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- We also prepared 2-Ts-CD by reacting β -CD with 3-nitrophenyl tosylate.⁸ This method gave overall <10% yield, whereas the procedure in Ref. 6 gave 25% yield.
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- Inclusion of the toluene group does not necessarily result in weaker binding of guests. When the guest is large and only partially included into the cavity, the hydrophobic interaction between the toluene group and the inserted portion of the guest molecule would lead stronger binding. This seems to be the case with ferrocene-monoacrylate which exhibits large binding constant with 6-Ts-CD than with β -CD, while ferrocene-diacylates show the reverse trend.⁴
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Synthesis of 2-Methylbenzo[*b*]Furan Derivatives from Aryl β -Chloroallyl Ethers with Aluminium Chloride

Jae Nyoung Kim, Sun Young Shin, and Eung K. Ryu*

Korea Research Institute of Chemical Technology,
P.O.Box 9 Taedeg-Tanji, Taejeon 305-606

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Although there are several synthetic methods of benzofuran derivatives,¹ they are often hampered by low yields or involve starting materials which are not easily accessible. One possible method for these compounds involves the use of Claisen rearrangement of aryl β -chloroallyl ethers² or aryl propargyl ethers.³ However, these methods have some limitations. In the case of aryl β -chloroallyl ethers, the use of solvents that have high boiling point with long reaction time is required and resulted in low yields of products in most cases.² Claisen rearrangement of aryl propargyl ethers needed electron withdrawing substituents on the aryl group to afford the desired benzofuran derivatives in reasonable yields. Otherwise, benzopyran derivatives or a mixture of products were obtained.³

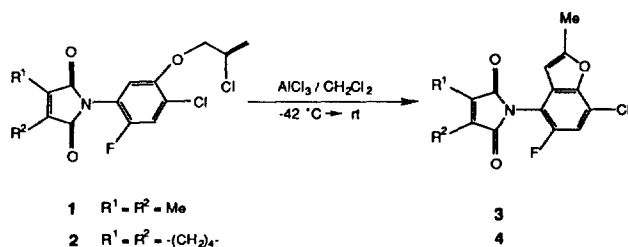
In our synthetic studies on the herbicidal maleimide derivatives⁴ such as **3** and **4** by the use of Claisen rearrangement, we found that treatment of **1** or **2** with AlCl_3 at low temperature ($-42^\circ\text{C} \rightarrow \text{rt}$) afforded the desired 2-methylbenzo[*b*]furan derivatives in good yields *via* tandem Claisen rearrangement-cyclization reaction. Aluminium chloride af-

Table 1. Synthesis of 2-Methylbenzo[*b*]Furan Derivatives

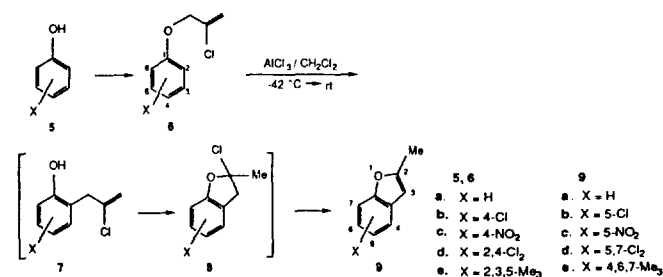
Entry	Starting material	Condition	Product	Yield (%)
1	1	$-42^\circ\text{C} \rightarrow \text{rt}$	3	72
2	1	<i>rt</i>	3	47
3	2	$-42^\circ\text{C} \rightarrow \text{rt}$	4	69
4	2	<i>rt</i>	4	59
5	6a	$-42^\circ\text{C} \rightarrow \text{rt}$	9a	36
6	6b	$-42^\circ\text{C} \rightarrow \text{rt}$	9b	75
7	6c	$-42^\circ\text{C} \rightarrow \text{rt}$	9c	45
8	6d	$-42^\circ\text{C} \rightarrow \text{rt}$	9d	63
9	6d	<i>rt</i>	9d	40
10	6e	$-42^\circ\text{C} \rightarrow \text{rt}$	9e	38

forded the best results for the formation of **3** and **4** in comparison with the other catalysts such as Et_2AlCl , SnCl_4 , or CF_3COOH . Various Lewis acids including AlCl_3 or Bronsted acids have been used in Claisen rearrangement.⁵ However, to our knowledge, there were no reports on the reaction of aryl β -chloroallyl ethers with AlCl_3 .

