Cesium Fluoride-Mediated Claisen Rearrangement of Aryl Propargyl Ether. Exclusive Formation of 2-Methylarylfuran and Its Availability as a Masked Salicylaldehyde[1)]

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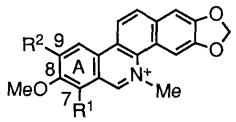
Claisen rearrangement of an aryl propargyl ether in the presence of CsF led to exclusive formation of 2-methylarylfuran in excellent yield. The result of a precise examination of the rearrangement is described. Satisfactory transformation of the 2-methylarylfuran to a salicylaldehyde derivative was achieved by stepwise oxidation. This combination of reactions serves as a useful method for regioselective introduction of a C_1 unit at the *ortho* position of a phenol group.

Keywords cesium fluoride; Claisen rearrangement; aryl propargyl ether; arylpyran; 2-methylarylfuran; furan ring cleavage; osmium tetroxide oxidation; masked salicylaldehyde

We have established a general synthetic method for the preparation of benzo[*c*]phenanthridine alkaloids[2)] showing anti-tumor activity. However, our method lacks applicability to the synthesis of 7,8-dialkoxy alkaloids such as chelerythrine (**1**) because the Bischler–Napieralski reaction, one of the key steps in the method, caused cyclization to the position *para* to the alkoxy group to yield 8,9-dialkoxy alkaloids such as nitidine (**2**). In the course of studies on the chemical constituents of Rutaceous plants, it became necessary to synthesize **1**. The best route for the synthesis of this target may be *via* lithiation of the phenyl ring. However, such an approach is generally not only unsuitable for large scale operation, but also less regioselective when applied to more functionalized aromatics.[3)]



1:R^1=OMe, R^2=H

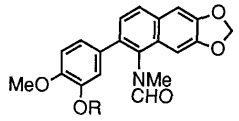
2:R^1=H, R^2=OMe

Thermal Claisen rearrangement of aryl propargyl ethers has been recognized as a general method for the preparation of arylpyrans[4)] since observation of the rearrangement by Iwai and Ide.[5)] In addition, Schmid and co-workers[6)] have reported generation of salicylaldehyde derivatives from 3,4-dihydroxy-2,2-dimethylbenzopyran derivatives. Thus, it is possible to introduce a C_1 unit regioselectively at the *ortho* position of a phenolic group by successive Claisen rearrangement of aryl propargyl ethers followed by oxidative cleavage of the pyran ring in the arylpyran products. We therefore planned to apply this strategy selectively to construct the tetra substituted pattern of ring A in **1**.

After a detailed examination of the Claisen rearrangement of an aryl propargyl ether (**4**), we discovered that the isomeric 2-methylarylfuran (**6**), but not the desired arylpyran (**5**), was exclusively formed on Claisen rearrangement in the presence of cesium fluoride (CsF). In this paper we present full details of the CsF-mediated Claisen rearrangement and the availability of the formed 2-methylarylfuran as a masked salicylaldehyde derivative.

Results and Discussion

It is known that tertiary propargyl ethers are the best substrates for thermal Claisen rearrangement.[7)] However, preparation of the tertiary ether[8)] can be tedious, although a synthetic approach has been described for coumarin derivatives.[9)] Strategically, therefore, a primary ether seemed to be the most suitable candidate for Claisen rearrangement because of its simple preparation. Thus we focussed on Claisen rearrangement of the primary propargyl ether (**4**)[10)] obtained quantitatively by treatment of the phenol (**3**)[11)] with propargyl bromide. However, Claisen rearrangement of **4**[12,13)] under various conditions resulted in little or no formation of the desired arylpyran (**5**),[12,13)] (mp 225 °C (softened at 200 °C) (Table I)), which showed coupled 1H multiplets due to olefinic protons of the pyran



3: R=H

4: R=CH_2-C≡CH

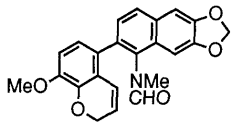


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TABLE I. Effect of Reaction Solvent upon the Yield (%) of the Pyran (**5**) from the Ether (**4**)

No.	Solvent	**4**/solvent (g/ml)	Additive (mol eq)	Conditions (°C/h)	Yield (%)
1	$PhNEt_2$	0.1		Reflux/7.5	17.6
2	HMPT[a)]			200/6	0[c)]
3	DEG[b)]			1.180/9; 2.200/8	0[d)]
4	$CHCl_3$	0.05	$AgBF_4$[e)] (2.4)	65/18.5	0[d)]

a) HMPT = hexamethylphosphoric triamide. *b*) DEG = diethyleneglycol. *c*) Formation of phenol (**3**). *d*) Formation of complex mixture. *e*) See ref. 14.

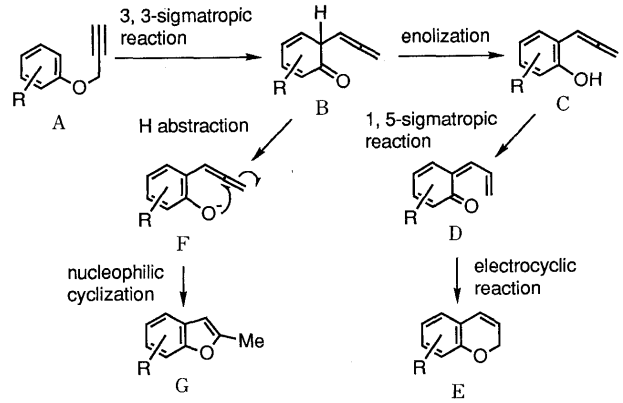


Chart 1

ring at δ 5.7 and 6.0 in the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum.

Chart 1 shows the accepted mechanism[15] for formation of arylpyran (E) from aryl propargyl ether (A) under the condition of Claisen rearrangement. The Claisen rearrangement was carried out in the presence of equimolar CsF, which possesses the ability to hydrogen bond,[16] on the basis of speculation that smooth cyclization to arylpyran (E) should be observed if the enolization of α-allenylketone (B) could be accelerated.

When diphenyl ether was used as a solvent the reaction smoothly proceeded to give a single cyclized product (**6**),[12,13] mp 233—235 °C, in 61.7% yield,[17] but not the expected **5** (Chart 2). The ^{1}H-NMR spectrum of **6** showed characteristic signals attributed to a methyl group and a proton on the furan ring in 2-methylbenzofuran at δ 2.44 and 6.10 as a 3H fine doublet (J=0.6 Hz) and 1H singlet,[18] respectively. These facts allowed us to deduce that **6** was a 2-methylarylfuran derivative, suggesting that a primary aryl propargyl ether would be favorably disposed to 2-methylarylfuran cyclization under the condition of Claisen rearrangement in the presence of CsF. Since thermal Claisen rearrangement of β-naphthyl propargyl ether (**7**) had been observed to yield β-naphthylpyran (**8**), this new type of reaction was fully investigated using **7** in place of **4**.

