trometer using tetramethylsilane as an internal standard. Vapor phase chromatography was performed on a Perkin-Elmer Model 226 capillary gas chromatograph equipped with 300 ft × 0.01 in. DC-550 silicone columns.

Hydrogenation of Phenylmercury Acetate. In a typical experiment a Parr low-pressure reactor[16] was charged with 6 g (17.8 mmol) of phenylmercury acetate, 90 mg (0.1 mmol) of tris(triphenylphosphine)rhodium(I) chloride, and 100 ml of methanol. The clear, yellow solution was pressurized with hydrogen to 36 psig at room temperature, and the reaction mixture was shaken overnight. The reactor pressure declined to $\sim$19 psig, corresponding to the consumption of $\sim$20 mmol of hydrogen. From the reaction was recovered 2.9 g of mercury (82%). The methanol was poured into water and was extracted with pentane. The extract was dried over magnesium sulfate and analyzed for benzene by VPC using *p*-xylene as an internal standard. The benzene yield was 1.2 g (85%).

Under similar conditions the following catalysts gave the benzene yields shown: tris(triphenylphosphine)ruthenium(II) chloride, 13%; hydridotris(triphenylphosphine)ruthenium(II) chloride, 17%; tetrakis(triphenylphosphine)palladium(0), 24%; tetrakis(triphenylphosphine)platinum(0), 16%; bis(triphenylphosphine)platinum(II) chloride, 14%.

Preparation of Bimetallic Complex (I). A solution of 264 mg (0.78 mmol) of phenylmercury acetate in 5 ml of chloroform was added to a solution of 691 mg (0.75 mmol) of tris(triphenylphosphine)rhodium(I) chloride in 5 ml of chloroform. The solution was stirred at room temperature for 15 min and the chloroform was removed by evaporation. The residue was recrystallized from 25 ml of methanol to yield 474 mg (63%) of yellow crystals, mp 184–186°.

Anal. Calcd for $C_{44}H_{38}ClO_2P_2HgRh$: C, 52.86; H, 3.83; Cl, 3.55; P, 6.20; Rh, Hg, 30.36. Found: C, 52.99; H, 3.93; Cl, 3.92; P, 6.79; Rh, Hg, 28.6.

The NMR spectrum ($CDCl_3$) showed a methyl singlet at 48 Hz and a broad multiplet of aromatic protons at 445 Hz. The observed proton areas were 6 (CH_3) and 94% (CH); the calculated values were 7.8 and 92.2%, respectively. The NMR and infrared spectra of the starting materials and product were totally different.

A 500 mg (0.5 mmol) sample of complex I was dissolved in methanol (50 ml) and hydrogenated at room temperature for 5 hr. Analysis of the methanol solution gave 30 mg (77%) of benzene. Filtration of the reaction mixture gave 70 mg of mercury (70%).

Hydroformylation of 1-Hexene. To an Autoclave Engineers 300-ml stainless steel autoclave were charged 30 ml of 1-hexene (20 g, 0.24 mol), 20 ml of benzene, and 0.3 g of complex I. The reaction was pressurized to 1500 psig with synthesis gas (H_2/CO 1:1) and stirred at 100° for 5 hr. Work-up of the benzene solution gave 26.8 g (98%) of C_7 aldehydes. The ratio of linear to branched isomers was 2.31.[17]

Carbonylation of Phenylmercury Acetate. To a 1-l. Parr 4500 Series autoclave was added 16.8 g (50 mmol) of phenylmercury acetate, 150 ml of methanol, and 0.1 g (0.10 mmol) of tris(triphenylphosphine)rhodium(I) chloride. The reactor was evacuated by a water aspirator, and carbon monoxide was pressured into the reactor to 110 psig. The reaction mixture was stirred at 85° for 25 min. Filtration of the reaction mixture gave 8.5 g (85%) of metallic mercury. From the methanol solution were recovered 2.5 g (38%) of methyl benzoate and 3.1 g (50%) of benzoic acid. The products were identified by comparison with authentic samples.

Registry No.—I, 54446-57-0; tris(triphenylphosphine)ruthenium(II) chloride, 15529-49-4; hydridotris(triphenylphosphine)ruthenium(II) chloride, 19631-00-6; tetrakis(triphenylphosphine)palladium(0), 14221-01-3; tetrakis(triphenylphosphine)platinum(0), 14221-02-4; bis(triphenylphosphine)platinum(II) chloride, 10199-34-5.

