), was carried out in 10 ml of xylene at 100° as described in the carbonylation of IVa. The reaction mixture was filtered to remove precipitated palladium, the solvent was evaporated under reduced pressure, and the residue was crystallized from benzene–hexane. There was obtained in 66% yield colorless crystals of compound XVIIb, mp 125–127°. The molecular weight found by mass spectroscopy was 281.105 (calcd 281.1052). The infrared spectrum showed a strong carbonyl absorption at 1720 cm^{-1}; NMR ($CDCl_3$) τ 2.50 (m, 8 aromatic and the tertiary proton), 7.65 (s, 3 acetate protons), 8.00 (s, 3 methyl protons).

Carbonylation of Complex IVc in Xylene. Carbonylation of 3.0 g (4.2 mmol) of complex IVc in 25 ml of xylene at 100° required 23 hr to reach completion. The crude product obtained after removal of the xylene under reduced pressure was purified by chromatography on silica gel. The only significant product was eluted with benzene–hexane. There was obtained 1.59 g (86%) of colorless crystals of XX, mp 97–98° (reported[21] mp 99–100°). The compound in chloroform solution had the expected infrared absorptions at 1730 and 1630 cm^{-1}. The molecular weight was found to be 221.084 (calcd 221.084); NMR ($CDCl_3$) τ 2.50 (m, 9 aromatic protons), 4.78 and 5.69 (2 d, J = 1.7 Hz, methylene protons).

Carbonylation of Complex Va in Xylene. The carbonylation of Va, 2.00 g (2.80 mmol), in 20 ml of xylene at 100° was complete in 10 hr. Filtration of the reaction mixture, evaporation of the xylene under reduced pressure, and two crystallizations of the residue from heptane gave 48% of compound XXII, mp 125–126°. The infrared spectrum showed a band at 1688 cm^{-1}. The molecular weight found was 281.104 (calcd 281.1052); NMR ($CDCl_3$–C_6D_6) τ 2.60 (m, 9 aromatic protons), 3.05 (s, tertiary proton), 5.30 (AB q, methylene group), 8.10 (s, 3 acetate protons).

Carbonylation of Complex Vb in Xylene. Carbonylation of 0.650 g (0.87 mmol) of Vb was carried out in 10 ml of xylene under 20 psi of carbon monoxide in a capped bottle at 130° for 2.5 hr. After cooling, the bottle was opened, the solvent was removed under reduced pressure, and the product was chromatographed on silica gel. Hexane–methylene chloride eluted 0.190 g (49%) of compound XXIII: mp 106–108°; molecular weight found 235.090 (calcd 235.100); NMR ($CDCl_3$–C_6D_6) τ 2.80 (m, 9 aromatic protons), 5.20 and 5.50 (2 d, J = 2.5 Hz, terminal methylene group), 5.30 (s, methylene protons).

Carbonylation of Complex VI in Xylene. One gram (1.34 mmol) of complex VI was carbonylated in 10 ml of xylene as usual at 100° in 5.5 hr. The product isolated by filtration and evaporation of the solvent was purified by two recrystallizations from heptane. There was obtained a 48% yield of compound XXIV, mp 102–103°. It had a carbonyl absorption at 1740 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.61, H, 4.79; N, 9.55.

NMR ($CDCl_3$) τ 0.81 (s, methine proton), 2.5 (9 aromatic protons), 7.87 (s, 3 acetate protons).

Carbonylation of Complex VII in Xylene. Carbonylation of 0.50 g (0.76 mmol) of VII in 10 ml of xylene was carried out at 100° in 3 hr, during which time 33 ml of carbon monoxide was absorbed. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel. Pentane–benzene eluted 61% of compound XXV, obtained as a viscous liquid. It had a strong carbonyl absorption at 1690 cm^{-1} in its infrared spectrum. The molecular weight observed was 188.094 (calcd 188.095); NMR (C_6D_6) τ 2.50 (m, 4 aromatic protons), 4.75 and 4.91 (2 d, J = 0.9 Hz, terminal methylene group), and 7.03 (s, 6 N-methyl protons).

