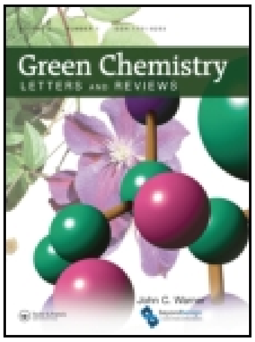

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RESEARCH LETTER

Efficient Prins cyclization in environmentally benign method using ion exchange resin catalyst

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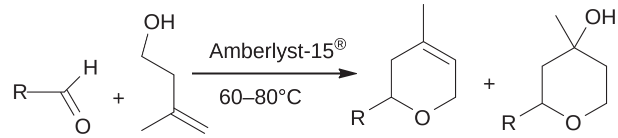
Amberlyst-15® (H^+) resin catalyzes efficient one-pot solvent free Prins cyclization of an aldehyde and a homoallylic alcohol to yield dihydropyrans and 4-hydroxytetrahydropyrans. The products, which display interesting olfactory property, are obtained under mild condition and by simple work up. The recovered resin can be used repeatedly.



Keywords: dihydropyrans; 4-hydroxytetrahydropyrans; Amberlyst-15®; Prins cyclization; olfactory property

Introduction

In recent years, the design of green methodologies to reduce energy consumption, use of toxic solvents, and waste products has gained prime importance. The efficient use of non-toxic and selective catalysts in solvent-free condition is desirable in the context of green chemistry (*1, 2*). The acid catalyzed condensation of olefins with carbonyl compounds, known as the Prins cyclization is an important reaction for carbon–carbon bond formation (*3–8*). The acid catalyzed reaction between a homoallylic alcohol and an aldehyde is direct and one of the most widely used methods for the preparation of dihydropyran and tetrahydropyran-4-ol derivatives (*9, 10*). The tetrahydropyran ring is a part of the skeleton of some important natural products including carbohydrates, avermectins, aplysiatoxin, oscillatoxin, talaromycins, acutiphycins, erythronolide B, monensin, cytovaricin, brevetoxin B, etc. (*11–13*). Similarly, several commercial perfumery molecules such as rose oxide, doremox, clarycet, etc. are 2-substituted-4-methyl-tetrahydropyran derivatives (Figure 1) (*14, 15*).

To achieve Prins condensation a number of methods have been developed using various Brønsted acids and Lewis acids (*16–27*). However, classical methods may need extended reaction times, or strongly acidic conditions, solvent extraction for product recovery, and they often produce mixtures of products. Hence, there is a need to find inexpensive and environmentally acceptable catalysts, which can effect this transformation under mild conditions.

In recent years, the use of solid acidic catalysts such as amberlyst, clays, and zeolites has received considerable attention in different areas of organic synthesis because of their environment compatibility, reusability, high selectivity, operation simplicity, non-corrosiveness, low cost, and ease of isolation of the products (*28, 29*). Prins-type cyclization reaction catalyzed by montmorillonite clay has been reported (*30, 31*).

We report herein amberlyst-15® catalyzed synthesis of dihydropyrans and 4-methyl-tetrahydropyran-4-ols. In particular, the use of amberlyst-15® catalyst makes reaction processes convenient, more economic, and environmentally benign.

Results and discussion

We have achieved the synthesis of dihydropyran and 4-methyl-tetrahydropyran-4-ols in the absence of solvent by treating the equimolar quantities of aldehyde and isoprenol with catalytic amount of Amberlyst-15® at 70–80°C for the period mentioned

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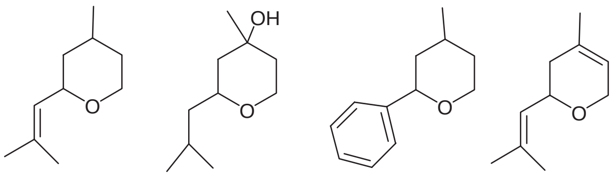


Figure 1. Some commercially important pyran derivatives.

in Table 1. The products were obtained by filtration of the reaction mixture and subjecting the filtrate to either fractional distillation *in vacuo* or to the column chromatography over silica gel to give the dihydropyrans **1a–3a, 5a–8a**, and 4-methyl-4-hydroxy-tetrahydropyrans **1b–9b** in the yields mentioned in Table 1.

The formation of 4-methyl-dihydropyran ring was indicated by ^{1}H NMR peaks due to –O-CH_2– group (δ~4.65–3.70) and 4-Me group (δ~1.7), and absence of the hydroxyl peak in the IR spectrum. Similarly the formation of 4-methyl-tetrahydropyran-4-ols was indicated by the presence of hydroxyl peak ~3410 cm^{-1} in the IR spectrum and the presence of peaks due to –O-CH_2– group (δ~4.65–3.70) and due to 4-methyl group (δ ~ 1.3) in the ^{1}H NMR spectrum. HRMS spectra of all products gave expected molecular ions.

