Regioselectivity of Palladium(II)-Induced Intramolecular Cyclization of 2-(3-Methyl-2-butenyl)phenol

Takahiro HOSOKAWA,* Shinji YAMASHITA, Shun-Ichi MURAHASHI, and Akio SONODA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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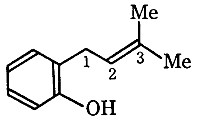
Reaction of 2-(3-methyl-2-butenyl)phenol (**1**) with $PdCl_2$ gives 2,2-dimethylchromene (**3**) and 2,2-dimethyl-4-methoxychroman (**4**) (six-membered products) predominantly, together with trace amounts of 2-isopropylbenzofuran (**5**) and 2-isopropenyl-2,3-dihydrobenzofuran (**6**) (five-membered products). The reaction involves attack of the oxygen atom of the phenoxyl group at 2- or 3-position of the allylic side chain. Addition of various sodium carboxylates to the reaction mixture changes the regioselectivity. In the presence of sodium salts of carboxylic acids bearing electron-releasing substituents, nearly equal amounts of five and six-membered products are formed. The presence of sodium salts of carboxylic acids bearing electron-withdrawing substituents results in the predominant formation of the six-membered products. These results are discussed on the basis of alternation of reactive Pd(II) species. Results obtained from 2-(2-butenyl)phenol (**2**) are also reported.

In 1973 a synthetic process of 2-substituted benzofurans *via* palladium(II)-induced intramolecular cyclization of 2-allylphenols was reported.[1] Thereafter, the cyclization has been applied to unsaturated ketoximes[2] and alcohols[3] for synthesizing various heterocyclic compounds.[4]

During the course of investigations on the cyclization of 2-allylphenols, it has been found that the cyclization of 2-(3-methyl-2-butenyl)phenol (**1**) involves attack of the oxygen atom of the phenoxyl group on either 2- or 3-position of the allylic side chain, and that the regioselectivity depends on the ligands of palladium(II) salts. Similar results were also obtained from the cyclization of 2-(2-butenyl)phenol (**2**). In order to elucidate factors controlling the regioselectivity, the reaction of **1** with palladium(II) salts, $PdCl_2$ or $Pd(OAc)_2$, was carried out in the presence of various sodium carboxylates. In the present paper, we report the effect of sodium carboxylates on the palladium(II)-induced cyclization of **1**.



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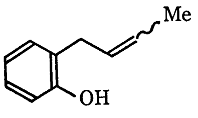

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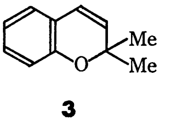
Results and Discussion

The reaction of **1** with $PdCl_2$ in aq methanol at 35 °C for 3 h in the air gave a 43% combined yield of six-membered products **3** and **4** (**3**: **4**=32: 11), along with trace amounts of benzofurans **5** and **6** in less than 2% yields. Addition of NaOAc to the reaction mixture or the use of $Pd(OAc)_2$ instead of $PdCl_2$ caused a change in the product distribution (Table 1); that is, substantial amounts of benzofurans **5** and **6** were formed along with chromene **3**, but no other product such as **4** was detected. The results given in Table 1 indicate the following. (1) In the $PdCl_2$ system, the total product yield increases by increasing the amount of added NaOAc, accompanied by an increase in the relative yield of **6** and a decrease in that of **5** and **3** (runs 1—5). (2) In the $Pd(OAc)_2$ system, the product distribution changes with the addition of six-fold excess of NaOAc (runs 6—7), further addition of NaOAc giving no significant effect (runs 7—8). (3) In the $PdCl_2$ system, the product distribution approaches that in the $Pd(OAc)_2$–NaOAc system by increasing the amount of added NaOAc (runs 5 and 7). The results suggest that both reaction systems involve analogous reactive Pd(II) species, and excess acetate ion must displace the chloride ligands in $PdCl_2$.[5]



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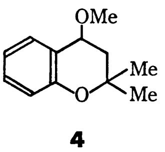

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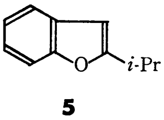

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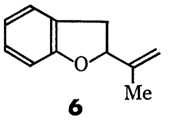

