dried and removed in vacuo. NMR of the red oil showed that the bicyclobutane had all reacted and been converted into cyclohepta[*jk*]phenanthrene (**20**). The two components were easily separated on an alumina column. The red **20** (568 mg) was recrystallized twice from ligroine/ether and sublimed to give analytically pure material having: mp 107–108 °C; mass spectrum, parent peak at *m/e* 228; NMR (CCl_4) δ 8.00–8.33 (m, 2 H, H-4 and H-5 of phenanthrene ring), 6.67–7.48 (m, 6 H, remaining aromatic), 5.87–6.32 (m, 2 H, vinyl adjacent to aromatic), and 5.18–5.62 (m, 2 H, remaining vinyl). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.58; H, 5.29.

1,10-Phenanthrobicyclo[3.2.0]hepta-2,6-diene (21). Two tubes, one containing 800 mg of a mixture of 80% 1,10-phenanthrotricyclo[4.1.0.$0^{2,7}$]heptene (**19**) and 20% 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) in 500 mL of cyclohexane and the other containing 120 mg of the same mixture in 50 mL of cyclohexane, were sealed in vacuo and heated at 150 °C for 8 h. After removing the cyclohexane, the residue was chromatographed on alumina eluting with ligroine and increasing amounts of ether in ligroine. The first component (690 mg) off the column was a mixture of 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**) (70%) and 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) (30%). The second component (101 mg) was shown by NMR to be cyclohepta[*jk*]phenanthrene (**20**).

Trituration of component 1 with ligroine/ether induced crystallization. Four recrystallizations of this solid from ligroine/ether afforded analytically pure 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**) having: mp 133 °C; mass spectrum, *m/e* 228 (parent peak); NMR (CCl_4) δ 8.17–8.70 (m, 2 H, H-4 and -5 of phenanthrene ring), 7.26–7.93 (m, 6 H, remaining aromatic), 6.30 (s, 2 H, vinyl), and 4.63 (s, 2 H, benzylic). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.61; H, 5.27.

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Registry No.—17, 63264-00-6; **18,** 198-73-2; **19,** 63212-63-5; **20,** 199-85-9; **21,** 63241-09-8; 7*H*-benz[*de*]anthracene, 199-94-0; butyllithium, 109-72-8; methylene chloride, 75-09-2.

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Oxidative Cyclization of 2-Allylphenols by Palladium(II) Acetate. Changes in Product Distribution

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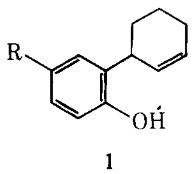
The cyclization of 2-allylphenols **1** having a cyclohexenyl moiety by an equimolar amount of $Pd(OAc)_2$ in air (MeOH, 25 °C) gives a mixture of *cis*-1,2,4a,9b- and *cis*-1,4,4a,9b-tetrahydrodibenzofurans **3** and **4** in nearly equal ratio, together with a small amount of 2,3-butanobenzofuran **5**. The addition of 9 equiv of cyclohexene to this reaction increases the proportion of **3** at the expense of those of **4** and **5**. Further, the distribution of these products changes with changing the substrate concentration. In the presence of excess substrate, the major product is again **3**. In the presence of O_2 (~1 atm), the cyclization proceeds catalytically with respect to Pd(II) without using another cooxidant such as Cu(II), and 0.5 molar equiv of O_2 is constantly consumed for the catalytic production of 1 mol of cyclized products (**3** + **4** + **5**). On the basis of these results, the observed change in product distribution is interpreted in terms of alternation of reacting Pd(II) species involved in the reactions and interaction of intermediate Pd(II) complexes with olefins. In relation to the stereochemistry of the intermediate oxypalladation adduct, the metal-exchange reaction of the trans oxymercurials I and II has been examined by using palladium(II) acetate.

The oxidative cyclization of 2-allylphenols by palladium(II) salts produces 2-substituted benzofurans or chromenes.[1,2] Cyclization of this type can be applicable to a variety of olefins bearing OH,[3] NOH,[4] COOH,[5] or NH_2[6] groups and provides a unique method for synthesizing heterocyclic compounds. The reaction is analogous to the oxidation of olefins by palladium(II),[7–9] and the isomer distribution of cyclized products is sensitively affected by small changes in the reaction conditions, the nature of ligands, and the structure of substrates. Thus, in the present study we have aimed to elucidate some of the fundamental factors controlling the distribution of isomeric benzofurans formed in the cyclization of 2-allylphenols by palladium(II) acetate. For this study, the allylphenols **1** and **2** (R = OMe or H) having cyclohexenyl and cyclopentenyl moieties were chosen since the product distri-



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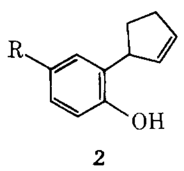

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a, R = OMe; **b**, R = H

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Table I. Product Distribution in the Cyclization of 1 and 2 with Palladium(II) Salts

