

# FeCl<sub>3</sub>-catalysed Zn-mediated allylation of cyclic enol ethers in water

P CHAKRABORTY and S C ROY\*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur,  
Kolkata 700 032, India  
e-mail: ocsr@iacs.res.in

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**Abstract.** A mild and environment-friendly Zn-mediated allylation of dihydrofuran and dihydropyran catalysed by iron(III) chloride in water has been developed.

**Keywords.** Zn-mediated; Fe(III) chloride; catalysis; enolethers; diols.

## 1. Introduction

Organic reactions in aqueous medium has attracted global attention from the chemists due to its safe environmentally benign character. Surprisingly, nature also permits aqueous medium for all the enzymatic processes. Since Breslow<sup>1</sup> introduced the Diels–Alder reaction in aqueous medium, there has been an increasing application of water as solvent in organic synthesis and sometime more advantageous in many respects compared to the common organic solvents.<sup>2</sup> In this connection metal-mediated Barbier type carbon–carbon bond forming reactions in aqueous media have been studied extensively.<sup>3</sup> Cyclic enol ethers like dihydropyrans (DHP) and dihydrofurans (DHF) are electron-rich alkenes that are widely used in various organic transformations.<sup>4</sup> But, the allylation of enol ethers are not much explored except a very few recent reports.<sup>5</sup> Loh and co-workers<sup>6</sup> described an InCl<sub>3</sub>-catalysed indium-mediated synthesis of polyols from the cyclic enol ethers in aqueous medium. Very recently, tin-mediated allylation of enol ethers in water has been reported.<sup>7</sup> But, they mainly dealt with aliphatic allylic bromides with longer reaction time, costly and sometimes toxic metals and metalhalides. Obviously, a further improvement of the method is always desirable.

## 2. Experimental

All melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. The <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> using TMS as an inter-

nal standard on 300 and 75 MHz spectrometer (Bruker) respectively and IR were recorded using a Shimadzu FT IR-8300 instrument. High-resolution mass spectra were obtained using a Qtof Micro YA263 instrument. Ethyl acetate was dried over anhydrous calcium chloride. Petroleum ether of boiling range 60–80°C was dried over sodium. Silica gel of 60–120 mesh were used for column chromatography.

### 2.1 Representative procedure for allylation of dihydropyran

To a stirred mixture of dihydropyran (84.2 mg, 1.0 mmol), water (5 mL), FeCl<sub>3</sub>·6H<sub>2</sub>O (54 mg, 0.2 mmol), Zn (130.8 mg, 2.0 mmol) allyl bromide **1a** (363 mg, 3.0 mmol) was added and the mixture was stirred at room temperature for 2 h. It was then extracted with ethyl acetate (3 × 10 mL), washed with brine (10 mL) and finally dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated under reduced pressure and the crude residue obtained was purified by column chromatography over silica gel (30% ethyl acetate in light petroleum) to afford oct-7-ene-1,5-diol (**2a**) (137 mg, 81%) as a viscous oil. IR (Neat): 3348, 3331, 2933, 1433, 914 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.5–1.38 (m, 6H), 2.31–2.09 (m, 2H), 2.78 (brs, 2H, -OH), 3.64–3.60 (m, 3H), 5.13–5.07 (m, 2H), 5.87–5.73 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 21.8, 32.4, 36.3, 42.0, 62.5, 70.7, 118.0, 134.9; HRMS: calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 167.1043, found 167.1048.

**2.1a 6-Methyloct-7-ene-1,5-diol (2b):** Compound **2b** (*syn/anti* = 1:1) was prepared from dihydropyran and **1b** following the procedure described for compound **2a**. Viscous oil. R<sub>f</sub> = 0.21 (30% ethyl acetate

\*For correspondence

in light petroleum). IR (Neat): 3350, 2935, 1454, 1261, 1057  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.02 (d, 3H,  $J = 6.8$  Hz), 1.03 (d, 3H,  $J = 6.8$  Hz), 1.39–1.69 (m, 6H), 2.15–2.30 (m, 1H), 3.11 (brs, 2H,  $-\text{OH}$ ), 3.40–3.51 (m, 1H), 3.62–3.69 (m, 2H), 5.03–5.12 (m, 2H), 5.68–5.82 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  13.1, 14.2, 18.1, 21.9, 22.3, 32.6, 33.7, 43.6, 44.3, 62.8, 74.7, 115.3, 116.3, 140.3, 140.9; HRMS: calcd. for  $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  181.1199, found 181.1205.

