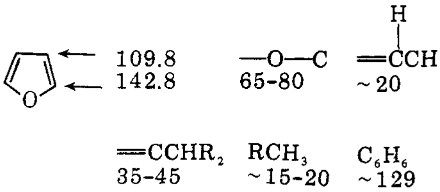
Chart II



"The Chemist's Companion" and are listed in Chart II.[24] Isomerization studies in this system were carried out in the same manner as the isomerization of enones already discussed.

In the reaction of 3,3-dimethylbutyryl chloride with vinylmercuric chloride, **5,5-dimethyl-1-hexen-3-one** was identified by its ^{1}H NMR spectrum: δ 1.0 (9 H, s, $C(CH_3)_3$), 2.4 (2 H, s, CH_2CO), 5.65 (1 H, d d, $J = 4, 8$ Hz, COCH=), 6.15 (2 H, m, $COCH{=}CH_2$). Further characterization was not carried out.

1-Chloro-5,5-dimethyl-3-hexanone was characterized fully: ^{1}H NMR (CCl_4) δ 1.0 (9 H, s, $C(CH_3)_3$), 2.25 (2 H, s, CCH_2CO), 2.75 (2 H, t, $J = 7$ Hz, $COCH_2CH_2Cl$), 3.6 (2 H, t, $J = 7$ Hz, CH_2Cl); IR (max) (thin film) 2940, 1710, 1360, 1180, 830 cm^{-1}; MS m/e 162.0812 ± 0.0008 (calcd for $C_8H_{15}OCl$, 162.0812).

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for financial support (R.C.L.) and the National Science Foundation for an NSF Traineeship (J.C.B.).

Registry No.—1-Acetoxy-4-chlorobutane, 6962-92-1; *trans*-11-chloromercuriundec-10-enoic acid, 56453-79-3; *cis*-11-chloromercuriundec-10-enoic acid, 56453-80-6; *trans*-12-carbomethoxy-3-dodecen-2-one, 61759-52-2; *cis*-12-carbomethoxy-3-dodecen-2-one, 61759-49-7; *cis*-3-octen-2-one, 51193-77-2; *cis*-5-decen-4-one, 64235-54-7; *trans*-5-decen-4-one, 64235-55-8; (*E*)-1-phenyl-2,4,4-trimethyl-2-penten-1-one, 64235-56-9; 4,5-dihydro-2-phenyl-3,4,5,5-tetramethylfuran, 64235-57-0; 2-methyl-3-*tert*-butyl-1-indanone, 64235-58-1; 3,3-dimethylbutyryl chloride, 7065-46-5; 5,5-dimethyl-1-hepten-3-one, 2177-33-5; 1-chloro-5,5-dimethyl-3-hexanone, 64235-59-2.

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(4) Alfred P. Sloan Foundation Fellow, 1977–1979.
(5) National Science Foundation Trainee, 1973–1977.
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Intramolecular Phenoxymercuration of 2-Allylphenols. Regioselectivity and Stereochemistry

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Intramolecular phenoxymercuration of 2-(2-cyclohexenyl)-4-methoxyphenol (**1**) using $Hg(OAc)_2$ gave 1,2,3,4,4a,9b-hexahydro-4-acetoxymercuri-8-methoxydibenzofuran (**2a**, 59%) as the sole product. The use of $HgCl_2$ in this reaction afforded only 2,4-propano-3-chloromercuri-6-methoxychroman (**3b**, 53%), indicating a change in the regioselectivity of the reaction. The stereochemistry of these mercurials was established by x-ray analyses which showed a trans arrangement of the Hg and the oxygen atom in both cases. That is, the reaction proceeds by an antarafacial addition to the C=C double bond of **1**. The use of mercuric chloroacetates in this reaction, e.g., $Hg(OCOCH_2Cl)_2$, gave both types of products, **2** and **3**, and the formation of the chroman compound **3** increased with increasing the electron-withdrawing property of the acetoxy ligands in $Hg(OCOCX_3)_2$: $OCOCH_3 < OCOCH_2Cl < OCOCHCl_2 < OCOCCl_3$. This suggests that the difference in regioselectivity observed with $Hg(OAc)_2$ and $HgCl_2$ depends on the electronic effect of the ligands on HgX_2. The use of HgX_2 having ligands more electronegative than acetate, such as $X = NO_3$ and ClO_4, led to the chroman compound **3**.

The reaction of 2-allylphenols with palladium(II) salts, which we have recently studied,[1,2] generally gives 2-substituted benzo- and/or dihydrobenzofurans. These products are considered to arise from an intramolecular phenoxypalladation process, but the palladation adduct is not isolated in this reaction. A way to produce this adduct may be by a metal-exchange reaction between the corresponding organomercury and palladium salts. Since palladium exchange with orga-

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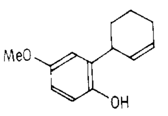
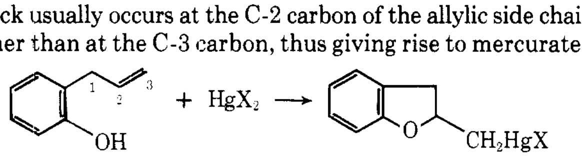
nomercurials has been shown to occur with retention of configuration at carbon,[3,4] the use of an organomercurial of known configuration may shed further light on the stereochemistry of the palladium adduct formed. From such a viewpoint, we planned to prepare the mercurated dihydrobenzofuran derived from 2-(2-cyclohexenyl)-4-methoxyphenol (1) and to define its stereochemistry.