Substrate	Palladium(II) salt	Yield, %	Product ratio[a]
1a	$Pd(OAc)_2$	73.3	46:49:5[e]
	$PdCl_2$–NaOAc (1:16)[b]	77.9	49:33:18[e]
1b	$Pd(OAc)_2$	86.0	39:56:5[e]
	$PdCl_2$–NaOAc (1:16)[b]	97.0	44:34:22[e]
2a	$Pd(OAc)_2$[c]	77.5	87:13:–[f]
2b	$Pd(OAc)_2$[c]	77.4	84:16:–[f]
	$PdCl_2$–NaOAc (1:16)[d]	46.4	80:20:–[f]

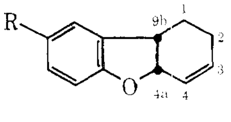
[a] The product ratio was determined by a combination of NMR and GLC analyses. [b] The reaction was carried out at 0 °C for 5 h. [c] The reaction was carried out at 55 °C for 3 h. [d] The reaction was carried out at 35 °C for 3 h. [e] Product ratio for **3**:**4**:**5**. [f] Product ratio for **6**:**7**:**8**.

butions from these substrates appeared to give an implication of the stereochemical process of this reaction.[1]

This paper mainly describes the following subjects: (i) the effect of substrate concentration on the isomer distribution; and (ii) elucidation of the catalytic process of this reaction.

Results

In this report, the product yields are all based on the palladium(II) salts used. The allylphenols **1** and **2** (**a**, R = OMe; **b**, R = H) were at first allowed to react with an equimolar amount of palladium(II) salt in $MeOH-H_2O$ at 25 °C for 2 h in air. Results are given in Table I. Thus, the reaction of **1** (**a** or **b**) with $Pd(OAc)_2$ gives a mixture of **3** and **4** along with a small amount of the benzofuran **5**. The use of $PdCl_2$ alone as the reagent affords at least seven products,[10] but addition of NaOAc (16 equiv) to this reaction leads to only the three cyclized products **3**, **4**, and **5**. The cyclization of **2** (**a** or **b**) by $Pd(OAc)_2$ or $PdCl_2$–NaOAc (1:16) gives a mixture of **6** and **7**, but no benzofuran **8** corresponding to **5** is obtained at all.



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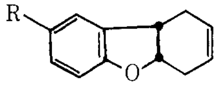

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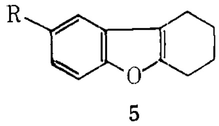

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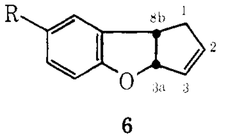

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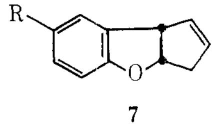

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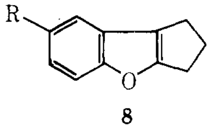

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a, R = OMe; **b**, R = H

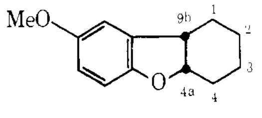
In the reactions using $Pd(OAc)_2$, no double-bond migration of the starting olefins was observed during the reactions. In addition, no secondary isomerization of the carbon–carbon double bonds in the products such as **3** → **5** occurred under the reaction conditions. However, the cyclized products **3** and **4** (**a** or **b**) underwent a small extent of disproportionation (vide infra).[11]

Hydrogenation of a mixture of **3a** and **4a** gives 1,2,3,4,4a,9b-hexahydro-8-methoxydibenzofuran (**9**) as the sole product. Similarly, a mixture of **6b** and **7b** affords 2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (**10**). Consequently, the products **3** and **4** or **6** and **7** are not stereoisomers between the C-4a and C-9b or C-3a and C-8b carbons, respectively. The stereochemistry of the fused furan ring at these carbons can be assigned as cis in all products since the NMR coupling constants of these protons (J = 7 ~ 8 Hz) are in agreement with reported values.[12] Table II, listing spectral and analytical data for these compounds, is given in the supplementary material.

Table III. Effect of Substrate Concentration on the Cyclization of 1a by Palladium(II) Acetate[a]

Run	Molar ratio **1a**/$Pd(OAc)_2$	Cyclized products: Yield,[b] %	Cyclized products: Product ratio[c] **3a**:**4a**:**5a**
1	0.5	34	37:57:6
2	1	73	46:49:5
3	2	176	56:40:4
4	5	254	66:32:2
5	10	606	74:24:2

[a] The reaction was carried out at 25 °C in $MeOH-H_2O$ for 2 h in air. A 0.5-mmol amount of $Pd(OAc)_2$ was used in all runs. [b] Yields based on Pd(II) were determined by GLC using an internal standard. [c] Product ratios were determined by a combination of GLC and NMR analyses. The data are reproducible within ±1 ~ 2% by at least two separate experiments.



