Journal of Oleo Science
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J. Oleo Sci. **59**, *(10) 549-555 (2010)*

JOURNAL OF OLEO SCIENCE

Synthesis of Cinnamyl Ethers from α-Vinylbenzyl Alcohol Using Iodine as Catalyst

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Abstract: Reactions of α-vinylbenzyl alcohol with other alcohols using iodine as a catalyst were investigated. The corresponding cinnamyl ethers were obtained as products. This suggested that α-vinylbenzyl alcohol was converted to cinnamyl ethers *via* 1-phenylallyl cation. Cinnamyl ethyl ether was obtained in 75% yield by the reaction of α-vinylbenzyl alcohol and ethanol in acetonitrile with iodine under the following conditions: temperature = 50 °C, molar ratio of α-vinylbenzyl alcohol:ethanol:iodine = 1:3.0:0.2, and time period = 6 h. Generally, the yields of the reactions using primary alcohols were higher than those using secondary and tertiary alcohols. Ether interchange also occurred by the reaction of α-vinylbenzyl alcohol and iodine, but proceeded smoothly only when an allyl group was used as the other substituent of the starting ether.

Key words: iodine, α-vinylbenzyl alcohol, 1-phenylallyl cation, cinnamyl ether

1 INTRODUCTION

Ether compounds are important in the perfume industry. In particular, cinnamyl ethers are used widely. Cinnamyl alcohol, which is a component of cinnamyl ethers, is synthesized from α-vinylbenzyl alcohol by allyl rearrangement using catalysts such as molybdenum complexes1), rhenium oxo catalysts2), cobalt chloride3), tin(Ⅱ)chloride with catalytic iridium(Ⅰ)4), and *o*-benzenedisulfonimide5). However, these catalysts are very expensive and/or toxic. Therefore, in this study, we investigated the synthesis of cinnamyl ethers from α-vinylbenzyl alcohol in one step without the isolation of cinnamyl alcohol using iodine as a catalyst. Iodine is easy to handle and has low toxicity, and it has been found to be an efficient catalyst in several organic reactions6-16). We previously reported iodine to be an efficient catalyst in the intramolecular etherification of 1,3-diols17). Sunghwa *et al.* reported that iodine is an efficient catalyst in the etherification of morroniside18).

2 EXPERIMENTAL

2.1 General

NMR spectra were obtained using a 400- or 300-MHz NMR spectrometer(JEOL JNM-LA-400 or Bruker DPX-300)with an internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Mass spectra (EI-MS)were recorded on JEOL JMS-HX110A and JEOL JMS-AX500 spectrometers.

2.2 Materials

α-Vinylbenzyl alcohol(**1**)used in this study is commercially available(SIGMA-ALDRICH Japan K. K.).

2.3 Etherification

A typical procedure is as follows.

2 mL of acetonitrile, 3.0 mmol of ethanol, 134.2 mg(1.0 mmol)of **1**, and 51 mg(0.2 mmol)of iodine were placed in a reaction tube and it was then sealed. The reaction mixture was stirred at 50℃ for 6 h. 10 mL of a 10% aqueous solution of sodium thiosulfate(10 mL)was added to the reaction mixture in order to remove iodine, and the mixture was then extracted with 20 mL of diisopropyl ether three

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Accepted April 16, 2010 (received for review February 3, 2010)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/

times. The organic layer was washed with 100 mL of water, dried with anhydrous sodium sulfate, and evaporated. The product was purified by column chromatography eluted with hexane/ethyl acetate (200:1). A total of 212 mg (0.75 mmol; 75% yield) of cinnamyl ethyl ether **2** was obtained.

2.3.1 Cinnamyl ethyl ether (**2**)

^{1}H-NMR (δ,$CDCl_3$): 1.25 (3H, t, $J = 7.0$ Hz), 3.55 (2H, q, $J = 7.0$ Hz), 4.14 (2H, dd, $J = 1.4$, 6.0 Hz), 6.31 (1H, dt, $J =$ 6.0, 15.9 Hz) 6.60 (1H, dt, $J = 15.9$, 1.4 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 15.7, 66.1, 71.7, 126.7, 126.9, 128.0, 129.0, 132.6, 137.2

IR (neat, cm^{-1}): 1121

HRMS calcd for $C_{11}H_{14}O$:162.1045; found: *m/z* 162.1045.

2.3.2 Cinnamyl methyl ether (**3**)

^{1}H-NMR (δ,$CDCl_3$): 3.39 (3H, s), 4.10 (2H, dd, $J = 1.4$, 4.6 Hz), 6.29 (1H, dt, $J = 6.0$, 15.9 Hz), 6.61 (1H, dt, $J = 15.9$, 1.4 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 58.0, 73.1, 125.9, 126.5, 127.7, 128.6, 132.5,136,7

IR (neat, cm^{-1}): 1120

HRMS calcd for $C_{10}H_{12}O$: 148.0888; found: *m/z* 148.0895.