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TABLE 1. PRODUCT DISTRIBUTION IN THE REACTION OF **1** WITH $PdCl_2$ OR $Pd(OAc)_2$ IN THE PRESENCE OF NaOAc[a]

Run	Molar ratio NaOAc/ PdX_2	Cyclized products Yield[b] (%)	Ratio 3	5	6	Unreacted 1 (%)
	X=Cl					
1	2	20	55	25	20	63
2	6	26	54	23	23	63
3	16	34	50	21	29	52
4	30	46	48	17	35	14
5	50	61	46	16	38	5
	X=OAc					
6	0	22	41	5	54	36
7	6	49	45	16	39	9
8	30	48	44	17	39	9

a) The reaction was carried out by using 0.5 mmol of **1**, 0.25 mmol of palladium(II) salt, and the corresponding amount of NaOAc in 9.5 ml of MeOH and 0.5 ml of H_2O at 35 °C for 3 h in the air. b) Yield was determined by GLC, and based on **1** used.

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* To whom correspondence should be addressed.

TABLE 2. PRODUCT DISTRIBUTION IN THE REACTION OF **1** WITH $PdCl_2$ IN THE PRESENCE OF VARIOUS SODIUM CARBOXYLATES OR SODIUM CHLORIDE[a]

Run	Sodium Salts	pK_a[b] (H_2O)	Cyclized products Yield[c] (%)	Ratio **3**	**4**	**5**	**6**	Unreacted **1** (%)
1	NaCl[d]		32	89	9	2	1	55
2	CF_3COONa	0.23	45	82	10	6	2	36
3	$CCl_2HCOONa$	1.25	36	80	4	8	8	51
4	CFH_2COONa	2.57	43	60	2	21	17	42
5	CH_3COONa	4.75	34	50	—	21	29	51
6	CH_3CH_2COONa	4.87	62	50	—	17	33	6
7	$(CH_3)_3CCOONa$	5.05	71[e]	51	—	12	37	3

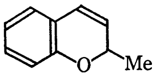
a) The reaction was performed by using 16 molar equivalents of sodium carboxylate to $PdCl_2$ under the conditions described in footnote a) in Table 1. b) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley & Son Inc., New York (1962), p. 124. c) Yield was determined by GLC, and based on charged **1**. d) 4 molar equivalents of NaCl to $PdCl_2$ was used. e) Reaction time was 1 h.

This is supported by the examination of absorption spectra of $PdCl_2$ in the presence of NaOAc. The solution of $PdCl_2$ in aq methanol showed a maximum absorption at 422 nm. Addition of NaOAc shifted the maximum to a shoulder peak around 400 nm,[6] which is similar to a spectrum of $Pd(OAc)_2$ in the presence of NaOAc.

On the basis of these results, we have carried out the reaction of **1** with $PdCl_2$ in the presence of various sodium carboxylates (16 molar equiv to $PdCl_2$) or NaCl.[7] The results summarized in Table **2** are as follows. (1) Formation of the six-membered products (**3** and **4**) predominates that of the five-membered products (**5** and **6**), when the reaction is performed in the presence of either sodium salts of carboxylic acids bearing electron-withdrawing group (runs 2—4) or NaCl, and the relative ratio of **3**+**4**/**5**+**6** (regioselectivity) correlates well with pK_a values of the corresponding carboxylic acids; thus, the higher ratio is observed with the lower pK_a value. (2) In the presence of sodium salts of carboxylic acids bearing electron-releasing group (runs 5—7), the amounts of six- and five-membered products formed are nearly equal, the ratio **3**/**5**+**6** not changing a great deal. These results can be ascribed to an alternation of reactive Pd(II) species through co-ordination of sodium carboxylates to $PdCl_2$, and the change in electron density of palladium appears to affect the regioselectivity. The following facts should be noted here. Firstly, in the reaction using $(CH_3)_3CCOONa$, if the total product yield is calculated on the basis of $PdCl_2$ used, it becomes 142%, suggesting that the reaction involves a catalytic process. When the reaction was carried out under an atmosphere of nitrogen or argon instead of air, the yield was reduced to ≈60% (≈30% based on charged **1**). Thus the catalytic process would be effected by oxygen in air. However, the relative ratios among the cyclized products did not change. Secondly, no double bond isomerization of **1** recovered took place.