Initially the thermal rearrangement was reexamined. Heating the ether (**7**)[19] at reflux in *N*,*N*-diethylaniline ($PhNEt_2$) gave the unstable naphthopyran (**8**)[5,20a] as the sole product in 88.5% yield. Compound **7** was next subjected to the CsF-mediated Claisen rearrangement in various solvents as a preliminary experiment (Table II). The naphthofuran (**9**)[20] was generated in each case and was isolated in high yield together with minute amounts of **8** when $PhNEt_2$ was used (entry 4). The use of sulfolane led to exclusive formation of **9**, but the yield was lower than that in $PhNEt_2$ (entry 5). Thus, $PhNEt_2$ was selected as the solvent for the reaction due to not only its contribution to arylfturan cyclization but also its easy removal from the reaction mixture by acid extraction.

The effects of varying the relative amount of CsF and presence of additives other than CsF were studied (Table III). The table shows that a catalytic amount of CsF was sufficient to produce the furan (**9**) (entry 1). However, in spite of its low solubility[21] in $PhNEt_2$ the use of equimolar CsF is recommended to obtain **9** in consistently high yield. Furthermore, CsF was demonstrated to play a crucial role in specific arylfuran cyclization in the Claisen rearrangement by the facts that use of a large excess of other metal fluorides (entries 5—8) or cesium chloride (entry 9) as additives resulted in no formation of **9** and that addition of tetra-*n*-butylammonium fluoride as a non-metal fluoride (entry 10) led to poor conversion[22] of **7** to the pyran (**8**) and the furan (**9**).

Since cyclization of an aryl propargyl ether to a 2-methylarylfuran has been observed under basic conditions[20a,23] we examined Claisen rearrangement in the presence of a variety of bases (Table IV). Schmid and co-workers[20a] have reported that potassium carbonate in sulfolane is effective for formation of the 2-methylfuran (**9**), but not in $PhNEt_2$. However, in our case this base in $PhNEt_2$ was also found to contribute to formation of the arylfuran (entry 3). These facts allowed us to rationalize favored arylfuran cyclization in the CsF-mediated Claisen rearrangement of an aryl propargyl ether by supposing that abstraction of the α-hydrogen atom in the α-allenylketone

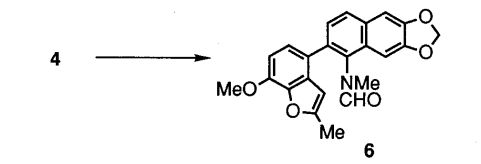
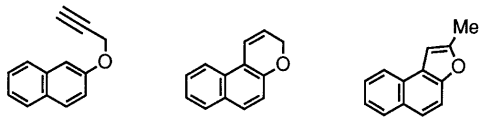


Chart 2



7 8 9

TABLE II. Claisen Rearrangement of the Ether (**7**) in the Presence of CsF[a]

No.	Solvent[b]	Condition (°C/h)	Yield (%)	
			8	**9**
1	Tetralin	100/3	++[c]	+[d]
2	Mesitylene	Reflux/4	++[c]	+[d]
3	Ph_2O	1.150/1; 2.180/3	+[d]	++[c]
4	$PhNEt_2$	Reflux/1	4.3	88.4
5	Sulfolane	200/1	0	56.9

a) A roughly equimolar amount (1.4 eq) of CsF to **7** was used. *b*) Compound **7** (0.1 g) was dissolved in the solvent (1 ml). *c*) The product was detected on TLC as a main component. *d*) The product was detected on TLC as a minor component.

TABLE III. Claisen Rearrangement of the Ether (**7**) in $PhNEt_2$ in the Presence of Additives[a]

No.	Additive (mol eq)		Additive/$PhNEt_2$ (g/ml)	Yield (%)	
				8	**9**
1	CsF	0.01	8.3×10^{-4}	25.4	59.6
2		0.1	8.3×10^{-3}	6.8	84.6
3		1.4	1.2×10^{-1}	4.3	88.4
4		10.0	8.4×10^{-1}	2.2	85.7
5	KF	26.3	8.5×10^{-1}	84.0	(+)[b]
6	RbF	14.6	8.4×10^{-1}	97.3	(+)[b]
7	CaF_2	19.4	8.3×10^{-1}	85.7	(+)[b]
8	BaF_2	8.7	8.5×10^{-1}	86.8	(+)[b]
9	CsCl	9.1	8.4×10^{-1}	88.8	(+)[b]
10	$(n\text{-Bu})_4NF$	5.8	8.4×10^{-1}	2.8	7.2

a) Compound **7** (0.1 g) was dissolved in $PhNEt_2$ (1 ml) and the solution was refluxed for 1 h. *b*) The product was faintly detected on TLC.

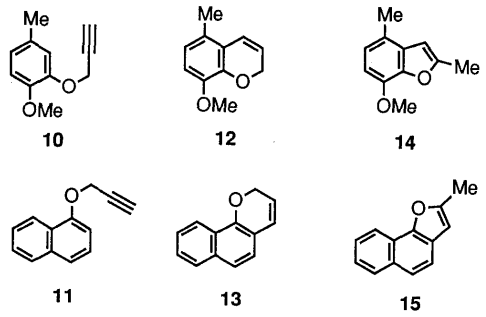
TABLE IV. Claisen Rearrangement of the Ether (**7**) in the Presence of Base[a]

No.	Solvent	Base (mol eq)	Base/solvent (g/ml)	Yield (%)	
				8	**9**
1	$PhNEt_2$	KOH (7.3)	2.6×10^{-1}	0	18.7
2		$NaHCO_3$ (19.2)	8.9×10^{-1}	72.2	6.9
3		K_2CO_3 (11.0)	8.4×10^{-1}	48.0	42.5
4	Sulfolane	K_2CO_3 (3.7)	1.4×10^{-1}	0	76.1[b]

a) Compound **7** (0.1 g) was dissolved in the solvent (1 ml) and refluxed for 1 h. *b*) In ref. 20*a* a lower yield (44%) was reported.