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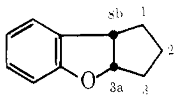

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All of the results described below are those derived from the reaction of **1a** (**a**, R = OMe) with $Pd(OAc)_2$. It is noted here that similar observations can be made by using **1b** (**b**, R = H). From Table III, firstly, it can be seen that the distribution of products **3a**–**5a** changes with changing the relative amount of substrate to $Pd(OAc)_2$ used. Thus, with increasing the concentration of **1a** relative to $Pd(OAc)_2$, the proportion of **3a** increases linearly at the expense of those of **4a** and **5a**. Furthermore, in the presence of excess **1a**, the reaction proceeds catalytically with respect to Pd(II). This result is remarkable in the regard that the catalytic reaction is effectively achieved without using another cooxidant such as Cu(II), which is required in most Pd(II)-catalyzed reactions of this type.[7a,13] For example, 0.5 mmol of $Pd(OAc)_2$ reacts with 5 mmol of **1a** to give 3.03 mmol of cyclized products; the catalytic turn-over is six times for Pd(II).[14] It should be noted here that the change observed in product distribution apparently correlates with the catalytic turn-over and that the proportion of **5a** is always extremely low.

When a nine-fold excess of cyclohexene, corresponding to the cyclohexenyl moiety of **1a**, was added to the 1:1 reaction, an 87% yield of cyclized products **3a**, **4a**, and **5a** was formed in a ratio of 70:21:9; the proportion of **3a** is evidently increased by this treatment (cf. run 2 in Table III). On the other hand, no significant effect was observed by a similar addition of *p*-methoxyphenol, corresponding to the phenolic moiety of **1a**. These results suggest that the predominant formation of **3a** in the presence of excess **1a** is due to an interaction between reactive Pd(II) species and the olefinic moiety of **1a**. The use of a highly coordinating solvent to Pd(II), such as acetonitrile, also resulted in the predominant formation of **3a**.

Under an atmosphere of nitrogen or argon, in place of air, no catalytic production of cyclized products was observed in the reaction of **1a**/$Pd(OAc)_2$ = 2. As shown in Table IV, the composition of products formed in this reaction changed with reaction time. Thus, the cyclized products **3a** and **4a** once formed were disproportionated into hexahydro-8-methoxydibenzofuran **9** and 8-methoxydibenzofuran (**11**), and the unreacted substrate **1a** was converted into a mixture of 2-

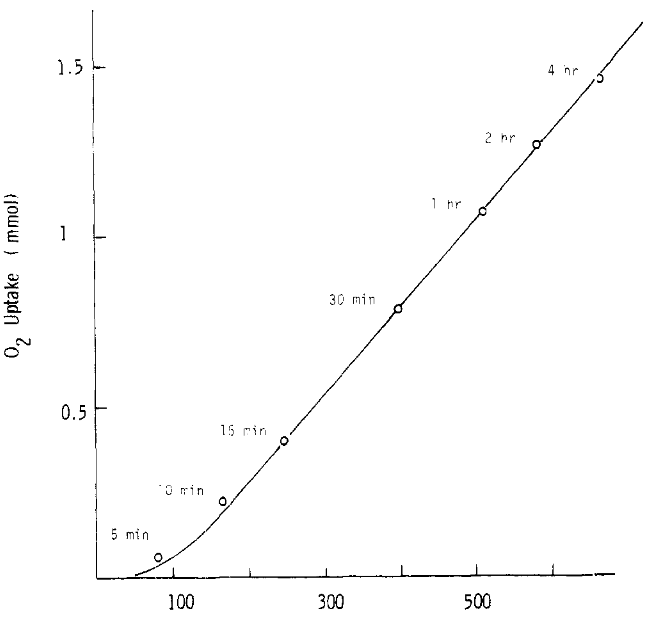


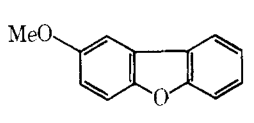
Figure 1. Plot of the O_2 uptake vs. the product yield of **3a** + **4a** + **5a** formed in the reaction of **1a** (5 mmol) and $Pd(OAc)_2$ (0.5 mmol) in $MeOH-H_2O$ at 25 °C under an atmosphere of O_2 (~1 atm).

Table IV. Product Distribution in the Cyclization of 1a under Inert Atmospheres[a]

Reaction time, h	Unreacted 1a, %	Product yield,[b] %				
		3a + 4a	5a	9	11	12 + 13
0.5[c]	118	43	2		6	
2[c]			11	8	15	134
0.5[d]	115	36			7	
2[d]		3	10	8	15	106

[a] Reaction conditions: 1 mmol of **1a**, 0.5 mmol of $Pd(OAc)_2$, and 21 mL of $MeOH-H_2O$ (18:3) at 25 °C under Ar or N_2. [b] Yields based on Pd(II) were determined by GLC using an internal standard. [c] Under Ar. [d] Under N_2.

cyclohexyl-4-methoxyphenol (**12**) and 2-phenyl-4-methoxyphenol (**13**). Therefore, the catalytic process of the foregoing reaction is evidently effected by atmospheric oxygen.