From these results we propose the following explanation for the regioselectivity of the cyclization. The cyclization would proceed *via* co-ordination of olefin to the reactive Pd(II) species, as has been generally accepted in many organic reactions using palladium(II).[8] On the co-ordinated olefin, an extensive positive charge may be induced by a decrease in electron density on palladium, if the reactive Pd(II) species bears electron-withdrawing ligands. Nucleophilic attack of the oxygen atom would thus occur predominantly at the 3-position of the allylic side chain, since a positive charge at this position is highly stabilized by two methyl groups. If so, one factor controlling the regioselectivity would be the electron density of palladium. This may be supported by the following results. (1) The use of $Pd(OCOCF_3)_2$ also led to a predominant formation of **3**. (2) The reaction of **1** with $Hg(OAc)_2$ (a more electrophilic reagent[9] than palladium(II)) in aq. methanol followed by $NaBH_4$ reduction gave a six-membered product, 2,2-dimethylchroman, as the sole product.

The reaction of 2-(2-butenyl)phenol (**2**) with palladium(II) salts gave cyclized products such as **7**, **8**, **9**, **10**, and **11**. As shown in Table 3, the reaction using $PdCl_2$ alone gives six-(**7**+**8**+**9**) and five-membered product (**10**) in the ratio 89: 21. The result shows a tendency similar to the case of **1**. Addition of NaOAc to $PdCl_2$ or the use of $Pd(OAc)_2$ instead of $PdCl_2$ leads to none of the six-membered products, only the five-membered products **10** and **11** being formed. Hence, the facile formation of the six-membered product(s) from **1** would be also governed by a favorable attack of Pd(II) on a less crowded carbon (2-position) of the allylic side chain of **1**.



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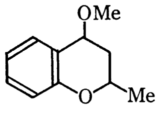

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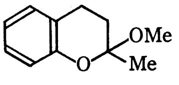

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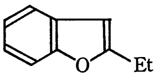

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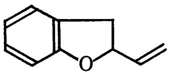

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TABLE 3. PRODUCT DISTRIBUTION IN THE REACTION OF **2** WITH PALLADIUM(II) SALTS[a]

Palladium(II) salts	Cyclized products Yield (%)	**7**	**8**	**9**	**10**	**11**
$PdCl_2$	34[b]	50	11	18	21	—[c]
$PdCl_2$–NaOAc[d]	40[e]	—	—	—	52	58
$Pd(OAc)_2$[f]	65	—	—	—	29	71

a) Palladium(II) salt was reacted with two molar equivalents of **2** in aq MeOH at 35 °C for 3 h in the air. b) The yield, based on charged **2**, was estimated from a mixture of isolated products by GLC. c) The ratio was determined by GLC peak areas. d) 16 molar equivalents of NaOAc to $PdCl_2$ was used. e) The yield was determined by GLC with biphenyl as an internal standard, and based on charged **2**. f) Data from Ref. 1b.

Experimental

Materials. 2-(2-Methyl-2-butenyl)phenol (**1**) was synthesized by C-alkylation of sodium phenoxide with 4-bromo-2-methyl-2-butene[10] according to the procedure of Hurd and Hoffman.[11] 2-(2-Butenyl)phenol (**2**) was prepared as reported previously.[1b] Palladium(II) chloride was prepared from a solution of palladium metal in *aqua regia* by diluting with aq hydrogen chloride and heating to dryness. Palladium(II) acetate was prepared by the method of Wilkinson *et al.*[12]