TABLE V. Thermal or the CsF-Mediated Claisen Rearrangements of the Ethers (**10** and **11**)

Ether (**10** or **11**)	Ether/$PhNEt_2$ (g/ml)	CsF (mol eq)	CsF/$PhNEt_2$ (g/ml)	Conditions (°C/h)	Yield (%) Pyrans	Yield (%) Furans
10	0.1	1.3	1.1×10^{-1}	Reflux/4	**12** 69.2	**14** 0
				Reflux/8	**12** 0	**14** 80.2
11	0.25	1.4	1.2×10^{-1}	180/4.5	**13** 62.0	**15** 0
	0.1			180/6	**13** 15.4	**15** 19.5



(B) with CsF results in nucleophilic attack of the phenolate (F) at the central carbon atom of the allenyl group in the molecule as shown in Chart 1.

For the purpose of extension of the reaction, other propargyl ethers (**10** and **11**)[24] were subjected to the CsF-mediated Claisen rearrangement after recognition of generation of the pyrans[25] (**12** and **13**)[26] in thermal rearrangement (Table V). Though in the case of the ether (**11**) the furan (**15**)[27] was produced along with the pyran (**13**), it was clear that CsF strongly contributed to furan cyclization since no formation of the furans (**14** and **15**) was observed in thermal rearrangement without CsF in each case. Thus, the CsF-mediated Claisen rearrangement has been confirmed to serve as a generally applicable reaction for 2-methylarylfuran formation from an aryl propargyl ether.

Oxidation with ozone or chromic acid has been used for cleavage of the furan ring in benzofuran derivatives.[28] However, in our case ozone seems to be an unsuitable reagent because our substrate contains an additional electron-rich aromatic ring oxidizable with ozone in the molecule. Therefore we examined oxidation of the furan ring in 2-methylbenzofuran using reagents other than ozone. 7-Methoxy-2,4-dimethylbenzofuran (**14**) was used as a model compound for the oxidation.

While oxidations with chromic acid, permanganate, peracid, or periodate resulted in either recovery of the starting material or generation of complex mixtures, those with osmium tetroxide (OsO_4) gave oxidized products according to the conditions used (Table VI).

Sodium metaperiodate and a catalytic amount of OsO_4[29] followed by hydrolysis transformed the furan (**14**) to the desired 3-methoxy-6-methylsalicylaldehyde (**18**) in poor yield (entry 1). Treatment of **14** with a stoichiometric amount of OsO_4 in pyridine or in diethyl ether containing pyridine led to formation of the same osmate, which was decomposed by acidic sodium hydrogen sulfite to afford the alcohol (**16**) in satisfactory yield (entry 2). Interestingly, decomposition of the osmate under basic conditions gave

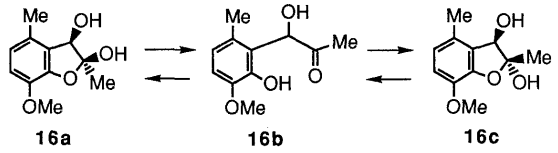


TABLE VI. Oxidation of the Furan (**14**) with Osmic Acid

No.	Reagent (mol eq)	Solvent	Conditions (°C/h)	Product (%)
1	OsO_4–$NaIO_4$ (0.2–2.0)	Dioxane–H_2O	r.t./24	**18**: 22.7
2	OsO_4 (1.2)	Pyridine	r.t./3	**16**: 88.2[a]
3	OsO_4 (1.3)	Et_2O–pyridine	r.t./24	**17**: 65.9[b]
4	OsO_4–NMMO (0.06—4.9)	*tert*-BuOH–pyridine	Reflux/27	**17**: 20.3

a) The osmate ester was decomposed with sodium hydrogen sulfite. *b*) The osmate ester was decomposed with sodium sulfite. r.t. = room temperature.

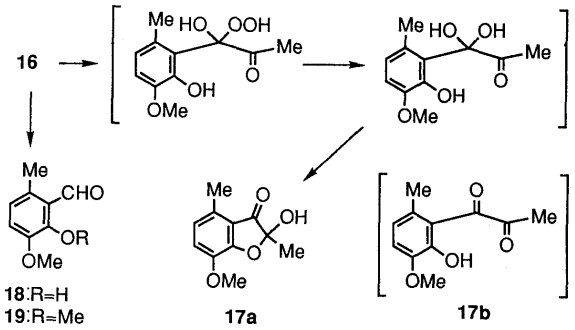


Chart 3

the ketone (**17**) instead of **16** (entry 3). Generation of the ketone was also found when a catalytic amount of OsO_4 in the presence of *N*-methylmorpholine *N*-oxide (NMMO)[30] was used (entry 4). The structures of the products were confirmed by spectroscopic analysis. Though two structures (**17a** and **17b**) could be drawn for the ketone (**17**), its ^{1}H-NMR spectrum showed a single signal of an aliphatic methyl group due to the cyclic structure (**17a**) at δ 1.65. On the other hand an aliphatic methyl group of the alcohol (**16**) appeared at δ 1.64, 1.78, and 2.10 as separated signals attributable to the cyclic structures (**16a** and **16c**) and the open form (**16b**) in the ratio of 4 : 1 : 10, respectively in the ^{1}H-NMR spectrum, indicating that **16** exists as an equilibrium mixture in solution.

Formation of the ketone (**17**) is reasonably explained by assuming that the alcohol (**16**) could be further oxidized by air in alkaline medium to give **17** (Chart 3). This assumption was supported by the fact that **17** was formed by treatment of **16** with 10% sodium carbonate solution.

Transformation of the alcohol (**16**) to the desired salicylaldehyde (**18**) was directly accomplished by oxidation with sodium metaperiodate followed by alkaline hydrolysis (Chart 3). Compound **18**, obtained as a yellow oil, was characterized as the methyl ether (**19**).

Thus, regioselective introduction of a C_1 unit at the *ortho* position of a phenolic group has been achieved through the CsF-mediated Claisen rearrangement of an aryl propargyl ether followed by oxidative cleavage of the furan ring of the resultant 2-methylarylfuran. We have succeeded in the total synthesis of chelerythrine (**1**)[31] by applying this method. 2-Methylarylfurans are relatively stable under various reaction conditions due to their aromaticity. In other

words, the furan ring in 2-methylfuran can act as not only a source of C_1 unit but also a protecting group for phenol. Further applications of this method to the synthesis of other natural products having four sequentially substituted benzene ring are in progress.