1

The reaction of 2-allylphenol with mercuric(II) salts was first reported by Adams in 1922 to give 2-mercurated methyl-2,3-dihydrobenzofurans.[5] Recently it has been shown that the reaction proceeds through electrophilic attack of Hg(II) on the double bond to produce a positively charged species which is trapped by the nucleophilic neighboring group.[6] In all such intramolecular phenoxymercurations of 2-allylphenols so far reported,[7–11] the internal nucleophilic attack usually occurs at the C-2 carbon of the allylic side chain rather than at the C-3 carbon, thus giving rise to mercurated



dihydrobenzofurans. However, when 1 was allowed to react with mercuric salts, the regioselectivity was found to be markedly affected by the anionic ligand of HgX_2. In order to understand this new observation, it was also required to clarify the stereochemistry of the mercurials obtained. Thus, in the present paper, our attention has been directed to the regioselectivity and stereochemistry of the intramolecular phenoxymercuration of 1.

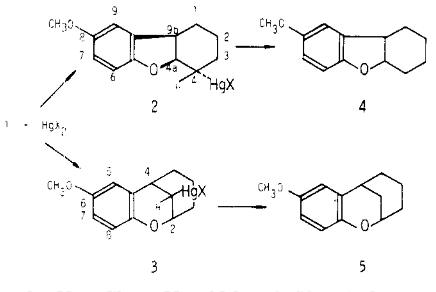
Results and Discussion

Cyclization of 1 with HgX_2. The reaction of 1 with $Hg(OAc)_2$ in water at room temperature for 24 h resulted in the formation of the mercurated dihydrobenzofuran **2a** in 59% yield (see Scheme I). By contrast, the use of $HgCl_2$ in this reaction gave a 53% yield of the mercurated chroman **3b**, indicating a change in the regioselectivity of the reaction. In neither reaction could any other product be detected, and unreacted starting material was recovered unchanged. Sodium borohydride reduction of **2a** and **3b** gave **4** and **5**, respectively (Experimental Section).

The use of $Hg(NO_3)_2$ also gave the chroman **3c** (53%) as the sole product. Similarly, the reaction of 1 with $Hg(ClO_4)_2$ followed by $NaBH_4$ reduction gave the chroman **5**. Again, no dihydrobenzofuran was detected in these reactions. These results indicate that the degree of dissociation of the Hg-X bond ($ClO_4 > NO_3 > OAc > Cl$) does not correlate with the difference in regioselectivity observed with $Hg(OAc)_2$ and $HgCl_2$.

When mercuric monochloroacetate was used in this reaction, both types of the products **2e** and **3e** were formed in a ratio of 56:44. The use of mercuric dichloroacetate changed the product ratio of **2**/**3**, the chroman **3f** being predominantly formed over the dihydrobenzofuran **2f** (Table I). Mercuric trichloroacetate or mercuric trifluoroacetate gave only the chroman **3g** or **3h**. These data indicate that the regioselectivity of this reaction depends on the electron-withdrawing property of the acetoxy ligands in $Hg(OCOCX_3)_2$. This parallels our previous observation that the regioselectivity in the Pd(II)-induced intramolecular cyclization of 2-(3-methyl-2-butenyl)phenol changes with the carboxylate ligands on Pd(II) salts.[2]

Scheme I



a, X = OAc; b, X = Cl; c, X = NO_3; d, X = ClO_4; e, X = $OCOCH_2Cl$; f, X = $OCOCHCl_2$; g, X = $OCOCCl_3$; h, X = $OCOCF_3$

Structures of the Mercurials 2 and 3. The NMR spectrum of **2a** shows that the H_{4a} proton is coupled to the H_{9b} and H_4 protons with equal coupling constants of 7 Hz. However, our observation that $J(H_{9b}–H_{4a}) = J(H_{9b}–H_{1,cis}) = J(H_{9b}–H_{1,trans}) = 7$ Hz indicates that no stereochemical information may be deduced from the coupling constants. The H_{4a} proton has the vicinal $^1H–^{199}Hg$ coupling constant of 144 Hz, which appears to suggest that H_{4a} and the Hg atom are cis since the value is close to the cis-vicinal coupling constant of $J(Hg–H)_{vic} = 99$ Hz reported for *trans*-1-chloromercuri-2-methoxycyclohexane. However, it has been shown that values of $J(Hg–H)_{vic}$ are generally around 100 Hz, except that it rises to around 600 Hz when the dihedral angle defined by the C,C,H plane and the C,C,Hg plane is close to 180°.[12] Thus, a configurational assignment based on the vicinal coupling constant of 144 Hz is not conclusive. Accordingly, we have carried out single crystal x-ray analyses of these mercurials to define the stereochemistry of structures 2 and 3.

Unfortunately, no crystal of **2a** (X = OAc) suitable for analysis could be obtained, and hence the acetate **2a** was converted into the chloride **2b** (X = Cl) by treatment with NaCl. Since the acetate **2a** was regenerated from the chloride **2b** by treatment with AgOAc and the NMR spectra of **2a** and **2b** were similar, it can be concluded that no stereochemical change of the furan moiety occurred during this transformation. The crystallographic studies were therefore carried out using the chlorides **2b** and **3b**.

The final positional and thermal parameters for the nonhydrogen atoms of the mercurials **2b** and **3b** are listed in Tables II and III, respectively. Interatomic distances and bond angles are collected in Tables IV and V. These tables are available as supplementary material.

Figures 1 and 2 show a perspective view of the molecules **2b** and **3b**, respectively. As seen in Figure 1, the cyclohexane ring of **2b** is in the chair form where the Hg and oxygen atoms are both equatorial, i.e., in a trans configuration. The C_{9a} atom occupies an axial position, and thus C_{9a} and the oxygen atom are in a cis configuration about the $C_{9b}–C_{4a}$ bond of the fused furan ring, which exists in the half-chair form. It is to be noted that the dihedral angle between the C_{4a},C_4,Hg plane and the C_{4a},C_4,H plane can be estimated to be 54° by assuming a normal position for the hydrogen atom.

