

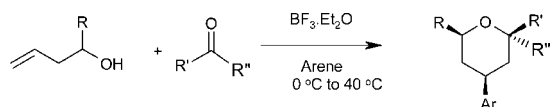
Stereoselective One-Pot, Three-Component Synthesis of 4-Aryltetrahydropyran via Prins–Friedel–Crafts Reaction

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where R=R'=R''=H, alkyl, aryl

A diastereoselective one-pot, three-component Prins–Friedel–Crafts reaction was developed for the synthesis of 4-aryltetrahydropyran derivatives from the reaction of carbonyl compounds with homoallylic alcohol in the presence of arene promoted by boron trifluoride etherate.

Multicomponent reactions are important in organic synthesis due to their ability to form multiple bonds in a single step.¹ Tetrahydropyran unit is found in many biologically active natural products.² These are prepared by hetero-Diels–Alder methods,³ manipulations of carbohydrates,⁴ intramolecular Michael reactions,⁵ and other methods.⁶ Prins reaction has long been used for the synthesis of 4-substituted tetrahydropyran such

as C-4 oxygenated, C-4 halogenated, and C-4 azido tetrahydropyran.⁷ The 4-aryltetrahydropyrans are core units of many naturally occurring biologically active compounds.^{8,2h} There are few methods for the synthesis of 4-aryltetrahydropyran. Li et al.^{8d} have reported the synthesis of 2,4-diaryltetrahydropyran by a three-component Prins–Friedel–Crafts reaction, but it suffers a major drawback. The method is limited to aromatic nucleophiles having a methoxy group. Rychnovsky and his group applied Prins reaction to 4-allyl-1,3-dioxanes²ⁱ and allyl α -acetoxy ether^{2h} for the synthesis of the 4-aryltetrahydropyran unit. Recently we have developed methodologies for the synthesis of symmetric 2,4-disubstituted-4-amido-⁹ and -4-aryltetrahydropyran¹⁰ by Sakurai–Hosomi–Prins–Ritter and Sakurai–Hosomi–Prins–Friedel–Crafts reaction, respectively. Although the Sakurai–Hosomi–Prins–Friedel–Crafts reaction provides symmetrical 4-aryltetrahydropyran with excellent stereochemistry it fails to afford unsymmetrical 2,6-disubstituted-4-aryltetrahydropyran. Here we wish to report an efficient method for the synthesis of unsymmetrical 2,6-disubstituted-4-aryltetrahydropyran from carbonyl compound, homoallyl alcohol, and arene mediated by boron trifluoride etherate in excellent yield and stereoselectivity.

Initially benzaldehyde was reacted with homoallyl alcohol in the presence of boron trifluoride etherate in benzene at rt. The product 2,4-diphenyltetrahydropyran was obtained with 75% yield in 6 h. The reaction is stereoselective and both substituents are in the equatorial position. The reaction can be generalized as shown in Scheme 1.

To prove its general applicability, aliphatic, aromatic, unsaturated, and heterocyclic aldehydes were examined and it was found that all types of aldehydes give good yields with high stereoselectivity (Table 1).

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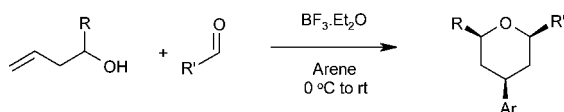
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(10) The reaction of aldehyde with allylsilane in arene gives symmetrical 2,6-disubstituted-4-aryltetrahydropyran in good yields. The reaction is highly stereoselective. Unpublished work.

SCHEME 1. Synthesis of 2,6-Disubstituted-4-phenyl-tetrahydropyran


where R = R' = H, alkyl, aryl, heterocyclic

In all the cases studied, 4-aryltetrahydropyrans **1b–21b** (Table 1) could be obtained in high purity without any side products. Both aliphatic and aromatic aldehydes give good yields with a high degree of diastereoselectivity as determined from the ^1H and ^{13}C NMR spectrum of the crude product. The substituents on the aromatic ring have a promising effect on this reaction. The aromatic aldehydes having electron-withdrawing groups and simple benzaldehyde gave good yields compared to electron-donating groups. Similarly saturated aliphatic aldehydes are found to be better substrates than the conjugated aliphatic aldehydes. This can be attributed to the stability of the oxocarbenium ion intermediate formed during the reaction (species **3**, Scheme 3).^{7a,d} The electron-donating groups on the aromatic ring stabilize the oxocarbenium ion whereas the electron-withdrawing groups destabilize the oxocarbenium ion. The conformation of the compounds is the chair form and all three substituents are in the equatorial position. This was confirmed by NOE experiment and single-crystal X-ray analysis.¹¹

