as in the above example, evaporation of the extracts gave 39.0 g (98%) of crude product: mp ~140 °C. The compound can be recrystallized from heptane, but even after several recrystallizations it was still a mixture of isomers as determined by GLC analysis of the amine hydrolysis product. Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.53; H, 5.04; N, 10.00.

Hydrolysis of the phthalimide group was achieved by heating 42.0 g (0.151 mol) of the crude *N*-[4-(3′-pyridyl)-3-butenyl]phthalimide with 17.73 g of 85% hydrazine hydrate and 375 mL of methanol. After boiling for 15 h and then cooling, 250 mL of water was added. The methanol was then removed under reduced pressure and 380 mL of concentrated hydrochloric acid was added. The mixture was heated at 100 °C for 5 h and cooled in an ice–salt bath. The crystallized phthalhydrazide was filtered and the filtrate was made strongly basic with sodium hydroxide. The solution was saturated with sodium chloride and the product extracted with five 250-mL portions of methylene chloride. The extracts were dried to give 12.63 g of crude amine. This material contained about 65% 4-(3′-pyridyl)-3-butenylamine (37% yield). Purification could be made by careful fractional distillation, although a completely pure sample could not be isolated. There was obtained 9.2 g, bp 89–90 °C (0.25 mm), 93% pure by GLC.

(±)-Nornicotine. Cyclization of 4-(3′-pyridyl)-3-butenylamine was effected by adding 6.09 g (0.037 mol) of the crude amine to a stirred suspension of 35.34 g (0.111 mol) of mercuric acetate, 70 mL of THF, and 70 mL of water in a 150-mL Pyrex bottle. The solution was heated to 56 °C with stirring for 15 h. The initial orange suspension was now a white suspension. The solution was cooled to room temperature, made basic with 3 N potassium hydroxide, and treated with a solution of 1.95 g (0.051 mmol) of sodium borohydride dissolved in a few milliliters of 3 N potassium hydroxide. After stirring for 30 min, solid sodium chloride was added to saturate the solution, and 50 mL of methylene chloride was added. The black suspension of mercury present was removed by filtration and the extract was separated from the aqueous layer in the filtrate. The aqueous phase was extracted five times more with 40-mL portions of methylene chloride. The combined extracts were dried and flash distilled under aspirator vacuum to give 4.87 g of 83% pure nornicotine (66%).

Further purification was achieved by adding 1.07 g of the mixture to a solution of 3.3 g of picric acid in 20 mL of ethanol. The yellow picrate formed was separated by filtration and recrystallized twice from a large volume of ethanol. There was obtained an 81% yield of the pure dipicrate: mp 191–192 °C (reported 191–192 °C).[11] Nornicotine was recovered from the dipicrate as described by Spath[12] in 80% yield. The pure material had an IR spectrum identical with the published spectrum.[13] Molecular weight (HRMS) 148.088 (calcd 148.099).

***N*-Acetyl-3-bromoindole.** A mixture of 20 g (0.17 mol) of indole and 17.5 mL (0.16 mol) of acetic anhydride with 0.1 g of sodium acetate was heated for 24 h at 145 °C under a reflux condenser. The mixture was then distilled under reduced pressure to give 11.61 g (41%) of *N*-acetylindole.

A solution of 7.34 g (0.05 mol) of the *N*-acetylindole, dissolved in 75 mL of carbon disulfide, was stirred at 0 °C and 2.57 mL (0.05 mol) of bromine was added dropwise. After stirring for 3 h at 25 °C, the solvent was removed under reduced pressure and the product was recrystallized four times from ethanol to form 5.05 g (46%) of long, colorless needles of *N*-acetyl-3-bromoindole: mp 106–108 °C. Molecular weight (HRMS) 236.979 (calcd 236.979). NMR ($CDCl_3$) δ 2.65 (s, 3), 7.60 (m, 4), 8.60 (m, 1).

Acknowledgment. We gratefully acknowledge financial assistance for this work from the University of Delaware Research Foundation and the National Science Foundation. The palladium used was loaned to us by Engelhard Industries, Inc.

