CESIUM FLUORIDE-MEDIATED CLAISEN REARRANGEMENTS OF PHENYL PROPARGYL ETHERS: EFFECT OF A SUBSTITUENT ON THE PHENYL RING ON THE REARRANGEMENT[1]

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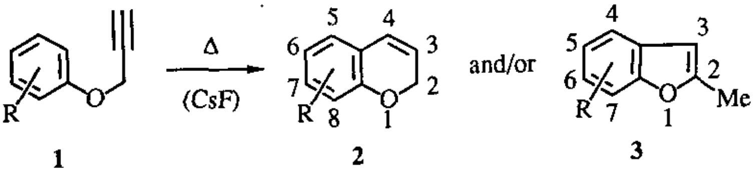
Abstract - Methoxy or methoxycarbonyl-substituted phenyl propargyl ethers were subjected to Claisen rearrangement either in the absence or in the presence of CsF. Substituent effect on the cyclization is discussed.

An aryl propargyl ether (**1**) thermally cyclized to give a benzopyran (**2**) but the yield was generally low in the case of a primary propargyl ether.[2] In contrast, we found the exclusive formation of a 2-methylbenzofuran (**3**) when heated a primary ether in the presence of cesium fluoride (CsF)[3] and applied the reaction to syntheses of natural products with a four-sequentially substituted benzene ring in the molecules by combination with oxidative cleavage of the formed furan ring.[4] Now we focused on effect of a substituent on the phenyl ring on the CsF-mediated Claisen rearrangement. Though thermal Claisen rearrangements have been reported on all of the possible isomers with an electron donative methoxy group,[5] only one example[5c] of the *m*-isomer with electron attractive ethoxycarbonyl one has appeared in literatures in which the structure of the cyclized product remained uncertain (Table 1). In this paper we describe substituent effects on Claisen rearrangement of propargyl ethers carrying a methoxy



1 **2** **3**

Table 1. Reported thermal Claisen rearrangements

ethers (**1**)	solvents	pyrans (**2**) (%)[a]	ref.
o-OMe (**1a**)	PhNEt$_2$	8-OMe (**2a**): 11.9 (58)	5a (5b)
m-OMe (**1b**)	PhNEt$_2$	5-OMe (**2b-1**): — (27.5) 7-OMe (**2b-2**): 12.5 (23.5)	5a (5b)
	PEG[b]	5-OMe (**2b-1**): 41.5 7-OMe (**2b-2**): 28.5	5c
p-OMe (**1c**)	PhNEt$_2$	6-OMe (**2c**): 30 (60)	5a (5b)
m-CO$_2$Et	PEG[b]	5- or 7-CO$_2$Et: 48	5c

a) The reported data by ref. 5b are given in parentheses.
b) Poly(ethylene glycol) (200).

or methoxycarbonyl group in the absence or in the presence of CsF.

The starting ethers (**1**) were easily prepared from the corresponding phenols in high yields. The Claisen rearrangements were carried out under the condition of heating in *N, N*-diethylaniline (PhNEt$_2$) under argon either without or with CsF. The crude products were purified by chromatography on silica gel and characterized by spectral data. In the nmr spectra benzopyrans (**2**) generally showed an AMX signal pattern consisting of a 2H double doublet, a 1H double triplet and a 1H diffused doublet at δ 4.7, 5.7 and 6.5, while 2-methylbenzofurans (**3**) an AX one consisting of a 3H finely splitted doublet (*ca.* 1 Hz) and a 1H diffused singlet at δ 2.4 and 6.3, respectively. In the case where separation of products was difficult the product ratio was estimated by the nmr comparison of the crude mixture with the separated authentic samples. The results obtained in the thermal rearrangements were given in Table 2 and those in the CsF-mediated ones in Table 3, respectively.

In both rearrangements were commonly observed quite smooth cyclization of *o*-substituted ethers, preferential cyclization to the *ortho* position of the substituent in *m*-substituted ethers, especially *m*-methoxycarbonyl one (**1e**), and acceleration of the reaction by an electron donative methoxy group. The methoxycarbonyl ethers gave the products in better yields in the CsF-mediated Claisen rearrangement than in the corresponding reaction without CsF.