To extend the utility of this method, various arenes as nucleophiles were systematically investigated under these reaction conditions. It was observed that methyl- and methoxy-substituted benzene reacts faster than benzene. Thus, the reaction with toluene gave **22o/p** as an inseparable regioisomer with a ratio of 4.7:1 and 90% overall yield. Similarly *o*- and *m*-xylene gave products **23o/p** (85% yield) and **24o/p** (88% yield) as a mixture of two inseparable regioisomers with a ratio of 1:1.2 and 1:2.7, respectively. On the other hand *p*-xylene gave **25** as a single isomer with 80% yield. Anisole gave ortho (**26o**) and para (**26p**) regioisomers with an *o/p*-ratio of 2:1 and 53% and 27% yields, respectively (80% overall yield). On the other hand 1-methoxy-4-methylbenzene gave the single isomer **27** in 82% yield (Table 2). But fused ring aromatic compounds, for example, naphthalene, 2-methoxynaphthalene, and deactivated aromatic compounds, remain unreactive.

The reaction can also be extended to cyclic and symmetrical acyclic ketones (Scheme 2). The reaction needs to be heated to 40 °C and takes a longer time. Reaction with an unsymmetrical ketone is not stereoselective. Thus, the reaction of cyclohexanone and 1,4-cyclohexanedione at 40 °C gave spirocyclic compounds **28** and **29** in 56% and 40% yields, respectively. On the other hand, symmetrical dichloroacetone gave 2,2-bis-chloromethyl-4-phenyltetrahydropyran **30** in 50% yield. Thus, it is evident that this reaction has widespread application for the synthesis of novel bicyclic heterocycles.

The major advantage of this reaction is that in a single step, two reactions, primarily the Prins cyclization and the Friedel–Crafts reaction, can be performed without any difficulties.

The mechanism of the reaction can be explained as follows. In the presence of Lewis acid, homoallylic alcohol **1** reacts with aldehyde to afford intermediate **2** (Scheme 3). Intermediate **2**

TABLE 1. Synthesis of 2,6-Disubstituted-4-aryltetrahydropyran

Sl No.	Aldehyde (a)	Homoallyl alcohol	Time /h	Product (b)	Yield ^a (%)
1			6		75
2			4		90
3			4		90
4			4		95
5			4		88
6			4		92
7			4		80
8			4		93
9			4		90
10			9		60
11			9		70
12			10		65
13			4		80
14			4		85
15			5		70
16			6		63
17			6		65
18			3		75
19			3		85
20			3		90
21			3		92

^a Yields refer to isolated yield.

(11) Crystallographic data for compound **2b** have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication number CCDC 68764.

TABLE 2. Reaction of 3-Buten-1-ol and *m*-Nitrobenzaldehyde with Other Nucleophiles (Arenes)

S.No.	Arene	Time / h	Product	%Yield ^a
1		1.5	 22o 22p	90
2		1	 23o 23p	85
3		1	 24o 24p	88
4		1	 25	80
5		6	 26o^b 26p^b	80
6		6	 27	82

^a Yields refer to isolated yield. ^b Otho/para ratio (**26o/26p** 2:1).

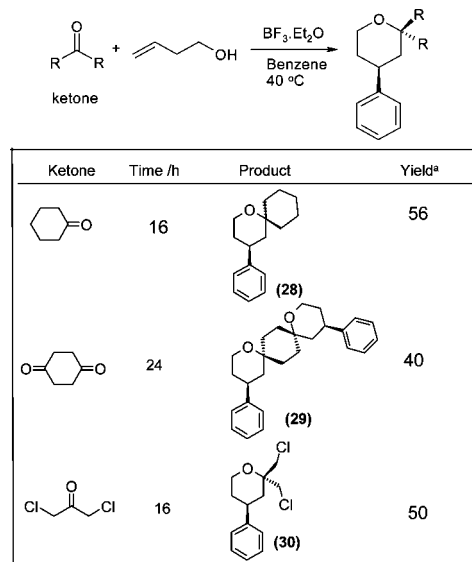
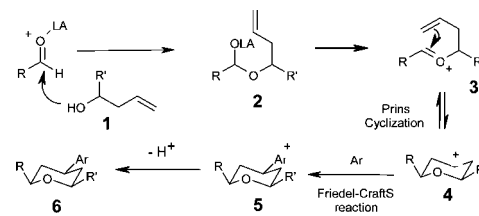
forms oxocarbenium ion **3**, which after cyclization gives tetrahydropyranyl cation **4**. Cation **4** in the presence of arene nucleophile gives intermediate **5**, which after deprotonation gives the 2,6-disubstituted-4-aryltetrahydropyran **6**.

