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Stereoselective Synthesis of 2,6-Disubstituted-4-Aryltetrahydropyrans Using Sakurai–Hosomi–Prins–Friedel–Crafts Reaction

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The reaction of aldehydes with allyltrimethylsilane in arene solvents gives symmetrical 2,6-disubstituted-4-aryltetrahydropyrans in good yields. The reaction is highly stereoselective.

Introduction

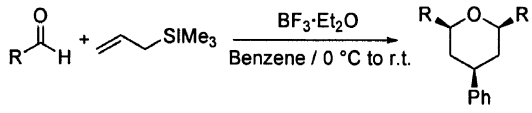
Multicomponent reactions are important in organic synthesis because of their ability to construct multiple bonds in a single step, which is crucial for pharmaceutically active and natural product synthesis.[1] The synthesis of the tetrahydropyran unit is important because of its presence in many natural products.[2] The all-*cis* 2,6-disubstituted-4-aryltetrahydropyrans have olfactory properties[3] and shows nonredox 5-lipoxygenase inhibiting properties.[4] These tetrahydropyrans are prepared by hetero-Diels–Alder methods,[5] manipulation of carbohydrates,[6] Prins cyclization,[7] and intramolecular Michael reactions.[8] Although the synthesis of 4-halo-,[9] 4-thio-,[10] 4-azido-,[11] 4-amino-,[12] and 4-hydroxytetrahydropyrans[7e,7f,9d,13] have been reported in the literature, the synthesis of 2,6-disubstituted-4-aryltetrahydropyrans is limited.[14,2h]

We have shown in our previous investigation that 2,6-disubstituted-4-amidotetrahydropyrans can be synthesized in high yields with excellent stereoselectivity through $BF_3{\cdot}Et_2O$-mediated cyclization of aldehydes and allyltrimethylsilane in acetonitrile. In this protocol, a Sakurai–Hosomi–Prins–Ritter reaction sequence was used.[12e]

We disclose here a stereoselective one-pot, three-component synthesis of 2,6-disubstituted-4-aryltetrahydropyrans from aldehydes, allyltrimethylsilane, and arenes by using a Sakurai–Hosomi–Prins–Friedel–Crafts reaction.

Results and Discussion

To start, benzaldehyde (1.0 mmol) was treated with allyltrimethylsilane (0.6 mmol) in benzene (5.0 mL) in the presence of $BF_3{\cdot}Et_2O$ (1.2 mmol) at 0 °C, and the reaction was warmed to room temperature. 2,4,6-Triphenyltetrahydropyran was obtained in 74% yield. To prove the general applicability of this reaction, a variety of alkyl and aryl aldehydes were investigated as shown in Scheme 1. The results are summarized in Table 1.



Scheme 1. Synthesis of symmetrical 2,6-disubstituted-4-aryltetrahydropyran (R = alkyl, aryl).

In all the cases studied, 4-aryltetrahydropyrans **1b**–**16b** (Table 1) could be obtained in high purity without any side products. Both aliphatic and aromatic aldehydes gave good yields with high diastereoselectivity, as determined from the ^1H and ^{13}C NMR spectra of the crude products. The substituents on the aromatic ring play an important role in this reaction: electron-withdrawing substituents and simple aldehydes gave better yields than those obtained when electron-donating groups were on the ring. Aliphatic aldehydes were found to be better substrates for this reaction. The substituents at the 2-, 4-, and 6-positions of the tetrahydropyran ring are in a *cis* relationship and are equatorial. This is revealed from the coupling constants of the 2,6-H (J = 11.2 and 2.0 Hz) and the 4-H (J = 11.2 and 2.0 Hz) hydrogen atoms of compound **2b** (Figure 1). This was also confirmed by an NOE experiment and single-crystal X-ray analysis.[15]

To explore further utility of the method, other arenes were also studied as nucleophiles as shown in Table 2. Thus, the reaction of *m*-nitrobenzaldehyde (**3a**) in toluene gave product **17** as an inseparable mixture of two regioisomers with a ratio of 4.7:1 and 97% overall yield. *o*-Xylene gave