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(17) Products analyzed by comparative VPC with authentic samples. The authors thank Dr. L. B. Taranko, Exxon Chemical Co., for performing this experiment.

Palladium-Promoted Cyclization of Diphenyl Ether, Diphenylamine, and Related Compounds

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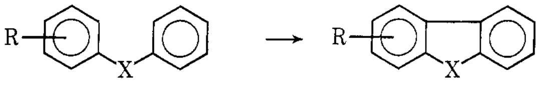
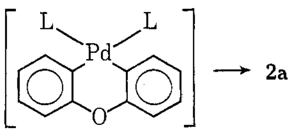
Aromatic compounds may be oxidatively coupled to biaryls and polyaryls by reaction with palladium acetate.[1–4] If diphenyl ether is used, a small amount of dibenzofuran, the product of intramolecular cyclization, is formed in addition to products from intermolecular coupling.[5] In fact, we have earlier shown that dibenzofuran is the only product if the reaction conditions are slightly modified.[6]

We now wish to present results which show that intramolecular cyclization is of general synthetic interest. When heated in acetic acid solution, which contained palladium acetate, diphenyl ether (**1a**), diphenylamine (**1b**), benzophenone (**1c**), and benzanilide (**1d**) gave high yields of cyclized products of the general structure **2** (Table I). An exception was diphenyl sulfide, which failed to yield a defined cyclization product.



1a, X = O; R = H	2a, X = O; R = H
b, X = NH; R = H	b, X = NH; R = H
c, X = CO; R = H	c, X = CO; R = H
d, X = CONH; R = H	d, X = CONH; R = H
e, X = NCH_3; R = H	e, X = NCH_3; R = H
f–m, X = NH; R = CH_3, CH_3O, Cl, Br, NO_2, CO_2H	f–m, X = NH; R = CH_3, CH_3O, Cl, Br, NO_2, CO_2H



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The investigation of a series of substituted diphenylamines showed that a large number of ring substituents were tolerated in the cyclization, e.g., methoxyl, methyl, carboxyl, and nitro groups (Table I). Therefore, the cyclization

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Table I
Results of the Cyclization

Compd, mmol	Palladium acetate, mmol	Solvent	Reaction time, hr	Product	Mp, °C	Yield, %
Diphenyl ether (**1a**), 2	4	Acetic acid	24	Dibenzofuran (**2a**)	85–86 (87)[8]	90
Diphenyl ether	2	Acetic acid	24	Dibenzofuran		45[a]
Diphenyl ether	2	Trifluoroacetic acid	1	Dibenzofuran		87[a]
Diphenyl ether	2	Acetic acid–methanesulfonic acid (15:1)	5 min	Dibenzofuran		40[a,b]
Diphenyl ether	2	Acetic acid–boron trifluoride (15:1)	1	Dibenzofuran		33[a,b]
Diphenylamine (**1b**), 1	1	Acetic acid	0.5	Carbazole (**2b**)	243.5–246 (246)[8]	70 (90[a])
Benzophenone (**1c**), 1	2	Acetic acid	48	9-Fluorenone (**2c**)	81–82 (83)[8]	65
Benzanilide (**1d**), 1	2	Acetic acid	48	6-Phenanthridone (**2d**)	294–296 (292–293)[9]	60
N-Methyldiphenylamine (**1e**), 1		Acetic acid	0.5	*N*-Methylcarbazole (**2e**)	138–139 (141)[10]	75 (90[a])
4-Methyldiphenylamine (**1f**), 1	1	Acetic acid	0.5	3-Methylcarbazole (**2f**)	206–208 (203)[11]	80 (90[a])
4-Methoxydiphenylamine (**1g**), 1	1	Acetic acid	0.5	3-Methoxycarbazole (**2g**)	149–151 (138–139)[12]	75 (90[a])
4-Chlorodiphenylamine (**1h**), 1	1	Acetic acid	0.5	3-Chlorocarbazole (**2h**)	198–200 (201.5)[13]	70 (90[a])
4-Bromodiphenylamine (**1i**), 1	1	Acetic acid	0.5	3-Bromocarbazole (**2i**)	193–195 (199)[14]	75 (90[a])
2-Chlorodiphenylamine (**1k**), 1	1	Acetic acid	1	1-Chlorocarbazole (**2k**)	113–114 (109–110)[15]	75 (90[a])
4-Nitrodiphenylamine (**1l**), 1	2	Acetic acid	2	3-Nitrocarbazole (**2l**)	214–216 (210)[16]	70 (90[a])
N-Phenylanthranilic acid (**1m**), 1	2	Acetic acid	2	Carbazole-1-carboxylic acid (**2m**)	273–274 (271–272)[17]	60

[a] Determined by GLC. [b] Longer reaction time gave no increase.

may be of interest as a general synthesis of condensed aromatic systems, e.g., alkaloids.