In the thermal rearrangements though the methoxy ethers led to exclusive formation of benzopyarns (**2**), consistent with the reported results shown in Table 1, the *o*- (**1d**) and *m*-methoxycarbonyl (**1e**) ethers produced a small amount of 2-methylbenzofurans (**3**) as additional products. Formation of a 2-methylbenzofuran (**3**) in thermal rearrangement has been reported in the case of presence of relatively

Table 2. Thermal Claisen rearrangements in $PhNEt_2$

	ethers (1)	time (h)	products (%)		
			pyrans (2)	furans (3)	(2+3)
o-	OMe (**1a**)	3.5	8-OMe (**2a**): 76.6	——	76.6[a)]
	CO_2Me (**1d**)	4[b) c)]	8-CO_2Me (**2d**): 53.6	7-CO_2Me (**3d**): 3.6	57.2[d)]
m-	OMe (**1b**)	8	5-OMe (**2b-1**): 41.5 7-OMe (**2b-2**): 32.7	——	74.2[d)]
	CO_2Me (**1e**)	14[b)]	5-CO_2Me (**2e-1**): 42.0 7-CO_2Me (**2e-2**): 11.6	4-CO_2Me (**3e-1**): 3.8	57.4[d)]
p-	OMe (**1c**)	7	6-OMe (**2c**): 48.3	——	48.3[a)]
	CO_2Me (**1f**)	10[b) c)]	6-CO_2Me (**2f**): 36.1	——	36.1[d)]

a) Isolated yield.
b) A starting material remained.
c) The prolonged reaction resulted in lowing the yields.
d) Estimation by nmr.

Table 3. The CsF-mediated Claisen rearrangements

	ethers (1)	time (h)	products (%)		
			pyrans (2)	furans (3)	(2+3)
o-	OMe (**1a**)	4.5	——	7-OMe (**3a**): 74.0	74.0[a)]
	CO_2Me (**1d**)	6	——	7-CO_2Me (**3d**): 63.1	63.1[a)]
m-	OMe (**1b**)	8	5-OMe (**2b-1**): 11.7 7-OMe (**2b-2**): 9.0	4-OMe (**3b-1**): 33.2 6-OMe (**3b-2**): 14.4	68.3[b)]
	CO_2Me (**1e**)	14[c)]	——	4-CO_2Me (**3e-1**): 55.5 6-CO_2Me (**3e-2**): 17.8	73.3[b)]
p-	OMe (**1c**)	6	——	5-OMe (**3c**): 58.9	58.9[a)]
	CO_2Me (**1f**)	48	——	5-CO_2Me (**3f**): 53.8	53.8[a)]

a) Isolated yield.
b) Estimation by nmr.
c) A starting material remained.

strong electron attractive substituents such as nitro or formyl groups on the phenyl ring.[5c] Our results indicate that presence of a methoxycarbonyl group could also lead to furan formation in some cases. In the CsF-mediated rearrangements the additive is always responsible for formation of 2-methylbenzofurans (3), especially in the case of methoxycarbonyl derivatives. However neither accelaration of reaction rates nor increase of product yields depending on a substituent were observed. Interestingly cyclization into an alternative ring size product was additionally observed on the reaction of the *m*-methoxy ether (**1b**). We have proposed a mechanism for the favored arylfuran cyclization in the CsF-mediated Claisen rearrangement, in which CsF can play an important role for generation of a phenolate ion by abstraction of the α-hydrogen atom in the rearranged α-allenylketone intermediate.[3] However the limited data in these experiments can not allow us to deduce the reason for an additional arylpyran formation in the CsF-mediated reaction of the *m*-methoxy ether (**1b**). Further investigation is now in progress.