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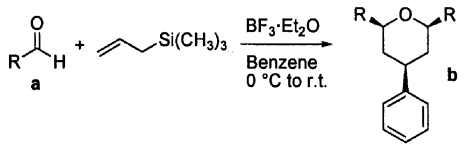
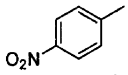
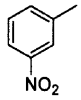
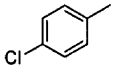
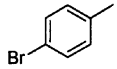
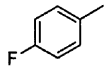
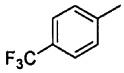
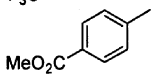
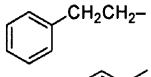
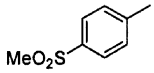
Table 1. Synthesis of 2,6-disubstituted-4-phenyltetrahydropyran.



Substrate	R	Time [h]	Product	Yield[a] [%]
1a		14	1b	74
2a		8	2b	93
3a		8	3b	95
4a		12	4b	80
5a		7	5b	85
6a		12	6b	60
7a		12	7b	85
8a		6.5	8b	90
9a		8	9b	85
10a		6.5	10b	89
11a		8	11b	87
12a		16	12b	80
13a		8	13b	88
14a		16	14b	72
15a	CH_3–	16	15b	50
16a	$CH_3(CH_2)_4CH_2$–	16	16b	85

[a] Yields refer to isolated products. Compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

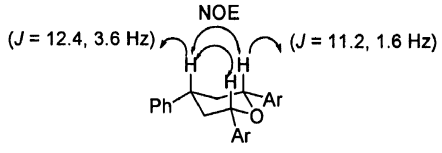
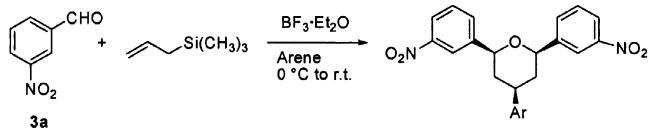
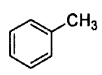
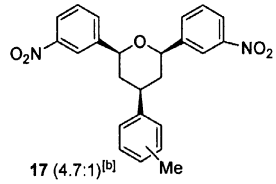
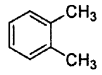
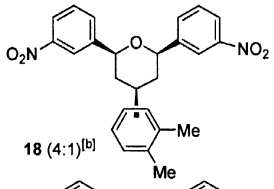
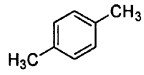
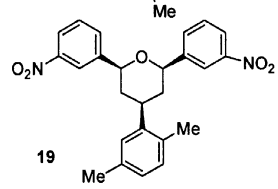
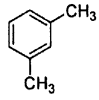
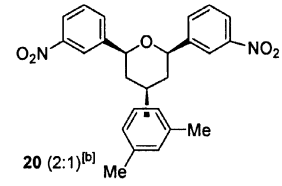
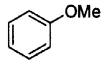
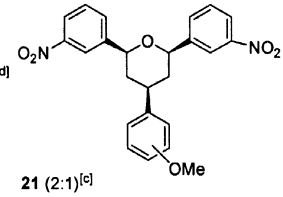


Figure 1. Coupling constants and NOE of compound **2b**.

product **18** as an inseparable mixture of two regioisomers with a ratio of 4:1 and 100% overall yield. In contrast, *p*-xylene gave single product **19** with 100% yield.

Table 2. Reaction of *m*-nitrobenzaldehyde with other aromatic nucleophiles.



Entry	Nucleophiles (Arenes)	Time [h]	Product	Yield[a] [%]
1		2	 **17** (4.7:1)[b]	97
2		1	 **18** (4:1)[b]	100
3		1	 **19**	100
4		1	 **20** (2:1)[b]	100
5		0.5 18[d]	 **21** (2:1)[c]	95 90[d]

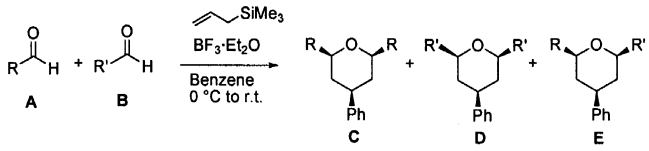
[a] Yields refer to isolated products. Compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. [b] Inseparable mixture of regioisomers. Ratio was determined by ^{1}H NMR spectroscopy. [c] *o*/*p*-Isomers were separated and their ratio was 2:1. [d] Reaction with 5.0 equiv. of anisole in CH_2Cl_2.