The rate of cyclization and the required relative amount of palladium acetate depend on the electron supply in the aromatic rings. Diphenylamine, where the connecting group is electron releasing, is rapidly cyclized in refluxing acetic acid. Only 1 equiv of palladium acetate is required to effect cyclization. This is also true for diphenylamines containing electron-releasing or moderately electron-attracting substituents, the time required for complete reaction being 0.5–1 hr. For diphenylamines containing strongly electron-attracting groups, 2 equiv of palladium acetate and a reaction time of 2 hr are necessary. Cyclization of diphenyl ether (**1b**) requires 2 equiv of palladium acetate and a reaction time of 24 hr, while the reactions of benzophenone (**1c**) and benzanilide (**1d**) are not quite completed after heating for 48 hr in the presence of 2 equiv of palladium acetate (Table I).

The cyclization is catalyzed by acids. When the reaction medium is changed from refluxing acetic acid to trifluoroacetic acid, the cyclization of diphenyl ether is complete within 1 hr and requires only 1 equiv of palladium acetate. Cyclization in acetic acid–methanesulfonic acid (15:1) is even more rapid, being essentially complete within 5 min at reflux (Table I). However, both hydrochloric and sulfuric acid inhibit cyclization. The influence of substituents and of the observed acid catalysis indicate that electrophilic attack by some palladium species on the aromatic rings is involved in the rate-determining step. A reactive intermediate of the type **3** has earlier been suggested[5–6] and is indicated indirectly by the fact that the reaction between a palladium chloride–phosphine complex and 2,2′-dilithiodiphenyl ether gave a high yield of dibenzofuran (**2a**) (X = O) while none of the anticipated palladium species **3**[7] could be observed. The mechanistic aspects and the synthetic scope of the cyclization are being studied.

Experimental Section

Materials. The starting materials **1a–m** and the expected products **2a–m** were either commercial samples or synthesized by standard methods.

Cyclization Procedure. A solution of the diaryl compound and palladium acetate in the appropriate solvent was heated at reflux until the starting material was consumed. The reaction was monitored by GLC and TLC. After evaporation of the solvent, the products were isolated by sublimation or column chromatography. The two procedures gave approximately the same yield. In most cases the yields were also determined by GLC of the reaction solution after addition of a known amount of biphenyl as an internal standard. The products were identified by comparison with authentic samples (ir, melting point, GLC, TLC).

Acknowledgment. We thank the Swedish Natural Science Research Council for financial support.

Registry No.—1a, 101-84-8; **1b**, 122-39-4; **1c**, 119-61-9; **1d**, 93-98-1; **1e**, 552-82-9; **1f**, 620-84-8; **1g**, 1208-86-2; **1h**, 1205-71-6; **1i**, 54446-36-5; **1k**, 1205-40-9; **1l**, 836-30-6; **1m**, 91-40-7; **2a**, 132-64-9; **2b**, 86-74-8; **2c**, 486-25-9; **2d**, 1015-89-0; **2e**, 1484-12-4; **2f**, 4630-20-0; **2g**, 18992-85-3; **2h**, 2732-25-4; **2i**, 1592-95-6; **2k**, 5599-70-2; **2l**, 3077-85-8; **2m**, 6311-19-9; palladium acetate, 3375-31-3.

