Preparation of Cyclopenta-Fused N-, O-, and S-Heterocycles by Lewis Acid Catalyzed Nazarov Reaction

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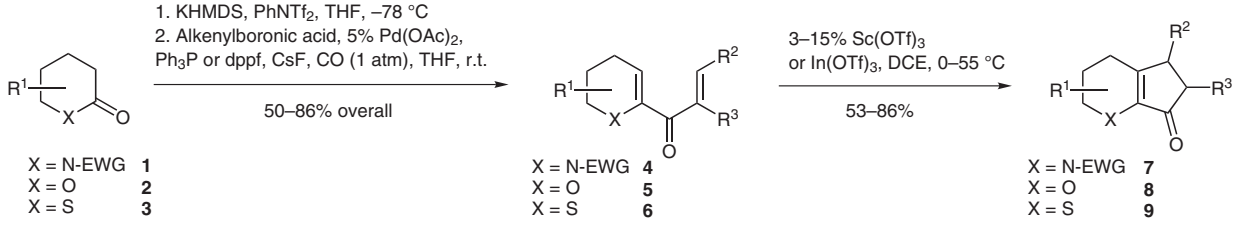
Received 7 February 2007

Abstract: The products of carbonylative coupling between lactam-, lactone- and thiolactone-derived vinyl triflates and alkenylboronic acids are suitable substrates for the Lewis acid catalyzed Nazarov reaction. The most efficient Lewis acids for the Nazarov reaction are scandium(III) and indium(III) triflates (3–15 mol%) in 1,2-dichloroethane, which provide the Nazarov products in moderate to excellent yield (53–86%). The electrocyclization rate depends also on the heteroatom (N, O, S) and the N-protecting group. On the whole, the entire procedure is an expeditious synthesis of hexahydro[1]pyrindenes, -cyclopenta[*b*]pyrans, and -cyclopenta[*b*]thiopyrans of noteworthy interest as they form the structural core of several natural molecules.

Key words: carbonylative couplings, electrocyclic reactions, Nazarov reaction, Lewis acids, bicyclic compounds



Scheme 1

Introduction

The acid-catalyzed cyclization of a doubly α,β-unsaturated ketone is referred to as the Nazarov reaction and it is currently one of the most versatile and powerful methods for the synthesis of five-membered carbocycles.[1] The abundance of five-membered carbocycles among natural products has inspired much research around the Nazarov reaction, so that the limitations of the original procedure such as the harsh reaction conditions (strong acids and high temperature) and the poor regioisomeric control have been fully surmounted.[2]

In several instances, Nazarov reactions have been carried out on substrates in which one of the double bonds involved in the electrocyclization is present in a carbocycle, thus leading to the formation of hexahydroindenes and other cyclopenta-fused carbocycles;[1] only a few examples of the Nazarov reaction involving nonaromatic heterocyclic compounds are known. The procedure summarized in Scheme 1 entails a short sequence which allows an expeditious synthesis of cyclopenta-fused N-, O-, and S-heterocycles that are of noteworthy interest as they form the structural core of several natural compounds.[3] The procedure encompasses the transformation of lactams, lactones, and thiolactones **1–3** into the corresponding enol triflates followed by carbonylative coupling with vinylboronic acids and, eventually, the Lewis acid catalyzed Nazarov reaction of coupling products **4–6**.

Scope and Limitation

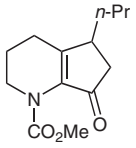
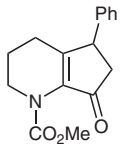
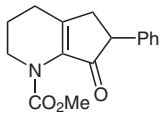
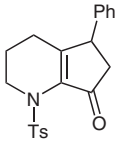
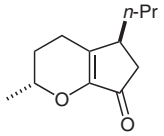
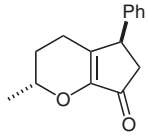
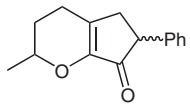
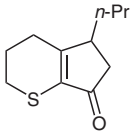
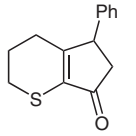
The carbonylative coupling of the triflates[4] with substituted vinylboronic acids (2.5 equiv) is carried out in the presence of palladium(II) acetate (5 mol%) and using triphenylphosphine (10 mol%) as a ligand (Scheme 1) as already reported by us for a N-heterocyclic triflate.[5] Under these conditions the reaction occurs at room temperature and under one atmosphere of carbon monoxide. With the O-heterocyclic triflates[6] the yield of the carbonylated products **5** can be increased by using 1,1′-bis(diphenylphosphino)ferrocene (dppf, 6.25 mol%) as a ligand, whereas with S-containing triflates[7] using cesium acetate as a base, instead of cesium fluoride (3 equiv), provides higher yields of the carbonylated products **6**.