Carbonylation of Complex VIIIa. A. In Xylene. Carbonylation of 0.50 g (0.84 mmol) of VIIIa in 10 ml of xylene for 6 hr at 100° was carried out as in the above examples. No reaction occurred at 25°. The product obtained after evaporation of the xylene, 0.282 g, was nearly pure XXVIa by NMR. Chromatography on silica gel, eluting with ether–benzene, gave a pure sample, 0.195 g (53%), of XXVIa as a pale yellow liquid. The infrared spectrum showed the expected carbonyl absorption at 1680 cm^{-1}. On standing the product solidified. Recrystallization from benzene–hexane gave colorless crystals, mp 160–161°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.05; H, 5.63; N, 12.78.

NMR ($CDCl_3$) τ 2.60 (m, 4 aromatic protons), 4.10 (s, 2 methylene protons), 6.75 (s, 3 N-methyl protons), 2.00 (s, 3 acetate protons).

B. In Ethanol. Carbonylation of 0.22 g (0.37 mmol) of VIIIa was carried out at room temperature in 10 ml of absolute ethanol. The reaction was over in a few minutes after the absorption of about 8 ml of CO. The reaction mixture was filtered, the solvent was removed under reduced pressure, and the products were separated by chromatography on silica gel. Benzene eluted 0.028 g (28%) of formaldehyde 1-methyl-1-phenylhydrazone. Ether–benzene (20:80) eluted ester XXVIa, 0.057 g (38%), as a colorless liquid. Finally, 50:50 ether–benzene eluted 0.019 g (12.5%) of XXVIb as a viscous yellow liquid.

Ester XXVIa had a carbonyl absorption at 1730 cm^{-1} and a molecular weight of 206.105 (calcd 206.105); NMR ($CDCl_3$) τ 2.80 (m, 4 aromatic protons), 3.90 (s, 2 terminal vinyl protons), 5.80 (q, 2 methylene protons), 6.90 (s, 3 N-methyl protons), 8.70 (t, 3 methyl protons).

Ether XXVIb had a carbonyl band at 1680 cm^{-1} and a molecular weight of 206.103 (calcd 206.105); NMR ($CDCl_3$) τ 2.70 (m, 4 aromatic protons), 4.80 (s, 2 methylene protons), 6.35 (q, 2 methylene protons), 6.70 (s, 3 N-methyl protons), 8.85 (t, 3 methyl protons).

Carbonylation of Complex VIIIb (Mixture of Isomers). A. In Benzene. A solution of 0.300 g (0.52 mmol) of VIIIb in 10 ml of benzene at room temperature in the gasometric apparatus absorbed about 15 ml of CO in less than 2 min and the reaction stopped. The products were isolated by chromatography on silica gel after evaporation of the solvent. Benzene–ether eluted as a pale yellow oil, 68% of compound XXVII. The infrared spectrum showed a strong carbonyl absorption at 1684 cm^{-1} and the molecular weight was 174.077 (calcd 174.079); NMR (CCl_4) τ 2.60 (m, 4 aromatic protons, 1 vinyl proton), 5.22 and 5.34 (2 d, J = 16 and 10 Hz, 2 terminal vinyl protons), 6.85 (s, 3 N-methyl protons).

Elution of a second fraction with 1:1 ether–benzene gave a very small amount of a colorless solid which appeared to be compound XXVIIIa: NMR (CCl_4) τ 2.50 (4 aromatic protons plus 1 tertiary proton), 6.77 (s, 3 N-methyl protons), 9.85 (3 acetate protons), 8.40 (d, 3 methyl protons).

B. In Methanol. A solution of 0.600 g (1.04 mmol) of VIIIb in 10 ml of methanol was carbonylated in the gasometric apparatus at room temperature. About 41 ml of CO was absorbed in 10 min and the reaction stopped. Evaporation of the solvent under reduced pressure at room temperature and chromatography on silica gel separated two major products. Elution with 1:4 ether–benzene separated 0.275 g (69%) of liquid XXIXb. The material had an infrared band at 1740 cm^{-1} and a molecular weight of 206.111 (calcd 206.105); NMR ($CDCl_3$) τ 3.00 (m, 4 aromatic protons, and the methine proton), 6.20 (s, 3 ester methyl protons), 6.90 (3 N-methyl protons), 8.10 (d, J = 5 Hz, ethylidene methyl protons).