Similarly, *m*-xylene gave product **20** as an inseparable mixture of two regioisomers with a ratio of 1:2 and 100% overall yield. Anisole is a good nucleophile, as it gave **21** with 95% yield within 30 min. (**21*p*/21*o***, 1:2). Even at a low concentration of anisole in dichloromethane a good yield was obtained (90%, Table 2). Electron-deficient aromatic compounds such as halobenzenes and nitrobenzene do not act as nucleophiles in the Friedel–Crafts reaction. Aromatic compounds having electron-donating groups, such as

methyl and methoxy groups, behave as strong nucleophiles in comparison to benzene, which is evident from their reaction times and yields (Tables 1 and 2). Other aromatic compounds like naphthalene, 2-methoxynaphthalene, and other fused-ring aromatic compounds were inactive under these reaction conditions. This might be due to steric hindrance.

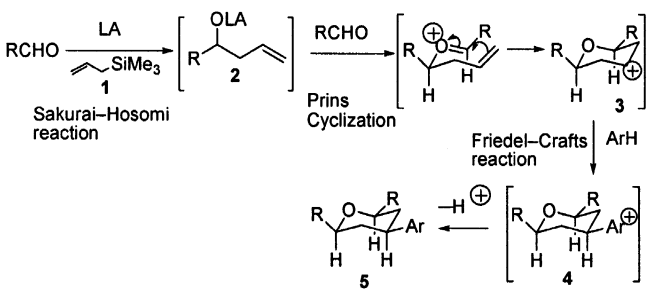
The reaction was also carried out with two different aldehydes. The reaction was performed by allowing aldehyde **A** to react with allyltrimethylsilane for 1 h, followed by the addition of aldehyde **B**. The reaction was not selective and gave three different products: symmetric products **C** and **D** and cross product **E** (Table 3). The yield of the cross product was always less than that of the symmetric products. Allowing the first aldehyde to react with allyltrimethylsilane for a longer time period resulted in lower amounts of cross products. This indicates that the rate of formation of homoallylic alcohol (Sakurai–Hosomi reaction) is slower than the Prins cyclization reaction. That is, all the molecules of aldehyde **A** do not form the homoallylic alcohol intermediate so that aldehyde **B** can take part in Prins cyclization to give only the cross product. The possibility of allyl transfer from the initially formed homoallyloxy intermediate (species **2**, Scheme 2) to the second aldehyde cannot be ruled out.

Table 3. Reaction with mixed aldehydes.



Entry	R	R'	Time [h]	Product (% Yield %)[a] C	D	E
1		O_2N	8	**1b** (32)	**2b** (32)	19
2		O_2N	8	**14b** (36)	**2b** (29)	15
3	$CH_3(CH_2)_4CH_2$–		14	**16b** (33)	**1b** (24)	15

[a] Yields refer to isolated products. Compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.



Scheme 2. Mechanism of the reaction.

The mechanism of the reaction can be explained as follows: In the presence of Lewis acid allyltrimethylsilane (**1**) reacts with the aldehyde to afford intermediate **2** (Scheme 2). Intermediate **2** reacts with another molecule of the aldehyde to give tetrahydropyranyl cation **3**, which in the presence of an aryl nucleophile, gives intermediate **4**. Species **4** after deprotonation gives 2,6-disubstituted-4-aryltetrahydropyran **5**.

Conclusions

In summary, an efficient, highly diastereoselective, one-pot method for the synthesis of 2,6-disubstituted-4-aryltetrahydropyrans in good yields has been developed. The scope and synthetic applications of this novel reaction is under investigation in our laboratory.

Experimental Section

General Procedure for the Synthesis of 2,6-Disubstituted-4-aryltetrahydropyrans: To a mixture of aldehyde (1.0 mmol), $BF_3{\cdot}Et_2O$ (1.2 mmol), and aryl compound (3.0 mL) was added a mixture of allyltrimethylsilane (0.6 mmol) and aryl compound (2.0 mL) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and 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 the title compounds.