Registry No.—*N*-[4-(3′-Pyridyl)-3-butenyl]phthalimide, 66417-81-0; (±)-nornicotine, 5746-86-1; indole, 120-72-9.

Supplementary Material Available: Table II contains melting points, molecular weights, and NMR spectra of the products prepared (2 pages). Ordering information is given on any current masthead page.

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Palladium-Catalyzed Vinylic Substitution Reactions of *N*-Vinyl Amides

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Received August 15, 1977

N-Vinyl amides undergo the palladium-catalyzed vinylic substitution reaction readily in many instances. *N*-Vinylpyrrolidinone gives a mixture of two isomers in the reaction with bromobenzene, resulting from additions in both possible directions to the vinyl group. *N*-Vinylphthalimide gives, predominantly, the product with the phenyl group added to the terminal carbon of the double bond. Derivatives with *p*-acetoxyl, 3,4-diacetoxyl, 2-bromo, and 4-nitro groups were prepared similarly in moderate to good yields. Catalytic hydrogenation of these compounds produced phenethylamine derivatives. Epoxides of two of the *N*-styrylphthalimide products were also prepared.

2-Arylethylamine structures occur very commonly in natural products and biologically active compounds. This structure might be produced in a new way by use of the palladium-catalyzed vinylic substitution reaction[1] between aryl halides and *N*-vinyl amides. Initial experiments were promising. Subsequent work reported herein demonstrates the simplicity and advantages of the method for producing various 2-styryl- and 2-arylethylamine derivatives.

Results and Discussion

We first investigated the reaction of bromobenzene with *N*-vinylpyrrolidinone. The reaction, which was catalyzed with 1 mol % of palladium acetate, based on the bromobenzene, and 4 mol % of tri-*o*-tolylphosphine,[2] proceeded rapidly at 100 °C producing a mixture of two products in quantitative yield. The two were formed by the addition of the intermediate phenylpalladium species in both possible directions to the

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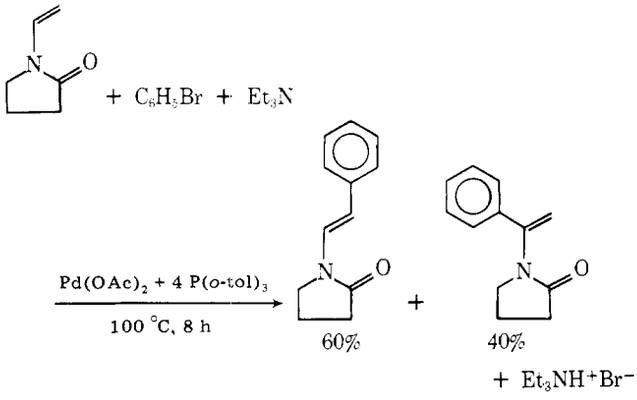
Table I. Vinylic Substitution Reactions of *N*-Vinyl Amides[a]