EXPERIMENTAL

All melting points were measured on a micro melting-point hot stage (Yanagimoto) and are uncorrected. Ir spectra were recorded on a Hitachi 260-10 or JASCO IR-700 spectrophotometer. Nmr spectra were recorded in $CDCl_3$ with a JEOL GSX-500 (500 MHz) spectrometers with tetramethylsilane (TMS) as an internal reference, unless otherwise stated. Diffused splitting pattern is abbreviated as dif. Ms were measured with a JEOL JMS-Automass 20 spectrometer using a direct inlet system and high resolution fast atom bombardment (HRFAB) ms with JEOL JMS-HX110 spectrometer. For column and flash chromatography silica gel 60 (70-230 mesh ASTM; Merck) and silica gel 60 (230-400 mesh; Nacalai Tesque) were used, respectively, while for tlc and preparative tlc (plc), silica gel 60 F_{254} (Art. 5715 and 5717, Merck) were used. Organic extracts were dried over K_2CO_3.

General Procedure for Preparation of Phenyl Propargyl Ethers A mixture of the phenol, propargyl bromide and K_2CO_3 in dimethylformamide (DMF) was stirred at room temperature. After addition of water the reaction mixture was extracted with ether. The ethereal solution was washed with 5 % NaOH and brine, dried and evaporated to dryness *in vacuo* to give a propargyl ether, which was purified by distillation or by recrystallization.

***o*-Methoxyphenyl Propargyl Ether (1a)** Guaiacol (10.1 g, 81.0 mmol), propargyl bromide (8.60 ml, 114 mmol) and K_2CO_3 (17.4 g, 126 mmol) in DMF (55.5 ml) were reacted for 4 h to give **1a** as a colorless oil (12.3 g, 94.0 %), bp 90-98 °C (6 mmHg) [lit.,[5a] bp 98-100 °C (2 mmHg)].

***m*-Methoxyphenyl Propargyl Ether (1b)** *m*-Methoxyphenol (10.0 g, 80.8 mmol), propargyl bromide (8.80 ml, 117 mmol) and K_2CO_3 (17.4 g, 126 mmol) in DMF (60 ml) were reacted for 23 h to give **1b** as a colorless oil (11.8 g, 89.8 %), bp 78-80 °C (3 mmHg) [lit.,[5a] bp 97-99 °C (1 mmHg)].

***p*-Methoxyphenyl Propargyl Ether (1c)** *p*-Hydroxyanisole (10.3 g, 82.7 mmol), propargyl bromide (10.2 ml, 136 mmol) and K_2CO_3 (17.7 g, 128 mmol) in DMF (60 ml) were reacted for 25 h to give **1c** as a colorless oil (12.1 g, 90.1 %), bp 100-102 °C (4 mmHg) [lit.,[5a] bp 106-108 °C (2 mmHg)].

***o*-Methoxycarbonylphenyl Propargyl Ether (1d)** Methyl salicylate (5.00 g, 32.9 mmol), propargyl bromide (3.60 ml, 47.8 mmol) and K_2CO_3 (7.09 g, 51.3 mmol) in DMF (30 ml) were reacted for 6 h to give **1d** as a colorless oil (5.89 g, 94.2 %), bp 124-127 °C (5 mmHg). HRFAB-ms *m/z*: 191.0703 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (neat): 3290, 2120, 1726 cm^{-1}. Nmr δ: 2.50 (1H, t, *J*=2.5 Hz, CH_2C-C$\underline{H}$), 3.85 (3H, s, OMe), 4.76 (2H, d, *J*=2.5 Hz, O$\underline{CH_2}$C-CH), 7.01 (1H, dif. t, *J*=7.8 Hz, 5-H), 7.10 (1H, dif. d, *J*=7.8 Hz, 3-H), 7.43 (1H, t like, *J*=7.8 Hz, 4-H), 7.78 (1H, dd, *J*=7.8, 1.7 Hz, 6-H).