2,4,6-Triphenyltetrahydropyran (1b): To a mixture of benzaldehyde (**1a**; 0.10 mL, 1.0 mmol), benzene (3.0 mL), and $BF_3{\cdot}Et_2O$ (0.15 mL, 1.2 mmol) was added allyltrimethylsilane (0.10 mL, 0.6 mmol.) in benzene (2.0 mL) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for 14 h. The progress of the reaction was monitored by TLC (EtOAc/hexane, 1:9). After completion of the reaction, the product was extracted with ethyl acetate and 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 **1b** (116 mg, 74%) as a gum. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.76–1.85 (m, 2 H, 3ax,5ax-CH), 2.16–2.20 (m, 2 H, 3eq,5eq-CH), 3.17 [tt, $J_{4ax,(3,5)ax}$ = 12.0 Hz, $J_{4ax,(3,5)eq}$ = 3.6 Hz, 1 H, 4ax-CH], 4.75 (dd, $J_{2ax,3ax}$ = 11.2 Hz, $J_{2ax,3eq}$ = 2.0 Hz, 2 H, 2ax,6ax-CH), 7.19–7.37 (m, 12 H, ArH), 7.47–7.49 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.4, 42.6, 80.0, 126.0, 126.6, 126.9, 127.5, 128.5, 128.7, 143.1, 145.3 ppm. IR: $\tilde{\nu}$ = 3063, 2915, 2874, 1598, 1573, 1476, 1443, 1208, 1133, 1079, 1051, 1035, 753 cm^{-1}. $C_{23}H_{22}O$ (314.42): calcd. C 87.86, H 7.05; found C 87.68, H 7.21.

4-(4-Methoxyphenyl)-2,6-bis(3-nitrophenyl)tetrahydro-2*H*-pyran (21*p*) and 4-(2-Methoxyphenyl)-2,6-bis(3-nitrophenyl)tetrahydro-2*H*-pyran (21*o*): To a solution of **3a** (302 mg, 2.0 mmol) and $BF_3{\cdot}Et_2O$ (0.30 mL, 2.4 mmol) in dichloromethane (2.0 mL) was added a solution of allyltrimethylsilane (0.22 mL, 1.4 mmol.) and anisole (1.10 mL, 10.0 mmol) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for 24 h. The progress of the

reaction was monitored by TLC (EtOAc/hexane; 1:9). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by thin-layer chromatography over silica gel to give **21*o*** and **21*p*** in a 2:1 ratio (390 mg, 90% of overall yield) as a solid. Data for **21*p***: Solid. M.p. 164–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74–1.84 (m, 2 H, 3ax,5ax-CH), 2.21–2.25 (m, 2 H, 3eq,5eq-CH), 3.20 [tt, $J_{4ax,(3,5)ax}$ = 12.4 Hz, $J_{4ax,(3,5)eq}$ = 3.6 Hz, 1 H, 4ax-CH], 3.78 (s, 3 H, -OCH_3), 4.88 (dd, $J_{2ax,3ax}$ = $J_{6ax,5ax}$ = 10 Hz, $J_{2ax,3eq}$ = $J_{6a,5eq}$ = 1.2 Hz, 2 H, 2ax,6ax-CH), 6.86 (d, J = 8.4 Hz, 2 H, ArH),7.18 (d, J = 8.4 Hz, 2 H, ArH), 7.56 (m, 2 H, ArH), 7.83 (d, J = 7.6 Hz, 2 H, ArH), 8.15 (d, J = 8.0 Hz, 2 H, ArH), 8.34 (s, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.2, 41.4, 55.5, 79.2, 114.3, 121.1, 122.8, 127.8, 129.7, 132.1, 136.3, 144.5, 148.5, 158.6 ppm. IR: $\tilde{\nu}$ = 2933, 2853, 1528, 1350, 1250, 1103, 1072, 810, 737 cm^{-1}. $C_{24}H_{22}N_2O_6$ (434.45): calcd. C 66.35, H 5.10, N 6.45; found C 66.50, H 5.27, N 6.57. Data for **21*o***: Solid. M.p. 124–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73–1.85 (m, 2 H, 3ax,5ax-CH), 2.20–2.24 (m, 2 H, 3ex,5ex-CH), 3.69 [tt, $J_{4ax,(3,5)ax}$ = 12.4 Hz, $J_{4ax,(3,5)eq}$ = 3.6 Hz, 1 H, 4ax-CH], 3.90 (s, 3 H, -OCH_3), 4.92 (dd, $J_{2ax,3ax}$ = $J_{6ax,5ax}$ = 10 Hz, $J_{2ax,3eq}$ = $J_{6a,5eq}$ = 1.2 Hz, 2 H, 2ax,6ax-CH), 6.88–6.95 (m, 2 H, ArH), 7.16–7.24 (m, 2 H, ArH), 7.56 (m, 2 H, ArH), 7.84 (d, J = 7.6 Hz, 2 H, ArH), 8.14–8.17 (m, 2 H, ArH), 8.33 (s, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.1, 39.6, 55.6, 79.4, 110.7, 121.0, 121.1, 122.7, 126.6, 127.8, 129.6, 132.2 (2 C), 144.7, 148.5, 156.9 ppm. IR: $\tilde{\nu}$ = 2920, 2850, 1528, 1348, 1241, 1102, 1070, 810, 736 cm^{-1}. $C_{24}H_{22}N_2O_6$ (434.44): calcd. C 66.35, H 5.10, N 6.45; found C 66.52, H 5.23, N 6.49.

