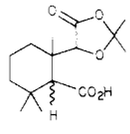
butanone **4a**. With this structure firmly established, examination of the data (^{1}H NMR and IR) included in our initial paper leads us to conclude that none of the adducts reported were cyclopropanes and that each should be reformulated as a cyclobutanone. In particular, the infrared spectra show two carbonyl absorptions—one in the range 1766–1782 cm^{-1}, typical of cyclobutanones, and a second in the range 1789–1801 cm^{-1}, characteristic of lactones of this type.[9] Further corroboration is provided from the ^{13}C NMR spectra of adducts **4a–d** and **7–9**. Each of these substances shows singlet resonances in the ranges 198.9–205.3 ppm (carbon a), 166.2–169.3 (carbon b), 110.5–112.0 (carbon c), and 92.3–96.5 (carbon d). In view of these findings, our additional claim[10,2b] to have effected homoconjugate openings of these "spiro-activated cyclopropanes" with various Grignard reagents must also be disregarded.

Acknowledgment. The financial support of the National Science Foundation (Grant No. NSF CHE76-84340 and NSF CHE76-05926, Instrument Grant for the Brucker NMR 200) and the National Institutes of Health (Grant No. CA25675) is gratefully acknowledged.

Registry No. 2, 7270-63-5; **4a**, 73466-63-4; **4b**, 73454-16-7; **4c**, 73466-64-5; **4d**, 73454-17-8; **6**, 73454-18-9; **7**, 73466-65-6; **8**, 73454-19-0; **9**, 73454-20-3; 1,3,3-trimethylcyclohexene, 503-47-9; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1-phenylcyclohexene, 771-98-2; 2-(2,2-dimethyl-1,3-dioxolan-4-on-5-yl)-2,6,6-trimethylbenzoic acid, 73466-66-7.

Supplementary Material Available: Complete ^{13}C NMR data for **4a–d** and **7–9**; tables of final structural parameters and intramolecular distances and angles (6 pages). Ordering information is given on any current masthead page.

(8) We have found that in the case of 1,3,3-trimethylcyclohexene the reaction is solvent dependent. Thus, photolysis in THF produces only cyclobutanone **4a**. However, in methylene chloride, in addition to **4a**, a second extremely unstable adduct is formed which reacts with moisture in the air to produce a carboxylic acid. The spectral data (^{1}H and ^{13}C NMR, IR, and mass spectra) are consistent with those of the following structure:



(9) Infrared data for lactones of this type have been recorded by M. Farines and J. Soulier, *Bull. Soc. Chim. Fr.*, 332 (1970).

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Conversion of 2-Halo-*N*-allylanilines to Indoles via Palladium(0) Oxidative Addition–Insertion Reactions

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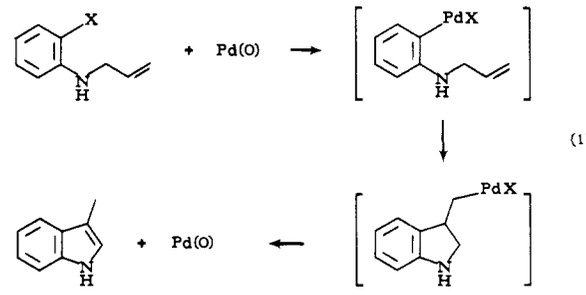
As part of an overall program directed toward the synthesis of the mitocenes, we have considered several organometallic approaches to the indole ring systems.[1,2] A potentially attractive approach involves an intramolecular "Heck" arylation[3] of 2-halo-*N*-allylanilines (eq. 1). This



procedure works rather well for systems in which the side-chain olefin is conjugated to a carbonyl group. Thus 2-halo-*N*-acryloyl- or -cinnamoylanilines are converted to oxindoles in fair yield, using both Pd(0)[4–6] and Ni(0)[7] catalysts. Similarly, 2-halo-*N*-allylanilines having ester groups γ to the nitrogen cyclize to 3-carbonyl-substituted indoles and/or quinoline in modest yield under related reaction conditions.[6,8,9] However, the only reported cyclization of this type of simple unactivated 2-halo-*N*-allylanilines involve Ni(0) catalysts and goes in rather low (20–45%) yield.[10] Since our further synthetic work required the cyclization of unactivated *N*-allylanilines, we developed closures for a number of simple systems. The results are summarized in Table I.