Thus, we examined the reactions with some aryl β -chloroallyl ethers **6**. Aryl β -chloroallyl ether derivatives **6** were readily prepared by treatment of the corresponding phenol derivatives **5** with 2,3-dichloropropene and potassium carbonate in acetone heated under reflux. The ether **6** were dissolved in dry dichloromethane and cooled to -42°C (dry ice in CH_3CN). Anhydrous AlCl_3 (1 equiv.) was added in one portion and stirred for 2 h. Then the reaction mixture was slowly warmed to room temperature and stirred for 2 h.



The reaction mixture was poured into cold water and extracted with dichloromethane. After usual work-up the crude products were purified by column chromatography to afford the desired compounds **9** in moderate yields. These results were summarized in Table 1.



As shown in Table 1, the reactions at room temperature (entry 2, 4, and 9) showed lower yields than the reactions performed at low temperature. The use of 1.0 equiv. of AlCl_3 was needed to obtain the optimal results. The sequence of

formation of 2-methylbenzo[*b*]furan derivatives is as follows: (1) Claisen rearrangement of **6** to **7**; (2) acid-catalyzed cyclization of **7** to **8**; (3) spontaneous loss of HCl to form **9**.

Characterization of Prepared Compounds. **3**: Yield 72%; ¹H-NMR (CDCl₃) δ2.09 (s, 3H), 2.17 (s, 3H), 2.48 (d, *J*=1 Hz, 3H), 6.26 (d, *J*=1 Hz, 1H), 7.15 (d, *J*=9.9 Hz, 1H); MS (70 eV) *m/z* 53 (43), 54 (43), 307 (M⁺, 100).

4: Yield 69%; ¹H-NMR (CDCl₃) δ1.80 (m, 4H), 2.43 (m, 4H), 2.46 (s, 3H), 6.28 (d, *J*=1.1 Hz, 1H), 7.13 (d, *J*=9.8 Hz, 1H); MS (70 eV) *m/z* 52 (34), 77 (59), 79 (100), 107 (32), 333 (M⁺, 70).

9a: Yield 36%; ¹H-NMR (CDCl₃) δ2.44 (s, 3H), 6.36 (d, *J*=1.1 Hz, 1H), 7.13-7.50 (m, 4H); MS (70 eV) *m/z* 103 (10), 131 (85), 132 (M⁺, 100).

9b: Yield 75%; ¹H-NMR (CDCl₃) δ2.39 (s, 3H), 6.25 (d, *J*=0.9 Hz, 1H), 7.09-7.39 (m, 3H); MS (70 eV) *m/z* 51 (39), 165 (100), 166 (M⁺, 81), 167 (39), 168 (25).

9c: Yield 45%; ¹H-NMR (CDCl₃) δ2.51 (s, 3H), 6.52 (d, *J*=0.7 Hz, 1H), 7.43-8.39 (m, 3H); MS (70 eV) *m/z* 77 (48), 103 (49), 131 (46), 177 (M⁺, 100).

9d: Yield 63%; ¹H-NMR (CDCl₃) δ2.47 (d, *J*=1 Hz, 3H), 6.33 (d, *J*=1 Hz, 1H), 7.17-7.30 (q, 2H); MS (70 eV) *m/z* 102 (27), 165 (25), 199 (85), 200 (M⁺, 100), 201 (64), 202 (60).

9e: Yield 38%; ¹H-NMR (CDCl₃) δ2.40 (s, 3H), 2.45 (s, 3H), 2.47 (s, 3H), 2.51 (s, 3H), 6.39 (d, *J*=1 Hz, 1H), 6.87 (s, 1H); MS (70 eV) *m/z* 159 (99), 173 (65), 174 (M⁺, 100).

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