Experimental

All melting points were measured on a micro melting-point hot stage (Yanagimoto) and are uncorrected. Infrared (IR) spectra were recorded for Nujol mulls on a Hitachi 260-10 or JASCO IR-700 spectrophotometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ solution with a JEOL FX- or GX-270 (270 MHz) or Hitachi R-24B (60 MHz) spectrometer, unless otherwise stated, with tetramethylsilane as internal reference. Peak multiplicities are quoted in Hz as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), double double doublet (ddd), and multiplet (m). Mass spectra (MS) were measured with a Hitachi M-60 spectrometer using a direct inlet system. For column and flash chromatography, Silica gel 60 (70—230 mesh ASTM, Merck) and Silica gel 60 (230—400 mesh ASTM, Merck) were used, while for thin layer chromatography (TLC) and preparative TLC (PLC), DC-Fertigplatten SIL-G 25 UV 254 (Macherey–Nagel) and Silica gel GF_{254} (Merck) were used. CsF was heated and powdered under argon before use.

Preparation of Aryl Propargyl Ethers. General Procedure A mixture of the phenol, propargyl bromide, and potassium carbonate in dimethylformamide or acetone was stirred. After addition of ethyl acetate or diethyl ether the mixture was washed with 5% aqueous sodium hydroxide and brine, dried, and evaporated. The crude product was purified by recrystallization, distillation, or column chromatographpy.

2-[4-Methoxy-3-(2-propynyloxy)phenyl]-1-(*N*-methylformamido)-6,7-methylenedioxynaphthalene (4) A mixture of the phenol (**3**)[11] (0.432 g, 1.23 mmol), propargyl bromide (0.185 g, 1.56 mmol), and potassium carbonate (0.255 g, 1.84 mmol) in dimethylfomamide (4.5 ml) was allowed to react at room temperature for 1.5 h. The ethyl acetate solution was dried over $MgSO_4$ and recrystallization gave colorless prisms (0.467 g, 97.6%) (from benzene–hexane), mp 140—143 °C (softened at 132 °C). *Anal.* Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 71.04; H, 4.94; N, 3.57. IR ν_{max} cm^{-1}: 3215 (C≡CH), 1670 (CO). ^{1}H-NMR (270 MHz) δ: 2.47 (1/6H, t, J=2.3 Hz, C≡CH), 2.52 (5/6H, t, J=2.3 Hz, C≡CH), 2.93 (1/2H, s, NMe), 3.04 (5/2H, s, NMe), 3.915 (5/2H, s, OMe), 3.924 (1/2H, s, OMe), 4.77 (2H, d, J=2.3 Hz, OCH_2C), 6.07 (1/3H, fine d, OCH_2O), 6.09 (5/3H, s, OCH_2O), 6.92—6.98 (2H, m, ArH), 7.01 (1H, d, J=1.7 Hz, 2′-H), 7.08 (5/6H, s, 5-H), 7.11 (1/6H, s, 5-H), 7.18 (1/6H, s, 8-H), 7.20 (5/6H, s, 8-H), 7.34 (1/6H, d, J=8.6 Hz, 4-H), 7.36 (5/6H, d, J=8.6 Hz, 4-H), 7.73 (1H, d, J=8.6 Hz, 3-H), 8.15 (5/6H, s, NCHO), 8.39 (1/6H, s, NCHO).

2-(2-Propynyloxy)naphthalene (7) A mixture of β-naphthol (5.09 g, 35.3 mmol), propargyl bromide (5.43 g, 45.7 mmol), and potassium carbonate (6.38 g, 46.2 mmol) in acetone (23 ml) was refluxed for 6.5 h. The ethereal solution was dried over K_2CO_3. Column chromatography with hexane–benzene (20:1) as the eluant gave colorless plates (5.86 g, 91.0%), mp 56.5—57 °C (lit. mp 62 °C[19]; mp 58.8—58.9 °C[20a]). This product was distilled at bp 78—83 °C (1 mmHg). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.47; H, 5.58. IR ν_{max} cm^{-1}: 3280 (C≡CH). ^{1}H-NMR (270 MHz) δ: 2.55 (1H, t, J=2.5 Hz, C≡CH), 4.81 (2H, d, J=2.5 Hz, OCH_2C), 7.19 (1H, dd, J=8.9, 2.7 Hz, 3-H), 7.24 (1H, d, J=2.7 Hz, 1-H), 7.35 (1H, ddd, J=8.2, 7.0, 1.2 Hz, 6- or 7-H), 7.45 (1H, ddd, J=8.6, 7.0, 1.2 Hz, 7- or 6-H), 7.74—7.79 (3H, m, 4-, 5-, and 8-H).

4-Methoxy-3-(2-propynyloxy)toluene (10) A mixture of 2-methoxy-5-methylphenol (isocreosol) (5.50 g, 39.8 mmol), propargyl bromide (6.62 g, 55.7 mmol), and potassium carbonate (8.25 g, 59.7 mmol) in dimethylformamide (28 ml) was reacted at room temperature for 5 h. The ethereal solution was dried over K_2CO_3. Distillation at 100—110 °C (5 mmHg) gave a colorless solid (5.62 g, 80.3%), mp 36.5—38 °C. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.54; H, 6.85. IR ν_{max} cm^{-1}: 3275 (C≡CH), 2110 (C≡C). ^{1}H-NMR (60 MHz) δ: 2.29 (3H, s, ArMe), 2.48 (1H, t, J=2.7 Hz, C≡CH), 3.83 (3H, s, OMe), 4.72 (2H, d, J=2.7 Hz, OCH_2C), 6.77 (2H, s, ArH×2), 6.85 (1H, s, ArH).

1-(2-Propynyloxy)naphthalene (11) A mixture of α-naphthol (5.01 g, 34.8 mmol), propargyl bromide (5.39 g, 45.3 mmol), and potassium carbonate (6.27 g, 45.3 mmol) in acetone (24 ml) was refluxed for 4 h. The ethereal solution was dried over K_2CO_3. Column chromatography with hexane as the eluant gave a pale yellow oil (5.10 g, 80.4%), which was distilled at 70—75 °C (1 mmHg) (lit.[24] bp 76 °C (0.12 mmHg)). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.78; H, 5.61. IR ν_{max} cm^{-1}: 3300 (C≡CH). ^{1}H-NMR (270 MHz) δ: 2.54 (1H, t, J=2.4 Hz, C≡CH), 4.89 (2H, d, J=2.4 Hz, OCH_2C), 6.94 (1H, dd, J=7.6, 0.9 Hz, 2-H), 7.38 (1H, q, J=7.6 Hz, 3-H), 7.43—7.53 (3H, m, ArH×3), 7.80 (1H, m, 5-H), 8.26 (1H, m, 8-H).

Thermal Claisen Rearrangement of Aryl Propargyl Ethers. General Procedure A solution of the ether in $PhNEt_2$ was heated under argon and then diluted with ethyl acetate or diethyl ether. The mixture was washed with 5% hydrochloric acid and brine, dried over K_2CO_3, and evaporated. The residue was purified by PLC or column chromatography.