The bond distances of Hg-Cl (2.33 Å) and Hg-C (2.11 Å) agree with the values of 2.53 and 2.34 Å reported for *trans*-1-chloromercuri-2-methoxycyclohexane,[13] and also the C-Hg-Cl bond angle of 174.8° is close to the reported value of 178°.[13]

Figure 2 shows that the cyclohexane ring of **3b** is also constructed with the chair form where both the Hg and the oxygen atom occupy the axial position. That is, the configuration of these atoms is trans.

These results indicate that the present reaction proceeds by antarafacial addition to the C=C double bond of 1, regardless of the anionic ligands of HgX_2. Thus, it may be safely concluded that the difference in regioselectivity observed with $Hg(OAc)_2$ and $HgCl_2$ is not related to the stereochemistry of the addition step.

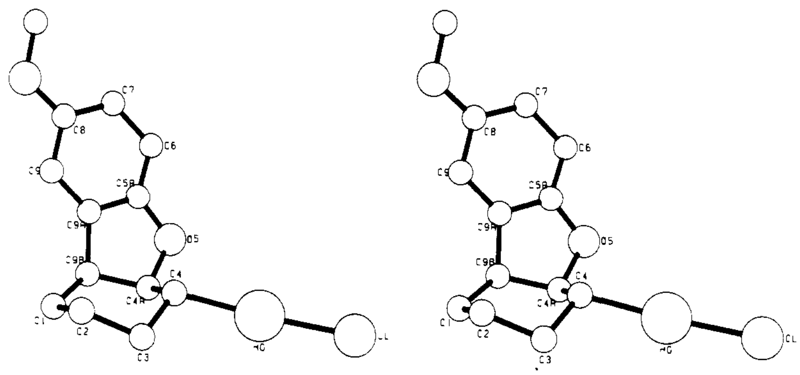


Figure 1. A stereoscopic view of the molecular structure of 1,2,3,4,4a,9b-hexahydro-4-chloromercuri-8-methoxydibenzofuran (**2b**).

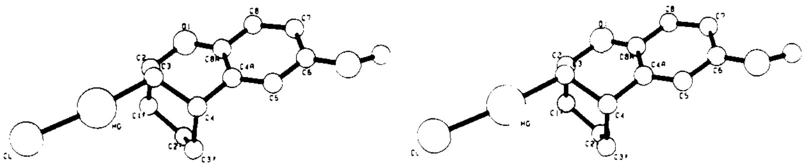


Figure 2. A stereoscopic view of the molecular structure of 2,4-propano-3-chloromercuri-6-methoxychroman (**3b**).

Table I. Cyclization of 1 with Mercuric Haloacetates

$1 + HgX_2 \rightarrow 2 + 3$

Mercuric salts (HgX_2) X^-	Cyclized products Yield,[a] %	2:3
$OCOCH_3$	59	100:
$OCOCH_2Cl$	79	56:44[b]
$OCOCHCl_2$	50	24:76[b]
$OCOCCl_3$[c]	40	:100
$OCOCF_3$	43	:100

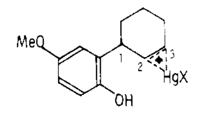
[a] Yields are of isolated products. [b] The ratio was determined from the NMR spectrum (100 MHz) of the crude reaction mixture by integrating the methoxy signals of **2** and **3**. These peaks appeared around δ 3.75 with a slightly different chemical shift (0.01 ppm). [c] The reagent was prepared in situ from mercuric oxide and trichloroacetic acid in water.

The trans-addition product is usually observed not only in solvomercuration of simple olefins[14–16] but also in the intramolecular carboxy- and hydroxymercuration of norbornenyl compounds.[17–20] However, the result described here is the first report as to the stereochemistry of intramolecular phenoxymercuration of 2-allylphenols.

Regioselectivity of the Reaction. Since the reversible nature of oxymercuration is well-known,[16,21,22] one could postulate that the formation of **2a** arises from a reversible deoxymercuration of the chroman **3a** (X = OAc) formed first during the reaction or that **3b** arises, similarly, from the dihydrobenzofuran **2b** (X = Cl). However, the following results indicate that no transformation of **3a** → **2a** occurs under the reaction conditions. (1) The acetate **3a** (X = OAc) prepared from **3b** (X = Cl) by treatment with AgOAc was stable in water in the presence of 1 equiv of HOAc. (2) The mercurial **3a** could be recovered unchanged after being added to a solution of **1** and $Hg(OAc)_2$ in water. Similarly, the dihydrobenzofuran **2b** (X = Cl) was not transformed into the chroman **3b** under the reaction conditions. Therefore, the mercurials **2a** (X = OAc) and **3b** (X = Cl) obtained are not interconvertible under the reaction conditions used.

In view of the results so far described, we propose that the difference of regioselectivity observed here may be ascribed to the electronic effect of the anionic ligands of HgX_2. A similar interpretation has been given for the stereospecificity of oxymercuration of allenes[23] and the stereoselectivity of the cyclopropane ring-opening reaction using mercuric salts.[24]

On the basis of mercurinium ion intermediate **6**, resulting from the electrophilic attack of Hg(II) at the double bond of **1**,[6,16] the present result would be rationalized as follows. When a more electronegative ligand, e.g., X = Cl, is attached to the Hg atom, carbenium ion character will increase at the C-3 carbon of the intermediate **6** because the development of a positive charge at the C-2 carbon is probably unfavored by the electron-withdrawing inductive effect of the neighboring phenoxy group. Therefore, the nucleophilic attack occurs predominantly at the C-3 carbon, leading to the chroman **3b**. A similar inductive effect which has been noted to affect the regioselectivity of nucleophilic scission of 3-methoxycyclohexene oxide[25] may support this explanation.