Typical literature procedures for "Heck arylation"[3–10] involve heating substrate, an amine, and, with bromides, a phosphine and 3% palladium acetate in acetonitrile in a sealed tube for several days at 110 °C. We have found that considerably better yields are obtained by addition of the catalyst in three successive 1% portions, one each day of reaction. Apparently the catalyst is deactivated during the reaction and periodic provision of fresh catalyst permits a higher overall yield, using the same total amount of catalyst. As is typical, the bromo aromatics are less reactive than the iodo aromatics and require the addition of 2 equiv of tris(2-tolyl)phosphine[3] per Pd to produce acceptable yields.[11]

Two substrates fail to cyclize. The *N*-cyclohexenylaniline is recovered unchanged from the reaction medium, thus prohibiting the synthesis of carbazoles by this method. The reason for this lack of reactivity is not apparent. Similarly the *N*-(2-methallyl)aniline also fails to cyclize. In this case, closure to a five-membered ring would produce a σ-alkylpalladium complex lacking β hydrogens and thus lacking the ability to β-hydride eliminate and regenerate the catalyst. However, closure to form a six-membered ring would permit β elimination. This does not occur, since the substrate is recovered unchanged from the reaction mixture. That six-membered ring formation *can* occur is shown by the closure of 2-bromo-*N*-(2-carbethoxyallyl)-

(1) L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. L. Waterman, *J. Am. Chem. Soc.*, **100**, 5800 (1978).

(2) L. S. Hegedus, G. F. Allen, and D. J. Olsen, *J. Am. Chem. Soc.*, in press.

(3) For a current review of this process, see R. F. Heck, *Acc. Chem. Res.*, **12**, 146 (1978).

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(9) M. Mori, K. Chiba, and Y. Ban, *Tetrahedron Lett.*, 1037 (1977).

(10) M. Mori and Y. Ban, *Tetrahedron Lett.*, 1803 (1976).

(11) It has been noted by J. T. Arrigo and A. K. Sparks (Universal Oil Products Company), U.S. Patent 3 707 481, 1972, that *N*-methyl-*N*-vinylaniline and *N*-methyl-*N*-allylaniline will cyclize in the presence of palladium acetylacetonate–Cu(OAc)$_2$ or palladium acetate–Cu(OAc)$_2$ to give *N*-methylindole and *N*-methyl-1,2-dihydroquinoline, respectively. No yields are reported.

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Table I. Palladium(0)-Catalyzed Cyclization of 2-Halo-*N*-allylanilines to 3-Substituted Indoles

aniline	product	yld, %[a]	charac-terizn	aniline	product	yld, %[a]	charac-terizn
2-iodo-*N*-allyl	3-methylindole	87	*b*	2-iodo-*N*-(2-methylallyl)	no reaction		
2-bromo-*N*-allyl	3-methylindole	60	*b*	2-bromo-4-methyl-*N*-allyl	3,5-dimethylindole	77	*f*
2-iodo-*N,N*-diallyl	1-allyl-3-methyl-indole	87	*c*	2-bromo-4-carb-ethoxy-*N*-allyl	3-methyl-5-carb-ethoxyindole	50	*g*
2-iodo-*N*-(3-methylallyl)	3-ethylindole	51	*d*	2-bromo-3,4-di-methoxy-*N*-allyl	3-methyl-5,6-di-methoxyindole	66	*g*
2-iodo-*N*-(3,3-dimethylallyl)	3-isopropylindole	73	*e*	2-iodo-*N*-(2-carb-ethoxyallyl)	3-carbethoxy-quinoline	49	*c*
2-iodo-*N*-(cyclo-hex-2-enyl)	no reaction						

[a] Yields are of isolated purified products. [b] Identical in all respects with authentic material. [c] Identical with material prepared by an alternate route. [d] Mp 37 °C (lit.[12] mp 37 °C). [e] Spectra identical with literature.[13] [f] Mp 75 °C (lit.[14] mp 75 °C). [g] These compounds have satisfactory IR and NMR spectra and acceptable elemental analyses or high-resolution exact-mass measurements.

aniline to 3-carbethoxyquinoline.

Experimental Section

The palladium acetate, tris(2-tolyl)phosphine, acetonitrile, and allyl bromide were obtained commercially and used without further purification. The triethylamine was distilled from KOH. The requisite 2-haloanilines were prepared by literature procedures.[1] NMR spectra were obtained with a Varian EM-360 instrument, and infrared spectra were obtained with a Beckman 4240 instrument. A typical procedure for each type of reaction is given below.

Preparation of 2-Iodo-*N*-allylaniline. 2-Iodoaniline (1.0 g, 4.54 mmol) was dissolved in 20 mL of dry tetrahydrofuran (THF) in a 100-mL round-bottom flask with a sidearm, and the flask was flushed with argon and cooled to −78 °C. Lithium diisopropylamide (4.5 mmol) (from 4.6 mmol of diisopropylamine and 4.6 mmol of *n*-butyllithium) in 5 mL of THF was slowly added, and the resulting mixture was allowed to warm to 0 °C over 10 min. After the resulting solution was recooled to −78 °C, allyl bromide (0.43 mL, 5.0 mmol) was added and the solution was stirred for 10 min, allowed to warm to room temperature, and stirred for 2 h at that temperature. The reaction mixture was partitioned between ether and saturated NaCl solution, and the ether phase was dried over anhydrous $MgSO_4$. After removal of solvent under vacuum, the crude material was purified by medium-pressure liquid chromatography (silica gel), using hexane as eluant. 2-Iodo-*N*-allylaniline (1.06 g, 89%) was obtained as a clear oil: NMR ($CDCl_3$) δ 3.55 (d, J = 6 Hz, 2, NCH_2), 4.09 (br s, 1, NH), 4.8–5.2 (m, 2, CH_2=C), 5.5–5.9 (m, 1, CH=C), 6.0–6.35 (m, 2, Ar H), 6.7–7.6 (m, 4, Ar H).