Rearrangement of the Ether (4): 2-[5-(8-Methoxy-2*H*-benzo[*b*]pyranyl)]-1-(*N*-methylformamido)-6,7-methylenedioxynaphthalene (5) A solution of **4** (0.057 g, 0.15 mmol) in $PhNEt_2$ (0.5 ml) was gently refluxed for 7.5 h and diluted with ethyl acetate. PLC with hexane–ethyl acetate (2:1) as the developing solvent gave slightly brown needles (0.010 g) (from MeOH), mp 225 °C (softened at 200 °C). *Anal.* Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.75; H, 4.94; N, 3.57. IR ν_{max} cm^{-1}: 1680 (CO). ^{1}H-NMR (270 MHz) δ: 2.90 (3/2H, s, NMe), 3.03 (3/2H, s, NMe), 3.905 (3/2H, s, OMe), 3.910 (3/2H, s, OMe), 4.82—4.87 (2H, m, $OC\underline{H}_2CH$), 5.69—5.77 (1H, m, $CH=C\underline{H}CH_2$), 5.97—6.05 (1H, m, $ArC\underline{H}=CH$), 6.10 (2H, s, OCH_2O), 6.65 (1/2H, d, J=8.2 Hz, 7′-H), 6.69 (1/2H, d, J=8.2 Hz, 7′-H), 6.82 (1H, d, J=8.2 Hz, 6′-H), 7.06 (1/2H, s, 5-H), 7.07 (1/2H, s, 5-H), 7.21 (1H, s, 8-H), 7.22 (1/2H, d, J=8.2 Hz, 4-H), 7.24 (1/2H, d, J=8.2 Hz, 4-H), 7.71 (1H, d, J=8.2 Hz, 3-H), 7.97 (1/2H, s, NCHO), 8.18 (1/2H, s, NCHO).

Rearrangement of the Ether (7): 3*H*-Naphtho[2,1-*b*]pyran (8) A solution of **7** (0.552 g, 3.03 mmol) in $PhNEt_2$ (5.5 ml) was refluxed for 1 h and diluted with diethyl ether. Column chromatography with hexane as the eluant gave colorless needles (0.489 g), mp 37.5—39 °C (lit. mp 40—41.5 °C[5a]; mp 35—38.5 °C[20a]; mp 32—33 °C[32]). This product was distilled at bp 115 °C (1 mmHg) (lit.[20a] bp 110 °C (0.25 Torr)). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.44; H, 5.58. ^{1}H-NMR (270 MHz) δ: 4.85 (2H, dd, J=3.8, 1.3 Hz, 3-H_2), 5.89 (1H, dt, J=9.9, 3.8 Hz, 2-H), 7.05 (1H, d, J=8.9 Hz, 5-H), 7.11 (1H, d, J=9.9 Hz, 1-H), 7.33 (1H, t, J=8.0 Hz, 8-H), 7.46 (1H, dt, J=8.0, 1.3 Hz, 9-H), 7.63 (1H, d, J=8.9 Hz, 6-H), 7.73 (1H, d, J=8.0 Hz, 7-H), 7.91 (1H, d, J=8.0 Hz, 10-H).

Rearrangement of the Ether (10): 8-Methoxy-5-methyl-2*H*-benzo[*b*]pyran (12) A solution of **10** (0.117 g, 0.67 mmol) in $PhNEt_2$ (1.2 ml) was refluxed for 4 h and diluted with diethyl ether. PLC with hexane–diethyl ether (5:1) as the developing solvent gave a yellow oil (0.081 g), which was distilled at bp 150—160 °C (14 mmHg). *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.83; H, 6.83. ^{1}H-NMR (60 MHz) δ: 2.23 (3H, s, 5-Me), 3.83 (3H, s, OMe), 4.78 (2H, dd, J=4.0, 1.9 Hz, 2-H_2), 5.81 (1H, dt, J=9.8, 4.0 Hz, 3-H), 6.58 (1H, dt, J=9.8, 1.9 Hz, 4-H), 6.65 (2H, s, 6- and 7-H).

Rearrangement of the Ether (11): 2*H*-Naphtho[1,2-*b*]pyran (13) A solution of **11** (0.466 g, 2.56 mmol) in $PhNEt_2$ (1.9 ml) was heated at 180 °C (bath temperature) for 4.5 h and diluted with diethyl ether. Column chromatography with hexane as the eluant gave a pale yellow oil (0.289 g), which was distilled at bp 65—70 °C (1 mmHg). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.42; H, 5.57. ^{1}H-NMR (270 MHz) δ: 4.99 (2H, dd, J=3.7, 1.7 Hz, 2-H_2), 5.79 (1H, dt, J=9.8, 3.7 Hz, 3-H), 6.52 (1H, dt, J=9.8, 1.7 Hz, 4-H), 7.12 (1H, d, J=8.1 Hz, 5- or 6-H), 7.34 (1H, d, J=8.1 Hz, 6- or 5-H), 7.38—7.45 (2H, m, 8- and 9-H), 7.82 (1H, m, 7-H), 8.12 (1H, m, 10-H).

Claisen Rearrangement of Aryl Propargyl Ethers in the Presence of CsF. General Procedure A suspension of the ether and CsF in diphenyl ether, $PhNEt_2$, or sulfolane was heated under argon with stirring and then diluted with diethyl ether. After removal of the insoluble material by filtration, the filtrate was washed with 5% hydrochloric acid and brine, dried over K_2CO_3, and evaporated. The residue was purified by PLC or column or flash chromatography.

Rearrangement of the Ether (4) in Diphenyl Ether: 2-[4-(7-Methoxy-2-methyl-2*H*-benzo[*b*]furanyl)]-1-(*N*-methylformamido)-6,7-methylenedioxynaphthalene (6) A suspension of **4** (0.304 g, 0.78 mmol) and CsF (0.165 g, 1.09 mmol) in diphenyl ether (3 ml) was heated at 200 °C (bath temperature) for 50 h, diluted with chloroform, and washed with water. Column chromatography with hexane–ethyl acetate (2:1) as the eluant gave colorless prisms (0.187 g) (from $CHCl_3$–MeOH), mp 233—235 °C. *Anal.* Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.68; H, 4.97; N, 3.58. IR ν_{max} cm^{-1}: 1670 (CO). ^{1}H-NMR (270 MHz) δ: 2.44 (3H, d, J=0.6 Hz, CMe), 2.83 (3/7H, s, NMe), 2.95 (18/7H, s, NMe), 4.04 (18/7H, s, OMe), 4.05 (3/7H, s, OMe), 6.10 (3H, s, OCH_2O, ArH), 6.77 (1/7H, d, J=7.9 Hz, 6′-H), 6.78 (6/7H, d, J=8.2 Hz, 6′-H), 6.94 (1H, d, J=7.9 Hz, 5′-H), 7.02 (1/7H, s, 5-H), 7.09 (6/7H, s, 5-H), 7.20 (1/7H, s,

8-H), 7.22 (6/7H, s, 8-H), 7.37 (1/7H, d, J=8.3 Hz, 4-H), 7.38 (6/7H, d, J=8.2 Hz, 4-H), 7.72 (1/7H, d, J=8.3 Hz, 3-H), 7.74 (6/7H, d, J=8.2 Hz, 3-H), 8.10 (6/7H, s, NCHO), 8.30 (1/7H, s, NCHO).