2.3.3 Cinnamyl propyl ether (**4**)

^{1}H-NMR (δ,$CDCl_3$): 0.95 (3H, t, $J = 7.4$ Hz), 1.64 (2H, sext., $J = 7.2$ Hz), 3.45 (2H, t, $J = 6.8$ Hz), 4.14 (2H, dd, $J =$ 1.3, 6.0 Hz), 6.31 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.21-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$):11.1, 23.4, 71.8, 72.6, 126.3, 126.9, 128.0, 128.5, 129.0, 132.5

IR (neat, cm^{-1}):1117

HRMS calcd for $C_{12}H_{16}O$: 176.1201; found: *m/z* 176.1190.

2.3.4 Butyl cinnamyl ether (**5**)

^{1}H-NMR (δ,$CDCl_3$): 0.93 (3H, t, $J = 7.3$ Hz), 1.40 (2H, sext., $J = 7.4$ Hz), 1.56-1.64 (2H, m), 3.48 (2H, t, $J = 6.6$ Hz), 4.13 (2H, dd, $J = 1.3$, 6.0 Hz), 6.30 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.21-7.43 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.4, 19.8, 32.3, 70.7, 71.4, 126.9, 128.0, 128.9, 132.5, 137.3

IR (neat, cm^{-1}): 1117

HRMS calcd for $C_{13}H_{18}O$: 190.1358; found: *m/z* 190.1351.

2.3.5 Cinnamyl pentyl ether (**6**)

^{1}H-NMR (δ,$CDCl_3$): 0.91 (3H, t, $J = 7.0$ Hz), 1.31-1.38 (2H, m), 1.58-1.65 (2H, m), 3.48 (2H, t, $J = 6.7$ Hz), 4.13 (2H, dd, $J = 1.3$, 6.0 Hz), 6.31 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.23-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.5, 23.0, 28.8, 29.9, 71.0, 71.8, 126.9, 128.0, 128.9, 132.5, 137.2

IR (neat, cm^{-1}): 1108

HRMS calcd for $C_{14}H_{20}O$: 204.1514; found: *m/z* 204.1523.

2.3.6 Cinnamyl hexyl ether (**7**)

^{1}H-NMR (δ,$CDCl_3$): 0.88 (3H, t, $J = 6.7$ Hz), 1.28-1.32 (2H, m), 1.35-1.38 (4H, m), 1.57-1.66 (2H, m), 3.47 (2H, t, $J =$ 6.7 Hz), 4.13 (2H, dd, $J = 1.3$, 6.2 Hz), 6.30 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.5, 23.1, 26.6, 29.7, 32.3, 71.0, 71.8, 126.9, 128.0, 128.9, 132.5, 137.2

IR (neat, cm^{-1}): 1111

HRMS calcd for $C_{15}H_{22}O$: 218.1671; found: *m/z* 218.1668.

2.3.7 Cinnamyl octyl ether (**8**)

^{1}H-NMR (δ,$CDCl_3$): 0.89 (3H, t, $J = 6.7$ Hz), 1.26-1.41 (10H, m), 1.57-1.64 (2H, m), 3.47 (2H, t, $J = 6.7$ Hz), 4.13 (2H, dd, $J = 1.2$, 6.0 Hz), 6.31 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.2 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.5, 23.1, 26.3, 30.2, 32.2, 71.0, 71.8, 126.9, 128.0, 128.9, 132.5, 137.2

IR (neat, cm^{-1}): 1109

HRMS calcd for $C_{17}H_{26}O$: 246.1984; found: *m/z* 246.1991.

2.3.8 Cinnamyl nonyl ether (**9**)

^{1}H-NMR (δ,$CDCl_3$): 0.88 (3H, t, $J = 6.7$ Hz), 1.27- 1.73 (14H, m), 3.74 (2H, t, $J = 6.7$), 4.13 (2H,dd, $J = 1.3$, 6.0 Hz), 6.31 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.5, 23.1, 26.6, 29.7, 29.9, 30.0, 30.2, 32.3, 71.0, 71.8, 126.9, 128.0, 128.9, 132.5, 137.2

IR (neat, cm^{-1}): 1110

HRMS calcd for $C_{18}H_{28}O$: 260.2140; found: *m/z* 260.2149.

2.3.9 Cinnamyl decyl ether (**10**)

^{1}H-NMR (δ,$CDCl_3$): 0.88 (3H, t, $J = 6.8$ Hz), 1.26-1.64 (16H, m), 3.47 (2H, t, $J = 6.7$ Hz), 4.13 (2H, dd, $J = 1.3$, 6.0 Hz), 6.30 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.3 Hz), 7.21-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.6, 23.1, 26.6, 29.9, 30.0, 30.2, 32.3, 71.0, 71,8, 126.9, 128.0, 128.9, 132.5, 137.2

IR (neat, cm^{-1}): 1113

HRMS calcd for $C_{19}H_{30}O$: 274.2297; found: *m/z* 274.2291.