A series of Lewis acids was tested in order to optimize the conditions for the Nazarov cyclization of dienones **4–6**. Metal triflates, in particular scandium(III) triflate and in-

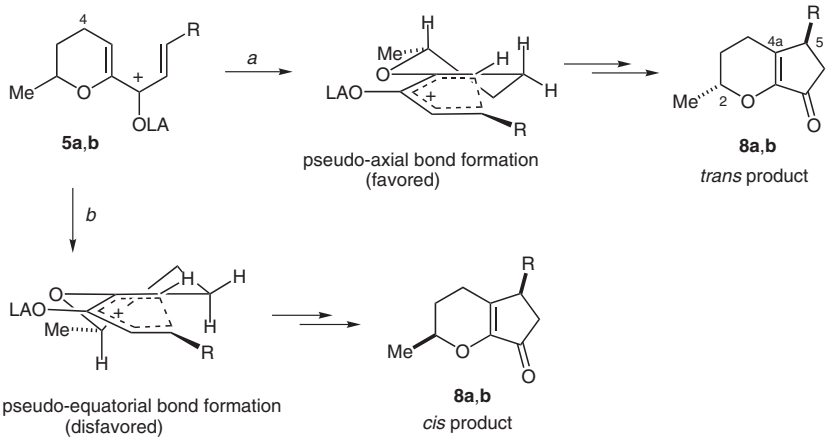
SYNTHESIS 2007, No. 11, pp 1733–1737
Advanced online publication: 28.02.2007
DOI: 10.1055/s-2007-965965; Art ID: Z03207SS

dium(III) triflate were the most efficient in catalyzing the electrocyclization process [$Zn(OTf)_2$, $Cu(OTf)_2$, $Yb(OTf)_3$, and $Y(OTf)_3$ were all inferior catalysts]. Scandium(III) and indium(III) triflates are the most Lewis acidic among the catalysts tested as the two cations Sc^{3+} and In^{3+} possess the highest charge-to-radius ratio.[8] A correlation between the efficiency of the electrocyclization and the Lewis acidity of the metal triflates thus exists.

Table 1 Nazarov Products Obtained by Treatment of the Corresponding Dienones **4**–**6** with a Lewis Acid

Entry	Lewis acid (mol%)	Temp (°C)	Time (h)	Product		Yield[a] (%)
1	$Sc(OTf)_3$ (3)	55	3		**7a**	86
2	$In(OTf)_3$ (15)	35	12		**7a**	85
3	$Sc(OTf)_3$ (3)	55	2.5		**7b**	83
4	$In(OTf)_3$ (10)	20	4		**7b**	81
5	$Sc(OTf)_3$ (10)	22	20		**7c**	64
6	$Sc(OTf)_3$ (3)	55	6.5		**7d**	55
7	$Sc(OTf)_3$ (3)	0	4		**8a**[b]	65
8	$Sc(OTf)_3$ (10)	0	1		**8b**[c]	63
9	$In(OTf)_3$ (3)	20	1		**8b**	64
10	$Sc(OTf)_3$ (3)	20	1.5		**8c**[d]	53
11	$Sc(OTf)_3$ (3)	20	1		**9a**	67
12	$Sc(OTf)_3$ (3)	20	1		**9b**	73
13	$In(OTf)_3$ (3)	20	1		**9b**	72

[a] Yield of isolated product.
[b] Ratio *trans*/*cis* 9:1.
[c] Ratio *trans*/*cis* 20:1.
[d] Ratio *trans*/*cis* 1.2:1.



Scheme 2 Torquoselectivity in the Nazarov reaction of dienones **5**

With *N*-methoxycarbonyl-protected dienones **4a**–**c**, all reactions were successfully carried out at either room temperature or by heating at 35–55 °C in the presence of 3–15 mol% of the catalyst (Table 1, entries 1–5) providing the Nazarov products **7a**–**c** in good yields. The *N*-tosyl protecting group had a slightly detrimental effect on the reaction rate (entry 6), as an acceptable yield (55%) of the Nazarov product **7d** was obtained only after heating for 6.5 hours in 1,2-dichloroethane at 55 °C in the presence of scandium(III) triflate (3 mol%); at room temperature with 0.1 equivalent of the Lewis acid the reaction was very slow and provided the Nazarov product in 26% yield after 24 hours.