Rearrangement of the Ether (7) in $PhNEt_2$ with 1.4 eq of CsF A suspension of **7** (0.566 g, 3.11 mmol) and CsF (0.662 g, 4.36 mmol) in $PhNEt_2$ (5.6 ml) was refluxed for 1 h. Column chromatography with hexane as the eluant gave two solid fractions (fr. A and fr. B).

2-Methylnaphtho[2,1-*b*]furan (**9**): Fraction A was obtained as colorless plates (0.501 g), mp 53.5—55 °C (lit. mp 53.5—55 °C[20a]; mp 56—57 °C[20b]; mp 52 °C[20c]), which could be distilled at bp 115 °C (1 mmHg) (lit. bp 50 °C (0.01 Torr)[20a]; bp 90 °C (8 mmHg)[27]). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.53; H, 5.62. ^{1}H-NMR (270 MHz) δ: 2.53 (3H, d, J=1.2 Hz, CMe), 6.83 (1H, br s, 1-H), 7.43 (1H, ddd, J=8.2, 7.9, 1.0 Hz, 7-H), 7.53 (1H, ddd, J=8.0, 7.9, 1.5 Hz, 8-H), 7.57 (1H, d, J=8.8 Hz, 4-H), 7.63 (1H, d, J=8.8 Hz, 5-H), 7.90 (1H, br d, J=8.2 Hz, 6-H), 8.05 (1H, dd, J=8.0, 1.0 Hz, 9-H).

3*H*-Naphtho[2,1-*b*]pyran (**8**): Fraction B gave **8** (0.024 g).

Rearrangement of the Ether (7) in $PhNEt_2$ with 0.01 eq of CsF A suspension of **7** (5.90 g, 32.4 mmol) and CsF (0.049 g, 0.32 mmol) in $PhNEt_2$ (59 ml) was refluxed for 1 h. Column chromatography with hexane as the eluant gave **9** (3.520 g) and **8** (1.501 g).

Rearrangement of the Ether (7) in $PhNEt_2$ with 0.1 eq of CsF A suspension of **7** (0.739 g, 4.05 mmol) and CsF (0.062 g, 0.41 mmol) in $PhNEt_2$ (7.4 ml) was refluxed for 1 h. Column chromatography with hexane as the eluant gave **9** (0.625 g) and **8** (0.050 g).

Rearrangement of the Ether (7) in $PhNEt_2$ with 10.0 eq of CsF A suspension of **7** (0.534 g, 2.93 mmol) and CsF (4.45 g, 29.3 mmol) in $PhNEt_2$ (5.3 ml) was heated at 180 °C (bath temperature) for 5 h. Column chromatography with hexane as the eluant gave **9** (0.457 g) and **8** (0.012 g).

Rearrangement of the Ether (7) in Sulfolane A suspension of **7** (0.478 g, 2.62 mmol) and CsF (0.566 g, 3.72 mmol) in sulfolane (4.8 ml) was heated at 220 °C (bath temperature) for 1 h, diluted with diethyl ether, and washed with water and brine. Column chromatography with hexane as the eluant gave **9** (0.272 g).

Rearrangement of the Ether (10) in $PhNEt_2$: 7-Methoxy-2,4-dimethylbenzo[*b*]furan (14) A suspension of **10** (5.43 g, 30.8 mmol) and CsF (6.12 g, 40.3 mmol) in $PhNEt_2$ (55 ml) was refluxed for 8 h. Column chromatography with hexane–diethyl ether (20 : 1) as the eluant gave a colorless oil (4.36 g), which was distilled at 140—145 °C (15 mmHg). *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.93; H, 6.85. ^{1}H-NMR (60 MHz) δ: 2.38 (3H, s, 4-Me), 2.46 (3H, d, J=1.2 Hz, 2-Me), 3.96 (3H, s, OMe), 6.33 (1H, q, J=1.2 Hz, 3-H), 6.60 (1H, d, J=8.0 Hz, 6-H), 6.87 (1H, d, J=8.0 Hz, 5-H).

Rearrangement of the Ether (11) in $PhNEt_2$ A suspension of **11** (0.404 g, 2.22 mmol) and CsF (0.472 g, 3.11 mmol) in $PhNEt_2$ (4.0 ml) was heated at 180 °C (bath temperature) for 6 h. Flash chromatography with hexane–benzene (50 : 1) as the eluant gave two solid fractions (fr. A and fr. B).

2-Methylnaphtho[1,2-*b*]furan (**15**): Fraction A was obtained as a colorless oil (0.079 g), which was distilled at bp 90—95 °C (2 mmHg) (lit.[27] bp 70—72 °C (6 mmHg)). *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.31; H, 5.59. ^{1}H-NMR (270 MHz) δ: 2.56 (3H, d, J=0.9 Hz, CMe), 6.49 (1H, q, J=0.9 Hz, 3-H), 7.43 (1H, ddd, J=8.2, 7.0, 1.2 Hz, 7-H), 7.55 (1H, ddd, J=8.2, 7.0, 1.2 Hz, 8-H), 7.56 (1H, d, J=8.6 Hz, 5-H), 7.61 (1H, d, J=8.6 Hz, 4-H), 7.89 (1H, d, J=8.2 Hz, 6-H), 8.25 (1H, d, J=8.2 Hz, 9-H).

2*H*-Naphtho[1,2-*b*]pyran (**13**): Fraction B gave **13** (0.062 g).

Rearrangement of the Ether (7) in $PhNEt_2$ in the Presence of an Additive Other than CsF. General Procedure A mixture of **7** and an additive in $PhNEt_2$ was refluxed for 1 h under argon with stirring and diluted with diethyl ether. After removal of the insoluble material the filtrate was washed with 5% hydrochloric acid and brine, dried over K_2CO_3, and evaporated. The residue was purified by column chromatography with hexane as the eluant.