2.3.10 Cinnamyl 3-methylbutyl ether (**11**)

^{1}H-NMR (δ,$CDCl_3$): 0.92 (6H, d, $J = 6.7$ Hz), 1.51-1.73 (3H, m), 3.50 (2H,t, $J = 6.8$ Hz), 4.14 (2H, d, $J = 6.0$ Hz), 6.30 (1H, dt, $J = 6.0$, 15.9 Hz), 6.60 (1H, d, $J = 15.9$ Hz), 7.21-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 23.1, 26.7, 39,0, 69.3, 71.9, 126.9, 127.0, 128.0, 128.9, 132.5, 137,2

IR (neat, cm^{-1}): 1113

HRMS calcd for $C_{14}H_{20}O$: 204.1514; found: *m/z* 204.1522

2.3.11 Cinnamyl 2-ethylpentyl ether (**12**)

^{1}H-NMR (δ,$CDCl_3$): 0.86-0.92 (6H, m), 1.25-1.42 (6H, m), 1.55-1.57 (1H, m), 3.36 (2H, d, $J = 5.9$ Hz), 4.12 (2H, dd, $J = 1.4$, 5.9 Hz), 6.30 (1H, dt, $J = 5.9$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.4 Hz), 7.21-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 11.8, 17.1, 23.1, 26.7, 35.5, 39.0, 69.3, 72.0, 126.9, 127.1, 128.0, 128.9, 132.3, 137.3

IR (neat, cm^{-1}): 1114

HRMS calcd for $C_{16}H_{24}O$: 232.1827; found: *m/z* 232.1822

2.3.12 Cinnamyl neopentyl ether (**13**)

^{1}H-NMR (δ,$CDCl_3$): 0.94 (9H, s), 3.13 (2H, s), 4.15 (2H, dd, $J = 1.4$, 5.8 Hz), 6.29 (1H, dt, $J = 5.8$, 15.9 Hz), 6.60 (1H, dt, $J = 15.9$, 1.4 Hz), 7.23-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 27.3, 32.6, 72.4, 81.4, 126.3, 126.9, 127.3, 127.9, 128.7, 132.0

IR (neat, cm^{-1}): 1112

HRMS calcd for $C_{14}H_{20}O$: 204.1514; found: *m/z* 204.1520

2.3.13 Cinnamyl 3-phenylpropyl ether (**14**)

^{1}H-NMR (δ,$CDCl_3$): 1.89-1.96 (2H, m), 2.72 (2H, t, *J* = 7.7 Hz), 3.50 (2H, t, *J* = 6.4 Hz), 4.14 (2H, dd, *J* = 1.2, 6.0 Hz), 6.31 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.2 Hz), 7.16-7.41 (10H, m)

^{13}C-NMR (δ,$CDCl_3$): 31.8, 32.8, 69.9, 71.9, 126.2, 126.7, 126.9, 128.1, 128.8, 128.9, 129.0, 132.6, 137.2, 142.4

IR (neat, cm^{-1}): 1117

HRMS calcd for $C_{18}H_{20}O$: 252.1514; found: *m/z* 252.1508

2.3.14 Cinnamyl isopropyl ether (**15**)

^{1}H-NMR (δ,$CDCl_3$): 1.21 (6H, d, *J* = 6.1 Hz), 3.69 (1H, sept., *J* = 6.1 Hz), 4.14 (2H, dd, *J* = 1.3, 6.0 Hz), 6.17 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.3 Hz), 7.20-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 22.6, 69.1, 71.4, 126.9, 127.3, 127.9, 128.9, 132.2, 137.3

IR (neat, cm^{-1}): 1125

HRMS calcd for $C_{12}H_{16}O$: 176.1201; found: *m/z* 176.1204

2.3.15 Cinnamyl 1-methylpropyl ether (**16**)

^{1}H-NMR (δ,$CDCl_3$): 093 (3H, d, *J* = 7.5 Hz), 1.17 (3H, d, *J* = 6.2 Hz), 1.35-1.52 (2H, m), 3.39-3.46 (1H, m), 4.15 (2H, dd, *J* = 1.4, 6.0 Hz), 6.31 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.4 Hz), 7.22-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 10.3, 19.7, 29.6, 69.4, 76.6, 126.9, 127.4, 127.9, 128.7, 132.1, 137.3