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11-Methoxyakuammicine from *Alstonia muelleriana*

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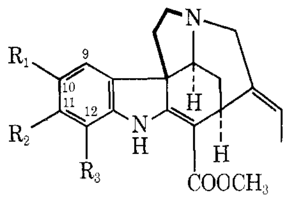
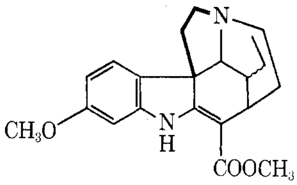
In our recent investigation of the alkaloids of *Alstonia muelleriana*[1] the isolation of a methoxyakuammicine alkaloid was reported. From spectral data, but without a direct comparison with authentic material, this alkaloid was judged to be identical with vinervinine (**1**), which had been isolated from *Vinca erecta* and assigned structure **1**, 11-methoxyakuammicine, by Yunusov and his coworkers.[2,3] Very recently,[4] the proposed structure 1 for vinervinine has been revised by Yunusov and coworkers to 12-methoxyakuammicine (**2**). We wish now to distinguish our alkaloid from vinervinine, and to support our original assignment of structure 1 to the compound from *A. muelleriana.*

The uv spectrum of our compound shows λ_{max} (MeOH) 232, 252 (sh), 298, 325 nm (ϵ 11,500, 9300, 7000, 6700), λ_{min} 272, 312 nm (ϵ 5600, 6400), which differs slightly from that which we reported previously.[1] These data are in better accord with those for 11-methoxy-14,19-dihydrocondylocarpine (**3**)[5] [λ_{max} (EtOH) 255, 286, 327 nm (ϵ 14,800, 10,900, 11,200), λ_{min} 275, 310 nm (ϵ 9500, 10,200)] than those for vinervinine [λ_{max} 237, 292, 334 nm (ϵ 13,000, 6600, 26,500)].[3] However, the definitive evidence for position assignment among phenolic functions of these alkaloids is from the NMR spectra of the aromatic region, as we have shown for sewarine (**4**, 10-hydroxyakuammicine),[6] the structure of which has also been confirmed crystallographically.[7]



$1,\ R_1 = R_3 = H;\ R_2 = OCH_3$
$2,\ R_1 = R_2 = H;\ R_3 = OCH_3$
$4,\ R_1 = OH;\ R_2 = R_3 = H;$
$9\text{-}H = H_A;\ R_2 = H_B;\ R_3 = H_C$



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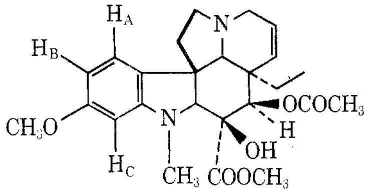

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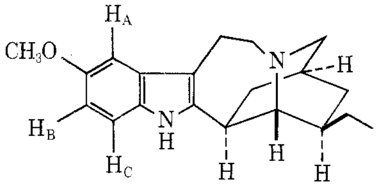

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Table I shows a comparison between the NMR spectra in the aromatic region for several indole alkaloids. It is clear that the spectrum of our alkaloid is very similar to those of vindoline (**5**) and 11-methoxy-14,19-dihydrocondylocarpine (**3**), but different from those for sewarine (**4**) and ibogaine (**6**). In particular, the spectrum in acetone-d_6 is especially revealing, and unequivocally indicates the identity of substitution pattern between our alkaloid and vindoline.[8] The spectra of 2,16-dihydrovinervinine and *N*-acetyldihydrovinervinine published in pictorial form by Yunusov et al.[4] are very different from any of these.

Table I
NMR Spectra (Aromatic Region) of Hydroxy- and Methoxyindole Alkaloids

Alkaloid	H_A, τ	J_{AB}, Hz	H_B	J_{BC}	H_C	Solvent	Ref
Vindoline (5)	3.09	8	3.70	2	3.92	$CDCl_3$	6
Ibogaine (6)	3.05	2	3.25	9	2.92	$CDCl_3$	6
Sewarine (4) HCl	3.02	2	3.30	7	3.17	CD_3OD	6
11-Methoxy-14,19-dihydrocondylocarpine (3)	3.02	9	3.5–3.8, 2 H multiplet			Probably $CDCl_3$	5
11-Methoxyakuammicine (1)[8]	3.0	8	~3.3, 2 H multiplet			$CDCl_3$	Present work and ref 1
	2.65	8	3.5	2	3.3	CD_3COCD_3	

The evidence for the akuammicine skeleton in the alkaloid from *Alstonia muelleriana* has been summarized previously.[1] From these data and the evidence discussed above we wish to retain the structure 11-methoxyakuammicine (for which a new trivial name seems unnecessary) for this alkaloid.

Acknowledgment. We thank Professor James P. Kutney for discussions.

Registry No.—1, 54484-54-7.