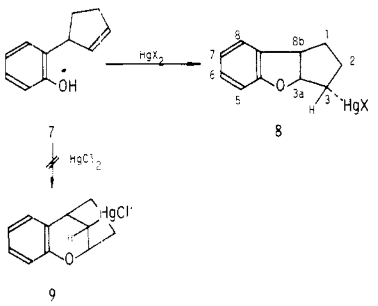


6

On the other hand, when the ligand is the less electronegative acetate (X = OAc), the positive charge on **6** will not be localized at a carbon atom, and the internal nucleophile will prefer to attack at the more sterically accessible C-2 position, forming the dihydrobenzofuran **2a**. The attack at this position could be conceivably facilitated by an interaction between the phenolic oxygen atom and the Hg atom as a specific directing effect[26–30] or by formation of an aryloxy–mercuric acetate species (ArO–HgOAc), as has been proposed in the cyclization of 2′-hydroxychalcones using $Hg(OAc)_2$.[31] However, such processes do not appear to be compatible with the trans stereochemistry of the addition product **2a**.

The dependence of regioselectivity on the electron-withdrawing property of the acetoxy ligands on Hg(II) as shown in Table I can be thus regarded as reflecting the extent of a localization of the positive charge on the carbon atoms.

The results obtained from the mercuration of 2-(2-cyclopentenyl)phenol (**7**) are also relevant to a discussion of regioselectivity. Thus, the reaction of **7** with $Hg(OAc)_2$ gave the acetoxymercuric dihydrobenzofuran **8a** (X = OAc, 60%) as expected, but the use of $HgCl_2$ also led to a dihydrobenzofuran **8b** (X = Cl, 65%), and no chroman **9** was formed (see Scheme II). Models indicate **9** to be a highly strained structure, and therefore a process leading to **9** is energetically unfavorable. The stereochemistry of the addition step in these reactions is also antarafacial since the observed $J(\text{Hg–H})_{vic}$ of 144 Hz for H_{3a} in the NMR spectra of **8a** and **8b** is the same as that of the mercurated dihydrobenzofurans **2a** and **2b**. Further, Scheme II



a, X = OAc; b, X = Cl

the acetate **8a** can be converted into the same chloride **8b** by treatment with NaCl. A cis configuration between the H_{3a} and the H_{8b} proton is indicated by the value of $J(H_{3a}–H_{8b})$ = 7 Hz.[32]

In brief, the regioselectivity of intramolecular phenoxymercuration of 2-allylphenols is largely dependent on the structure of the substrates. In fact, 2-allylphenol itself always gives 2-mercurated methyl-2,3-dihydrobenzofurans, regardless of the nature of the ligands of HgX_2,[5] whereas only 3-mercurated 2,2-dimethylchroman is formed from 2-(3-methyl-2-butenyl)phenol, even with $Hg(OAc)_2$.[2] In the latter reaction, a positive charge developing at the C-3 carbon of the allylic side chain is highly stabilized by the two methyl substituents at this position, while the former reaction will produce the secondary carbenium ion at the C-2 carbon since it is obviously more stable than the primary one at the C-3 carbon. Thus, either the chroman or the dihydrobenzofuran compound is formed in these reactions.

Conclusions

(1) The Hg(II)-mediated cyclization of 2-allylphenols proceeds by an antarafacial addition, as is usually observed in oxymercuration of alkenes. (2) The difference in regioselectivity observed here is ascribed to the electronic effect of the anionic ligands on HgX_2. This result appears to give a rationale to our previous interpretation[2] on the regioselectivity in the Pd(II)-induced cyclization of 2-(3-methyl-2-butenyl)phenol.

Experimental Section

NMR spectra were recorded on a 100-MHz Model JNM-4H-100 (JEOL) spectrometer or on 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 Y. Harada at the Department of Chemistry, Faculty of Engineering Science, Osaka University. All temperatures were uncorrected.

Materials. 2-(2-Cyclohexenyl)-4-methoxyphenol (1) was prepared from 3-bromocyclohexene and *p*-methoxyphenol by the reported procedures.[33] 2-(2-Cyclopentenyl)phenol (7) was similarly prepared from 3-chlorocyclopentene and phenol. Mercuric monochloro- and dichloroacetate were prepared from mercuric oxide (yellow) and the corresponding acetic acids by the known procedures.[34] Preparation of mercuric trichloroacetate was carried out by the same procedures as above, but isolation of this compound was as unsuccessful as that reported in the literature.[34] Accordingly, this reagent was used in situ by preparing it from mercuric oxide and trichloroacetic acid in water. Mercuric trifluoroacetate was obtained by treatment of mercuric oxide with trifluoroacetic acid in the presence of trifluoroacetic anhydride.[35] The other mercuric salts used were commercial products.

Reaction of 1 with HgX_2. 2-(2-Cyclohexenyl)-4-methoxyphenol (**1**, 3 mmol) was added to a solution of mercuric salt (3 mmol) in water (9 mL). The resulting heterogeneous mixture was stirred at 25 °C for 24 h, during which time a heavy, grayish oil setted out. After the aqueous solution was poured off by decantation, a small amount of methanol was added to the residue, and the resulting white precipitate was filtered and dried. The crude reaction product was purified by recrystallization from methanol. From the filtrate only unreacted **1** was recovered.