IR (neat, cm^{-1}): 1121

HRMS calcd for $C_{13}H_{18}O$: 190.1358; found: *m/z* 190.1366

2.3.16 Cinnamyl 1-methylpentyl ether (**17**)

^{1}H-NMR (δ,$CDCl_3$): 0.91 (3H, t, *J* = 7.0 Hz), 1.18 (3H, d, *J* = 6.1 Hz), 1.25-1.39 (2H, m), 1.41-1.43 (2H, m), 1.55-1.60 (2H, m), 3.46-3.50 (1H, m), 4.15 (2H, dd, *J* = 1.3, 6.0Hz), 6.30 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.3 Hz), 7.22-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 14.5, 20.1, 23.2, 28.2, 36.8, 69.3, 75.4, 126.9, 127.4, 127.9, 128.9, 132.1, 137.3

IR (neat, cm^{-1}): 1121

HRMS calcd for $C_{15}H_{22}O$: 218.1671; found: *m/z* 218.1672

2.3.17 Cinnamyl 1-ethylpentyl ether (**18**)

^{1}H-NMR (δ,$CDCl_3$): 0.87-0.95 (6H, m), 1.30-1.39 (4H, m), 1.50-1.61 (4H, m), 3.44-3.50 (1H, m), 4.13 (2H, dd, *J* = 1.3, 6.0 Hz), 6.31 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.3 Hz), 7.22-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 10.0, 14.5, 23.4, 26.9, 28.1, 33.6, 71.8, 80.7, 126.9, 127.5, 127.9, 128.0, 128.9, 132.5

IR (neat, cm^{-1}): 1120

HRMS calcd for $C_{16}H_{24}O$: 232.1827; found: *m/z* 232.1831

2.3.18 Cinnamyl cyclopentyl ether (**19**)

^{1}H-NMR (δ,$CDCl_3$):1.53 (4H, m), 1.73 (4H, m), 4.01 (1H, m), 4.11 (2H, dd, *J* = 1.3, 6.0 Hz), 6.30 (1H, dt, *J* = 6.0, 15.9 Hz), 6.59 (1H, dt, *J* = 15.9, 1.3 Hz), 7.20-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 24.0, 32.8, 69.9, 81.3, 126.9, 127.2, 127.9, 128.9, 132.2, 137.3

IR (neat, cm^{-1}): 1096

HRMS calcd for $C_{14}H_{18}O$: 202.1358; found: *m/z* 202.1362

2.3.19 Cinnamyl cyclohexyl ether (**20**)

^{1}H-NMR (δ,$CDCl_3$): 1.23-1.35 (6H, m), 1.52-1.58 (4H, m), 3.40 (1H, m), 4.18 (2H, dd, *J* = 1.4, 6.0 Hz), 6.31 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.4 Hz), 7.20-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 24.7, 26.2, 32.8, 68.8, 81.9, 126.9, 127.5, 127.9, 128.9, 132.1, 137.3

IR (neat, cm^{-1}): 1072

HRMS calcd for $C_{15}H_{20}O$: 216.1514; found: *m/z* 216.1512

2.3.20 *t*-Butyl cinnamyl ether (**21**)

^{1}H-NMR (δ,$CDCl_3$): 1.27 (9H, s), 4.09 (2H, dd, *J* = 1.4, 5.9 Hz), 6.30 (1H, dt, *J* = 5.9, 15.9 Hz), 6.60 (1H,dt, *J* = 15.9, 1.4 Hz), 7.20-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 28.1, 63.2, 73.8, 126.9, 127.8, 128.1, 128.9, 131.4, 137.5

IR (neat, cm^{-1}): 1121

HRMS calcd for $C_{13}H_{18}O$: 190.1358; found: *m/z* 190.1353

2.3.21 Cinnamyl propenyl ether (**22**)

^{1}H-NMR (δ,$CDCl_3$): 3.96-4.08 (2H, m), 4.17 (2H, dd, *J* = 1.3, 6.0 Hz), 5.19-5.35 (2H, m), 5.88-6.02 (1H, m), 6.30 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.3 Hz), 7.24-7.41 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 69.3, 70.8, 126.0, 126.5, 126.9, 127.7, 128.5, 128.6, 132.5, 137.2

IR (neat, cm^{-1}): 1071

HRMS calcd for $C_{12}H_{14}O$: 174.1045; found: *m/z* 174.1041

2.3.22 3-Butenyl cinnamyl ether (**23**)

^{1}H-NMR (δ,$CDCl_3$): 2.29-2.41 (2H, m), 3.54 (2H, t, *J* = 6.8 Hz), 4.15 (2H, dd, *J* = 1.2, 6.0 Hz), 5.01-5.24 (2H, m), 5.80-5.92 (1H, m), 6.30 (1H, dt, *J* = 6.0, 15.9 Hz), 6.60 (1H, dt, *J* = 15.9, 1.2 Hz), 7.21-7.40 (5H, m)