Elution with 2:3 ether–benzene gave 0.078 g (20%) of compound XXVIIIb as a pale yellow liquid. An infrared absorption at 1700 cm^{-1} was observed and the molecular weight found was 206.102 (calcd 206.105); NMR (CCl_4) τ 2.60 (m, 4 aromatic protons), 4.20 (q, tertiary proton, J = 6 Hz), 6.60 (s, 3 methyl protons), 6.70 (s, 3 methyl protons), 8.50 (d, J = 6 Hz, 3 methyl protons).

Elution with ether gave 0.004 g of colorless crystals of a compound of unknown structure, mp ~120°.

C. In Ethanol. The carbonylation of 0.160 g (0.26 mmol) of VIIIb in 10 ml of absolute ethanol at room temperature required about 2 hr to reach completion when about 2 equiv of CO had been absorbed. After filtration and evaporation of the ethanol there was obtained 0.130 g of a pale yellow oil, which by NMR was fairly pure XXIXc. Chromatography on silica gel with elution with benzene–ether gave 0.076 g (68%) of a pure sample of XXIXc. Its infrared spectrum showed a strong carbonyl band at 1728 cm^{-1} and the observed molecular weight was 220.119 (calcd 220.121); NMR ($CDCl_3$) τ 2.70 (m, 4 aromatic protons plus tertiary proton), 5.70 (q, J = 7.5 Hz, methylene protons), 6.80 (s, 3 *N*-methyl protons), 8.05 (d, J = 6 Hz, 3 methyl protons), 8.65 (t, 3 methyl protons).

Carbonylation of Complex IXa in Xylene. Carbonylation of 1.50 g (2.5 mmol) of IXa in 15 ml of xylene at 100° was complete in 0.5 hr with the absorption of 70 ml of CO. After removal of the xylene under reduced pressure the products were chromatographed on alumina. Benzene eluted 0.350 g of colorless crystals of XXXa (72%) (crystallized from hexane): mp 114–115° (reported[22] mp 114–116°); NMR ($CDCl_3$) τ 2.50 (m, 4 aromatic protons), 5.65 (s, methylene group), 6.80 (3 *N*-methyl protons). The molecular weight observed was 147.069 (calcd 147.068).

Elution with methanol gave acid XXXIa as a colorless solid which, after crystallization from benzene–hexane, weighed 0.020 g (4.5%): mp 123–125°; NMR ($CDCl_3$) τ 2.00 (m, 8 aromatic protons), 6.09 (s, 4 methylene protons), 7.45 (s, 12 *N*-methyl protons). The molecular weight found was 179.099 (calcd 179.095).

Anal. Calcd for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.27; H, 7.56; N, 7.39.

Carbonylation of IXb in Xylene. Carbonylation and purification was carried out exactly as in the preceding example. The reaction was complete in 15 min at 100°. Benzene elution in the chromatography gave a 27% yield of (liquid) 2-ethylphthalimidine (XXXb). The molecular weight by mass spectroscopy was found to be 161.085 (calcd 161.084); NMR ($CDCl_3$) τ 2.50 (m, 4 aromatic protons), 5.70 (s, methylene protons), 6.30 (q, J = 8 Hz, methylene protons), 8.80 (t, methyl protons). This was apparently the same compound prepared by Brewster et al.[22]

Elution with methanol and crystallization from benzene–hexane gave 36% of colorless crystals of acid XXXIb, mp 104–106°. A second recrystallization sharpened the melting point to 105–106° (reported[23] mp 105°); NMR ($CDCl_3$) τ 2.20 (m, 8 aromatic protons), 6.00 (s, 4 methylene protons), 7.10 (q, J = 6 Hz, 8 methylene protons), 8.70 (t, 12 methyl protons). The molecular weight observed was 207.124 (calcd 207.126).