2a (X = OAc). Into a stirring solution of $Hg(OAc)_2$ (0.960 g, 3 mmol) in water (9 mL) was added **1** (0.612 g, 3 mmol). The resulting precipitate of **2a** (0.828 g, 59%) was recrystallized from methanol: mp 127–128 °C; IR (Nujol) 1590, 1475, 1375, 1307, 1275, 1240, 1220, 1197, 1177, 1150, 1141, 1130, 1090, 1025, 935, 911, 890, 868, 847, 808, 770, 748, 725, 673 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.44–2.42 (m, 6 H), 2.03 (s, 3 H, $OCOCH_3$), 3.09 (ddd, 1 H, J = 7, 8.5, 3.5 Hz, H_4), 3.40 (q, 1 H, J = 7 Hz, H_{9b}), 3.76 (s, 3 H, OCH_3), 4.95 (t, 1 H, J = 7 Hz and $J(^1H–^{199}Hg)$ = 144 Hz, H_{4a}). The assignment of these protons was supported by a double-irradiation experiment. Double irradiation of H_4 (δ 3.09) simplified the signal of H_{4a} (δ 4.95) to show a doublet (J = 7 Hz). The signal of H_{4a} was also transformed into a doublet (J = 7 Hz) by irradiating the C_{9b} proton (δ 3.40). Double irradiation of H_{4a} simplified both the signals of H_4 and H_{9b} to show a double doublet (J = 3.5, 8.4 Hz) and a triplet (J = 7 Hz), respectively.

Anal. Calcd for $C_{15}H_{18}O_4Hg$: C, 38.89; H, 3.89. Found: C, 38.50; H, 3.85.

3b (X = Cl). Into a stirring solution of $HgCl_2$ (1.310 g, 5 mmol) in water (15 mL) was added **1** (1.620 g, 5 mmol). The reaction gave a 53% yield of **3b**. Recrystallization from methanol afforded an analytically pure sample of **3b:** mp 201–202 °C; IR (Nujol) 1490, 1425, 1365, 1353, 1335, 1320, 1307, 1263, 1240, 1210, 1183, 1145, 1102, 1080, 1043, 1020, 995, 950, 935, 895, 882, 830, 802, 750, 720, 700 cm^{-1}; NMR (60 MHz) δ ($CDCl_3$) 1.4–2.3 (m, 6 H), 3.26 (m, 2 H), 3.73 (s, 3 H, OCH_3), 4.77 (m, 1 H), 6.50 (m, 1 H, phenyl), 6.71 (m, 2 H, phenyl).

Anal. Calcd for $C_{13}H_{15}HgClO_2$: C, 35.52; H, 3.42. Found: C, 35.64; H, 3.45.

3c (X = NO_3). Into a stirring solution of $Hg(NO_3)_2 \cdot H_2O$ (1.000 g, 3 mmol) in water (9 mL) was added **1** (0.612 g, 3 mmol). The resulting precipitate of **3c** (0.730, 53%) was recrystallized from methanol: mp 145 °C dec; IR (Nujol) 1520, 1490, 1443, 1427, 1320, 1303, 1270, 1238, 1205, 1140, 1102, 1080, 1040, 1022, 950, 953, 925, 898, 883, 807, 798, 737, 700 cm^{-1}; NMR (60 MHz) δ ($CDCl_3$) 1.5–2.2 (m, 6 H), 3.28 (m, 1 H), 3.43 (m, 1 H), 3.75 (s, 3 H, OCH_3), 4.78 (m, 1 H), 6.51 (m, 1 H, phenyl), 6.73 (m, 2 H, phenyl).

Anal. Calcd for $C_{13}H_{15}O_5NHg$: C, 33.51; H, 3.25. Found: C, 33.32; H, 3.24.

3d (X = ClO_4). Into a stirring solution of $Hg(ClO_4)_2$ (1.360 g, 3 mmol) in water (9 mL) was added **1** (0.612 g, 3 mmol). No solid product was obtained from this reaction. The resulting oily substance was indicated by NMR to contain only the mercurial **3d** and unreacted starting material **1**. The NMR spectrum (60 MHz) of **3d** as a 1:1 mixture of **3d** and **1** in $CDCl_3$ showed the following resonances: δ 1.4–2.3 (m, 6 H), 3.11 (m, 1 H), 3.30 (m, 1 H), 3.71 (s, 3 H, OCH_3), 4.75 (m, 1 H), 6.45 (m, 1 H, phenyl), 6.67 (m, 2 H, phenyl). Deoxymercuration of this mixture by a manner described below gave the chroman **5**, and no dihydrobenzofuran **4** was obtained.

2e and 3e (X = $OCOCH_2Cl$). Into a stirring solution of $Hg(OCOCH_2Cl)_2$ (1.164 g, 3 mmol) in water (9 mL) was added **1** (0.612 g, 3 mmol). The resulting colorless solid (1.220 g, 79%) was shown by NMR to contain the mercurials **2e** and **3e** in a ratio of 56:44. The mercurated chroman **3e** could be readily separated by recrystallization from methanol. **3e:** mp 141–142 °C; IR (Nujol) 1660, 1600, 1500, 1433, 1400, 1348, 1307, 1262, 1237, 1207, 1145, 1100, 1080, 1040, 995, 948, 932, 890, 882, 833, 805, 778, 700, 685 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.4–2.3 (m, 6 H), 3.24 (m, 2 H), 3.74 (s, 3 H, OCH_3), 4.11 (s, 2 H, $OCOCH_2Cl$), 4.72 (m, 1 H), 6.47 (m, 1 H, phenyl), 6.68 (m, 2 H, phenyl).

Anal. Calcd for $C_{15}H_{17}O_4HgCl \cdot 0.5H_2O$:[36] C, 35.61; H, 3.49. Found: C, 35.56; H, 3.37.

Isolation of **2e** in a pure form was unsuccessful. Repeated recrystallization of the reaction products afforded a 70% purity of **2e**. The following data were deduced from a 3:7 mixture of **2e** and **3e**. **2e:** NMR (100 MHz) δ ($CDCl_3$) 1.4–2.3 (m, 6 H), 2.96–3.54 (m, 2 H), 3.76 (s, 3 H, OCH_3), 4.11 (s, 2 H, $OCOCH_2Cl$), 4.92 (t, 1 H, J = 7 Hz), 6.68 (m, 3 H, phenyl).

Anal. Calcd for $C_{15}H_{17}O_4HgCl \cdot 0.5H_2O$: C, 35.61; H, 3.49. Found: C, 35.55; H, 3.41.