N-vinyl amide (mmol)	organic halide (mmol)	registry no.	PR_3	PR_3/ $Pd(OAc)_2$	time	product (% yield)	registry no.
N-vinylpyrrolidone[c,b] (12.5)	C_6H_5Br (10)	108-86-1	P(*o*-tol)$_3$	4	8 h	*N*-(2-phenylvinyl)pyrrolidone (60)[d]	6908-67-4
						N-(1-phenylvinyl)pyrrolidone (40)[d]	66373-96-4
N-vinylpyrrolidone[c] (12.5)	C_6H_5Br (10)		P(2,5-*i*-PrPh)$_3$	4	9.5 h	*N*-(2-phenylvinyl)pyrrolidone (55)[d]	
						N-(1-phenylvinyl)pyrrolidone (44)[d]	
N-vinylpyrrolidone[e] (12.5)	4-$(CH_3)_2NC_6H_4Br$ (10)	586-77-6	P(*o*-tol)$_3$	4	2 days	4-$(CH_3)_2NC_6H_4COCH_3$ (57)	2124-31-4
N-vinylpyrrolidone[e] (12.5)	(*E*)-2-bromostyrene (10)	588-72-7	P(*o*-tol)$_3$	4	4 days	*N*-(4-phenyl-1,3-butadienyl)-pyrrolidone (25)	66373-97-5
N-vinylphthalimide[c,h] (11)	C_6H_5Br (10)		P(*o*-tol)$_3$	4	4.5 days	*N*-(2-phenylvinyl)phthalimide (74)	23092-87-7
N-vinylphthalimide[c] (11)	4-$AcOC_6H_4Br$ (10)	1927-95-3	P(*o*-tol)$_3$	8	18 h	*N*-[2-(4′-acetoxyphenyl)vinyl]-phthalimide (75)	66373-98-6
N-vinylphthalimide[c] (11)	3-4-$(AcO)_2$-C_6H_3Br (10)	66373-95-3	P(*o*-tol)$_3$	6	15 h	*N*-[2-(3′,4′-diacetoxyphenyl)-vinyl]phthalimide (68)	66373-99-7
N-vinylphthalimide[c,f] (25)	2-BrC_6H_4I (20)	583-55-1			20 h	*N*-[2-(2′-bromophenyl)vinyl]-phthalimide (75)	66374-00-3
N-vinylphthalimide[c,g] (10)	4-$O_2NC_6H_4Br$ (11)	586-78-7	P(*o*-tol)$_3$	2	17 h	*N*-[2-(4′-nitrophenyl)vinyl]-phthalimide (64)	66374-01-4
N-vinylphthalimide[c,g] (12.5)	2-$H_2NC_6H_4I$ (10)	615-43-0			45 h	indole (26)[d]	120-72-9

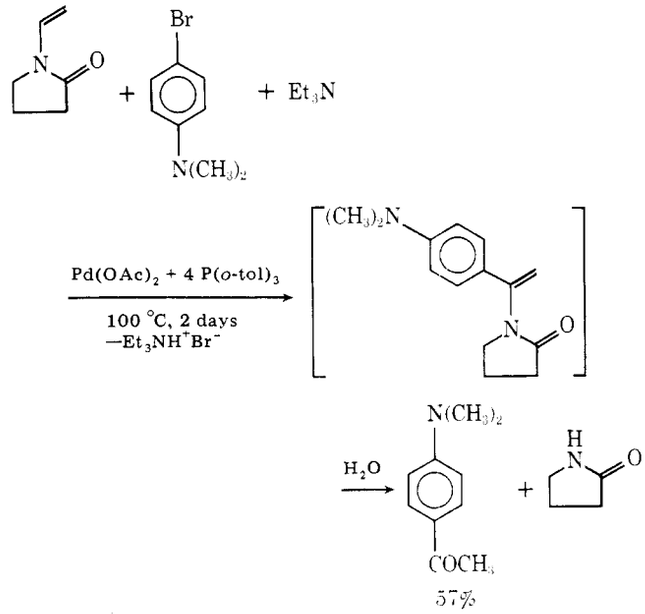
[a] All reactions were carried out at 100 °C with 12.5 mmol of triethylamine using 0.10 mmol of palladium acetate as catalyst. [b] Yield of purified product except where indicated. [c] Acetonitrile (4 mL) used as solvent. [d] GLC yields. [e] Experiment carried out by Mr. William Gorak. [f] Experiment carried out by Mr. Joseph Plevyak. [g] Experiment carried out by Mr. Bruce Hrnjez. [h] Registry no.: *N*-vinylpyrrolidone, 88-12-0; *N*-vinylphthalimide, 3485-84-5.

vinyl amide double bond, followed by the "palladium hydride" elimination. Double bonds substituted with electron-donating substituents tend to produce significant amounts of 2-aryl adducts in addition to the major 1-aryl isomers.[1-3] The strongly electron-donating 2-pyrrolidinone group in this example caused 40% of the addition to occur on the internal