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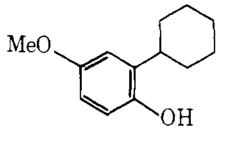

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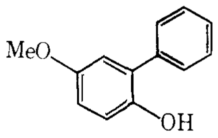

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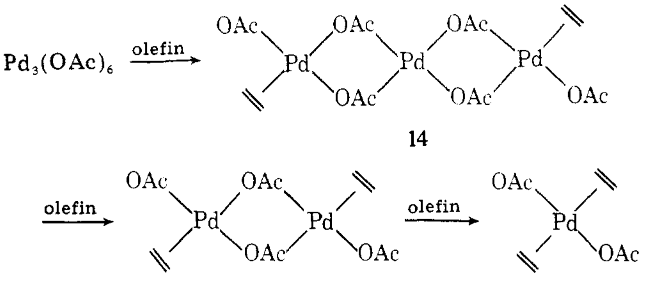
When the reaction of **1a**/$Pd(OAc)_2$ = 10 was performed under an atmosphere of oxygen (~1 atm), the oxygen uptake was found to correlate with the yield of cyclized products (Figure 1). Namely, 0.5 mmol of O_2 was constantly consumed for the production of 1 mmol of cyclized products (**3a** + **4a** + **5a**) formed in the region where the product yield is over 100%. When the reaction was carried out in anhydrous benzene, a stoichiometric amount of H_2O was detected from the reaction mixture by means of Karl Fischer titration. Therefore, the stoichiometry of the catalytic reaction can be represented as eq 1. When benzene was the solvent, a 736% yield of cyclized products was formed in a ratio of **3a**:**4a**:**5a** = 71:22:7. Again, the proportion of **5a** was quite low.

$$\mathbf{1a} + 0.5O_2 \rightarrow \mathbf{3a} + \mathbf{4a} + \mathbf{5a} + H_2O \qquad (1)$$

Discussion

Since the distribution of products formed in a cyclization of this type has been found to be remarkably affected by the anionic ligand of palladium(II) salts,[2] our attention here has been directed to the reaction using palladium(II) acetate. Palladium(II) acetate as a solid is a trimeric ring structure bearing acetate bridges[15] which are necessarily cleaved in the initial stage of reaction. Since the cleavage is induced by the coordination of olefins or additives to the metal to give a trimeric, dimeric, and/or monomeric species such as **14**–**16**,[7,8,16] it is obvious that variations in the concentration of olefinic substrate give rise to changes in the degree of aggregation of palladium(II) acetate. Thus, in the presence of excess substrate, the substrate itself may act out the part of a ligand in reacting Pd(II) acetate. Accordingly, we propose that the observed dependence of product distribution on the substrate concentration (Table III) may be fundamentally ascribed to the different nature of reacting Pd(II) species involved in these reactions.[17]



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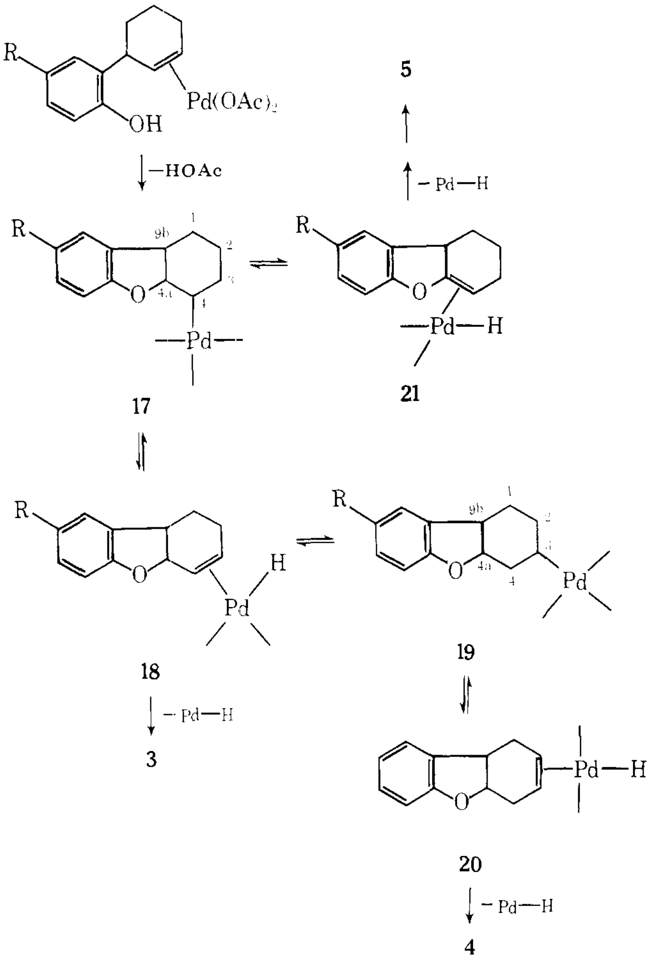
The product distribution itself can be rationalized in terms of intramolecular oxypalladation and palladium(II) hydride elimination–readditions, as shown in Scheme I. The first step in this reaction will proceed by intramolecular nucleophilic attack of the phenoxy group at the C=C bond of **1** coordinated to palladium(II) acetate. This process is accompanied by the loss of HOAc to give the oxypalladation adduct **17**. In the intermediate **17**, β palladium hydride elimination from the C-3 carbon produces the hydridopalladium olefin complex **18**. The complex **18** rearranges into the σ complex **19** by readdition of Pd–H in the opposite direction or gives product **3** with liberation of the Pd–H species. Hydride elimination from the C-2 carbon of **19** results in the formation of **4** via the hydridopalladium olefin complex **20**. The rearrangement of intermediate hydridopalladium olefin complexes, such as **18**, is most likely reversible in the coordination sphere of Pd(II)[18,19] The benzofuran **5** is formed from **21**, which is derived via β palladium hydride elimination from the C-4a carbon of **17**. The double-bond migration of **21** → **5** would, however, occur irreversibly since it gives rise to the thermodynamically more stable benzofuran **5**.

