Enantioselective 1,3-Dipolar Cycloaddition Reactions Using Complexes of (-)-Sparteine

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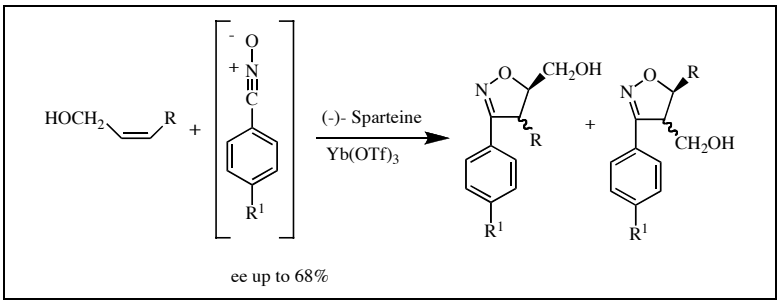

Regio- and stereoselective 1,3-dipolar cycloaddition of nitrile oxides to internal 2-pentenols and α,β-unsaturated esters catalyzed by (-) sparteine-lanthanide complexes affords corresponding 3-aryl-2-isoxazolines with enantioselectivities up to 68% ee.

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INTRODUCTION

1,3-Dipolar cycloaddition of nitrile oxides to alkenes is the most useful method of preparation of 2-isoxazolines [1], useful intermediates which can be easily transformed by reductive N-O bond cleavage to several synthetically important compounds such as β-hydroxy ketones, β-hydroxy esters, α,β-unsaturated carbonyl compounds or iminoketones [2]. The nitrile oxides can be formed either by Huisgen method from aldoximes by chlorination and base-induced dehydrochlorination [1] or by Mukayama method from primary nitro compounds and phenyl isocyanates [3]. While reactions with terminal alkenes give almost exclusively 5-substituted 2-isoxazolines problems of weak regio- and stereoselectivity appear for 1,2-disubstituted olefins. Diastereoselective and enantioselective cycloadditions have been studied extensively with application of optically active substrates and chiral catalysts [4]. Several obstacles such as propensity of nitrile oxides to dimerize and form unreactive complexes with metal catalysts as well as interaction of tertiary amines used to generate nitrile oxides with Lewis acids had to be overcome [5]. Cycloaddition of the nitrile oxides to the optically active internal α-silyl allyl alcohols in the presence of alkoxymagnesium bromides afforded trisubstituted 2-isoxazolines without loss of chirality [6]. Ukaji *et al* applied a related approach to the first asymmetric metal-catalyzed 1,3-dipolar cycloaddition reaction of nitrile oxides to γ-substituted allylic alcohols with diethylzinc and (*R,R*)-diisopropyl tartrate as the chiral auxiliary [7,8]. A catalytic version of this reaction was also developed. Sibi *et al* achieved excellent regio- and enantioselectivity in the cycloaddition of nitrile oxide to crotonamide derivatized as achiral pyrazolidinone using a chiral Lewis acid obtained from bisoxazoline derivative of amino indanol and magnesium iodide [9]. Coordination of amine bases to Lewis acid was circumvented by application of Amberlyst 21 as a base to generate nitrile oxides from hydroximinoyl chlorides.

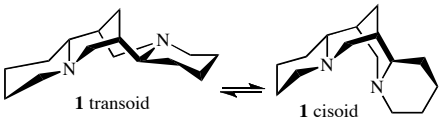
RESULTS AND DISCUSSION

These results underlined the importance of creating a chiral sphere around a metal center where by aggregation of dipole and dipolarophile a good control of regio- and stereoselectivity may be achieved. Such a sphere may comprise a chiral diamine such as bisoxazoline applied as a ligand for magnesium ion [9,10] or nickel ion [11,12], isoxazolidinylpyridine derivative (PyBox) [13], Kemp's triacid derivative [14], and Rebeck benzoxazole [15].