^{13}C-NMR (δ,$CDCl_3$): 34.7, 70.0, 71.9, 116.9, 126.6, 126.9, 128.1, 129.0, 132.7, 135.7, 137.2

IR (neat, cm^{-1}): 1110, 1639

HRMS calcd for $C_{13}H_{16}O$: 188.1201; found: *m/z* 188.1208

2.3.23 Dicinnamyl ether (**24**)

^{1}H-NMR (δ,$CDCl_3$): 4.21 (4H, dd, *J* = 1.2, 6.0 Hz), 6.34 (2H, dt, *J* = 6.0, 15.9 Hz), 6.64 (2H, dt, *J* = 15.9, 1.2 Hz), 7.21-7.42 (10H, m)

^{13}C-NMR (δ,$CDCl_3$): 71.2, 126.4, 126.9, 128.1, 129.0, 133.0, 127.8

IR (neat, cm^{-1}): 1271

HRMS calcd for $C_{18}H_{18}O$: 250.1358; found: *m/z* 250.1359

2.3.24 Benzyl cinnamyl ether (**25**)

^{1}H-NMR (δ,$CDCl_3$): 4.20 (2H, dd, *J* = 1.3, 6.0 Hz), 4.58 (2H, s), 6.34 (1H, dt, *J* = 6.0, 15.9Hz), 6.84 (1H, dt, *J* = 15.9, 1.3 Hz), 7.21-7.41 (10H, m)

^{13}C-NMR (δ,$CDCl_3$): 71.2, 72.6, 126.4, 126.9, 128.1, 128.3, 128.6, 128.7, 128.8, 129.0, 130.1, 133.0

IR (neat, cm^{-1}): 1111

HRMS calcd for $C_{16}H_{16}O$: 224.1201; found: *m/z* 224.1195

2.3.25 Cinnamyl *o*-methylbenzyl ether(**26**)

^{1}H-NMR(δ,$CDCl_3$): 2.36(3H, s), 4.21(2H, dd, J=1.1, 6.0 Hz), 4.57(2H, s), 6.34(1H, dt, J=6.0, 15.9 Hz), 6.64(1H, dt, J=15.9, 1.1 Hz), 7.19-7.46(9H, m)

^{13}C-NMR(δ,$CDCl_3$): 19.3, 71.0, 71.3, 126.2, 126.9, 128.1, 128.3, 129.0, 129.1, 130.6, 130.7, 132.9, 136.6, 137.2

IR(neat, cm^{-1}): 1072

HRMS calcd for $C_{17}H_{18}O$: 238.1358; found: *m/z* 238.1362

2.3.26 Cinnamyl *m*-methylbenzyl ether(**27**)

^{1}H-NMR(δ,$CDCl_3$): 2.36(3H, s), 4.20(2H, dd, J=1.1, 6.0 Hz), 4.54(2H, s), 6.37(1H, dt, J=6.0, 15.9 Hz), 6.63(1H, dt, J=15.9, 1.1 Hz), 7.02-7.44(9H, m)

^{13}C-NMR(δ,$CDCl_3$): 21.8, 71.2, 72.7, 125.3, 126.5, 127.0, 127.7, 128.1, 128.7, 128.8, 129.0, 129.3, 132.9, 137.2, 138.6

IR(neat, cm^{-1}): 1074

HRMS calcd for $C_{17}H_{18}O$: 238.1358; found: *m/z* 238.1355

2.3.27 Cinnamyl *p*-methylbenzyl ether(**28**)

^{1}H-NMR(δ,CDC_{13}): 2.35(3H, s), 4.18(2H, dd, J=1.3, 6.0 Hz), 4.53(2H,s), 6.33(1H, dt, J=6.0, 15.9 Hz), 6.62(1H, dt, J=15.9, 1.2 Hz), 7.15-7.41(9H, m)

^{13}C-NMR(δ,$CDCl_3$): 21.6, 71.0, 72.5, 126.6, 126.9, 128.1, 128.4, 129.0, 129.5, 132.9, 135.6, 137.2, 137.8

IR(neat, cm^{-1}): 1072

HRMS calcd for $C_{17}H_{18}O$: 238.1358; found: *m/z* 238.1361

2.3.28 Cinnamyl *p*-nitrobenzyl ether(**29**)

^{1}H-NMR(δ,$CDCl_3$): 4.26(2H, dd, J=1.3, 6.1 Hz), 4.67 (2H, s), 6.34(1H dt, J=6.1, 15.9 Hz), 6.65(1H, dt, J=15.9, 1.3 Hz),7.21-7.42(5H, m), 7.53(2H, d, J=8.7 Hz), 8.22 (2H, dd, J=7.0 Hz)

^{13}C-NMR(δ,$CDCl_3$): 71.2, 71.9, 124.1, 125.7, 127.0, 128.2, 128.4, 129.1, 133.6, 136.8, 146.4