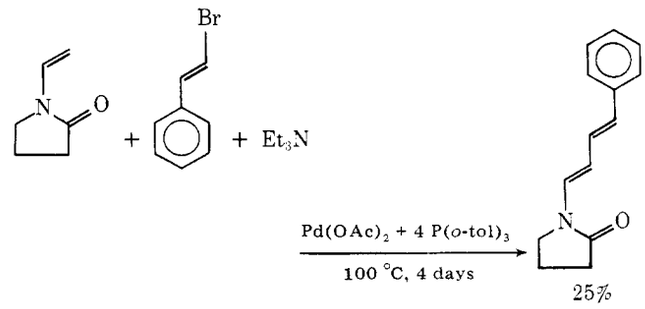


carbon of the double bond. This reaction also was carried out with a larger phosphine to determine if steric factors might influence the direction of addition of the arylpalladium group. The use of tris(2,5-diisopropylphenyl)phosphine instead of tri-*o*-tolylphosphine gave exactly the same ratio of products, indicating that the ratio is controlled by electronic factors. The results of these and related experiments are summarized in Table I. The use of *p*-(dimethylamino)bromobenzene in place of bromobenzene led to the formation of the 2-aryl derivative, which apparently hydrolyzed very easily from atmospheric moisture on attempted isolation, since only *p*-(dimethylamino)acetophenone was isolated in 57% yield. It is not known whether the other isomer was formed and if it either decomposed or was not detected.

The reaction of (*E*)-2-bromostyrene with *N*-vinylpyrrolidinone, on the other hand, gave only the terminal adduct.

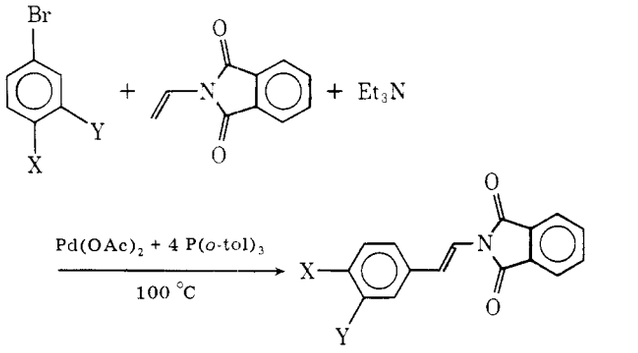


However, the yield was only 25% again leaving unanswered the question of whether or not the other isomer had been formed.



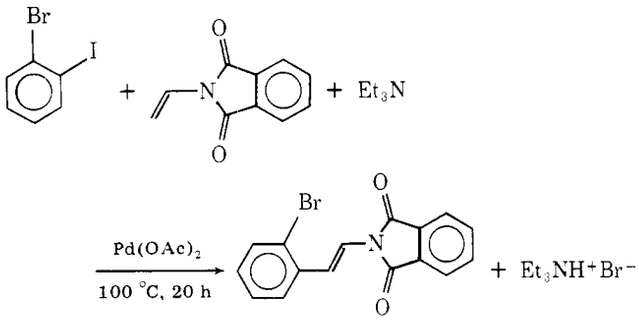
Since these reactions did not appear very promising for synthetic purposes, we turned to another readily available *N*-vinyl amide, *N*-vinylphthalimide.

N-Vinylphthalimide and bromobenzene reacted readily at 100 °C with 4:1 tri-*o*-tolylphosphine–palladium acetate as catalyst and triethylamine, forming *N*-2-styrylphthalimide in 74% yield. We did not isolate any of the 1-styryl adduct; however, it may have been formed, but lost during recrystallization. Similar yields of products were obtained with 4-acetoxybromobenzene and 4-bromocatechol diacetate. The latter reaction gave a 28% higher yield when the more basic diisopropylamine was used instead of triethylamine in the reaction. Only dark viscous oils were obtained in this reaction when either 4-bromophenol or 4-bromocatechol were used rather than their acetates. Presumably, the phenolic groups were reacting with the *N*-vinyl double bond.



Ia, X = Y = H
b, X = OAc; Y = H
c, X = Y = OAc

2-Iodoaniline reacts with *N*-vinylphthalimide to form indole, but only in 26% yield. 2-Nitroiodobenzene gave no identifiable product with *N*-vinylphthalimide. 2-Bromoiodobenzene, however, reacted, using palladium acetate as catalyst, giving *N*-2-(2′-bromostyryl)phthalimide (II) in 75% yield.