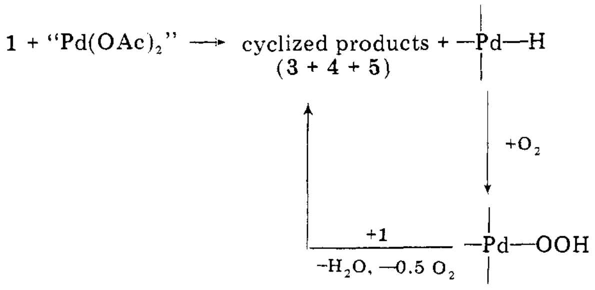
In view of all of this, the observed change in product distribution is ascribed to the change in equilibria among the intermediate complexes such as **17** ⇌ **18** ⇌ **19**. Thus, if the tetrahydrodibenzofuran **3** coordinated to Pd(II) in **18** is replaced by a free olefin such as the substrate itself or added cyclohexene, the proportion of **3** increases at the expense of those of **4** and **5**. Alternatively, it may simply be considered that the change in these equilibria is responsible for the difference in ligands of reactive Pd(II) species.[20]

The Pd–H species formed, whatever it is free or not, will

Scheme I

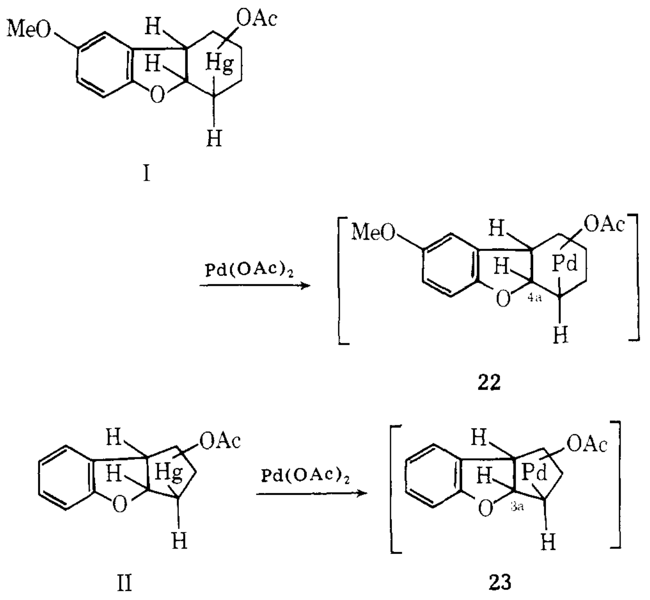


Scheme II



react with O_2, affording a hydroperoxypalladium(II) complex as a catalytic species. The existence of such a species is not unlikely since a rhodium hydride complex has been shown to react with O_2 to give a hydroperoxyrhodium complex.[21] The catalytic cycle given in Scheme II, wherein the ring closure of 1 proceeds by the loss of HOOH to give $0.5O_2$ and H_2O, is consistent with the observed stoichiometry of eq 1. Under the condition of an inert atmosphere, the Pd–H species decomposes to Pd(0), which could be active enough to catalyze the disproportionation of cyclohexenyl moieties of products and substrate.[22]

Finally, we will note here the stereochemistry of the oxypalladation adduct, which may be responsible for the formation of benzofuran **5** or **8**. Since the elimination of Pd–H generally occurs in a cis manner,[23] the trans oxypalladation adduct, e.g., **22** or **23**, is expected to give a relatively higher proportion of **5** or **8** via elimination of the cis hydrogen at the C-4a or C-3a carbons, respectively, but the cis adduct is not. When the trans adduct **22** was produced in situ by treating the trans oxymercurial I[24] with palladium(II) acetate in benzene for 5 min,[25] a 27% combined yield of **3a**, **4a**, and **5a** was formed in a ratio of 77:9:14. The proportion of **5a** was, however, not as high as we expected. The same treatment of *trans*-II afforded a 24% combined yield of **6b** and **7b** in a ratio of 90:10, but none of the expected benzofuran **8b** was formed at all. These results indicate that the hydride elimination from the C-4a or C-3a carbons does not occur with great facility, probably because it gives rise to an olefin of highly strained structure. Therefore, it can be said that a lower proportion of **5a** in the parent reaction is not necessarily dependent on the stereochemistry of the oxypalladation adduct.