In summary, an efficient and highly diastereoselective one-pot method has been developed for the synthesis of unsymmetrical 2,6-disubstituted-4-aryltetrahydropyran. The same method can also be used for the synthesis of spirocyclic compounds in good yields. This method should be useful in natural product synthesis.

Experimental Section

General Procedure for the Synthesis of Compounds 1b–21b and 22–25. To a mixture of aldehydes (1.0 equiv) in arene (3.0 mL) was added boron trifluoride etherate (1.2 equiv). The mixture was cooled to 0 °C and then homoallyl alcohol (1.0 equiv) in arene (2.0 mL) was added drop by drop over 10 min. The temperature was slowly brought to rt in 1 h. The reaction mixture was stirred at rt for a specified time. The progress of the reaction was monitored by TLC with ethyl acetate and hexane as eluents. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel to give the title compounds.

Synthesis of 2,4-Diphenyltetrahydropyran (1b, Table 1). To a solution of benzaldehyde **1a** (0.20 mL, 2.0 mmol) in benzene (3.0 mL) was added boron trifluoride etherate (0.30 mL, 2.4 mmol). The mixture was cooled to 0 °C and then buten-1-ol (144 mg, 2.0

SCHEME 2. Reaction of 3-Buten-1-ol with Ketone**SCHEME 3.** Mechanism of the Reaction

mmol) in benzene (2.0 mL) was added drop by drop over 10 min. The temperature was slowly brought to rt in 1 h. The reaction mixture was stirred at rt for 6 h. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel to give 2,4-diphenyltetrahydropyran **1b** (358 mg, 75%) as a gum. ¹H NMR (400 MHz, CDCl₃) δ 1.80 (q, *J* = 12.0 Hz, 1 H), 1.85–1.95 (m, 2 H), 2.08 (dq, *J* = 13.2 and 2.0 Hz, 1 H), 2.97 (tt, *J* = 11.6 and 4.0 Hz, 1 H), 3.77 (dt, *J* = 11.2 and 3.2 Hz, 1 H), 4.29 (ddd, *J* = 11.2, 4.0, and 2.4 Hz, 1 H), 4.48 (dd, *J* = 11.2 and 2.0 Hz, 1 H), 7.19–7.40 (m, 10 H); ¹³C NMR (100 MHz, CDCl₃) δ 33.3, 41.5, 42.0, 68.5, 79.8, 125.7, 126.4, 126.7, 127.4, 128.3, 128.5, 142.9, 145.4; IR 3061, 3029, 2938, 2845, 1494, 1452, 1374, 1252, 1128, 1088, 1041, 961, 918, 751, 701 cm⁻¹. Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.55; H, 7.78.

General Procedure for the Synthesis of Compounds 26 and 27. To a mixture of *m*-nitrobenzaldehyde (1.0 equiv) in CH₂Cl₂ (2.0 mL) was added boron trifluoride etherate (1.2 equiv). The mixture was cooled to 0 °C and then homoallyl alcohol (1.0 equiv) and nucleophile (arene) (5.0 equiv) in CH₂Cl₂ (1.0 mL) were added drop by drop over 10 min. The temperature was slowly brought to rt in 1 h. The reaction mixture was stirred at rt for a specified time. The progress of the reaction was monitored by TLC with ethyl acetate and hexane as eluents. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel to give the title compounds.

4-(2-Methoxyphenyl)-2-(3-nitrophenyl)tetrahydropyran (26o) and 4-(4-Methoxyphenyl)-2-(3-nitrophenyl)tetrahydropyran (26p, Table 2). To a mixture of *m*-nitrobenzaldehyde (302 mg, 2.0 mmol) in CH₂Cl₂ (2.0 mL) was added boron trifluoride etherate (0.30 mL, 2.4 mmol). The reaction mixture was cooled to 0 °C and then a