For the Nazarov reaction of 2-alkoxy-1,4-dien-3-ones,[9] we chose 6-methyl-substituted compounds **5** (X = O, R^1 = 6-Me) in order to address, besides the reactivity, the problem of torquoselectivity in the Lewis acid catalyzed cyclization, an issue that has been examined by us in the case of Brønsted acid catalyzed Nazarov reaction,[10] which could be of crucial importance in synthetic applications of the methodology. Cyclization of dienone **5a** (R^2 = Pr, R^3 = H) in the presence of 3 mol% of scandium triflate at 0 °C for four hours provided the Nazarov product **8a** (entry 7) in 65% yield after chromatography. Cyclization of **7b** (R^2 = Ph, R^3 = H) was rapid with 10 mol% of scandium triflate at 0 °C (entry 8) as well as in the presence of 3 mol% of indium(III) triflate (entry 9) at 20 °C. Both compounds **8a** and **8b** were obtained as a mixture of diastereomers in 9:1 and 20:1 ratio, respectively. The major isomers were assigned the 2,5-*trans* relative stereochemistry by NOE studies, which is in accordance with the results obtained in the mineral acid catalyzed Nazarov reaction of analogous substrates.[10a] The cyclization of **7c** (R^2 = H, R^3 = Ph) was carried out at room temperature in the presence of 3 mol% of scandium triflate (entry 10). In this case a 1.2:1 mixture of diastereomers **8c** (not separated) was isolated by chromatography in 53% yield. TLC monitoring showed that some degradation of the starting material and/or the Nazarov product had occurred.

The cyclization of thiopyranyl derivatives **6** was also rapid, as the Nazarov products (entries 11–13) were obtained in good yield just after one hour at room temperature. When the reaction was carried out on **6a** (R^2 = Pr, R^3 = H) at 55 °C, we observed a rapid darkening of the solution and, by TLC, degradation of the substrate and/or the Nazarov product into several byproducts. By lowering the reaction temperature and using the same low amount of scandium triflate (3 mol%) the reaction was still rapid, as the conversion of **6a** into **9a** was complete after one hour (entry 11), without any appreciable degradation (67% yield after chromatography). Treatment of dienone **6b** (R^2 = Ph, R^3 = H) with both Lewis acids (entries 12 and 13) provided good yields of the Nazarov product **9b** after one hour at room temperature.

The (high) relative rates of cyclization of heteroatom-containing dienones **4**–**6** can be explained on the basis of the role of the heteroatom in stabilizing the positive charge that develops at the α-position in the transition state of the process (Scheme 2).[10a,b,11] Also, bidentate binding of the Lewis acid to the substrate (C=O and X) could help the two vinyl moieties in adopting the proper s-*cis*/s-*trans* orientation for the cyclization.[9]

As for the torquoselectivity in the cyclization of **5a**,**b**, it is interesting to notice that the Lewis acid has no effect in varying the sense of conrotation with respect to the mineral acid catalyzed process,[10a] as the 2,5-*trans*-products **8a**,**b** are obtained as the major diastereomers. The electrocyclization of the pentadienyl cations deriving from **5a**,**b** (Scheme 2) occurs through a transition state in which the methyl group is equatorially placed. On the basis of previous DFT studies,[11] the formation of the new bond along the axial direction (path a) should occur through a more stable transition state and allow for the maximum orbital overlap in the formation of the new C4a–C5 bond.

Finally, irrespective of the sense of conrotation, the formation of the thermodynamic 1.2:1 mixture **8c** is due to equilibration at C6 after cyclization and loss of H4a.

The typical procedures for the three classes of dienones depicted in Scheme 1 are described. For the carbonylative coupling procedure and characterization of **7a** and 7**b** see ref. 5. Analytical data for all new compounds are provided in detail.

Methyl 7-Oxo-5-propyl-2,3,4,5,6,7-hexahydro-1*H*-[1]pyrindine-1-carboxylate (7a);[5] Typical Procedure

To a soln of **4a** (72 mg, 0.3 mmol) in anhyd DCE (1.5 mL) was added $Sc(OTf)_3$ (4.5 mg, 0.009 mmol) and the resulting soln was stirred at 55 °C for 3 h under an N_2 atmosphere. The dark soln was diluted with Et_2O (8 mL) and washed with 5% aq $NaHCO_3$ (30 mL). The aqueous layer was extracted with Et_2O (2 × 25 mL) and the combined organic layers were dried (Na_2SO_4). Chromatography (silica gel 60, EtOAc–petroleum ether, 1:2) provided **7a** (62 mg, 86%) as a colorless oil.