2f and 3f (X = $OCOCHCl_2$). Into a stirring solution of $Hg(OCOCHCl_2)_2$ (1.370 g, 3 mmol) was added **1** (0.612 g, 3 mmol). The resulting colorless solid (0.790 g, 50%) was shown by NMR to contain the mercurials **2f** and **3f** in a ratio of 24:76. The mercurated chroman **3f** could be readily separated by recrystallization from methanol. This compound showed no clear decomposition point, although it started to decompose at 139 °C. **3f:** IR (Nujol) 1675, 1495, 1450, 1335, 1350, 1262, 1240, 1220, 1205, 1145, 1100, 1077, 1035, 993, 945, 885, 868, 835, 805, 782, 756, 700 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.2–2.4 (m, 6 H), 3.24 (m, 2 H), 3.75 (s, 3 H, OCH_3), 4.73 (m, 1 H), 6.00 (s, 1 H, $OCOCHCl_2$), 6.46 (m, 1 H, phenyl), 6.70 (m, 2 H, phenyl).

Anal. Calcd for $C_{15}H_{16}O_4Cl_2Hg$: C, 33.87; H, 3.03. Found: C, 33.84; H, 2.99.

Isolation of **2f** in a pure form was also unsuccessful. The NMR (100 MHz) spectrum of the reaction products showed the following resonances, except for those due to **3f:** ($CDCl_3$) δ 1.2–2.4 (m, 6 H), 3.28–3.60 (m, 2 H), 3.76 (s, 3 H, OCH_3), 4.92 (t, 1 H, J = 8 Hz), 6.00 (s, 1 H, $OCOCHCl_2$), 6.68 (m, 3 H, phenyl).

An elemental analysis showed the mixture to have a formula of $C_{15}H_{16}O_4Cl_2Hg$. Anal. Calcd: C, 33.87; H, 3.03. Found: C, 33.32; H, 2.98.

The formation of **2f** was further confirmed by converting it to the chloride **2b** (X = Cl). Thus, a mixture of the reaction products **2f** and **3f** was treated with NaCl in water, and the resulting crystals were recrystallized from chloroform. The mercurial **3b** was readily crystallized from the solution. Crystals obtained from the mother liquid were found by NMR to contain a 1:1 mixture of **2b** and **3b.**

3g (X = $OCOCCl_3$). A solution of HgO (0.620 g, 3 mmol) and CCl_3COOH (0.980 g, 3 mmol) in water (9 mL) was stirred for 15 min, and then **1** (0.612 g, 3 mmol) was added to this solution. After 24 h, the aqueous solution was decanted, and the residue was dissolved in chloroform. The chloroform solution was filtered and concentrated, leaving an oily substance which was crystallized by adding a small amount of ether. The resulting crystals of **3g** (0.680 g, 40%) were recrystallized from methanol. This compound showed no clear decomposition point, although it started to decompose at 135 °C. **3g:** IR (Nujol) 1670, 1437, 1423, 1360, 1310, 1260, 1235, 1200, 1168, 1140, 1097, 1077, 1045, 993, 945, 878, 865, 830, 815, 760, 695, 680 cm^{-1}; NMR (60 MHz) δ ($CDCl_3$) 1.4–2.3 (m, 6 H), 3.30 (m, 2 H), 3.72 (s, 3 H, OCH_3), 4.73 (m, 1 H), 6.49 (m, 1 H, phenyl), 6.72 (m, 2 H, phenyl).

Anal. Calcd for $C_{15}H_{15}O_4Cl_3Hg$: C, 31.82; H, 2.67. Found: C, 32.76; H, 2.94.

3h (X = $OCOCF_3$). Into a stirring solution of $Hg(OCOCF_3)_2$ (1.280 g, 3 mmol) in water (9 mL) was added **1** (0.612 g, 3 mmol). The resulting amorphous solid was filtered to give a 43% yield of **3h** (0.685 g): mp 124–128 °C; IR (Nujol) 1690, 1585, 1500, 1415, 1380, 1310, 1240, 1190, 1140, 1110, 1080, 1037, 997, 950, 885, 853, 835, 810, 790, 733, 700 cm^{-1}; NMR (60 MHz) δ ($CDCl_3$) 1.4–2.3 (m, 6 H), 3.28 (m, 1 H), 3.75 (s, 3 H, OCH_3), 4.72 (m, 1 H), 6.50 (m, 1 H, phenyl), 6.73 (m, 2 H, phenyl). Owing to the difficulty of purification by recrystallization, no satisfactory analytical data were obtained for this compound.

Sodium Borohydride Reduction of 2a and 3b. Sodium borohydride reduction of **2a** was performed by the procedure of Bordwell and Douglass.[37] A solution of sodium borohydride (0.019 g, 0.5 mmol) in 2.5 M sodium hydroxide was added to a stirring solution of **2a** (0.231 g, 0.5 mmol) in 2 mL of water–ethanol (80:20). The reaction mixture was stirred at room temperature for 20 min and filtered. The aqueous solution was extracted with carbon tetrachloride. The extract was found to contain the dihydrobenzofuran **4** (22%) and the original olefin **1** (57%) by GLC analysis. The two compounds could be separated by means of alumina column chromatography. An analytically pure sample of **4** was obtained by preparative GLC. The spectral data of **4** were identical with those of an authentic sample prepared by the procedure of Fráter and Schmid.[33] **4** (colorless liquid): IR (neat) 2925, 2850, 1600, 1480, 1433, 1430, 1265, 1255, 1215, 1187, 1175, 1130, 1027, 945, 902, 880, 847, 803, 793, 738 cm^{-1}; NMR (100 MHz) δ (CCl_4) 1.12–2.12 (m, 8 H), 3.04 (q, 1 H, J = 7 Hz, H_{9b}), 3.67 (s, 3 H, OCH_3), 4.50 (dt, 1 H, J = 7, 4.5 Hz, H_{4a}), 6.55 (m, 3 H, phenyl). The signal at a lower field (δ 4.50) can be assigned to the tertiary proton (H_{4a}) on the C_{4a} carbon adjacent to the oxygen atom. Thus, the quartet at δ 3.04 is assigned to the benzylic proton of H_{9b}. Double irradiation of cyclohexene protons at δ 1.60 simplified the quartet to a doublet (J = 7 Hz).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 75.76; H, 8.00.