When the above reaction was allowed to continue for 5 hr at 100° (CO absorption ceased in 15 min) and the products isolated as above, there was obtained from the chromatography a new fraction which was eluted with 1:1 benzene–hexane. This material was a colorless liquid with properties indicating that it was the ethyl ester of acid XXXIb. The molecular weight observed was 235.166 (calcd 235.157); NMR ($CDCl_3$) τ 2.40 (m, 4 aromatic protons), 5.60 (q, 2 methylene protons of the ethyl ester group), 6.70 (s, 2 benzylic protons), 7.40 (q, 4 methylene protons of *N,N*-diethyl group), 8.60 (t, 3 methyl protons in the ester ethyl group), 8.80 (t, 6 methyl protons in the *N,N*-diethyl group).

There was also eluted from the chromatography 53% of XXXb and 0.6% of XXXIb.

Carbonylation of IXb in benzene at room temperature was also carried out. The reaction was complete in about 3 hr. Filtration of the reaction mixture and addition of hexane gave a 63% yield of acid XXXIb, mp 103–106°. After recrystallization from benzene–hexane the melting point was 105–106° (reported[23] mp 105°).

Carbonylation of IXc in Xylene. The carbonylation of 0.400 g (0.61 mmol) of IXc was carried out in 10 ml of xylene at 100°. The reaction was over in about 10 min when 20 ml of CO had been absorbed. The products were isolated as in the carbonylation of IXa above. Benzene–ether eluted the major product, ester XXXII, in 51% yield as a pale yellow liquid. The infrared spectrum of the product had carbonyl absorptions at 1680 and 1730 cm^{-1}. The molecular weight found was 247.122 (calcd 247.121); NMR ($CDCl_3$) τ 2.50 (m, 4 aromatic protons), 5.70 (s, 2 methylene protons), 5.95 and 6.40 (2 t, 4 methylene protons), 8.00 (s, 3 acetate protons), 8.30 (m, 4 methylene protons).

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Registry No.—I, 54865-84-8; III, 55740-67-5; IVa, 39963-25-2; IVb, 55740-68-6; IVc, 39963-30-9; Va, 55740-69-7; Vb, 55740-70-0; VI, 55740-71-1; VII, 55740-72-2; VIIIa, 55740-73-3; VIIIb, 55740-74-4; VIIIb monomer, pyridine analog, 55740-75-5; IXa, 40243-08-1; IXb, 55740-76-6; IXc, 55740-77-7; XI, 3848-48-4; XVIIa, 55740-87-9; XVIIb, 55740-88-0; XVIIIa, 19339-69-6; XVIIIb, 52920-25-9; XIIIc, 25770-48-3; XIXa, 55740-89-1; XIXb, 52920-28-2; XX, 19339-67-4; XXII, 55740-91-5; XXIII, 55740-90-4; XXIV, 55740-92-6; XXV, 55740-93-7; XXVIa, 55740-94-8; XXVIb, 55740-95-9; XXVII, 55740-96-0; XXVIIIa, 55740-97-1; XXVIIIb, 55740-98-2; XXIXb, 55740-99-3; XXIXc, 55741-00-9; XXXa, 5342-91-6; XXXb, 23967-95-5; XXXIa, 55741-01-0; XXXIb, 55741-02-1; XXXIb ethyl ester, 55741-03-2; XXXII, 55741-04-3; azobenzene, 103-33-3; palladium acetate, 3375-31-3; *N*-benzylbenzaldehyde imine, 780-25-6; *N*-benzylacetophenone imine, 14428-98-9; benzaldazine, 588-68-1; acetophenone dimethylhydrazone, 13466-32-5; 1-methyl-1-phenylhydrazone of formaldehyde, 15754-28-6; methylene chloride, 75-09-2; 1-methyl-1-phenylhydrazone of acetaldehyde, 52163-09-4; acetone, 67-64-1; *N,N*-dimethylbenzylamine, 103-83-3; *N,N*-diethylbenzylamine, 772-54-3; *N*-benzylpyrrolidine, 29897-82-3; CO, 630-08-0; 2-ethoxycarbonylazobenzene, 18277-91-3.

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