IR(neat, cm^{-1}): 1345, 1520

HRMS calcd for $C_{16}H_{15}NO_3$: 269.1052; found: *m/z* 269.1054

2.3.29 Cinnamyl α-vinylbenzyl ether(**30**)

^{1}H-NMR(δ,$CDCl_3$): 4.15(2H, dd, J=1.6, 5.9 Hz), 4.87 (1H, d, J=6.7 Hz), 5.15- 5.26(2H, m), 5.90-6.22(1H, m), 6.32(1H, dt, J=5.9, 15.9 Hz), 6.60(1H, dt, J=15.9, 1.6 Hz), 7.21-7.40(10H, m)

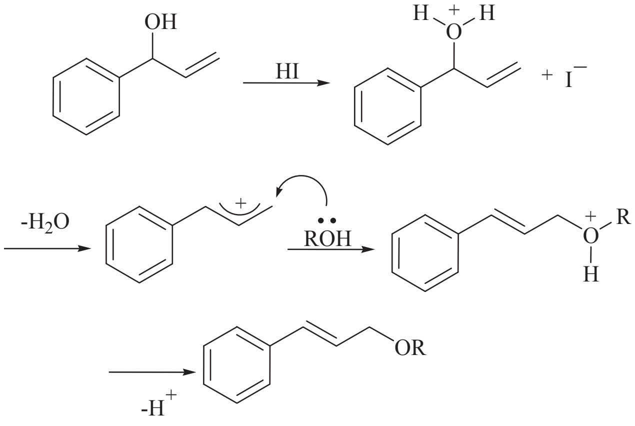
^{13}C-NMR(δ,$CDCl_3$): 69.3, 82.5, 116.8, 126.6, 126.9, 127.4, 128.0, 128.1, 128.9, 129.0, 132.7, 137.2, 139.3, 141.4

IR(neat, cm^{-1}):1060, 966, 745, 693

HRMS calcd for $C_{18}H_{18}O$: 250.1358; found: *m/z* 250.1357

3 RESULTS AND DISCUSSION

The reaction of α-vinylbenzyl alcohol(**1**)with ethanol was performed as follows. Acetonitrile, ethanol, α-vinylbenzyl alcohol, and iodine were placed in a reaction tube, and the mixture was stirred with heating. After the reaction, an aqueous solution of sodium thiosulfate was added to remove iodine, and the product was isolated. Spectroscopic data of the purified product indicated the structure of cinnamyl ethyl ether(**2**). Thus, cinnamyl ethyl ether **2** was obtained from **1** *via* **1**-phenylallyl cation. A possible reaction mechanism is shown in **Scheme 1**. α-Vinylbenzyl alcohol reacts with iodine to form hydroiodide, which acts as an acid catalyst to produce a benzyl cation intermediate. The hydroxyl group of ethanol attacks the cation intermediate to cause allyl rearrangement. It is possible for both ethanol and excess α-vinylbenzyl alcohol to attack the cation intermediate. Therefore, the concentration of ethanol is considered to be important in the reaction.



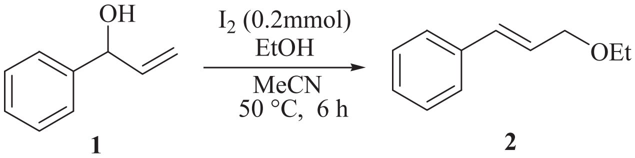
Scheme 1

The optimum conditions for the reaction of **1** with ethanol were investigated and the results are summarized in **Table 1**. As previously reported, the most suitable molar ratio of the starting material to iodine is 1:0.2$^{15)}$. The reaction was attempted under conditions of excess ethanol(entry 1). The yield was 73%. The amount of solvent(acetonitrile)was decreased by half(1.0 mL), and the amount of ethanol was varied from 8.3 mmol to 2.0 mmol(entries

Table 1 Synthesis of cinnamyl ethyl ether from α-vinylbenzyl alcohol.

Entry	MeCN (mL)	EtOH (mmol)	Yield (%)
1	2.0	16.7^a	73
2	1.0	8.3^b	68
3	1.0	3.0	75
4	1.0	2.0	64

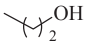
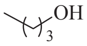
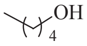
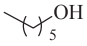
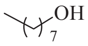
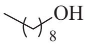
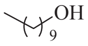
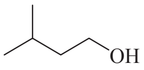
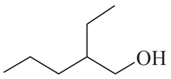
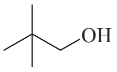
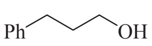
^{a} 16.7 mmol = 1.0 mL ^{b} 8.3 mmol = 0.5 mL



1
(1.0 mmol)

2

Table 2 Synthesis of alkyl cinnamyl ethers from α-vinylbenzyl alcohol and primary alcohols.