**2.1b 6,6-Dimethyloct-7-ene-1,5-diol (2c):** Compound **2c** was prepared from dihydropyran and **1c** following the procedure described for compound **2a**. Viscous oil.  $R_f = 0.19$  (30% ethyl acetate in light petroleum). IR (Neat): 3471, 3452, 2943, 1450, 1068, 914  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.97 (s, 6H), 1.22–1.62 (m, 6H), 2.83 (brs, 2H,  $\text{OH}$ ), 3.23 (appeared as a doublet,  $J = 9$  Hz, 1H) 3.60 (t,  $J = 6.0$  Hz, 2H), 4.97–5.05 (m, 2H), 5.79 (dd,  $J = 10.8$ , 17.4 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  22.4, 22.9, 23.2, 30.9, 32.4, 41.7, 62.4, 78.3, 113.2, 145.5; HRMS: calcd. for  $\text{C}_{10}\text{H}_{20}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  195.1356, found 195.1362.

**2.1c 6-Phenyloct-7-ene-1,5-diol (2d):** Compound **2d** was prepared from dihydropyran and **1d** following the procedure described for compound **2a**. Viscous oil.  $R_f = 0.22$  (30% ethyl acetate in light petroleum). IR (Neat): 3304, 3271, 2937, 1454, 1253, 1074, 916, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.66–1.25 (m, 6H), 2.95 (brs, 2H), 3.20–3.32 (m, 1H), 3.55–3.62 (m, 2H), 3.76–3.87 (m, 1H), 5.09–5.23 (m, 2H), 6.05–6.17 (m, 1H), 7.17–7.35 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  20.7, 21.9, 32.5, 34.0, 57.5, 62.7, 74.0, 74.2, 116.9, 118.0, 126.8, 127.02, 128.0, 128.8, 138.4, 141.0, 141.6; HRMS: calcd. for  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  243.1356, found 243.1360.

**2.1d Hept-6-ene-1,4-diol (2e):** Compound **2e** was prepared from dihydrofuran and **1a** following the procedure described for compound **2a**. Viscous oil.  $R_f = 0.19$  (30% EtOAc in light petroleum): IR (Neat): 3365, 3350, 2935, 1437, 1057  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.44–1.64 (m, 4H), 2.12–2.27 (m, 2H), 3.49–3.63 (m, 5H), 5.06–5.11 (m, 2H), 5.86–5.73 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  29.1, 33.8, 42.1, 62.7, 70.8, 117.8, 134.9.

**2.1e 5-Methylhept-6-ene-1,4-diol (2f):** Compound **2f** was prepared from dihydrofuran and **1b** following

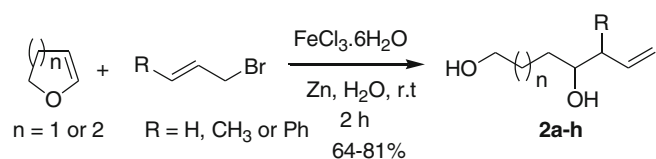
the procedure described for compound **2a**. Viscous oil.  $R_f = 0.21$ ; (30% ethyl acetate in light petroleum). IR (Neat): 3365, 3350, 2941, 1454, 1001, 914  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.02 (dd,  $J = 1.5$ , 6.8 Hz, 3H), 1.61–1.69 (m, 4H), 2.15–2.30 (m, 1H), 3.11 (brs, 2H), 3.40–3.51 (m, 1H), 3.62–3.69 (m, 2H), 5.12–5.03 (m, 2H), 5.68–5.82 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  14.7, 16.2, 29.3, 29.6, 31.1, 31.3, 43.9, 44.4, 63.0, 74.8, 75.4, 115.4, 116.4, 140.9, 141.0.

**2.1f 5,5-Dimethylhept-6-ene-1,4-diol (2g):** Compound **2g** was prepared from dihydrofuran and **1c** following the procedure described for compound **2a**. Viscous oil.  $R_f = 0.18$  (30% ethyl acetate in light petroleum). IR (Neat): 3365, 3350, 2960, 1415, 1055, 758  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.97 (s, 6H), 1.21–1.29 (m, 1H), 1.59–1.70 (m, 3H), 3.21–3.24 (m, 1H), 3.30 (brs, 2H), 3.53–3.66 (m, 2H), 4.96–5.04 (m, 2H), 5.79 (dd,  $J = 10.9$ , 17.4 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  22.5, 22.8, 28.5, 41.7, 30.3, 62.7, 78.5, 113.1, 145.5; HRMS: calcd. for  $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  181.1199, found 181.1205.