Reaction of 1 with Palladium(II) Salts. *A) Analyses of Product Distributions*: A suspension of palladium(II) salt ($PdCl_2$ or $Pd(OAc)_2$, 0.25 mmol) and a given amount of NaOAc in MeOH (4.5 ml)–H_2O (0.5 ml) was stirred at 35 °C for 10 min in the air, and then a mixture of allylphenol **1** (0.081 g, 0.5 mmol) and appropriate amount of biphenyl (internal standard for GLC analysis) in MeOH (5 ml) was added to the suspension, stirring being continued for 3 h. Product distributions were analyzed by gas chromatography (a JEOL Model JGC-20KFP gas chromatography) equipped with a FID detector using 10% PEG-20 M Celite Column (1 m × 4 mm). Peaks attributed to chromene **3**, benzofurans **5** and **6**, chroman **4**, biphenyl (internal standard), and unreacted **1** appeared with retention times of 10.0, 11.6, 14.3, 20.3, and 28.8 min, respectively, under the conditions of injection temperature 300 °C and column temperature 120 °C which was raised up at the rate of 5 °C/min after 7 min. The results are summarized in Table 1.

Analyses of product distribution in the presence of various sodium carboxylates were performed by the same procedure, the results being given in Table **2**. All the product yields are based on **1** used. Isolation, purification, and identification of cyclized products were carried out as follows.

B) Isolation and Identification of 2,2-Dimethylchromene (3) and 2,2-Dimethyl-4-methoxychroman (4): For isolation of cyclized products **3** and **4**, the reaction was carried out by using a catalytic amount of $PdCl_2$. A mixture of **1** (1.620 g, 10 mmol), $PdCl_2$ (0.035 g, 0.2 mmol), and $CuCl_2$ (0.670 g, 5 mmol) in MeOH (25 ml)–H_2O (2 ml) was stirred at 65 °C under a slow stream of oxygen. After 24 h, the reaction mixture was filtered and extracted with ether. The ether extract was washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was distilled under reduced pressure, giving 1st fraction (0.506 g) at 85—90 °C/4 mmHg and 2nd fraction (0.658 g) at 101—105 °C/4 mmHg. GLC analyses showed that the 1st fraction contained chromene **3**, chroman **4**, unreacted **1**, and an unidentified product in 55, 15, 9, and 21% on GLC peak areas, respectively, and the 2nd fraction in 27, 28, 15, and 30%. The unidentified compound is a phenolic material since it can be removed from the mixtures by treating with Claisen's alkali. Although its isolation was unsuccessful owing to decomposition during the course of preparative GLC, the compound is probably 2-(2-methoxy-3-methylbutyl)phenol. The other products were isolated by preparative GLC using 10% PEG-20 M Celite Column at 165 °C. 2,2-Dimethylchromene (**3**), NMR (CCl_4), δ 1.37 (s, 6H), 5.44 (d, J=10 Hz, 1H), 6.18 (d, J=10 Hz, 1H), and 7.1—6.4 (m, 4H). (Found: C, 82.41; H, 7.48%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%). The spectral properties of this compound were identical with those of the authentic sample prepared by the method of Campbell *et al.*[13] 2,2-Dimethyl-4-methoxychroman (**4**), NMR (CCl_4), δ 1.27 (s, 3H, Me), 1.35 (s, 3H, Me), 1.92 (d, J=7 Hz, 2H, C-3 proton), 3.32 (s, 3H, OMe), 4.27 (t, J=7 Hz, 1H, benzylic proton), and 7.2—6.2 (m, 4H); IR, cm^{-1} 1608 (m), 1580 (s), 1482 (s), 1485 (s), 1367 (m), 1258 (s), 1203 (s), 1128 (s), 1090 (s), 920 (s), 908 (m), and 748 (s); Found: C, 75.19; H, 8.53%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%. The position of the methoxyl group was assigned on the basis of the downfield shift of benzylic proton (δ 4.27) caused by both phenyl ring and methoxyl group. The benzylic protons of 2,2-dimethylchroman (see below) show resonance at δ 2.72 as a triplet. The assignment is also supported by comparison with the NMR spectrum of 2-methyl-4-methoxychroman (**7**).