Entry	Alcohol	Yield (%)
1	MeOH	74 (**3**)
2		70 (**4**)
3		67 (**5**)
4		70 (**6**)
5		70 (**7**)
6		64 (**8**)
7		74 (**9**)
8		70 (**10**)
9		66 (**11**)
10		60 (**12**)
11		53 (**13**)
12		62 (**14**)

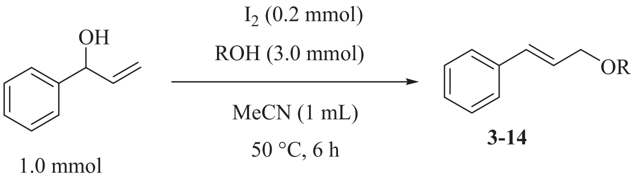
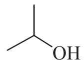
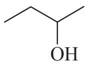
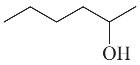
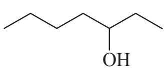
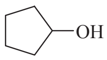
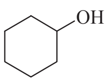
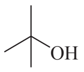
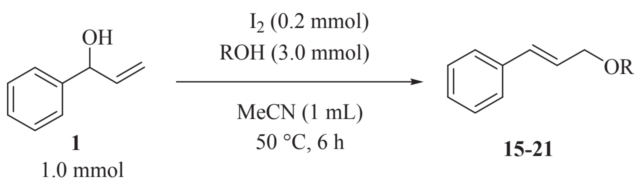


Table 3 Synthesis of alkyl cinnamyl ethers from α-vinylbenzyl alcohol with secondary, tertiary and cyclic alcohols.

Entry	Alcohol	Yield (%)
1		52 (**15**)
2		45 (**16**)
3		42 (**17**)
4		44 (**18**)
5		43 (**19**)
6		51 (**20**)
7		32 (**21**)



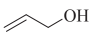
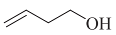
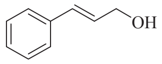
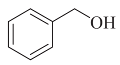
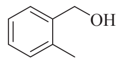
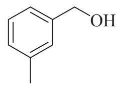
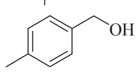
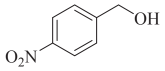
2-4). While a significant difference in the yield was not observed, the yield was highest with 3.0 mmol of ethanol. Therefore, the optimum molar ratio of α-vinylbenzyl alcohol to the other alcohol used was determined to be 1.0:3.0.

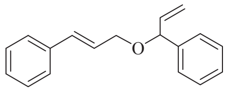
The reactions of α-vinylbenzyl alcohol with various primary alcohols were carried out under the conditions mentioned above. The results are listed in Table 2. The yield was above 50% in all cases. For straight-chain alcohols, the chain length did not affect the reaction (entries 1-8). The yields of the reactions using alcohols having branched chains (entries 9-12) were somewhat lower than those of the reactions using straight-chain alcohols.

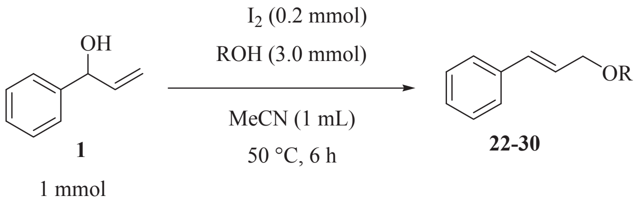
The reactions of α-vinylbenzyl alcohol with various secondary alcohols, cyclic alcohols and a tertiary alcohol (*t*-butyl alcohol) were performed. The results are summarized in Table 3. The yields of the reactions using the secondary alcohols (entries 1-4) were somewhat lower than those using the primary alcohols (Table 2), but comparable to those using alcohols with cycloalkyl groups (entries 5 and6). The yield of the reaction using *t*-butyl alcohol was the lowest, 32%, among the alcohols used (entry 7). This was attributed to the steric hindrance of the three methyl groups.

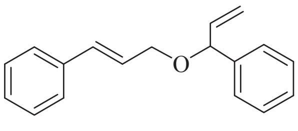
The reactions of α-vinylbenzyl alcohol with unsaturated alcohols and benzylic alcohols were studied. The results are listed in Table 4. When aliphatic unsaturated alcohols were used (entries 1 and 2), the yields were as high as those of reactions using the corresponding saturated alcohols. When cinnamyl alcohol was used (entry 3), the yield of the expected product, dicinnamyl ether 24, decreased dramatically, but by-product cinnamyl α-vinylbenzyl ether 30 was obtained in 21% yield. It is likely that some α-vinylbenzyl alcohol did not rearrange due to the high concentration of cinnamyl alcohol, and that the hydroxyl group of α-vinylbenzyl alcohol attacked the cation intermediate, which may have originated from either α-vinylbenzyl alcohol or cinnamyl alcohol, as shown in Scheme 2. When benzyl alcohol was used, the yield of the corresponding ether (benzyl cinnamyl ether 25) was 74% (entry 4). However,