***m*-Methoxycarbonylphenyl Propargyl Ether (1e)** Methyl *m*-hydroxybenzoate (5.03 g, 33.1 mmol), propargyl bromide (3.52 ml, 46.8 mmol) and K_2CO_3 (7.10 g, 51.4 mmol) in DMF (30 ml) were reacted for 4 h to give **1e** (6.13 g, 97.4 %) as pale yellow prisms (hexane), mp 56-57 °C. HRFAB-ms *m/z*: 191.0704 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (nujol): 3282, 2120, 1712 cm^{-1}. Nmr δ: 2.54 (1H, t, *J*=2.4 Hz, CH_2C-C$\underline{H}$), 3.91 (3H, s, OMe), 4.74 (2H, d, *J*=2.4 Hz, O$\underline{CH_2}$C-CH), 7.18 (1H, dif. dd, *J*=8.2, 1.9 Hz, 4-H), 7.36 (1H, dd, *J*=8.2, 7.6 Hz, 5-H), 7.64 (1H, dif. d, *J*=1.9 Hz, 2-H), 7.68 (1H, d, *J*=7.6 Hz, 6-H).

***p*-Methoxycarbonylphenyl Propargyl Ether (1f)** Methyl *p*-hydroxybenzoate (5.05 g, 33.2 mmol), propargyl bromide (3.60 ml, 47.8 mmol) and K_2CO_3 (7.11 g, 51.4 mmol) in DMF (30 ml) were reacted for 2.5 h to give **1f** (5.92 g, 93.8 %) as colorless plates (ether-hexane), mp 66-67 °C. HRFAB-ms *m/z*: 191.0701 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (nujol): 3246, 2126, 1705 cm^{-1}. Nmr δ: 2.55 (1H, t, *J*=2.4 Hz, CH_2C-C$\underline{H}$), 3.89 (3H, s, OMe), 4.75 (2H, d, *J*=2.4 Hz, O$\underline{CH_2}$C-CH), 7.00 (2H, dt, *J*=9.0, 2.2 Hz, 2- and 6-H), 8.01 (2H, dt, *J*=9.0, 2.2 Hz, 3- and 5-H).

General Procedure for Thermal Claisen Rearrangement A solution of **1** in $PhNEt_2$ was refluxed under argon. After diluted with ether the ethereal solution was washed with 5 % HCl and brine, dried and evaporated to dryness *in vacuo*. The crude product(s) was purified by column or flash chromatography. For determination of a product ratio by nmr spectrum a reaction mixture was through a short column chromatography before measurement.

On *o*-Methoxyphenyl Propargyl Ether (1a) **1a** (1.12 g, 6.29 mmol) in $PhNEt_2$ (5.3 ml) was reacted for 3.5 h to give 8-methoxybenzo[*b*]pyran (**2a**) (0.781 g, 76.6 %) as a colorless oil, bp 110-120 °C (5 mmHg) [lit.,[5a] bp 110-115 °C (1 mmHg)]. *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.07; H, 6.17. Nmr δ: 3.87 (3H, s, OMe), 4.88 (2H, dd, *J*=3.6, 1.8 Hz, 2-H_2), 5.79 (1H, dt, *J*=9.8, 3.6 Hz, 3-H), 6.41 (1H, dt, *J*=9.8, 1.8 Hz, 4-H), 6.62 (1H, dd, *J*=7.3, 1.5 Hz, 7-H), 6.78 (1H, dd, *J*=8.1, 1.5 Hz, 5-H), 6.82 (1H, t, *J*=7.7 Hz, 6-H).