With Potassium Fluoride: The use of **7** (0.526 g, 2.89 mmol), KF (4.42 g, 76.0 mmol), and $PhNEt_2$ (5.2 ml) gave **8** (0.442 g).

With Calcium Fluoride: The use of **7** (0.538 g, 2.95 mmol), CaF_2 (4.47 g, 57.3 mmol), and $PhNEt_2$ (5.4 ml) gave **8** (0.461 g).

With Barium Fluoride: The use of **7** (0.496 g, 2.72 mmol), BaF_2 (4.15 g, 23.6 mmol), and $PhNEt_2$ (4.9 ml) gave **8** (0.431 g).

With Rubidium Fluoride: The use of **7** (0.479g, 2.63 mmol), RbF (4.40 g, 42.1 mmol), and $PhNEt_2$ (4.8 ml) gave **8** (0.466 g).

With Cesium Chloride: The use of **7** (0.553 g, 3.04 mmol), CsCl (4.64 g, 27.7 mmol), and $PhNEt_2$ (5.5 ml) gave **8** (0.491 g).

With Tetra-*n*-butylammonium Fluoride: A mixture of **7** (0.500 g, 2.74 mmol), $(n\text{-Bu})_4NF$ obtained by evaporation of a 1.0 M solution (16 ml, 16.0 mmol) of $(n\text{-Bu})_4NF$ in tetrahydrofuran, and $PhNEt_2$ (5.0 ml) was used. Column chromatography of the residue with hexane as the eluant gave **9** (0.036 g) and **8** (0.014 g).

Claisen Rearrangement of the Ether (7) in the Presence of Base. General Procedure A mixture of **7** and base in $PhNEt_2$ or sulfolane was heated under argon with stirring. After work-up, the organic solution was washed with 5% hydrochloric acid, water, and brine, dried over K_2CO_3, and evaporated. The residue was purified by PLC or column chromatography.

With Potassium Hydroxide in $PhNEt_2$: A mixture of **7** (2.15 g, 11.8 mmol) and potassium hydroxidte (5.39 g, 86.4 mmol) in $PhNEt_2$ (21 ml) was heated at 180 °C (bath temperature) for 3.5 h, poured into water, and extracted with benzene. Column chromatography with hexane and the eluant gave **9** (0.403 g).

With Sodium Hydrogen Carbonate in $PhNEt_2$: A mixture of **7** (0.501 g, 2.75 mmol) and sodium hydrogen carbonate (4.44 g, 52.9 mmol) in $PhNEt_2$ (5.0 ml) was refluxed for 1 h, diluted with diethyl ether, and filtered. Column chromatography with hexane as the eluant gave **9** (0.035 g) and **8** (0.362 g).

With Potassium Carbonate in $PhNEt_2$: A mixture of **7** (0.461 g, 2.53 mmol) and potassium carbonate (3.84 g, 27.8 mmol) in $PhNEt_2$ (4.6 ml) was refluxed for 1 h, diluted with diethyl ether, and filtered. Column chromatography with hexane as the eluant gave **9** (0.196 g) and **8** (0.221 g).

With Potassium Carbonate in Sulfolane: A mixture of **7** (0.592 g, 3.25 mmol) and potassium carbonate (1.67 g, 12.1 mmol) in sulfolane (12 ml) was heated at 200 °C (bath temperature) for 1.5 h, poured into water, and extracted with diethyl ether. Column chromatography with hexane as the eluant gave **9** (0.450 g).

Oxidation of the Furan (14) with Equimolar of OsO_4 in Pyridine Followed by Decomposition with Sodium Hydrogen Sulfite: 2,3-Dihydroxy-7-methoxy-2,4-dimethyl-2,3-dihydrobenzo[*b*]furan[33] (16) OsO_4 (0.957 g, 3.76 mmol) was added to a solution of **14** (0.553 g, 3.14 mmol) in dry pyridine (11 ml). The mixture was stirred at room temperature for 4 h, then a solution of sodium hydrogen sulfite (1.44 g, 13.8 mmol) in water (22 ml) and pyridine (15 ml) was added dropwise. The reaction mixture was stirred at room temperature for 1.5 h, poured into water, and extracted with ethyl acetate. The ethyl acetate solution was washed with saturated aqueous copper (II) sulfate and brine, dried over $MgSO_4$, and evaporated. Recrystallization of the residue from diethyl ether gave colorless prisms (0.583 g), mp 109—110 °C. *Anal.* Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.66; H, 6.73. IR ν_{max} cm^{-1}: 3488 and 3170 (OH).[34] ^{1}H-NMR (270 MHz) δ: 1.64 (12/15H, s, CMe), 1.78 (3/15H, s, CMe), 2.10 (30/15H, s, CMe), 2.13[35] (s, OH), 2.30 (2/3 × 3H, s, ArMe), 2.34 (1/3H × 3H, s, ArMe), 2.90[35] (s, OH), 3.84 (3/3H, s, OMe), 3.87 (6/3H, s, OMe), 4.09 (10/15H, d, J=4.6 Hz, OH), 4.58 (4/15H, s, OH), 4.77 (4/15H, d, J=7.0 Hz, ArC<u>H</u>(OH)), 4.87 (1/15H, d, J=8.5 Hz, ArC<u>H</u>(OH)), 5.44 (10/15H, d, J=4.6 Hz, ArC<u>H</u>(OH)), 5.89 (10/15H, s, OH), 6.65—6.80 (2H, m, ArH).

Oxidation of the Furan (14) with Equimolar of OsO_4 in Diethyl Ether–Pyridine Followed by Decomposition with Sodium Sulfite: 2-Hydroxy-7-methoxy-2,4-dimethyl-2,3-dihydrobenzo[*b*]furan-3(2*H*)-one[36] (17) A solution of OsO_4 (0.113 g, 0.445 mmol) in dry diethyl ether (1.5 ml) was added to a solution of **14** (0.062 g, 0.35 mmol) in dry diethyl ether (1 ml) containing dry pyridine (0.03 ml). The mixture was stirred at room temperature for 24 h, then a solution of sodium sulfite (0.443 g, 3.51 mmol) in ethanol (2 ml) and water (4 ml) was added dropwise. The resulting mixture was stirred at 75 °C (bath temperature) for 1 h and the precipitate which separated was filtered off. The filtrate was extracted with ethyl acetate. The ethyl acetate solution was washed with saturated aqueous copper (II) sulfate and brine, dried over $MgSO_4$, and evaporated. PLC of the residue with chloroform–ethyl acetate (5 : 1) as the developing solvent gave colorless prisms (0.048 g), mp 100.5—101.5 °C (from diethyl ether–hexane). *Anal.* Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.57; H, 5.93. IR ν_{max} cm^{-1}: 3440 sh and 3320 (OH), 1711 (CO). ^{1}H-NMR (60 MHz) δ: 1.65 (3H, s, CMe), 2.44 (3H, s, ArMe), 3.83 (1H, s, OH), 3.89 (3H, s, OMe), 6.69 (1H, d, J=7.5 Hz, ArH), 7.00 (1H, d, J=7.5 Hz, ArH). MS m/z: 208 (M^+, 7.1%), 166 (11.3), 165 (100), 69 (12.6).