1-Allyl-3-methylindole was prepared from 3-methylindole and allyl bromide by using the same procedure to give 0.81 g (62%): NMR ($CDCl_3$) δ 2.35 (s, 3, CH_3), 4.25 (m, 2, NCH_2), 4.6–6.16 (m, 2, CH_2=C), 5.3–6.0 (m, 1, CH=C), 6.60 (s, 1, indole 2 H), 7.0–7.6 (m, 4, Ar H).

Cyclization of 2-Iodo-*N*-(3,3-dimethylallyl)aniline to 3-Isopropylindole. A Fischer–Porter aersol compatibility tube (3.5 × 13 cm) was charged with 0.287 g (1.00 mmol) of the iodoaniline, 2.2 mg (0.01 mmol) of $Pd(OAc)_2$, 0.21 mg (1.5 mmol) of NEt_3, and 6 mL of CH_3CN. The bottle was capped with a rubber serum cap, clamped into place by the pressure bottle head supplied with the unit, and flushed several times with argon. The mixture was heated at 110 °C for a total of 72 h. After 24 h and 48 h, the mixture was cooled to room temperature, an additional 2.2 mg of $Pd(OAc)_2$ and 0.07 mL of Et_3N in 1 mL of CH_3CN was added, and the mixture was reheated to 110 °C. After completion, the crude product was purified by medium-pressure liquid chromatography, eluting with 4:1 hexane/ether to give 3-isopropylindole[13] (0.116 g, 73%).

Cyclization of 2-Bromo-4-carbethoxy-*N*-allylaniline to 3-Methyl-5-carbethoxyindole. The reaction was run as above except 0.02 equiv of tris(2-tolyl)phosphine (based on substrate) was added in addition to the rest of the components. An additional 0.02 equiv of this phosphine was added with each subsequent addition of $Pd(OAc)_2$. From 0.32 g (1.12 mmol) of the allylaniline was obtained 0.113 g (49%) of 3-methyl-5-carbethoxyindole: NMR (CCl_4) δ 1.48 (t, J = 7 Hz, 3, CH_3CH_2O), 2.38 (s, 3, CH_3), 4.45 (q, J = 7 Hz, 2, CH_3CH_2O), 6.95 (s, 1, indole 2 H), 7.25 (d), 7.90 (d of d), 8.35 (s, 3, Ar H), 9.00 (br, 1, NH); IR (CCl_4) 3330 (NH), 1700 (C=O) cm^{-1}.

Acknowledgment. Support for this research under Grant 1 R01 GM26178 from the National Institutes of Health is gratefully acknowledged.

Registry No. 2-Iodo-*N*-allylaniline, 73396-87-9; 2-iodoaniline, 615-43-0; 1-allyl-3-methylindole, 1914-05-2; 3-methylindole, 83-34-1; allyl bromide, 106-95-6; 2-iodo-*N*-(3,3-dimethylallyl)aniline, 73396-88-0; 3-isopropylindole, 16886-00-3; 2-bromo-4-carbethoxy-*N*-allylaniline, 73396-89-1; 3-methyl-5-carbethoxyindole, 73396-90-4; 2-bromo-*N*-allylaniline, 73396-91-5; 2-iodo-*N,N*-diallylaniline, 73396-92-6; 2-iodo-*N*-(cyclohex-2-enyl)aniline, 73396-93-7; 2-iodo-*N*-(2-methylallyl)aniline, 73396-94-8; 2-bromo-4-methyl-*N*-allylaniline, 73396-95-9; 2-bromo-3,4-dimethoxy-*N*-allylaniline, 73396-96-0; 2-iodo-*N*-(2-carbethoxyallyl)aniline, 73396-97-1; 3-ethylindole, 1484-19-1; 3,5-dimethylindole, 3189-12-6; 3-methyl-5,6-dimethoxyindole, 73396-98-2; 3-carbethoxyquinoline, 50741-46-3; Pd(O), 7440-05-3.

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Osmium-Catalyzed Vicinal Oxyamination of Olefins by *N*-Chloro-*N*-metallocarbamates

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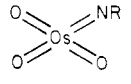
We have previously reported four procedures for the vicinal oxyamination of olefins. One method employs stoichiometric amounts of preformed (*tert*-alkylimido)-osmium compounds (**1a**).[1] The other methods are catalytic in osmium. Two of the catalytic methods rely on Chloramine-T (TsNClNa) for the in situ regeneration of the imidoosmium species **1b**.[2,3] These procedures produce



1a, R = *tert*-alkyl
b, R = Ts
c, R = R′OCO

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0022-3263/80/1945-2710$01.00/0