It struck us that a similar chiral cavity as in the above mentioned synthetic diamines could be provided by a natural quinolizidine alkaloid (-)-sparteine (**1**). This alkaloid in a free form shows a transoid conformation with the C-ring in the boat form and *trans* C/D ring juncture [16,17]. On protonation or formation of metal complexes inversion of configuration on N-16 takes place resulting in adoption of cisoid conformation with *cis* C/D ring juncture [18,19] (Scheme 1), and a cavity between two nitrogen atoms allowing sparteine to function as a bidendate ligand. Following a pioneering contribution of Hoppe [20] there has been recent upsurge of interest in

sparteine as a chiral ligand in asymmetric synthesis. Initially organolithium compounds were applied in asymmetric deprotonation, substitution and addition reactions [21,22]. Later chiral complexes of sparteine with other metal ions were used, such as complexes of magnesium [23], tin [24], titanium [25,26], copper [27,28], manganese [29], and palladium [30,31].

Scheme 1



In search of new chiral Lewis acid catalysts we examined participation of lanthanides, metals of strong oxophilicity which due to large ionic radii (1.1 – 0.9 Å) show high coordination numbers (6-12) [32]. These catalysts were successfully applied in asymmetric 1,3-dipolar cycloaddition of nitrones and alkenes in the presence of chiral amines and/or phenols [14,33]. We have just achieved regio- and stereoselective 1,3-dipolar cycloaddition of nitrile oxides to α,β-unsaturated esters and internal 2-pentenols catalyzed by *R*-(+) BINOL-lanthanide complexes affording corresponding 3-aryl-2-isoxazolines with good enantioselectivities [34].

These data induced us to examine for the first time application of chiral complexes of lanthanides with (-)-sparteine in cycloaddition reaction of aryl nitrile oxides to alkenols (Scheme 2). A catalyst formed from sparteine and anhydrous ytterbium triflate showed the best regioselectivity and yield of the reaction as compared to praseodymium, scandium, and ytterbium triflate hydrate. Nitrile oxides were generated by dehydrochlorination of hydroximinoyl chlorides on Amberlyst A-21 column [9] or *in situ* with triethylamine. The effects of catalyst amount, addition order, solvent, structure of the dipole, and presence of additional base on regio- and stereoselectivity of the reaction with *Z*-2-pentol were studied. Preliminary results are presented in Table 1. Trifluoromethyl-substituted dipole was applied most frequently because this group often enhances biological activity of compounds.

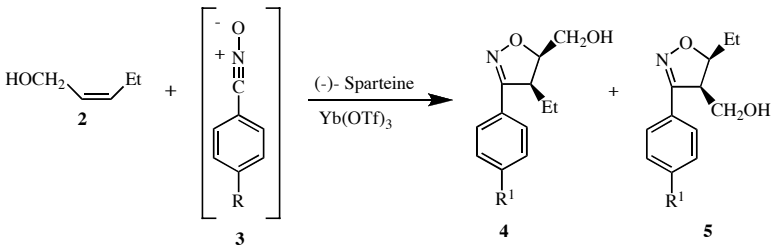
Reaction run without any catalyst (entry 16) showed low regioselectivity and yield. When nitrile oxide was generated in the presence of one equivalent of (-)-sparteine (entry 17) regioselectivity of the reaction was much improved, although the yield was still unsatisfactory.

With increase of the catalyst amount (from 0.5 to 1.1 equivalent) direction of regioselectivity changed from prevalence of regioisomer **4** (entries 1-2) to favoring of isomer **5** (entries 3-5). Reactions carried out in diethyl ether were more regioselective than those run in dichloromethane, although the yields were lower. Structure of the dipole influenced both the regio- and enantioselectivity of the cycloaddition. Reaction of nitrile oxides with electron-donating substituents (entries 12-15) were more regioselective and enantioselective in comparison with nitrile oxides bearing electron-with-drawing substituents. In reaction 12, 13, and 15 only regioisomer **5** was detected. Conversion of pentenols to metal alkoxides with *n*-butyl lithium or Grignard reagent increased the proportion of regioisomer **5** (entries 12, 14).