Oxidation of the Furan (14) with a Catalytic Amount of OsO_4 in the Presence of NMMO To a solution of NMMO (0.396 g, 2.84 mmol) in water (1.2 ml) and pyridine (0.2 ml) was added a solution of **14** (0.113 g, 0.64 mmol) in *tert*-butanol (2.5 ml) and then an aqueous solution (1 ml, *ca.* 0.074 mmol) prepared from OsO_4 (0.096 g, 0.378 mmol) and water (5.1 ml). The mixture was refluxed for 20 h. Further NMMO (0.308 g, 2.21 mmol) and pyridine (0.5 ml) were added and the mixture was refluxed for 7 h. After addition of a solution of sodium hydrogen sulfite (0.525 g,

5.0 mmol) in water (2.1 ml), the reaction mixture was stirred at room temperature for 0.5 h, poured into 10% hydrochloric acid containing ice, and extracted with 20% methanol in chloroform. The organic solution was washed with 5% hydrochloric acid and brine, dried over $MgSO_4$, and evaporated. PLC of the residue with hexane–ethyl acetate (2 : 1) as the developing solvent gave the ketone (**17**) (0.027 g).

Treatment of the Alcohol (16) with 10% Sodium Carbonate A mixture of **16** (0.035 g, 0.168 mmol), sodium carbonate (0.180 g, 1.70 mmol), ethanol (0.8 ml), and water (1.6 ml) was refluxed for 14 h, poured into water, acidified with 10% hydrochloric acid, and extracted with diethyl ether. The ethereal solution was washed with brine, dried over $MgSO_4$, and evaporated. PLC of the residue with hexane–ethyl acetate (2 : 1) as the developing solvent gave **17** (0.024 g, 68.1%).

Oxidation of the Furan (14) with a Catalytic Amount of OsO_4 and Sodium Metaperiodate: 2-Hydroxy-3-methoxy-6-methylbenzaldehyde (18) An aqueous solution (0.7 ml, *ca.* 0.05 mmol) prepared from OsO_4 (0.065 g, 0.256 mmol) and water (3.5 ml) was added to a solution of **14** (0.056 g, 0.319 mmol) in dioxane (1.5 ml). The mixture was stirred at room temperature for 0.5 h, then sodium metaperiodate (0.123 g, 0.575 mmol) was added. The resulting mixture was stirred at room temperature for 24 h, poured into water, and extracted with diethyl ether. The ethereal solution was washed with saturated aqueous sodium sulfite, dried over $MgSO_4$, and evaporated. The residue was dissolved in ethanol (0.3 ml) and 1% aqueous sodium hydrogen carbonate (0.3 ml) was added. The reaction mixture was stirred at 80 °C (bath temperature) for 1 h, poured into water, acidified with 5% hydrochloric acid, and extracted with diethyl ether. The ethereal solution was washed with brine, dried over $MgSO_4$, and evaporated. PLC of the residue with hexane–diethyl ether (1 : 1) as the developing solvent gave a light brown oil (0.010 g), which was identical with the sample obtained by oxidation of **16** with sodium metaperiodate as described below.

2-Hydroxy-3-methoxy-6-methylbenzaldehyde (18) Sodium metaperiodate (0.237 g, 1.11 mmol) was added to a solution of **16** (0.156 g, 0.743 mmol) in methanol (4.7 ml) and water (1.6 ml). The mixture was stirred at room temperature for 5 h, poured into water, and extracted with diethyl ether. The ethereal solution was dried over $MgSO_4$ and evaporated. The residue was dissolved in ethanol (23 ml) and 1% aqueous sodium hydrogen carbonate (9.4 ml), refluxed for 5 h, poured into water, carefully acidified with 5% hydrochloric acid to pH 5—6, and extracted with diethyl ether. The ethereal solution was washed with brine, dried over $MgSO_4$, and evaporated. Distillation of the residue at bp 90—100 °C (1 mmHg) gave a yellow oil (0.103 g, 83.7%). IR ν_{max} cm^{-1}: 3500—3200 (br, OH), 1639 (C=O). ^{1}H-NMR (60 MHz) δ: 2.52 (3H, s, CMe), 3.88 (3H, s, OMe), 6.63 (1H, d, J=7.5 Hz, 5-H), 6.97 (1H, d, J=7.5 Hz, 4-H), 10.23 (1H, s, CHO), 12.03 (1H, s, OH).

2,3-Dimethoxy-6-methylbenzaldehyde (19) Sodium hydroxide (0.019 g, 0.41 mmol), benzyl tri-*n*-butylammonium chloride (0.016 g, 0.051 mmol), and dimethyl sulfate (0.08 ml, 0.844 mmol) were successively added to a solution of the aldehyde (**18**) (0.027 g, 0.164 mmol) in methylene chloride (0.8 ml) and water (0.8 ml). The mixture was stirred at room temperature for 1.5 h, poured into water, and extracted with diethyl ether. The ethereal solution was washed with 5% aqueous ammonium hydroxide, dried over K_2CO_3, and evaporated to give pale yellow prisms (quant.), mp 62—64 °C, which could be purified by distillation at bp 140—150 °C (17 mmHg). *Anal.* Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.51; H, 6.77. IR ν_{max} cm^{-1}: 1684 (C=O). ^{1}H-NMR (60 MHz) δ: 2.49 (3H, s, CMe), 3.88 (3H, s, OMe), 3.93 (3H, s, OMe), 6.86 (1H, d, J=8.0 Hz, 5-H), 7.04 (1H, d, J=8.0 Hz, 4-H), 10.51 (1H, s, CHO).

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References and Notes

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36) This nomenclature is based on the cyclic structure (**17a**) {1-[2-(1-hydroxy-6-methoxy-3-methylphenyl)propan-1,2-dione for the open structure (**17b**)}.