On *m*-Methoxyphenyl Propargyl Ether (1b) **1b** (0.941 g, 5.80 mmol) in $PhNEt_2$ (5.0 ml) was reacted for 6 h. The crude products were separated by flash chromatography using hexane to afford two products[6]: (a) 5-Methoxybenzo[*b*]pyran (**2b-1**), a colorless oil, bp 95-100 °C (4 mmHg). Ms *m/z*: 162 (M^+, 77.8 %). Nmr δ: 3.81 (3H, s, OMe), 4.74 (2H, dd, *J*=3.7, 2.0 Hz, 2-H_2), 5.72 (1H, dt, *J*=10.0, 3.7 Hz, 3-H), 6.44 (1H, d, *J*=8.3 Hz, 6- or 8-H), 6.45 (1H, d, *J*=8.3 Hz, 8- or 6-H), 6.76 (1H, dif. d, *J*=10.0 Hz, 4-H), 7.04 (1H, t, *J*=8.3 Hz, 7-H); (b) 7-Methoxybenzo[*b*]pyran (**2b-2**), a slightly yellow oil, bp 95-100 °C (4 mmHg) [lit.,[5a] bp 115-118 °C (1 mmHg)]. *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.07; H, 6.09. Nmr δ: 3.76 (3H, s, OMe), 4.79 (2H, dd, *J*=3.7, 1.7 Hz, 2-H_2), 5.62 (1H, dt, *J*=9.8, 3.7 Hz, 3-H), 6.36 (1H, d, *J*=2.5 Hz, 8-H), 6.37 (1H, dif. d, *J*=9.8 Hz, 4-H), 6.41 (1H, dd, *J*=8.3, 2.5 Hz, 6-H), 6.87 (1H, d, *J*=8.3 Hz, 5-H).

For determination of a product ratio **1b** (0.190 g, 1.17 mmol) in $PhNEt_2$ (1 ml) was reacted for 8 h. Two components of **2b-1** and **2b-2** in the crude product (0.141 g, 74.2 %) were estimated as a ratio of 1.27 : 1.

On *p*-Methoxyphenyl Propargyl Ether (1c) **1c** (2.00 g, 12.3 mmol) in $PhNEt_2$ (10 ml) was reacted for 7 h to give 6-methoxybenzo[*b*]pyran (**2c**) (0.965 g, 48.3 %) as a colorless oil, bp 120-125 °C (4 mmHg) [lit.,[5a] bp 115-118 °C (1 mmHg)]. *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.10; H, 5.95. Nmr δ: 3.68 (3H, s, OMe), 4.67 (2H, dd, *J*=3.7, 1.8 Hz, 2-H_2), 5.74 (1H, dt, *J*=9.8, 3.7 Hz, 3-H), 6.32 (1H, dif. d, *J*=9.8 Hz, 4-H), 6.46 (1H, d, *J*=3.1 Hz, 5-H), 6.58 (1H, dd, *J*=8.8, 3.1 Hz, 7-H), 6.64 (1H, d, *J*=8.8 Hz, 8-H).

On *o*-Methoxycarbonylphenyl Propargyl Ether (1d) **1d** (0.496 g, 2.61 mmol) in $PhNEt_2$ (2.5 ml) was reacted for 8 h. The crude products were separated by flash chromatography using a mixed solvent of hexane and acetone (10 : 1, v/v) to afford two products[6]: (a) 7-Methoxycarbonyl-2-methylbenzo[*b*]furan (**3d**), a colorless oil, which was identified with a product isolated from the CsF-mediated reaction of **1d**; (b) 8-Methoxycarbonylbenzo[*b*]pyran (**2d**), a colorless oil, bp 115-130 °C (4 mmHg). HRFAB-ms *m/z*: 191.0706 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (neat): 1728 cm^{-1}. Nmr δ: 3.88 (3H, s, OMe), 4.93 (2H, dd, *J*=3.4, 1.8 Hz, 2-H_2), 5.83 (1H, dt, *J*=9.8, 3.4 Hz, 3-H), 6.41 (1H, dt, *J*=9.8, 1.8 Hz, 4-H), 6.86 (1H, dd, *J*=7.9, 7.4 Hz, 6-H), 7.07 (1H, dd, *J*=7.4, 1.5 Hz, 5-H), 7.61 (1H, dd, *J*=7.9, 1.5 Hz, 7-H).

For determination of a product ratio **1d** (0.210 g, 1.10 mmol) in $PhNEt_2$ (1 ml) was reacted for 4 h. Three components of the starting **1d**, **3d** and **2d** in the crude product (0.145 g, 69.0 %) were estimated as a ratio of 3.32 : 1 : 15.1.