These experiments clearly demonstrate an effect of sparteine and its complex with the lanthanide on regioselectivity and enantioselectivity of the reaction. This complex enables agglomeration of dipole and dipolarophile in the chiral cavity of cisoid sparteine, which results in facial selectivity. Electron-donating substituents of the dipole increase the negative charge on the oxygen atom, which seems to stabilize complex with electro-positive lanthanide (entry 15) and sparteine, resulting in enhanced regio- and stereoselectivity of the reaction. Similar effect exert electron-donating substituents of the dipole on interaction of sparteine with lithium alkoxide (dipolarophile) and dipoles (entries 12 and 13), where excellent regioselectivity was achieved.

We tried also in one case application of the chiral sparteine catalyst to the enantioselective cycloaddition reaction of aryl nitrile oxides to unsaturated ester – methyl crotonate (Scheme 3). It was gratifying to find

Scheme 2



R = CF_3, Et, i-Pr, OMe

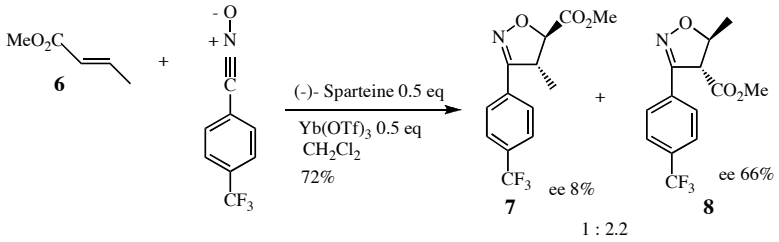
Table 1

Reactions of *Z*-2-penten-1-ol with nitile oxides in the presence of chiral (-)-sparteine catalyst

Entry	R	Sparte-ine eq	$Yb(OTf)_3$ eq	Addnl base eq	Solvent	Yield %	**5:4** ratio	**5** ee %	**4** ee %
1[a]	CF_3	0.5	0.5	-	CH_2Cl_2	36	1:2.1	24	38
2	CF_3	0.6	0.3	-	CH_2Cl_2	48	1:1.5	18	22
3	CF_3	1	1	-	Et_2O	17	3.8:1	38	22
4	CF_3	1.1	1.1	-	Et_2O	42	1.9:1	19	42
5	CF_3[b]	1.1	1.1	-	CH_2Cl_2	61	1.7:1	34	28
6[a]	CF_3	2	1	-	Et_2O	20	1:5.7	28	30
7	CF_3	0.5	-	0.5 BuLi	CH_2Cl_2	40	1.2:1	40	24
8[a]	CF_3	0.7	-	0.7 BuLi	CH_2Cl_2	33	1:1.3	26	30
9	CF_3	1	-	1 BuLi	Et_2O	51	1:1.6	30	30
10[a]	CF_3[b]	1	-	1 BuLi	Et_2O	21	1.6:1	49	28
11	CF_3	1	-	1 iPrMgBr	Et_2O	35	4.9:1	42	40
12	*i*-Pr	1	-	1 BuLi	Et_2O	39	0:100	50	-
13	Et	1	-	1 BuLi	Et_2O	37	0:100	48	-
14	*i*-Pr	1	1	-	Et_2O	62	1:1.4	68	34
15	OMe	1	1	-	CH_2Cl_2	55	0:100	60	-
16	CF_3	-	-	-	CH_2Cl_2	20	1:1.2	-	-
17	CF_3	1	-	-	CH_2Cl_2	18	1:6.1	15	16

[a] *N*-oxide was generated with NEt_3, in other cases on the Amberlyst A-21 column;[b] Dipolarophile was added after dipole.

Scheme 3



unexpectedly good ee of 66% for regioisomer 4 (Scheme 3). This result broadens the synthetic utility of sparteine-lanthanide catalyst. Further studies are in progress to improve efficiency of the catalyst and to explore it in other asymmetric reactions.