Conclusion

The oxidative cyclization of 2-(2-cyclohexenyl)-4-methoxyphenol by palladium(II) acetate in the presence of O_2 is catalytic with respect to Pd(II) without using the usual carrier, Cu(II), which is required in most Pd(II)-catalyzed reactions of this type.[7a,13] Variations in the substrate concentration or the presence of cyclohexene change the product distribution observed. This may be responsible for the change in equilibria among intermediate complexes.

Experimental Section

NMR spectra were recorded on a 100-MHz Model JNM-4H-100 (JEOL) or a 60 MHz Model JNM-MH-60 (JEOL) spectrometer; chemical shifts (δ) are expressed in parts per million relative to Me_4Si. IR spectra were recorded on a Hitachi 215 spectrophotometer. Elemental analyses were performed by Mr. Y. Harada, Department of Chemistry, Faculty of Engineering Science, Osaka University. All temperatures were uncorrected.

Materials. Palladium(II) acetate was prepared by the following procedure. Palladium metal (>99.9% pure; 5.2 g) was dissolved in aqua regia (80 mL), and to this solution was added 40 mL of an aqueous solution of sodium formate (11.6 g). After the solution was heated at 80–90 °C for 5 min, pellets of sodium hydroxide (40 g) were slowly added at room temprature. The resulting palladium sponge was carefully washed with water by decantation until no Cl ion was detected by adding a few drops of $AgNO_3$ solution, and it was filtered with suction. After the palladium sponge was dried in vacuo, it was converted into palladium(II) acetate by nitric acid and glacial acetic acid according to the procedure of G. Wilkinson et al.[26] The glacial acetic acid, prepurified by $KMnO_4$ treatment,[8] was used for the preparation of pure palladium(II) acetate. The palladium(II) acetate of brown color was recrystallized from purified acetic acid containing a small amount of palladium sponge. The recrystallization was repeated two or three times. Palladium(II) chloride was prepared from a solution of palladium metal in aqua regia by repeated dilution with aqueous hydrogen chloride and heating to dryness. The allylphenols 1 and 2 (a or b) were synthesized by the Claisen rearrangement of the corresponding cycloalkenyl phenyl ethers.[27]

General Procedure for the Determination of Product Yield

and Its Distribution. The product ratio was determined by a combination of GLC and NMR analyses. The GLC analysis was performed on a JEOL flame ionization Model JGC-20KFP chromatograph using a 1 m × 4 mm, 10% PEG 20M Celite column under the conditions of injection temperature 250–300 °C and column temperature 110–250 °C. Since the isomeric tetrahydrodibenzofurans **3** and **4** (**a** or **b**) appear at the same retention time under the above conditions, the ratio of (**3** + **4**):**5** was first determined by GLC analysis and then the ratio of **3**:**4** was determined by NMR analysis. The determination of the ratio of **3a**:**4a** was performed by the measurment of peak areas of methoxy signals appearing at slightly different chemical shifts (**3a**, δ 3.68; **4a**, δ 3.67). In a similar way, the ratio of **3b**:**4b** was approximately determined by measuring peak areas of olefinic protons (**3b**, δ 5.90; **4b**, δ 5.78) simplified by a double irradiation technique. The product ratio of (**3a** + **4a**):**5a** was obtained at least three times by GLC analyses on each run and was reproducible within ±1% by at least two separate experiments. The ratios of **3a**:**4a** given in Table III are the average of five measurements by NMR spectroscopy from two separate experiments. Deviations from the average were ±2%.

For the determination of product yield by GLC, either biphenyl or naphthalene was chosen as an internal standard. The yield of **3** + **4** was determined by using the response factor of **3** (**a** or **b**) since the factor of a mixture of **3** and **4** was identical with that of purely isolated **3** (**a** or **b**).

At a final stage of this study, it was found that the products **3** and **4** (**a** or **b**) could be separated well by GLC using a 2 m × 4 mm, 15% silicon DC-QF-1 Celite column. The product ratio of **3a**:**4a** determined by the use of this column was nearly identical with that obtained by the NMR analysis (less than a 3% difference).

Isomerization of products during the process of GLC analysis of reaction mixtures did not occur.