On *m*-Methoxycarbonylphenyl Propargyl Ether (1e) **1e** (0.496 g, 2.61 mmol) in $PhNEt_2$ (5 ml) was reacted for 15 h. The crude products were separated by flash chromatography using a mixed solvent of hexane and benzene (3 : 2, v/v) to afford two pyrans[6]: (a) 5-Methoxycarbonylbenzo[*b*]pyran (**2e-1**), a colorless oil, bp 110-125 °C (4 mmHg). HRFAB-ms *m/z*: 191.0713 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (neat): 1715 cm^{-1}. Nmr δ: 3.82 (3H, s, OMe), 4.70 (2H, dd, *J*=3.7, 1.8 Hz, 2-H_2), 5.86 (1H, dt, *J*=10.4, 3.7 Hz, 3-H), 6.89 (1H, dt, *J*=7.9, 1.2 Hz, 8-H), 7.06 (1H, t, *J*=7.9 Hz, 7-H), 7.24 (1H, dif. d, *J*=10.4 Hz, 4-H), 7.41 (1H, dd, *J*=7.9, 1.2 Hz, 6-H); (b) 7-Methoxycarbonylbenzo[*b*]pyran (**2e-2**), a slightly yellow oil, bp 120-130 °C (4 mmHg). HRFAB-ms *m/z*: 191.0703 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} (neat): 1717 cm^{-1}. Nmr δ: 3.81 (3H, s, OMe), 4.80 (2H, dd, *J*=3.4, 1.8 Hz, 2-H_2), 5.82 (1H, dt, *J*=9.7, 3.4 Hz, 3-H), 6.37 (1H, d, *J*=9.7 Hz, 4-H), 6.92 (1H, d, *J*=7.9 Hz, 5-H), 7.33 (1H, br s, 8-H), 7.47 (1H, dd, *J*=7.9, 1.2 Hz, 6-H).

For determination of a product ratio **1e** (0.207 g, 1.09 mmol) in $PhNEt_2$ (1 ml) was reacted for 14 h. Four components of the starting **1e**, **2e-1**, **2e-2** and **3e-1** in the crude product (0.124 g, 59.9 %) were estimated as a ratio of 1 : 1.51 : 16.9 : 4.68. The authentic 4-methoxycarbonylfuran (**3e-1**) was obtained in the CsF-mediated reaction of **1e**.

On *p*-Methoxycarbonylphenyl Propargyl Ether (1f) **1f** (0.499 g, 2.62 mmol) in $PhNEt_2$ (5 ml) was reacted for 30 h. The crude products were separated by flash chromatography using a mixed solvent of hexane and acetone (50 : 1, v/v) to give 6-methoxycarbonylbenzo[*b*]pyran (**2f**) as a colorless oil (0.075 g, 15.0 %), bp 105-130 °C (4 mmHg). *Anal.* Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.19; H, 5.24. Ir ν_{max} (neat): 1714 cm^{-1}. Nmr δ: 3.80 (3H, s, OMe), 4.84 (2H, dd, *J*=3.3, 2.0 Hz, 2-H_2), 5.71 (1H, dt, *J*=10.0, 3.3 Hz, 3-H), 6.35 (1H, dif. d, *J*=10.0 Hz, 4-H), 6.68 (1H, d, *J*=8.5 Hz, 8-H), 7.56 (1H, d, *J*=2.0 Hz, 5-H), 7.72 (1H, dd, *J*=8.5, 2.0 Hz, 7-H).

For determination of a product ratio **1f** (0.502 g, 2.64 mmol) in $PhNEt_2$ (2.5 ml) was reacted for 10 h. Two components of the starting **1f** and **2f** in the crude product (0.391 g, 77.9 %) were estimated as a ratio of 1.16 : 1.

General Procedure for the CsF-Mediated Claisen Rearrangement A mixture of **1** and CsF in $PhNEt_2$ was refluxed under argon. After diluted with ether insoluble materials were removed by decantation. The ethereal solution was treated as mentioned in the thermal reaction.