The recovered resin was repeatedly used (five times) for this conversion without much loss in cyclization efficiency. The catalyst is inexpensive, non-toxic, and reusable, which makes the process more economic and environmentally benign. Thus, green and economic synthesis of dihydropyrans and 4-hydroxytetrahydropyrans has been achieved. The products show excellent perfumery property.

Experimental

General procedure for Prins cyclization in the presence of Amberlyst-15®

A mixture of aldehyde (0.1 mol), isoprenol (0.1 mol), and Amberlyst-15® (0.2 g) was heated at 70°C for the period mentioned in Table 1. The completion of reaction was checked by gas chromatography (GC). The catalyst was filtered and washed with acetone. The solvent was removed from the filtrate and the residue was subjected either to distillation *in vacuo* or to column chromatography over silica gel to get the reaction products dihydropyrans **1a–3a**, **5a–8a**, and 4-methyl-4-hydroxy-tetrahydropyrans **1b–9b**. The yields and reaction time are mentioned in Table 1. The α-substituted aldehydes, namely isobutyraldehyde (entry 4) and melonal (entry 9) did not yield dihydropyran. The recovered resin was reused five times without appreciable loss of activity.

Spectral data of selected compounds

*3,6-Dihydro-2-isobutyl-4-methyl-2H-pyran (**1a**, Table 1, entry 1)*: Colorless liquid; IR: neat, ν_{max} cm^{-1} 2871, 1470, 1384, 1265, 1161, 1021; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.10 (t, J = 6 Hz, 1H), 4.09–3.99 (m, 2H), 2.87 (m, 2H), 2.21–1.96 (m, 2H), 1.83 (m, 1H), 1.51 (d, J = 2 Hz, 3H), 0.90 (d, J = 7 Hz, 6H); HRMS: m/z found: 154.2518 (calc. for $C_{10}H_{18}O$: 154.2523), 139 (15), 97 (28), 69 (100), 57 (35), 43 (100).

*Tetrahydro-2-isobutyl-4-methyl-2H-pyran-4-ol (**1b**, Table 1, entry 1)*: Colorless liquid; IR: neat, ν_{max} cm^{-1} 3410, 2956, 1468, 1378, 1169, 1112; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.80–3.60 (m, 3H), 2.70 (s, –OH), 2.10–1.54 (m, 4H), 1.25–1.83 (m, 1H), 1.23 (s, J = 6 Hz, 3H), 0.90 (d, J = 7 Hz, 6H); HRMS: m/z found 172.2670 (calc. for $C_{10}H_{20}O_2$: 172.2676), 154 (22), 139 (21), 97 (32), 69 (100), 57 (32), 43 (86).

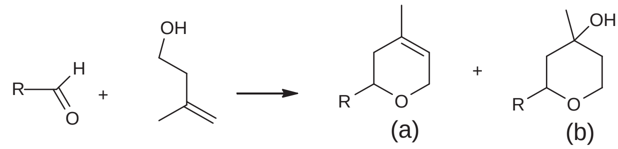
*3,6-Dihydro-4-methyl-2-propyl-2H-pyran (**2a**, Table 1, entry 2)*: Colorless liquid; IR: neat, ν_{max} cm^{-1} 2932, 1465, 1382, 1140, 1107, 1015; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.39 (t, 1H), 4.80–4.60 (m, 2H), 3.90 (m, 1H), 1.80–1.65 (m, 2H), 1.31 (d, J = 2Hz, 3H), 1.60–1.30 (m, 4H), 0.90 (t, J = 7 Hz, 3H); HRMS: m/z found 140.2248 (calc. for $C_9H_{16}O$: 140.2254) 140, 125 (13), 110 (87), 97 (100), 82 (46), 68 (87), 55 (30), 41 (43).

*Tetrahydro-4-methyl-2-propyl-2H-pyran-4-ol (**2b**, Table 1, entry 2)*: Colorless liquid; IR: neat, ν_{max} cm^{-1} 3418, 2949, 1463, 1384, 1172, 1109, 1004, 937; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H 3.65–3.55 (m, 3H), 2.10 (s, 1H, –OH), 1.80–1.55 (m, 4H), 1.52–1.33 (m, 4H), 1.30 (s, 3H), 0.90 (t, J = 7 Hz, 3H); HRMS: m/z found 158.2412 (calc. for $C_9H_{18}O_2$: 158.2407) 158, 140 (100), 125 (7), 112 (4), 71 (15), 43 (29).