EXPERIMENTAL

Reagent grade chemicals were used without further purifycation unless otherwise noted. Elemental analyses were performed at Microanalysis Laboratory of Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw. Spectra were obtained as follows: IR spectra on JASCO FTIR-420 spectrometer, ^{1}H NMR spectra on Varian 500 UNITY plus-500 and Varian 200 UNITY plus 200 spectrometers in deuterated chloroform using TMS as internal standard. Flash-chromatography was carried out using silica gel S 230-400 mesh (Merck).

Hydroximinoyl acid chlorides were prepared from the corresponding aryl aldehyde oximes and NCS in DMF [35]. The corresponding nitrile oxides were generated *in situ* by dehydrohalogenation with triethylamine or on Amberlyst A-21 column [9].

General procedure for the cycloaddition reactions with application of sparteine-lanthanide complexes: A mixture of (-)-sparteine and ytterbium triflate in dry dichloromethane was stirred at room temperature for 30 minutes. *Z* 2-penten-1-ol (1 mmol) was added to the clear solution and stirring was continued for 30 minutes. A solution of dipole in the same solvent generated by passing a hydroximinoyl chloride (1 mmole) solution through a column of Amberlyst 21 was added dropwise over 30 minutes. The obtained solution was stirred for *ca*. 19 h, water was added to quench the reaction and the reaction mixture was diluted with dichloromethane. The organic phase was washed with water, dilute hydrochloric acid and water, dried (magnesium sulfate) and the solvent was evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel and the enantiomeric excess of separated regioisomers was determined by HPLC analysis (Astec Cyclobond I 2000 RN).

General procedure for the cycloaddition reactions with application of sparteine and lithium alkoxides. *N*-butyl lithium (2.5 *M* solution in hexanes) was added to a solution of (-)-sparteine in dry diethyl ether at -78 °C. *Z* 2-penten-1-ol (1 mmol) was added dropwise and the mixture was stirred at 0 °C for 30 minutes. A solution of nitrile oxide was added dropwise over 30 minutes and a milky reaction mixture was stirred at 0 °C for 5 hours and overnight at room temperature. A clear reaction mixture was neutralized with ammonium chloride solution and worked-up as above.

[4-Ethyl-3(4-trifluoromethylphenyl)-4,5-dihydroisoxazol-4-yl]methanol (4a) and [5-ethyl-3(4-trifluoromethylphenyl)-4,5-dihydroisoxazol-4-yl]methanol (5a). These compounds were obtained as colorless oils. Regioisomer-5 (**4a**): ir (neat) OH 3330, 3140, 1619, 1520 (Ph), 1324 (CF_3) cm^{-1}; ^{1}H nmr

($CDCl_3$, 200 MHz) δ 7.77 (d, J = 8.5 Hz, 2H, 5'-H, 3'-H), 7.66 (d, J = 8.5 Hz, 2H, 6'-H, 2'-H), 4.81 (m, 1H, 5-H), 4.01 (m, 2H, CH_2OH), 3.64 (m, 1H, 4-H), 2.18 (s, 1H, OH) 1.69 (m, 2H, CH_2CH_3), 0.94 (t, J = 7.6 Hz, 3H). *Anal*. Calcd. for $C_{13}H_{14}NO_2$: C, 57.14; H, 5.16. Found: C, 56.81; H, 5.01. Regioisomer 4 (**5a**): ir (neat) OH 3328, phenyl 1619, 1530, CF_3 1326 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz) δ 7.96 (d, J = 8.4 Hz, 2H, 5'-H, 3'-H) 7.66 (d, J = 8.4 Hz, 2H, 6'-H, 2'-H), 5.57 (m, 2H, 4-H, 5-H), 4.24 (m, 2H, CH_2OH), 2.08 (m, 2H, CH_2CH_3), 0.98 (t, J = 7,6 Hz, 3H). *Anal*. Calcd. for $C_{13}H_{14}NO_2$: C, 57.14; H, 5.16. Found: C, 56.95; H, 4.98.