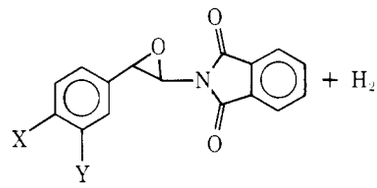
II

p-Bromonitrobenzene and *N*-vinylphthalimide produced the expected 2-*N*-(4′-nitrostyryl)phthalimide in 64% yield.

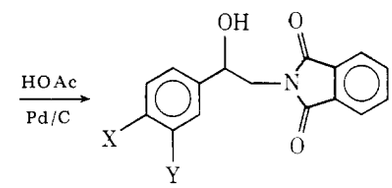
Attempts to react *N*-2-propenylphthalimide[4] with bromo- or iodobenzene were unsuccessful. It appears that the reactions of the *N*-vinyl amides are very sensitive to steric effects around the reacting groups.

We looked briefly at some reactions of the *N*-styryl amides prepared to determine if they could be converted into phenylethylamine derivatives. Compounds Ia and Ic were hydrogenated with a palladium on charcoal catalyst. Compound Ia reduced easily at atmospheric pressure and room temperature, but Ic required elevated temperatures (100 °C) and pressure (600 psi). Only the double bond reduced in the first example, but Ic gave *N*-2-(3′,4′-diacetoxyphenyl)ethylhexahydrophthalimide. The ^{13}C NMR spectrum clearly showed that the phthalimide ring had reduced. We were unable to reduce the double bond in the *o*-bromo derivative II with platinum on charcoal as catalyst without removing the bromo group also.

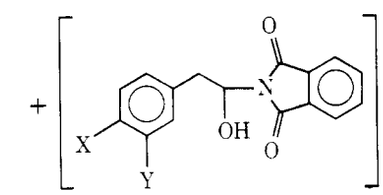
Compounds Ib and Ic were epoxidized in 70–80% yields using *m*-chloroperbenzoic acid. Reduction of the epoxides to alcohols using hydrogen and palladium on charcoal gave mixtures of products under neutral conditions. Compound IIIb, in the presence of a few drops of acetic acid, reduced partially to the 2-hydroxy-2-(*p*-acetoxyphenyl)ethyl derivative (IVb; 39%), but the compound was not obtained pure.



IIIb, X = OAc; Y = H
c, X = Y = OAc



IV



V

Compound IIIc under these conditions gave, at least mainly, the 1-hydroxy product (Vc), which decomposed to phthalimide and 3,4-diacetoxyphenylacetaldehyde on isolation judging by the NMR spectrum of the crude reaction product mixture.

We attempted to prepare phenylalanine derivatives by the vinylic substitution reaction with 2-acetamidoacrylic acid and with its methyl ester, but neither bromobenzene nor iodobenzene gave any identifiable products from the reactions under our standard conditions.

The experiments carried out demonstrate a useful new method for the synthesis of 2-styryl- and 2-phenylethylamine derivatives from various aryl halides.

Experimental Section

p-Bromophenyl acetate [bp 100 °C (2 mm)], bromohydroquinone diacetate (mp 67–69 °C), 4-bromoresorcinol diacetate (mp 46–47 °C), and 4-bromocatechol diacetate [bp 126–132 °C (0.5 mm)] were prepared by heating the phenols with acetic anhydride and a few drops of pyridine. The 4-bromocatechol was prepared by the oxidation of 5-bromosalicylaldehyde with hydrogen peroxide.[5] *N*-Vinylphthalimide was obtained from Polysciences, Inc., Warrington, Pa. Other reagents used were commercial products and they were used as received. The properties of the products prepared are listed in Table II, which will appear only in the microfilm edition of this journal. (See note on supplementary material at the end of the paper.)

General Procedure for the Vinylic Substitution Reaction. Essentially the same procedure as described previously was used.[1,2] The *N*-vinylphthalimide reactions gave more easily purified products, however, if little or no excess *N*-vinylphthalimide over the aryl halide was used. Since these products were rather insoluble in the reaction mixtures, acetonitrile was usually used as solvent. Examples are given below.