Methyl 7-Oxo-6-phenyl-2,3,4,5,6,7-hexahydro-1*H*-[1]pyrindine-1-carboxylate (7c)

R_f = 0.31 (EtOAc–petroleum ether, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96–2.02 (m, 2 H), 2.46–2.50 (m, 2 H), 2.60 (d, *J* = 18.2 Hz, 1 H), 3.07 (dd, *J* = 18.2, 7.2 Hz, 1 H), 3.65–3.73 (m, 2 H + 1 H), 3.74 (s, 3 H), 7.19–7.36 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 22.4 (t), 26.5 (t), 37.6 (t), 44.3 (t), 50.7 (d), 53.2 (q), 126.8 (d), 127.6 (d, 2 C), 128.6 (d, 2 C), 137.7 (s), 139.4 (s), 154.4 (s), 156.0 (s), 198.6 (s).

MS (EI, 70 eV): *m*/*z* (%) = 271 (M^+, 100), 243 (12), 226 (12), 212 (23), 77 (18).

Anal. Calcd for $C_{16}H_{17}NO_3$ (271.31): C, 70.83; H, 6.32; N, 5.16. Found: C, 70.49; H, 6.14; N, 5.27.

5-Phenyl-1-tosyl-1,2,3,4,5,6-hexahydro-7*H*-[1]pyrindin-7-one (7d)

R_f = 0.41 (CH_2Cl_2–MeOH, 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90–1.96 (m, 2 H), 2.08–2.16 (m, 2 H), 2.43 (s, 3 H), 2.44 (dd, *J* = 18.3, 2.2 Hz, 2 H), 2.98 (dd, *J* = 18.3, 7.0 Hz, 1 H), 3.40–3.49 (m, 2 H), 3.87 (d, *J* = 7.0 Hz, 1 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 7.25–7.35 (m, 5 H), 8.04 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 21.6 (q), 21.7 (t), 24.1 (t), 43.7 (t), 45.4 (d), 46.2 (t), 127.2 (d, 2 C), 127.3 (d), 127.8 (d, 2 C), 129.1 (d, 2 C), 129.4 (d, 2 C), 138.0 (s), 141.3 (s), 143.6 (s), 161.2 (s), 199.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 367 (M^+, 100), 261 (37), 212 (76), 184 (94), 91 (100).

Anal. Calcd for $C_{21}H_{21}NO_3S$ (367.46): C, 68.64; H, 5.76; N, 3.81. Found: C, 68.33; H, 5.49; N, 3.44.

2-Methyl-5-propyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (8a)

To a soln of **5a** (78 mg, 0.4 mmol) in anhyd DCE (3 mL) was added $Sc(OTf)_3$ (6 mg, 0.012 mmol) and the resulting soln was stirred at 0 °C for 4 h under an N_2 atmosphere. Usual workup and chromatography (silica gel 60, EtOAc–hexane, 1:4, 1% Et_3N) provided **5b** (51 mg, 65%) as a pale yellow oil (9:1 diastereomeric mixture).

Major diastereomer

R_f = 0.24 (EtOAc–hexane, 1:4, 1% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H), 1.08–1.26 (m, 1 H), 1.09–1.40 (m, 2 H), 1.37 (d, *J* = 6.4 Hz, 3 H), 1.56–1.73 (m, 2 H), 1.91–1.97 (m, 1 H), 2.02 (d, *J* = 18.4 Hz, 1 H), 2.16–2.22 (m, 1 H), 2.39–2.48 (m, 1 H), 2.51 (dd, *J* = 18.4, 6.1 Hz, 1 H), 2.57–2.65 (m, 1 H), 3.95–4.03 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (q), 20.2 (t), 20.6 (q), 22.8 (t), 28.4 (t), 35.7 (t), 37.4 (d), 39.4 (t), 73.2 (d), 148.3 (s), 150.9 (s), 200.2 (s).

MS (EI, 70eV): *m*/*z* (%) = 194 (33), 151 (100), 123 (28), 55 (30).

Anal. Calcd for $C_{12}H_{18}O_2$ (194.27): C, 74.19; H, 9.34. Found: C, 70.33; H, 9.01.