**2.1g 5-Phenylhept-6-ene-1,4-diol (2h):** Compound **2h** was prepared from dihydrofuran and **1d** following the procedure described for compound **2a**. Viscous oil.  $R_f = 0.21$  (30% ethyl acetate in light petroleum). IR (Neat): 3379, 3369, 2926, 1452, 1242, 1043, 987, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.31–1.71 (m, 4H), 3.22–3.59 (m, 5H), 3.78–3.83 (m, 1H), 5.09–5.20 (m, 2H), 5.97–6.19 (m, 1H), 7.18–7.30 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  29.1, 31.5, 31.6, 57.3, 57.4, 62.6, 74.1, 74.2, 116.7, 117.5, 126.6, 127.7, 128.0, 128.5, 128.6, 138.5, 138.6, 141.1, 141.7; HRMS: calcd. for  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  229.1199, found 229.1205.

### 3. Results and discussion

We report here a very efficient one pot procedure for the synthesis of enediols from DHP and DHF by the reaction with diallyl zinc catalysed by  $\text{FeCl}_3$  in water medium. Thus, a mixture of DHP or DHF (1.0 mmol),



**Scheme 1.** Synthesis of enediols.

**Table 1.** Allylation of DHP.

Entry	Allylic bromide	Product	Yield(%) <sup>a</sup>	Ref.
1			81	5-7
2			77 <i>syn/anti</i> (1:1)	5-7
3			73	6
4			67 <i>syn/anti</i> (1:1)	5

<sup>a</sup>Yields refer to isolated products**Table 2.** Allylation of DHF.

Entry	Allylic bromide	Product	Yield(%) <sup>a</sup>	Ref.
1			80	5-7
2			78 <i>syn/anti</i> (1:1)	5-7
3			66	6
4			64 <i>syn/anti</i> (1:1)	5

<sup>a</sup>Yields refer to isolated products

water (5 mL), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.2 mmol), zinc (2.0 mmol) and allyl bromide (3.0 mmol) was stirred for 2 h at room temperature to furnish the enediols (**1a–h**) in good yield (scheme 1).

Thus, a series of diallylzinc were reacted with DHP and the results are summarized in table 1.

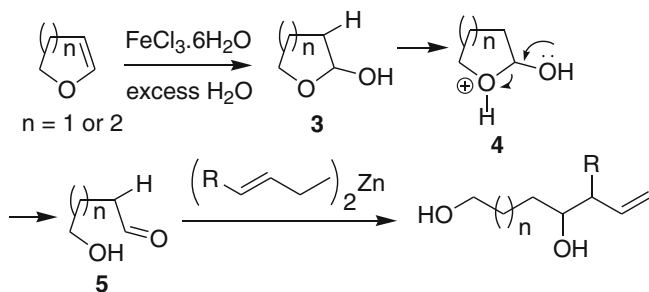
It is obvious that FeCl<sub>3</sub> catalyses the hydration of the cyclic enol. Probably, water plays an important role in the formation of aldehyde **5** in the presence of FeCl<sub>3</sub> from the hemiacetal **3** via the intermediate **4** and then the aldehyde **5** reacts immediately with diallyl zinc to form the enediols. The probable mechanism with the analogy of the report by Kresge<sup>8</sup> is shown in scheme 2.

All the compounds obtained were characterized by IR, NMR and HRMS and were compared with the data reported in the literature. A series of allyl bromides also

reacted with dihydrofuran in the presence of Zn and FeCl<sub>3</sub> (catalytic) in aqueous medium and the results are summarized in table 2.

It is noteworthy that methyl (entry 3, table 1) and phenyl (entry 4, table 1) substituted allyl bromides also smoothly reacted with DHP and DHF to yield the desired products. The allylation reaction did not respond at all when Zn was used without a catalytic amount of FeCl<sub>3</sub> or using only FeCl<sub>3</sub> without Zn. It was found that using Zn and a catalytic amount of FeCl<sub>3</sub> without water could not produce the desired product (table 3).

It has to be mentioned here that the reaction lacks *syn/anti* selectivity. The allylation of both dihydrofuran and dihydropyran with methyl 4-bromocrotonate ended up with a mixture of uncharacterizable products without giving any desired enediols.

**Scheme 2.** Probable mechanism.**Table 3.** Optimization of allylation reaction.

Entry	Reaction condition	Yield (%) of enediol
1	FeCl <sub>3</sub> ·6H <sub>2</sub> O, H <sub>2</sub> O, rt, 2 h	0
2	FeCl <sub>3</sub> ·6H <sub>2</sub> O, Zn, rt, 2 h	0
3	Zn, H <sub>2</sub> O, rt, 2 h	0
4	FeCl <sub>3</sub> ·6H <sub>2</sub> O, Zn, H <sub>2</sub> O, rt, 2 h	80

#### 4. Conclusions

In conclusion, we have developed a new methodology for one-pot synthesis of different enediols from dihydropyran and dihydrofuran in an efficient and environment friendly approach.

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