On *o*-Methoxyphenyl Propargyl Ether (1a) **1a** (1.91 g, 11.7 mmol) and CsF (2.33 g, 15.4 mmol) in $PhNEt_2$ (20 ml) were reacted for 4 h. The crude products were separated by column chromatography using a mixed solvent of hexane and ethyl acetate (10 : 1, v/v) to give 7-methoxy-2-methylbenzo[*b*]furan (**3a**) (1.41 g, 74.0 %) as a colorless oil, bp 75-110 °C (4 mmHg) [lit.,[7] bp 125-127 °C (1 mmHg)]. *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.34; H, 6.13. Nmr (60 MHz) δ: 2.48 (3H, d, *J*=1.0 Hz, 2-Me), 4.00 (3H, s, OMe), 6.47 (1H, dif. d, *J*=1.0 Hz, 3-H), 6.63-7.18 (3H, m, ArH).

On *m*-Methoxyphenyl Propargyl Ether (1b) **1b** (1.08 g, 6.66 mmol) and CsF (1.37 g, 9.01 mmol) in $PhNEt_2$ (10 ml) were reacted for 6 h. The crude products were repeatedly separated by flash chromatography and plc using hexane as a solvent to give two furans[6]: (a) 4-Methoxy-2-methylbenzo[*b*]furan (**3b-1**), a colorless oil, bp 80-90 °C (4 mmHg). *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.15; H, 6.08. Nmr δ: 2.43 (3H, d, *J*=1.2 Hz, 2-Me), 3.91 (3H, s, OMe), 6.45 (1H, dif. s, 3-H), 6.62 (1H, d, *J*=8.0 Hz, 5-H), 7.04 (1H, d, *J*=8.0 Hz, 7-H), 7.12 (1H, t, *J*=8.0 Hz, 6-H); (b) 6-Methoxy-2-methylbenzo[*b*]furan (**3b-2**), a colorless oil, bp 85-95 °C (4 mmHg) [lit.,[8] bp 138 °C (15 mmHg)]. Ms *m/z*: 162 (M^+, 78.5 %). Nmr δ: 2.41 (3H, d, *J*=0.9 Hz, 2-Me), 3.83 (3H, s, OMe), 6.28 (1H, dif. d, *J*=0.9 Hz, 3-H), 6.81 (1H, dd, *J*=8.5, 2.2 Hz, 5-H), 6.96 (1H, d, *J*=2.2 Hz, 7-H), 7.31 (1H, d, *J*=8.5 Hz, 4-H).

For determination of a product ratio **1b** (0.199 g, 1.23 mmol) and CsF (0.241 g, 1.59 mmol) in $PhNEt_2$ (2 ml) were reacted for 8 h. Four components of **3b-1, 3b-2, 2b-1** and **2b-2** in the crude product (0.137 g, 66.8 %) were estimated as a ratio of 3.69 : 1.60 :1.30 : 1.

On *p*-Methoxyphenyl Propargyl Ether (1c) **1c** (0.518 g, 3.18 mmol) and CsF (0.896 g, 5.90 mmol) in $PhNEt_2$ (5 ml) were reacted for 6 h to give 5-methoxy-2-methylbenzo[*b*]furan (**3c**) (0.304 g, 58.9 %) as a colorless oil, bp 110-120 °C (4 mmHg) [lit.,[9] bp 130-140 °C (24 mmHg)]. *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.33; H, 5.96. Nmr δ: 2.42 (3H, d, *J*=1.0

Hz, 2-Me), 3.82 (3H, s, OMe), 6.30 (1H, dif. s, 3-H), 6.79 (1H, dd, *J*=8.8, 2.7 Hz, 6-H), 6.94 (1H, d, *J*=2.7 Hz, 4-H), 7.27 (1H, d, *J*=8.8 Hz, 7-H).