*3,6-Dihydro-4-methyl-2-phenyl-2H-pyran (**5a**, Table 1, entry 5)*: Pale yellow liquid; IR: neat, ν_{max} cm^{-1} 3031, 1452, 1381, 1118, 1031, 755, 699; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.15 (s, 5H), 5.35 (s, 1H), 4.80–4.10 (m, 3H), 2.50–1.90 (m, 2H), 1.71 (s, 3H); HRMS: m/z found 174.2418 (calc. for $C_{12}H_{14}O$: 174.2425), 160 (13), 105 (55), 67 (100), 53 (50), 41 (50).

*Tetrahydro-4-methyl-2-phenyl-2H-pyran-4-ol (**5b**, Table 1, entry 5)*: Pale yellow liquid; IR (neat cm^{-1}): neat, ν_{max} cm^{-1} 3398, 2966, 1604, 1454, 1378, 1258, 1175, 1091, 699; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H

Table 1. Amberlyst - 15® catalyzed Prins reaction of aldehydes with isoprenol.



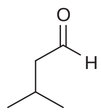
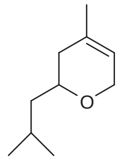
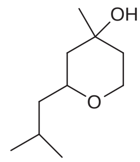
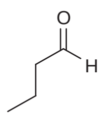
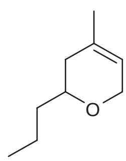
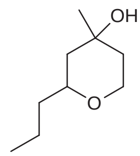
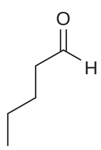
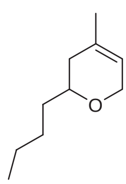
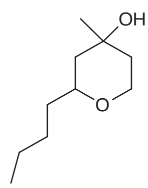
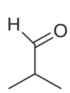
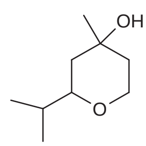
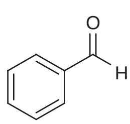
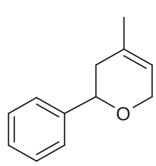
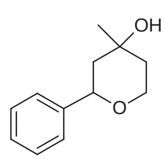
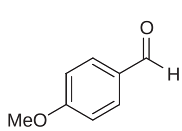
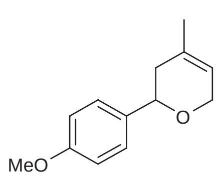
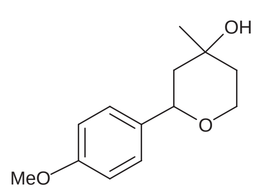
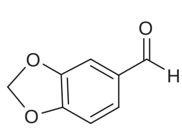
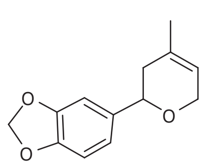
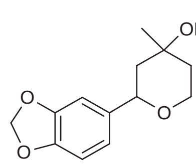
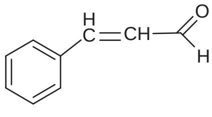
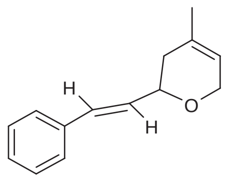
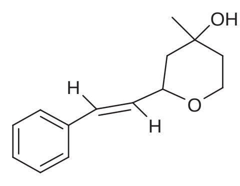
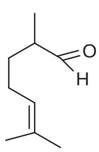
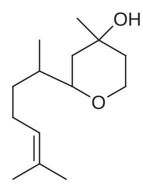
Entry	Aldehyde	Products: Dihydropyran (a)	Products: 4-Hydroxy-tetrahydropyran	Time (hr)	Compound (yield %)	
1				11	**1a** (32)	**1b** (51)
2				10	**2a** (27)	**2b** (62)
3				6	**3a** (69)	**3b** (31)
4				16		**4b** (64)
5				12	**5a** (24)	**5b** (45)
6				12	**6a** (19)	**6b** (44)
7				16.5	**7a** (36)	**7b** (28)

Table 1 (*Continued*)

		Products				
Entry	Aldehyde	Dihydropyran (a)	4-Hydroxy-tetrahydropyran	Time (hr)	Compound (yield %)	
8				9	**8a** (57)	**8b** (41)
9				9		**9b** (72)

7.30–7.11 (bs, 5H), 4.65–3.70 (m, 3H), 1.85–1.70 (m, 4H), 1.25 (s, 3H); HRMS: *m/z* found 192.2571 (calc. for $C_{12}H_{16}O_2$: 192.2578), 174 (81), 159 (100), 145 (5), 131 (5), 105 (25), 77 (4), 43 (44).