General Procedure for Cyclization Using Palladium(II) Acetate. Palladium(II) acetate (0.112 g, 0.5 mmol) and an appropriate amount of internal standard for GLC analysis were placed in a 100-mL open flask containing a magnetic stirring bar, and a given amount of the substrate dissolved in methanol (18 mL) and water (3.3 mL) was added to the flask. The heterogeneous solution was stirred at 25 °C, and the reaction mixture was sequentially analyzed by GLC. After 2 h, the resulting palladium black was filtered off and the filtrate extracted with ether. The extract was washed with 10% aqueous sodium hydroxide and dried over anhydrous magnesium sulfate. After the solvent was removed in vacuo, the residue was allowed to pass through a short column of alumina using pentane as the eluent. A mixture of cyclized products was obtained by distillation under reduced pressure. For the determination of the product ratio of **3**, **4**, and **5** (**a** or **b**), the distillate was subjected to GLC and NMR analyses. The results are given in Tables I and III. The boiling points of a mixture of cyclized products are as follows: **3a**, **4a**, and **5a**, 125–130 °C (6 mmHg); **3b**, **4b**, and **5b**, 82–86 °C (6 mmHg); **6a** and **7a**, 88–92 °C (4 mmHg); and **6b** and **7b**, 80–84 °C (6 mmHg). Isolation of pure products was performed by preparative GLC. The analytical and spectral data of the products are given in Table II (see supplementary material).

Check for Secondary Isomerization of Cyclized Products. In order to check secondary isomerization of the carbon–carbon double bond of products, blank experiments were carried out by using a mixture of isolated **3a** and **4a**. When a 67:33 mixture of **3a** and **4a** was treated with an equimolar amount of palladium(II) acetate in the presence or absence of a drop of acetic acid or palladium black, no formation of **5a** was observed and the ratio of **3a**:**4a** was invariant after 2 h. When the reaction of **1a** with an equimolar amount of palladium(II) acetate was followed by GLC, no significant change was observed in the GLC ratio of **3a**:**4a**:**5a**. In this case, the GLC analysis was performed using a 15% silicon DC-QF-1 Celite column. Similar observation was obtained in the reaction of **2b** with palladium(II) acetate.

Reaction of 1a with an Equimolar Amount of Palladium(II) Acetate in the Presence of Cyclohexene or *p*-Methoxyphenol. The allylphenol **1a** (0.102 g, 0.5 mmol) was allowed to react with palladium(II) acetate (0.112 g, 0.5 mmol) in the presence of cyclohexene (0.368 g, 4.5 mmol) for 2 h under the usual conditions. Analysis of the products showed that an 87% combined yield of **3a**, **4a**, and **5a** was formed in a ratio of 70:21:9.

The treatment of **1a** with palladium(II) acetate in the presence of *p*-methoxyphenol (9 equiv) gave a 75% combined yield of **3a**, **4a**, and **5a** in a ratio of 45:52:3.

Cyclization of 1 (a or b) and 2b by Palladium(II) Chloride in the Presence of Sodium Acetate. A suspended solution of palladium(II) chloride (0.5 mmol) and sodium acetate (8 mmol) in methanol (4 mL) and water (3.3 mL) was stirred at 0 °C for 5–10 min. Into the suspension was added **1** (0.5 mmol) and an internal standard dissolved in methanol (4 mL), and stirring was continued for 5 h at 0 °C. When the reaction temperature was 25 °C, the disproportionation of cyclized products **3**, **4**, and **5** predominantly occurred. Product yields and their distribution given in Table I were analyzed by the method described above.

The cyclization of **2b** was performed at 35 °C for 3 h under otherwise identical conditions.

Hydrogenation of a Mixture of Cyclized Products. A solution of a 56:44 mixture of **3a** and **4a** (0.150 g) in methanol (8 mL) was stirred in the presence of palladium on charcoal under a hydrogen atmosphere (~1 atm) at room temperature for 5 h. After the usual workup, 1,2,3,4,4a,9b-hexahydro-8-methoxydibenzofuran (**9**) was quantitatively obtained as a single product. Similarly, a 80:20 mixture of **6b** and **7b** gave 2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (**10**) as the sole product. The spectral and analytical data for **9** and **10** are listed in Table II.