***p*-(Dimethylamino)acetophenone from *N*-Vinylpyrrolidinone.**[6] A mixture of 2.00 g (10 mmol) of *p*-bromodimethylaniline, 1.39 g (12.5 mmol) of *N*-vinylpyrrolidinone, 0.121 g (0.4 mmol) of tri-*o*-

tolylphosphine, 0.022 g (0.10 mmol) of palladium acetate, and 1.75 mL (12.5 mmol) of triethylamine was heated in a steam bath in a capped heavy-walled Pyrex tube for 2 days. At this time GLC showed all of the p-bromodimethylaniline had reacted. After cooling the reaction mixture was diluted with ether and filtered to remove the triethylamine hydrobromide. Evaporation of the filtrate followed by distillation of the brown residue under reduced pressure gave 0.93 g (57%) of a yellow liquid, bp 190 °C (0.4 mm), which solidified on standing. The NMR spectrum of the product was identical with that reported for p-(dimethylamino)acetophenone.[7]

***N*-2-(3',4'-Diacetoxystyryl)phthalimide (Ic).** A mixture of 2.37 g (10 mmol) of 4-bromocatechol diacetate, 1.82 g (10.5 mmol) of *N*-vinylphthalimide, 1.26 g (12.5 mmol) of diisopropylamine, 0.1824 g (0.6 mmol) of tri-o-tolylphosphine, 0.022 g (0.10 mmol) of palladium acetate, and 4 mL of acetonitrile was heated in a capped nitrogen-filled tube at 100 °C for 15 h. The cooled reaction mixture was diluted with 150 mL of cold water and the crude yellow product was filtered. The dried product was heated with 25 mL of acetic anhydride and 5 drops of pyridine for 1 h at 100 °C to reacetylate any hydrolyzed material. After cooling the mixture was poured into ice and the solid recovered by filtration. After air drying the product was recrystallized from benzene–heptane to give 2.5 g (68%) of the product as small yellow crystals: mp 162–164 °C. Anal. Calcd for $C_{20}H_{15}NO_6$: C, 65.75; H, 4.14. Found: C, 66.02; H. 4.30.

***N*-[2-(3',4'-Diacetoxyphenyl)ethyl]hexahydrophthalimide.** A mixture of 1.0 g (2.74 mmol) of *N*-[2-(3',4'-diacetoxystyryl)]-phthalimide, 0.21 g of 10% palladium on charcoal, and 20 mL of toluene was put in a 60-mL bomb and hydrogenated at 100 °C and 600 psi for 16 h. The reduction did not go to completion under milder conditions. The cooled reaction mixture was filtered through Celite and the solvent was distilled under reduced pressure. The colorless oil that remained was crystallized from methylene chloride–heptane to give 0.55 g (55%) of colorless crystals: mp 96–99 °C. NMR ($CDCl_3$) δ 7.1 (m, 3 H), 3.75 (t, 2 H, J = 6 Hz), 2.85 (m, 2 H), 2.25 (s, 6 H), 1.55 (m, 10 H). ^{13}C NMR 142.04, 140.90, 136.59, 127.09, 124.01, 123.42. Anal. Calcd for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.62; H, 6.48; N, 3.63.

Epoxidation of Ic. A solution of 1.0 g (2.63 mmol) of Ic and 0.679 g (3.95 mmol) of m-chloroperbenzoic acid in 10 mL of methylene chloride was stirred at room temperature for 43 h. The solution was then diluted with 25 mL more of methylene chloride and the solution was extracted with aqueous sodium bicarbonate. After drying the methylene chloride phase was concentrated under reduced pressure and the solid remaining was recrystallized from methylene chloride–hexane to give 0.78 g (77%) of epoxide IIIc: mp 205–207.5 °C. NMR (90 MHz, $CDCl_3$) δ 7.58 (m, 9 H), 5.32 (d, J = 1 Hz, 1 H), 4.85 (d, J = 1 Hz, 1 H), 2.3 (s, 6 H). Anal. Calcd for $C_{20}H_{15}NO_7$: C, 62.99; H, 3.96. Found: C, 62.77; H, 3.60.