On *o*-Methoxycarbonylphenyl Propargyl Ether (1d) **1d** (0.512 g, 2.69 mmol) and CsF (0.700 g, 4.61 mmol) in $PhNEt_2$ (5 ml) were reacted for 6 h to give 7-methoxycarbonyl-2-methylbenzo[*b*]furan (**3d**) (0.323 g, 63.1 %) as a colorless oil, bp 107-115 °C (4 mmHg). *Anal.* Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.38; H, 5.18. Ir ν_{max} (neat): 1720 cm^{-1}. Nmr δ: 2.53 (3H, d, *J*=0.9 Hz, 2-Me), 3.99 (3H, s, OMe), 6.42 (1H, dif. d, *J*=0.9 Hz, 3-H), 7.22 (1H, t, *J*=7.6 Hz, 5-H), 7.65 (1H, dd, *J*=7.6, 1.0 Hz, 4-H), 7.85 (1H, dd, *J*=7.6, 1.0 Hz, 6-H).

On *m*-Methoxycarbonylphenyl Propargyl Ether (1e) **1e** (6.02 g, 3.17 mmol) and CsF (0.834 g, 5.49 mmol) in $PhNEt_2$ (6 ml) were reacted for 7 h. The crude products were repeatedly separated by plc using a mixed solvent of CCl_4 and $CHCl_3$ (3 : 1, v/v) to give two furans[6]: (a) 4-Methoxycarbonyl-2-methylbenzo[*b*]furan (**3e-1**), a colorless oil, bp 120-130 °C (4 mmHg). *Anal.* Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.20; H, 5.04. Ir ν_{max} ($CHCl_3$): 1712 cm^{-1}. Nmr δ: 2.40 (3H, d, *J*=1.0 Hz, 2-Me), 3.87 (3H, s, OMe), 6.89 (1H, dif. s, 3-H), 7.15 (1H, dd, *J*=8.3, 7.5 Hz, 6-H), 7.48 (1H, dif. d, *J*=8.3 Hz, 7-H), 7.82 (1H, dif. d, *J*=7.5 Hz, 5-H); (b) 6-Methoxycarbonyl-2-methylbenzo[*b*]furan (**3e-2**), a colorless oil, bp 110-120 °C (4 mmHg). HRFAB-ms *m/z*: 191.0706 (Calcd for $C_{11}H_{11}O_3$: 191.0708). Ir ν_{max} ($CHCl_3$): 1711 cm^{-1}. Nmr δ: 2.42 (3H, d, *J*=1.0 Hz, 2-Me), 3.86 (3H, s, OMe), 6.35 (1H, dif. s, 3-H), 7.41 (1H, d, *J*=8.3 Hz, 4-H), 7.83 (1H, dd, *J*=8.3, 1.4 Hz, 5-H), 8.01 (1H, s, 7-H).

For determination of a product ratio **1e** (0.199 g, 1.05 mmol) and CsF (0.471 g, 3.10 mmol) in $PhNEt_2$ (2 ml) were reacted for 14 h. Three components of the starting **1e**, **3e-1** and **3e-2** in the crude product (0.149 g, 74.9 %) were estimated as a ratio of 1 : 35.8 : 11.5.

On *p*-Methoxycarbonylphenyl Propargyl Ether (1f) **1f** (0.504 g, 2.65 mmol) and CsF (0.970 g, 6.39 mmol) in $PhNEt_2$ (5 ml) were reacted for 48 h. The crude products were separated by flash chromatography[10] using a mixed solvent of hexane and acetone (50 : 1, v/v) to give 5-methoxycarbonyl-2-methylbenzo[*b*]furan (**3f**) (0.271 g, 53.8 %), bp 124-138 °C (4 mmHg), which was solidified into colorless fine prisms, mp 60-61 °C. *Anal.* Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.25; H, 5.25. Ir ν_{max} (nujol): 1727 cm^{-1}. Nmr δ: 2.47 (3H, d, *J*=1.0 Hz, 2-Me), 3.92 (3H, s, OMe), 6.43 (1H, dif. d, *J*=1.0 Hz, 3-H), 7.41 (1H, d, *J*=8.6 Hz, 7-H), 7.94 (1H, dd, *J*=8.6, 1.8 Hz, 6-H), 8.20 (1H, d, *J*=1.8 Hz, 4-H).

REFERENCES AND NOTES

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10. Methyl *p*-methoxybenzoate was also isolated as a by-product in 6.1 % yield.

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