Deoxymercuration of **3b** was carried out in an identical manner with that described above. In this case, a large amount of **3b** remained unreacted. The GLC analysis of the extract showed that the chroman **5** and the original olefin **1** were formed in 19% and 17% yield, respectively, based on the starting material charged. **5** (colorless liquid): IR (neat) 2930, 2850, 1493, 1463, 1463, 1450, 1430, 1302, 1255, 1200, 1153, 1083, 1055, 1040, 962, 927, 825, 807, 740, 695 cm^{-1}; NMR (100 MHz) δ (CCl_4) 1.12–2.00 (m, 8 H), 2.88 (m, 1 H), 3.64 (s, 3 H, OCH_3), 4.46 (m, 1 H), 6.46 (m, 1 H, phenyl), 6.64 (2 H, phenyl).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.38; H, 7.96.

Preparation of Authentic Samples 4 and 5. A solution of **1** (5 mmol) in benzene (300 mL) was irradiated at 10–15 °C for 48 h by means of a 500-W high-pressure mercury lamp. After the solvent was removed, the residue was distilled under reduced pressure to afford a mixture of **4**, **5**, and unreacted **1**. The phenol **1** was removed by washing the mixture with Claisen's alkali. After this treatment, a 45:55 mixture of **4** and **5** was obtained in 19% yield.

Table VI. Summary of X-Ray Diffraction Experiments

	2b	**3b**
Formula	$C_{13}H_{15}O_2HgCl$	$C_{13}H_{15}O_2HgCl$
Formula weight, g	439.3	439.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	8	4
Unit-cell parameters		
a, Å	8.219 (5)	9.075 (3)
b, Å	11.952 (2)	6.726 (3)
c, Å	26.855 (3)	21.144 (4)
β, deg	95.68 (5)	98.59 (5)
V_c, Å^3	2625.1	1276.1
Density (calcd), g/cm^3	2.222	2.286
Crystal dimensions, mm	0.05 × 0.03 × 0.2	0.2 × 0.15 × 0.3
μ, cm^{-1}	243.2	124.7
Radiation	Cu Kα (β filter)	Mo Kα (β filter)
2θ range	$3° < 2\theta < 113°$	$3° < 2\theta < 52.5°$
Scan mode	ω scan	$\omega-2\theta$ scan
Scan range, °ω	$2.4 + 0.15 \tan \theta$	$1.5 + 0.35 \tan \theta$
Reflections measured	4010	2804
Radiation damage	10% in F(obsd)	8% in F(obsd)

Transformation of 2a (X = OAc) into 2b (X = Cl). Into a solution of **2a** (0.46 g, 1 mmol) in methanol (5 mL) was added sodium chloride (0.059 g, 1 mmol) dissolved in a small amount of water. The solution precipitated a white solid which was filtered off after 15 min. An analytically pure sample was crystallized from methanol. **2b:** mp 154–155 °C; IR (Nujol) 1480, 1380, 1330, 1267, 1215, 1195, 1175, 1115, 1082, 1030, 980, 950, 925, 860, 805, 800, 770, 760, 721, 700 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.3–2.2 (m, 6 H), 2.96 (ddd, 1 H, J = 8.5, 7, 4 Hz, H_4), 3.40 (q, 1 H, J = 6.5, 7 Hz, H_{9b}), 3.76 (s, 3 H, OCH_3), 4.91 (t, 1 H, J = 7 Hz and $J(^1H-^{199}Hg)$ = 144 Hz, H_{4a}), 6.68 (m, 3 H, phenyl).

Anal. Calcd for $C_{13}H_{15}HgClO_2$: C, 35.52; H, 3.42. Found: C, 35.35; H, 3.33.

Transformation of 3b (X = Cl) into 3a (X = OAc). To a solution of **3b** (0.439 g, 1 mmol) in acetone (15 mL) was added silver acetate (0.167 g, 1 mmol) dissolved in water, After the solution was stirred for 30 min in the dark, the resulting precipitate (AgCl) was filtered off, and the solvent was removed to leave an amorphous material which could not be crystallized by adding methanol or other solvents. The NMR spectrum of this material showed only the presence of **3a:** IR ($CHCl_3$) 2920, 2830, 1623, 1600, 1363, 1305, 1142, 1076, 947 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.40–2.28 (m, 6 H), 2.04 (s, 3 H, $OCOCH_3$), 3.11 (m, 2 H), 3.71 (s, 3 H, OCH_3), 4.69 (m, 1 H), 6.48 (m, 1 H, phenyl), 6.70 (m, 2 H, phenyl).

Crystallographic Procedures. Crystals **2b** and **3b** were grown from methanol solutions as transparent thin needles and prisms, respectively, which were both slightly light-sensitive. Preliminary oscillation and Weissenberg photographs of both crystals indicated them to be monoclinic. The systematic absences, $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$, uniquely showed the space group to be $P2_1/c$ for both crystals. Accurate cell dimensions were obtained through least-squares refinements of the setting angle of high-angle reflections measured on a four-circle Rigaku automatic diffractometer. Since the crystals of **2b** were very thin needles, the intensity data for this compound were collected using Cu Kα radiation generated from a rotating anode in order to get sufficient diffracted intensities. The intensities for **3b** were obtained with Mo Kα radiation from a sealed tube, and only those reflections whose peak intensities were greater than 10 Hz at the calculated setting positions were collected in order to minimize the radiation damage of this compound. During the course of collection of each data set, the intensities of three monitoring reflections were measured on every 50 reflections. Since the intensities were gradually decreased for both crystals, all the data were corrected using the decay curve obtained from the monitoring reflections. The reflections were also corrected for Lorentz–polarization factors, but not absorption effects. The experimental details are given in Table VI.