C) Isolation and Identification of 2-Isopropylbenzofuran (5) and 2-Isopropenyl-2,3-dihydrobenzofuran (6): For the isolation of **5** and **6**, allylphenol **1** (1.620 g, 10 mmol) was similarly reacted with a catalytic amount of $Pd(OAc)_2$ (0.046 g, 0.2 mmol) in the presence of $Cu(OAc)_2 \cdot H_2O$ (0.998 g, 5 mmol) for 48 h. The usual work-up followed by distillation (~105 °C/6 mmHg) gave an oil (1.260 g) which contained largely unreacted **1**. The distillate was then treated with Claisen's alkali, and the organic products were extracted with petroleum ether. The extract was washed with water and dried over $MgSO_4$. Removal of the solvent afforded colorless oil (0.358 g) which was found to contain **3**, **5**, and **6** in the ratio 47: 3: 50 on GLC peak areas. Isolation of these products was performed by preparative GLC under the same conditions as above. 2-Isopropylbenzofuran (**5**), NMR (CCl_4), δ 1.41 (d, J=7 Hz, 6H, Me) 3.06 (h, J=7 Hz, 1H), 6.31 (s, 1H, C-3 proton), 7.1—7.3 (m, 2H), and 7.3—7.5 (m, 2H): IR, cm^{-1} 1582 (s), 1592 (s), 1462 (s), 1425 (s), 1223 (s), 1158 (m), 930 (m), 783 (s) and 725 (s); Found: C, 82.45; H, 7.61%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. 2-Isopropenyl-2,3-dihydrobenzofuran (**6**), NMR (CCl_4), δ 1.70 (broad s, 3H, Me), 2.89 (dd, J=16 and 8 Hz, 1H, C-3 proton), 3.21 (dd, J=16 and 8.5 Hz, 1H, C-3 proton), 4.74 (broad s, 1H, olefinic proton), 4.94 (broad s, 1H, olefinic proton), 4.95 (t, J=8 Hz, 1H, C-2 proton), 6.58 (2H, phenyl proton), and 6.86 (2H, phenyl proton): IR, cm^{-1} 1643 (w), 1590 (s), 1476 (s), 1458 (s), 1368 (m), 1318 (m), 1210 (s), 1160 (w), 1090 (w), 1010 (m), 950 (m), 890 (m), 850 (m), and 738 (s): Found: C, 82.31; H, 7.54%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

D) Reaction of 1 with $Pd(OCOCF_3)_2$: $Pd(OCOCF_3)_2$ was prepared by the procedure of Wilkinson *et al.*[12] $Pd(OCOCF_3)_2$ (0.083 g, 0.25 mmol) was reacted with **1** (0.081 g, 0.5 mmol) according to the same procedures as above. GLC analysis showed that **3**, **5**, and **6** were formed in 45% combined yield, based on charged **1**, in the ratio 83: 14: 3. The yield was determined with biphenyl as an internal standard.

Reaction of 1 with $Hg(OAc)_2$. $Hg(OAc)_2$ (0.318 g, 1 mmol) was reacted with **1** (0.162 g, 1 mmol) in MeOH (19 ml)–H_2O (1 ml) at 35 °C for 3 h. The reaction mixture was extracted with ether, washed with water, and dried over $MgSO_4$–$NaHCO_3$. After evaporation of ether, the residue was dissolved in carbon tetrachloride. Organomercurial, probably 3-acetoxymercuri-2,2-dimethylchroman, was precipitated (0.247 g, 59%) by adding petroleum ether to the solution. The mercurial (0.247 g, 0.59 mmol) was added to a solution of $NaBH_4$ (0.022 g, 0.58 mmol) in 2 M sodium hydroxide (2 ml). The reaction mixture was stirred for 45 min at 15 °C, and extracted with ether. The extract was washed with water and dried over $MgSO_4$. Removal of ether gave a colorless oil (0.079 g, 83%) which was found to contain only 2,2-dimethylchroman by GLC analysis. 2,2-Dimethylchroman, NMR (CCl_4), δ 1.28 (s, 6H, Me), 1.73 (t, 2H, J=7 Hz, C-3 proton), 2.72 (t, 2H, J=7 Hz, benzylic proton), and 7.1—6.4 (m, 4H): (Found: C, 81.58; H, 8.78%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.). The structure was confirmed by comparison with an authentic sample prepared by hydrogenation of **3** with palladium on charcoal.