*3,6-Dihydro-2-(4-methoxyphenyl)-4-methyl-2H-pyran (**6a**, Table 1, entry 1)*: Light brown liquid; IR (neat cm^{-1}): neat, ν_{max} cm^{-1} 2930, 2835, 1614, 1515, 1463, 1248, 1175, 1036, 828, 772; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.14 (d, $J=9$ Hz, 2H), 6.74 (d, $J=9$ Hz, 2H), 5.10 (s, 1H), 4.30–3.80 (m, 3H), 3.30 (s, $-OCH_3$, 3H), 2.30–1.60 (m, 2H), 1.33 (s, 3H); HRMS: *m/z* found 204.2682 (calc. for $C_{13}H_{16}O_2$: 204.2688), 189 (6), 175 (12), 162 (24), 135 (100), 119 (4), 77 (9), 61 (4), 40 (57).

*Tetrahydro-2-(4-methoxyphenyl)-4-methyl-2H-pyran-4-ol (**6b**, Table 1, entry 6)*: Light brown liquid; IR (neat cm^{-1}): neat, ν_{max} cm^{-1} 3413, 3011, 2940, 1612, 1515, 1378, 1248, 1216, 1086, 1035, 830, 605; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.20 (d, $J=9$ Hz, 2H), 6.70 (d, $J=9$ Hz, 2H), 5.10–3.70 (m, 3H), 3.50 (s, $-OCH_3$, 3H), 2.60 (s, –OH), 1.45–1.10 (m, 4H), 1.01 (s, 3H); HRMS: *m/z* found 222.2848 (calc. for $C_{13}H_{18}O_3$: 222.2841), 204 (29), 189 (95), 150 (5), 135 (100), 119 (8), 103 (11), 89 (13), 77 (11).

*5-(3,6-Dihydro-4-methyl-2H-pyran-2-yl) benzo[d]-[1,3]dioxole (**7a**, Table 1, entry 7)*: Pale yellow liquid; IR (neat cm^{-1}): neat, ν_{max} cm^{-1} 2963, 1608, 1489, 1443, 1383, 1257, 1095, 933, 809; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.69 (s, 1H), 6.35 (s, 2H), 5.63 (s, 2H), 5.21 (s, 1H), 4.74 (s, 1H), 4.42–4.21 (m, 2H), 2.50–2.10 (m, 2H), 1.71 (s, 3H); HRMS: *m/z* found 218.2518 (calc. for $C_{13}H_{14}O_3$: 218.2523), 203 (9), 149 (100), 134 (4), 120 (4), 108 (4), 97 (2).

*2-(Benzo[d][1,3]dioxol-5-yl)-tetrahydro-4-methyl-2H-pyran-4-ol (**7b**, Table 1, entry 7)*: Light brown liquid; IR: neat, ν_{max} cm^{-1} 3437, 2777, 1609, 1504, 1489, 1383, 1251, 1094, 1040, 934, 667; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.67 (s, 1H), 6.35 (s, 2H), 5.70 (s, 2H), 4.61–4.32 (m, 1H), 3.92–3.61 (m, 2H), 2.10 (s, 1H, –OH), 1.80–1.30 (m, 4H), 1.20 (s, 3H); HRMS: *m/z* found 236.2672 (calc. for $C_{13}H_{16}O_4$: 236.2676), 218 (12), 203 (69), 189 (3), 175 (7), 149 (100), 135 (7), 121 (12), 71 (16), 54 (2i3).

*3,6-Dihydro-4-methyl-2-styryl-2H-pyran (**8a**, Table 1, entry 8)*: Pale yellow liquid; IR: neat, ν_{max} cm^{-1} 2924, 1725, 1677, 1449, 1123, 1020, 973, 748, 689; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.40–7.12 (m, 5H), 6.81 (d, $J=16$ Hz, 1H), 6.31 (dd, $J=16$ and 6 Hz, 1H), 5.42 (bs, 1H), 4.81–4.62 (m, 1H), 4.44–4.01 (m, 2H), 2.41–1.92 (m, 2H), 1.71 (s, 3H); HRMS: *m/z* found 200.2812 (calc. for $C_{14}H_{16}O$: 200.2804), 185 (6), 155 (10), 101 (16), 91 (39), 77 (20).

*Tetrahydro-4-methyl-2-styryl-2H-pyran-4-ol (**8b**, Table 1, entry 8)*: Pale yellow liquid**;** IR: neat, ν_{max} cm^{-1} 3427, 2962, 1707, 1649, 1599, 1495, 1375, 1075, 967; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.30–7.14 (m, 5H), 6.45 (d, $J=16$ Hz, 1H), 6.02 (dd, $J=16$ and 6 Hz, 1H), 4.50–4.28 (m, 1H), 4.10–3.70 (m, 2H), 2.35 (bs, 1H), 1.72–1.41. (m, 4H), 1.31 (s, 3H); HRMS: *m/z* found 218.2951 (calc. for $C_{14}H_{18}O_2$: 218.2957), 198 (100), 184 (50), 128 (57), 115 (29), 102 (14), 89 (20).

Acknowledgements

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