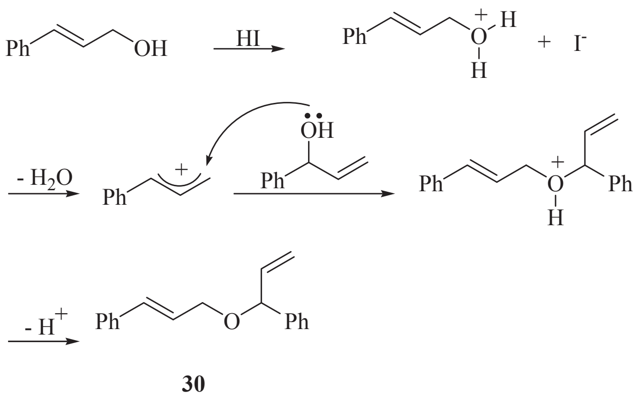
Table 4 Synthesis of alkyl cinnamyl ethers from α-vinylbenzyl alcohol with unsaturated and benzylic alcohols.

Entry	Alcohol	Yield (%)
1		69 (**22**)
2		58 (**23**)
3		23^a (**24**)
4		74 (**25**)
5		48 (**26**)
6		63 (**27**)
7		67 (**28**)
8		36 (**29**)

a  (**30**) was also obtained (21%).

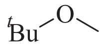
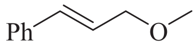
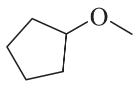
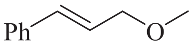
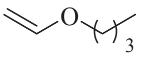
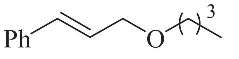


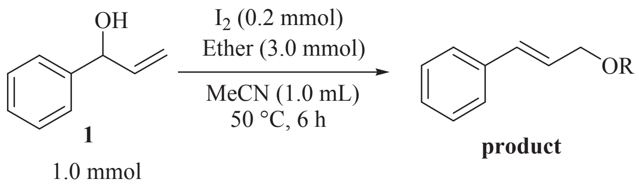
a  (**30**) was also obtained (21%).



Scheme 2

Table 5 Reaction of α-vinylbenzyl alcohol with ethers.

Entry	Ether	Product	Yield (%)
1		 (**3**)	34
2		 (**3**)	15
3		 (**5**)	65



when *o*-methylbenzyl alcohol was used, the yield decreased to 48% (entry 5). This may be due to the steric hindrance of the *ortho*-methyl group because the yield with *m*-methylbenzyl cinnamyl alcohol (27) was 63% (entry 6) and that with *p*-methylbenzyl cinnamyl alcohol (28) was 67% (entry 7).

Then, the reactions of α-vinylbenzyl alcohol with ethers were investigated (Table 5). The product of the reaction of α-vinylbenzyl alcohol with t-butyl methyl ether was spectroscopically determined to be cinnamyl methyl ether (3). This indicated that, after allyl rearrangement, the lone pair of electrons on the oxygen atom in *t*-butyl methyl ether attacked the benzyl cation intermediate. The dissociation of the starting material ether occurred, resulting in the ether interchange, which produced 3. However, the yield of 3 by the reaction of α-vinylbenzyl alcohol with methanol (74%; entry 1 in Table 2) was higher than that by the reaction of α-vinylbenzyl alcohol with *t*-butyl methyl ether (34%; entry 1 in Table 5). The reaction of α-vinylbenzyl alcohol with cyclopentyl methyl ether was also attempted, but the yield decreased further (entry 2). Therefore, because the stability of the eliminated cation after the breakage of the ether bond is increased, a vinyl group was used as the other substituent of the starting ether (entry 3). Butyl cinnamyl ether (5) was produced from butyl vinyl ether in 65% yield. This value was as high as that of the reaction of α-vinylbenzyl alcohol with butanol (67%; entry 3 in Table 2).

Barbero *et al*. reported that the reaction of α-vinylbenzyl alcohol with ethanol, using *o*-benzenedisulfonimide as a catalyst gave the corresponding cinnamyl ether in 56%

yield[5]. As mentioned above, the similar reaction performed using iodine as a catalyst produced cinnamyl ether in 75% yield.

In conclusion, the reactions of α-vinylbenzyl alcohol with various alcohols using iodine as a catalyst produced the corresponding cinnamyl ethers *via* 1-phenylallyl cation. Reactions using primary alcohols proceeded more smoothly than those using secondary or tertiary alcohols. Ether interchange also occurred by the reaction of α-vinylbenzyl alcohol and iodine, but proceeded smoothly only when an allyl group was used as the other substituent of the starting ether.

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