Cyclization of 1a with Palladium(II) Acetate under an Atmosphere of Nitrogen or Argon. Palladium(II) acetate (0.112 g, 0.5 mmol) was placed in a 50-mL round-bottle flask equipped with a three-way stopcock and a magnetic stirring bar, and the flask was flushed with N_2 or Ar. A solution of **1a** (0.204 g, 1 mmol) and biphenyl (internal standard for GLC analysis) in methanol (18 mL) and water (3.3 mL) was introduced into the flask at room temperature, and stirring was continued for 2 h. An aliquot of the reaction mixture was periodically analyzed by GLC using a 10% PEG 20M Celite column (1 m × 4 mm). Peaks attributed to biphenyl (internal standard), **9**, **3a** + **4a**, **5a**, **11**, **1a**, and **12** + **13** appeared with retention times of 6, 14, 15, 16, 18, 24.5, and 25.5 min, respectively, under the conditions of injection temperature 250 °C and column temperature 170 °C, which was increased at the rate of 5, 10, and 5 °C/min after 6, 8, and 12 min, respectively. After the reaction was completed, the resulting palladium black was filtered off and the filtrate was extracted with 10% aqueous sodium hydroxide. From the ether extract, the cyclized products were obtained. The alkaline solution was acidified, and the phenolic products were extracted with ether. The ether solution was dried and distilled under reduced pressure. Isolation of products was performed by preparative GLC. However, the isolation of the phenolic products **12** and **13** in a pure form was unsuccessful because of very poor separation by GLC. A 62:38 mixture of **12** and **13**,[28] when isolated by preparative GLC, showed the following resonances in the NMR spectrum (60 MHz, CCl_4). **12:** δ 1.03–2.03 (m, 10 H), 2.53–3.05 (m, 1 H), 3.70 (s, 3 H, OCH_3), 5.36 (broad s, 1 H, OH), and 6.60 (m, 3 H, phenyl). **13:** δ 3.73 (s, 3 H, OCH_3), 5.55 (broad s, 1 H, OH), 6.76 (m, 3 H, phenyl), and 7.37 (m, 5 H, phenyl). These assignments were confirmed by comparison with the NMR spectrum of compound **12**, which was independently synthesized by the hydrogenation of **1a** with palladium on charcoal. Further, a 41:59 mixture of **12** and **13** was obtainable by heating the cyclohexylphenol **12** at 240 °C for 8 h in the presence of palladium on charcoal.[29]

The compound **11** isolated by preparative GLC showed the following data: IR (neat) 1600, 1482, 1450, 1437, 1318, 1295, 1225, 1185, 1163, 1100, 1028, 835, 800, 740, and 718 cm^{-1}; NMR (60 MHz) δ (CCl_4) 3.84 (s, 3 H) and 6.8–7.9 (m, 7 H).

Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.82; H, 5.09. Found: C, 78.51; H, 5.30.

The spectral and analytical data for other products are given in Table II.

Cyclization of 1a with Palladium(II) Acetate Under an Atmosphere of Oxygen. A 50-mL three-neck flask equipped with an addition tube for the solid palladium(II) acetate, a three-way stopcock with a serum cap, and a magnetic stirring bar was connected to a low-pressure hydrogenation apparatus filled with O_2. A solution of **1a** (1.020 g, 5 mmol) and biphenyl (internal standard for GLC analysis) in methanol (18 mL) and water (3.3 mL) was introduced into the reaction flask, and palladium(II) acetate (0.112 g, 0.5 mmol) was placed in the addition tube. The system was first evacuated with an aspirator from one side of the three-way stopcock and then flushed with O_2. After the procedure was repeated several times, the solid palladium(II) acetate was added to the solution at 25 °C by inverting the reaction flask, and the oxygen uptake was immediately measured. An aliquot of the reaction mixture was periodically taken out by a syringe from the top of the three-way stopcock and analyzed by GLC. The results are shown in Figure 1.

When the reaction was carried out in dry benzene (10 mL) under otherwise identical conditions, a stoichiometric amount of water was detected from the reaction mixture by means of a Yanagimoto Karl Fisher reagent titrator (Model KY-100, Yanagimoto Manufacturing Co., Ltd.).

Reaction of the Mercurials I and II with Palladium(II) Acetate. The mercurial I[24] (0.231 g, 0.5 mmol) was added to a solution of palladium(II) acetate (0.112 g, 0.5 mmol) in benzene (6 mL) at room temperature with stirring. After 5 min, GLC analysis of the reaction mixture showed that only the three products **3a**, **4a**, and **5a** were formed in 27% combined yield. In prolonged reaction it was found that the reaction was accompanied by the production of 2-(2-cyclohexenyl)-4-methoxyphenol (**1a**). The product ratio of **3a**:**4a**:**5a**, determined by averaging four experiments, was 77:9:14.

The reaction of the mercurial II with palladium(II) acetate under the same conditions as above gave a mixture of **6b** and **7b** (24% combined yield) in a ratio of 90:10.

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Registry No.—**1a**, 64252-19-3; **1b**, 14003-77-1; **2a**, 61076-48-0; **2b**, 6627-83-4; **3a**, 66324-22-9; **3b**, 66324-24-1; **4a**, 66324-23-0; **4b**, 66324-25-2; **5a**, 7291-77-2; **5b**, 13130-19-3; **6a**, 66324-26-3; **6b**, 66324-28-5; **7a**, 66324-27-4; **7b**, 66324-29-6; **8a**, 7196-06-7; **9**, 66324-30-9; **10**, 14855-05-1; **11**, 20357-70-4; **12**, 16790-05-9; **13**, 13522-82-2; palladium(II) acetate, 3375-31-3.

Supplementary Material Available: A listing of analytical and spectral data for **3**–**7** (**a** or **b**), **9**, and **10** in Table II (4 pages). Ordering information is given on any current masthead page.

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