General Procedure for Crossed 2,6-Disubstituted-4-phenyltetrahydropyrans: To a mixture of aldehyde (1.0 mmol) and $BF_3{\cdot}Et_2O$ (1.2 mmol) in benzene (2.0 mL) was added allyltrimethylsilane (0.6 mmol) in benzene (1.0 mL) drop by drop at 0 °C. The reaction mixture was stirred for 1 h at the same temperature, and the other aldehyde (1.2 mmol) and $BF_3{\cdot}Et_2O$ (1.4 mmol) in benzene (2 mL) was added drop by drop at same temperature. The temperature was then slowly brought to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and 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 the title compounds.

6-(4-Nitrophenyl)-2,4-diphenyltetrahydropyran (1E): To a mixture of benzaldehyde (106 mg, 1.0 mmol) and $BF_3{\cdot}Et_2O$ (0.20 mL, 1.2 mmol) in benzene (2.0 mL) was added allyltrimethylsilane (0.10 mL, 0.6 mmol) in benzene (1.0 mL) drop by drop at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and then *p*-nitrobenzaldehyde (181 mg, 1.2 mmol) and $BF_3{\cdot}Et_2O$ (1.8 mg, 1.4 mmol) in benzene (2 mL) were added drop by drop at the same temperature. The temperature was slowly brought to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and 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 compounds **1b** (100 mg, 32%), **2b** (129 mg, 32%), and **1E** (68 mg, 19%). Data for **1E**: Solid. M.p. 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.70 (q, J = 12.4 Hz, 1 H), 1.80 (q, J = 12.8 Hz, 1 H), 2.15–2.18 (m, 2 H), 3.17 (tt, J = 12.0, 3.6 Hz, 1 H), 4.73 (dd, J = 11.2, 2.0 Hz, 1 H), 4.80 (dd, J = 11.2, 2.0 Hz, 1 H), 7.18–7.39 (m, 8 H), 7.46 (d, J = 8.8 Hz, 2 H), 7.59 (d, J = 8.4 Hz, 2 H), 8.16 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.0, 41.2, 42.3, 78.9, 80.1, 123.7, 125.9, 126.3, 126.6, 126.9, 127.7, 128.6, 128.8, 142.5, 144.6, 147.2, 150.3 ppm. IR: $\tilde{\nu}$ = 3062, 3029, 2941, 2849, 1602, 1516, 1495, 1345, 1287, 1102, 1078, 1030, 987, 851, 748 cm^{-1}. $C_{23}H_{21}NO_3$ (359.42): calcd. C 76.86, H 5.89, N 3.90; found C 76.92, H 5.78, N 3.88.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of **1b**–**8b**, **11b**–**16b**, and **17**–**21**; ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds **9b** and **10b**; crude ^{1}H NMR spectra of compound **11b**; NOESY spectrum of **2b**; X-ray structure and crystal parameters of compound **8b**.

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[15] CCDC-692425 (for **8b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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