The structure of **2b** was solved by a Patterson function and subsequent Fourier synthesis. The positional and anisotropic thermal factors of all nonhydrogen atoms were refined by block-diagonal least squares with unit weights using the 3071 nonzero reflections. The final reliability index, R (defined as $\sum||F_o| - |F_c||/|F_o|$), was 0.073.

The structure of **3b** was solved by means of the automatic crystal structure analysis processing program, developed by Tanaka et al.[38] in 1975, based on the heavy-atom method. Refinements of the atomic parameters for the nonhydrogen atoms using block-diagonal least squares with unit weights led to an *R* of 0.094 for the 1567 nonzero reflections observed.

Reaction of 7 with $Hg(OAc)_2$ or $HgCl_2$. The reaction was carried out in a manner identical with that described in the reaction of 1 with HgX_2. The mercurials **8a** (**a**, X = OAc) and **8b** (**b**, X = Cl) were readily crystallized from methanol. **8a:** 60% yield; mp 116–117 °C; IR (Nujol) 1610, 1480, 1420, 1370, 1295, 1260, 1230, 1200, 1183, 1165, 1155, 1100, 1047, 1015, 1003, 940, 920, 867, 827, 807, 740, 725, 680 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.75–2.32 (m, 4 H), 2.02 (s, 3 H, $OCOCH_3$), 3.16 (m, 1 H, H_3), 3.96 (nearly triplet, 1 H, J = 7.5, H_{8b}), 5.55 (dd, 1 H, J = 7.5, 2 Hz and $J(^1H-^{199}Hg)$ = 144 Hz, H_{3a}), 6.6–7.2 (m, 4 H, phenyl).

Anal. Calcd for $C_{13}H_{14}HgO_3$: C, 37.27; H, 3.38. Found: C, 37.19; H, 3.37.

8b: 65% yield; mp 164–165 °C; IR (Nujol) 1610, 1480, 1420, 1370, 1295, 1260, 1230, 1200, 1183, 1165, 1155, 1100, 1047, 1015, 1003, 940, 920, 867, 827, 807, 740, 725, 680 cm^{-1}; NMR (100 MHz) δ ($CDCl_3$) 1.5–2.4 (m, 4 H), 3.14 (m, 1 H), 3.96 (nearly triplet, 1 H, J = 7.5 Hz, H_{8b}), 5.54 (dd, 1 H, J = 7, 2.5 Hz and $J(^1H-^{199}Hg)$ = 144 Hz, H_{3a}), 6.6–7.2 (m, 4 H, phenyl).

Anal. Calcd for $C_{11}H_{11}OHgCl$: C, 33.42; H, 2.81. Found: C, 33.38; H, 2.85.

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Supplementary Material Available: Tables II and III, listing the final positional and thermal parameters for the nonhydrogen atoms, and Tables IV and V, listing the bond distances and bond angles (5 pages). Ordering information is given on any current masthead page.

Registry No.—**1,** 64252-19-3; **2a,** 64252-20-6; **2b,** 64252-21-7; **2e,** 64252-22-8; **2f,** 64252-23-9; **3a,** 64252-24-0; **3b,** 64252-25-1; **3c,** 64252-26-2; **3d,** 64252-27-3; **3e,** 64252-28-4; **3f,** 64252-29-5; **3g,** 64252-30-8; **3h,** 64252-31-9; **4,** 27124-68-1; **5,** 64252-32-0; **7,** 6627-83-4; **8a,** 64252-33-1; **8b,** 64252-34-2; 3-chlorocyclopentene, 96-40-2; phenol, 108-95-2; $Hg(OAc)_2$, 1600-27-7; $HgCl_2$, 7487-94-7; $Hg(NO_3)_2$, 10045-94-0; $Hg(ClO_4)_2$, 7616-83-3; $Hg(OCOCH_2Cl)_2$, 26719-07-3; $Hg(OCOCHCl_2)_2$, 26788-74-9; HgO, 21908-53-2; CCl_3COOH, 76-03-9; $Hg(OCOCF_3)_2$, 13257-51-7; AgOAc, 563-63-3.

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Addition Reaction of Benzene to α-Substituted Chalcone Derivatives by Means of Palladium(II) Acetate

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The reaction of several α-substituted chalcone derivatives with benzene and acetic acid in the presence of palladium(II) acetate was investigated. When the α substituents are bulky and powerfully electron withdrawing, such as benzoyl, nitro, ethoxycarbonyl, and carboxyl groups, the addition of benzene to their carbon–carbon double bond occurs. The formation of the benzene adducts proceeded catalytically with respect to palladium(II) acetate. A mechanism involving the carbanion derived from heterolytic fission of the initially formed intermediate σ-palladium complex is suggested.

The aromatic substitution reaction of olefins by use of palladium(II) salts has received wide attention since Moritani and Fujiwara et al.[1] and Heck et al.[2] independently reported their pioneering work. In the previous work on the Moritani–Fujiwara arylation, the authors reported that electron-withdrawing groups such as a nitro on the olefinic carbon atom affect the arylation very strongly[3] and that β-substituted β-methylstyrenes did not give the usual phenylation compounds, but exclusively the corresponding β-diphenylmethylstyrenes because of a steric effect.[4] In the present paper is described a novel catalytic addition reaction of benzene to the carbon–carbon double bond of some α-substituted chalcones in the

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