solution of 3-buten-1-ol (144 mg, 2.0 mmol) and anisole (1.0 mL, 9.2 mmol) in CH_2Cl_2 (1.0 mL) was added drop by drop over 10 min. The temperature was then slowly increased to rt in 1 h. The reaction mixture was stirred at rt for 6 h. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel to give **26o/p** as two regioisomers with a ratio 2:1. **26o** (334 mg, 53%): solid; mp 79–83 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.67 (q, $J = 12.0$ Hz, 1 H), 1.80–1.95 (m, 2 H), 2.10 (dq, $J = 13.2$ and 2.0 Hz, 1 H), 3.45 (tt, $J = 12.0$ and 3.6 Hz, 1 H), 3.77–3.82 (m, 1 H), 3.86 (s, 3 H), 4.31 (ddd, $J = 11.6$, 4.4, and 1.6 Hz, 1 H), 4.63 (dd, $J = 11.2$ and 2.0 Hz, 1 H), 6.86–7.00 (m, 2 H), 7.16–7.23 (m, 2 H), 7.50 (t, $J = 8.0$ Hz, 1 H), 7.71 (d, $J = 7.6$ Hz, 1 H), 8.10 (d, $J = 8.4$ Hz, 1 H), 8.28 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.8, 34.8, 40.4, 55.5, 69.1, 78.9, 110.6, 120.9, 121.1, 122.5, 126.7, 127.5, 129.4, 132.2, 133.1, 145.4, 148.4, 156.9; IR 2939, 2841, 1600, 1528, 1493, 1349, 1240, 1132, 1083, 1030, 846, 810, 753 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.95; H, 6.14; N, 4.52. **26p** (167 mg, 27%): gum; ^1H NMR (400 MHz, CDCl_3) δ 1.65 (q, $J = 12.0$ Hz, 1 H), 1.82–1.91 (m, 2 H), 2.09 (dq, $J = 13.2$ and 2.0 Hz, 1 H), 2.93 (tt, $J = 12.0$ and 3.6 Hz, 1 H), 3.71–3.80 (m, 1 H), 3.77 (s, 3 H), 4.31 (dt, $J = 10.8$ and 1.2 Hz, 1 H), 4.56 (dd, $J = 10.8$ and 1.6 Hz, 1 H), 6.85 (d, $J = 8.8$ Hz, 2 H), 7.15 (d, $J = 8.8$ Hz, 2 H), 7.48 (t, $J = 8.0$ Hz, 1 H), 7.69 (d, $J = 7.6$ Hz, 1 H), 8.10 (dd, $J = 8.4$ and 1.2 Hz, 1 H), 8.27 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 33.4, 41.1, 41.9, 55.3, 68.7, 78.6, 114.1, 120.9, 122.4, 127.7, 129.4, 132.0, 137.2, 145.2, 148.3, 158.3; IR 2935, 2847, 1610, 1528, 1463, 1351, 1249, 1180, 1086, 1036, 830, 807, 738 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.04; H, 6.08; N, 4.55.

General Procedure for the Three-Component Reaction with Ketones 28–30. To a solution of ketone (1 equiv) and 3-buten-ol (1 equiv) in benzene (3.0 mL) was added boron trifluoride etherate (1.2 equiv). The reaction mixture was stirred for the specified time at 40 °C. The progress of the reaction was monitored by TLC with

ethyl acetate and hexane as eluents. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel.

Synthesis of 4-Phenyl-1-oxa-spiro[5.5]undecane (28, Scheme 2). To a solution of cyclohexanone (196 mg, 2.0 mmol) and 3-buten-1-ol (144 mg, 2.0 mmol) in benzene (3.0 mL) was added boron trifluoride etherate (0.30 mL, 2.4 mmol). The reaction mixture was stirred at 40 °C for 16 h. After completion of the reaction, the product was extracted with ethyl acetate, then washed with brine and water. The organic layer was dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by short column chromatography over silica gel to give 4-phenyl-1-oxa-spiro[5.5]undecane **28** (258 mg, 56%) as a gum. ^1H NMR (400 MHz, CDCl_3) δ 1.26–1.80 (m, 14 H), 2.10–2.14 (m, 1 H), 2.90–2.97 (m, 1 H), 3.73–3.85 (m, 1 H), 7.18–7.23 (m, 3 H), 7.28–7.33 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.6, 21.8, 26.3, 29.7, 33.7, 36.7, 40.5, 43.6, 60.7, 72.4, 126.3, 126.8, 128.5, 146; IR 3027, 2927, 2855, 1603, 1492, 1445, 1375, 1175, 1101, 1079, 974, 910, 759, 698 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}$: C, 83.43; H, 9.63. Found: C, 83.54; H, 9.54.

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Supporting Information Available: Experimental procedures and ^1H , ^{13}C NMR spectra of all compounds, ^{19}F NMR spectra of **4b** and **8b**, and X-ray crystallographic data and ORTEP diagram of **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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