Hydrogenation of Ia. A mixture of 0.56 g (2.25 mmol) of Ia, 0.21 g of 10% palladium on charcoal, and 20 mL of toluene was stirred under 1 atm of hydrogen at room temperature for about 1 h when gas absorption stopped. The mixture was then filtered through Celite, rinsing with toluene, and the filtrate was concentrated under reduced pressure. The solid residue was recrystallized from heptane to give colorless crystals: mp 131–132 °C (reported 131 °C).[8] NMR ($CDCl_3$) δ 8.05 (m, 4 H), 7.55 (s, 5 H), 4.1 (t, J = 6 Hz, 2 H), 3.1 (t, J = 6 Hz, 2 H).

Epoxidation of Ib. A mixture of 4.13 g (13.4 mmol) of Ib and 4.16 g (24.2 mmol) of m-chloroperbenzoic acid in 80 mL of benzene was stirred at room temperature for 20 h. After extraction of the solution with aqueous sodium bicarbonate and drying, the benzene was distilled under reduced pressure and the product was recrystallized from chloroform–heptane. There was obtained 3.15 g (70%) of colorless epoxide IIIb: mp 174–176 °C. NMR ($CDCl_3$) δ 7.6 (m, 8 H), 5.35 (d, J = 1 Hz, 1 H), 4.9 (d, J = 1 Hz, 1 H), 2.3 (s, 3 H). Anal. Calcd for $C_{18}H_{13}NO_5$: C, 66.87; H, 4.05. Found: C, 66.88; H. 4.10.

***N*-[2-(p-Acetoxyphenyl)-1-hydroxyethyl]phthalimide (Vb).** A mixture of 0.42 g of the epoxide of Ib and 0.1 g of 10% palladium on charcoal in 25 mL of ethyl acetate containing 2 drops of acetic acid was reduced at room temperature with 1 atm of hydrogen. In 2 h 1 equiv of hydrogen was absorbed. The solution was filtered through Celite and the solvent was removed under reduced pressure. The solid remaining was recrystallized from chloroform–heptane to give 0.162 g (39%) of colorless (impure) crystals: mp 220–233 °C dec. NMR ($CDCl_3$) δ 7.55 (m, 8 H), 5.95 (t, J = 7 Hz, 1 H), 4.3 (s, 1 H), 3.5 (d, J = 7 Hz, 2 H), 2.2 (s, 3 H). Anal. Calcd for $C_{18}H_{15}NO_5$: C, 66.46; H, 4.65. Found: C, 65.31; H, 3.66.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We also are grateful to the Matthey-Bishop Co., Inc., for the loan of the palladium used in this work.

Registry No.—Ia epoxide, 66374-02-5; IIIb, 66374-03-6; IIIc, 66374-04-7; IVb, 66374-07-0; Vb, 66374-06-9; *N*-[2-(3',4'-diacetoxyphenyl)ethyl]hexahydrophthalimide, 66374-05-8.

Supplementary Material Available: Table II listing melting points, molecular weights, and NMR spectra of the products prepared (2 pages). Ordering information is given on any current masthead page.

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Palladium-Catalyzed Synthesis of 2-Quinolone Derivatives from 2-Iodoanilines

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Several new examples of the use of 1,2-disubstituted olefins in the palladium-catalyzed vinylic substitution reaction have been studied. Stereochemical results are reported. This reaction was used with substituted acrylic acid derivatives and o-iodoanilines to form 2-quinolones in moderate to good yields.

The recent discovery that o-aminoaryl and hydroxyaryl halides underwent the palladium-catalyzed vinylic substitution reaction in good yields in several instances[1] suggested that quinolone and coumarin derivatives might be formed via these reactions. In the previous study monosubstituted olefins—methyl acrylate, acrylic acid, acrylonitrile, and styrene—were found *not* to undergo cyclization when reacted with 2-bromo- or 2-iodoaniline or the corresponding halophenols.

Palladium hydride elimination from the intermediate adduct (I, for example) must have been faster than ring closure. The elimination selectivity formed trans products which did not isomerize and cyclize under the reaction conditions

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