Reaction of 2-(2-Butenyl)phenol (2) with $PdCl_2$. A mixture of *cis*- and *trans*-**2** (*cis*/*trans*= 1/1.9) was reacted with $PdCl_2$ (0.177 g, 1 mmol) in MeOH (38 ml)–H_2O (2 ml) at 35 °C for 5 h in the air. After filtration of precipitated metallic palladium, organic products were extracted with ether in the usual way. After removal of ether, the residue was subjected to alumina column chromatography (Al_2O_3, 8 g). Elution with petroleum ether (50 ml) gave colorless oil (0.110 g) containing **7**, **8**, **9**, and **10** in the ratio 50: 11: 18: 21 on GLC peak areas and unidentified products in less than 4%. The combined yield of cyclized products was approximately 34% based on charged **2**. These products were isolated by preparative GLC using 5% PEG-20 M Celite Column at 125 °C. 2-Methylchromene (**7**), NMR (CCl_4), δ 1.32 (d, 3H, J=6.5 Hz, Me), 4.90 (ddq, 1H, J=6.5, 3, and 1.8 Hz, C-2 proton), 5.56 (dd, 1H, J=3 and 9 Hz, olefinic proton), 6.28 (dd, 1H, J=9 and 1.8 Hz, olefinic proton), and 7.5—6.7 (m, 4H); Found: C, 82.25; H, 6.82%. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90%. 2-Methyl-4-methoxychroman (**8**), NMR (CCl_4), δ 1.40 (d, 3H, J=6.5 Hz, Me), 1.62 (ddd, 1H, J=13, 9.5, and 3 Hz, C-3 proton), 2.05 (ddd, 1H, J= 13, $\approx$1, and $\approx$2 Hz, C-3 proton), 3.33 (s, 3H, OMe), 4.10 (dd, 1H, J=3 and $\approx$2 Hz, benzylic proton), 4.32 (m, 1H, C-2 proton), 6.7—6.9 (m, 2H), and 7.0—7.3 (m, 2H). Found: C, 73.98; H, 7.75%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%. The assignment of structure **8** is supported by the double irradiation experiment in NMR. Double irradiation of benzylic proton (δ 4.10) simplified the signals of C-3 protons (δ 1.62 and 2.05), showing two sets of double doublet (J= 13 and 9.5 Hz and J= 13 and $\approx$1 Hz). The signals of C-3 protons were transformed into two sets of broad doublet by irradiating on the C-2 proton (δ 4.32). The multiplet of C-2 proton was simplified by double irradiation of the methyl signal at δ 1.04 to show a broad doublet (J=9.5 Hz). The C-2 proton signal was also simplified by double irradiation of C-3 proton at δ 1.62 and 2.05 to show a doublet of quartet, in each case, bearing coupling constants of J=6.5 and $\approx$1 Hz, and J=6.5 and 9.5 Hz, respectively. 2-Methyl-2-methoxychroman (**9**) was identified by comparison with the spectral data reported by Dolby *et al.*[14] (Found: C, 74.29; H, 7.69%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%). Identification of 2-ethylbenzofuran (**10**) and 2-vinyl-2,3-dihydrobenzofuran (**11**) was described previously.[2b]

*Reaction of **2** with $PdCl_2$ in the Presence of NaOAc.* Allylphenol **2** (0.445 g, 3 mmol) was reacted with $PdCl_2$ (0.276 g, 1.5 mmol) in the presence of NaOAc (1.968 g, 24 mmol) in MeOH (57 ml)–H_2O (3 ml) at 35 °C for 3 h in the air. GLC analysis showed that only benzofurans **5** and **6** were formed in 40% combined yield based on charged **2**, in the ratio 52: 58. The yield was determined with biphenyl as an internal standard.

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4) Other workers have also succeeded in preparing some heterocyclic compounds by using cyclizations of this type; a) A. Kasahara, T. Izumi, and M. Ooshima, *Bull. Chem. Soc. Jpn.*, **47**, 2526 (1974); b) T. Izumi and A. Kasahara, *ibid.*, **48**, 1673 (1975); c) L. S. Hegedus, G. F. Allen, and E. L. Waterman, *J. Am. Chem. Soc.*, **98**, 2674 (1976).

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