(2*R,5*R**)-2-Methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (8b)**

R_f = 0.18 (EtOAc–hexane, 1:5, 0.5% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.2 Hz, 3 H), 1.57–1.78 (m, 1 H), 1.84–2.00 (m, 1 H), 2.07–2.19 (m, 2 H), 2.33 (dd, *J* = 18.7, 1.5 Hz, 1 H), 2.91 (dd, *J* = 18.7, 6.6 Hz, 1 H), 3.81 (dd, *J* = 6.6, 1.5 Hz, 1 H), 4.03–4.17 (m, 1 H), 7.15–7.18 (m, 2 H), 7.20–7.40 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 20.6 (q), 22.6 (t), 28.4 (t), 43.2 (t), 43.7 (d), 73.5 (d), 126.9 (d, 2 C), 127.0 (d), 128.8 (d, 2 C), 141.6 (s), 146.9 (s), 151.5 (s), 199.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 228 (M^+, 100), 200 (94), 129 (58), 115 (55), 91 (22).

Anal. Calcd for $C_{15}H_{16}O_2$ (228.29): C, 78.92; H, 7.06. Found: C, 78.63; H, 7.19.

2-Methyl-6-phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]pyran-7(2*H*)-one (8c)

Major diastereomer

R_f = 0.15 (EtOAc–hexane, 1:5, 0.5% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.2 Hz, 3 H), 1.64–1.87 (m, 1 H), 1.94–2.10 (m, 1 H), 2.38–2.51 (m, 3 H), 2.96 (dd, *J* = 17.6, 6.9 Hz, 1 H), 3.59 (d, *J* = 6.9 Hz, 1 H), 4.06–4.22 (m, 1 H), 7.10–7.38 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 20.6 (q), 24.3 (t), 28.6 (t), 35.9 (t), 49.7 (d), 73.5 (d), 126.8 (d, 2 C), 127.5 (d), 128.6 (d, 2 C), 139.5 (s), 144.4 (s), 150.5 (s), 199.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 228 (M^+, 100), 199 (16), 129 (35), 91 (22).

5-Propyl-3,4,5,6-tetrahydrocyclopenta[*b*]thiopyran-7(2*H*)-one (9a)

To a soln of **6a** (52 mg, 0.27 mmol) in anhyd DCE (2 mL) was added $Sc(OTf)_3$ (3.9 mg, 0.008 mmol) and the resulting soln was stirred at r.t. for 1 h under an N_2 atmosphere. Usual workup and chromatography (silica gel 60, EtOAc–petroleum ether, 1:8, 0.5% Et_3N,) provided **9a** (35 mg, 67%) as a colorless oil.

R_f = 0.28 (EtOAc–petroleum ether, 1:8, 0.5% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.0 Hz, 3 H), 1.18–1.40 (m, 3 H), 1.64–1.68 (m, 1 H), 1.96–2.07 (m, 1 H), 2.10 (dd, *J* = 18.7, 2.9 Hz, 1 H), 2.11–2.20 (m, 1 H), 2.33 (dt, *J* = 18.7, 5.6 Hz, 1 H), 2.48–2.56 (m, 1 H), 2.57 (dd, *J* = 18.7, 6.4 Hz, 1 H), 2.73–2.80 (m, 1 H), 2.82–2.92 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.3 (q), 20.3 (t), 22.4 (t), 25.6 (t), 26.0 (t), 35.1 (d), 40.2 (t), 43.5 (t), 132.8 (s), 166.8 (s), 200.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 196 (M^+, 47), 153 (100), 125 (7).

Anal. Calcd for $C_{11}H_{16}OS$ (196.31): C, 67.30; H, 8.22. Found: C, 67.46; H, 8.04.

5-Phenyl-3,4,5,6-tetrahydrocyclopenta[*b*]thiopyran-7(2*H*)-one (9b)

Mp 108–135 °C (dec); R_f = 0.24 (EtOAc–petroleum ether, 1:6, 0.5% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96–2.07 (m, 2 H), 2.07–2.27 (m, 2 H), 2.42 (dd, *J* = 18.7, 2.0 Hz, 1 H), 2.86–2.91 (m, 2 H), 2.97 (dd, *J* = 18.7, 6.7 Hz, 1 H), 3.91 (d, *J* = 6.7 Hz, 1 H), 7.10–7.13 (m, 2 H), 7.23–7.35 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 22.3 (t), 25.6 (t), 26.0 (t), 44.0 (t), 49.6 (d), 127.0 (d, 3 C), 128.9 (d, 2 C), 134.0 (s), 141.3 (s), 165.3 (s), 204.0 (s).

MS (EI, 70 eV): *m*/*z* (%) = 230 (M^+, 100), 202 (47), 141 (46), 115 (55), 77 (55).

Anal. Calcd for $C_{14}H_{14}OS$ (230.33): C, 73.01; H, 6.13. Found: C, 72.88; H, 6.23.

Acknowledgment

We thank MIUR and University of Florence for financial support, and Cassa di Risparmio di Firenze for granting a 400 MHz NMR spectrometer.

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