[4-Ethyl-3-(4-isopropylphenyl)-4,5-dihydroisoxazol-5-yl]-methanol (4b) and [5-ethyl-3-(4-isopropylphenyl)-4,5-dihydro-isoxazol-4-yl]methanol (5b). These compounds were obtained as colorless oils; regioisomer-5 (**4b**): ir (neat) OH 3400, phenyl 1610, 839 cm-1; ^1H nmr ($CDCl_3$, 200 MHz) δ 7.67 (d, J = 8.2 Hz, 2H, 2'-H, 6'-H), 7.27 (d, J = 8.2 Hz, 2H, 3'-H, 5'-H), 7.20 (s, 1H, OH), 4.51 (dt, J = 8.3; 6.4 Hz, 1H, 5-H), 3.85 (d, J = 6.4 Hz, 1H, CH-CH_2-OH), 3.61 (dt, J = 8.3; 6.7 Hz, 1H, 4-H), 2.93 (septuplet, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 1.99 (qd, J = 6.7 Hz, 2H, CH_2CH_3), 1.26 (d, J = 6.8 Hz, 6H, $(CH_3)_2CH$-), 1.16 (t, J = 6.7 Hz, 3H, CH_3CH_2). *Anal*. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.53; H, 8.41. Regioisomer 4 (5b): ir (neat) OH 3309, phenyl 1620, 841 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz) δ 7.87 (s, 1H, OH), 7.56 (d, J = 8.0 Hz, 2H, 2'-H, 6'-H), 7.25 (d, J = 8.0 Hz, 2H, H–3', H–5'), 5.63 (m, 2H, 4-H, 5-H), 4.75 (d, J = 5.5 Hz, 2H, CH-CH_2OH), 2.93 (septuplet, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 1.97 (dq, J = 6.9; 3.0 Hz, 2H, CH_2CH_3), 1.25 (d, J = 6.5 Hz, 6H, $(CH_3)_2CH$), 0.91 (t, J = 7.8 Hz, 3H, CH_3CH_2). *Anal*. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.46; H, 8.39.

[5-Ethyl-3-(4-ethylphenyl)-4,5-dihydroisoxazol-4-yl]-methanol (5c). This compound was obtained as colorless oil; ir (neat) OH 3380, phenyl 1636, 840 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz) δ 7.96 (d, J = 8.2 Hz, 2H, 6'-H, 2'-H), 7.25 (d, J = 8.2 Hz, 2H, 3'-H, 5'-H), 5.65 (m, 2H, 4-H, 5-H), 4.86 (d, J = 6 Hz, 2H, CH_2OH), 2.71 (q, J = 7.5 Hz, 2H, CH_2Ar), 2.19 (m, 2H, CH-CH_2CH_3), 1.25 (t, J = 7.5 Hz, 2H, Ar-CH_2CH_3), 1.02 (t, J = 7.5 Hz, 3 H, CH_3CH_2CH-). *Anal*. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 72.36; H, 8.59.

[5-Ethyl-3-(4-methoxyphenyl)-4,5-dihydroisoxazol-4-yl]-methanol (5d). This compound was obtained as a colorless oil; ir (neat) OH 3429, phenyl 1608, 832 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz) δ 6.93 (d, J = 8.5 Hz, 2H, 5'-H, 3'-H), 6.84 (d, J = 8.5 Hz, 2H, 6'-H, 2'-H), 4.05 (m, 2H, 4-H, 5-H), 3.91 (m, 2H, CH_2OH), 3.78 (s, 3H, CH_3O), 1.65 (m, 2H, CH_3CH_2CH), 0.88 (m, 3H, $CHCH_2CH_3$). *Anal*. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28. Found: C, 66.08; H, 7.06.

Methyl trifluoromethylphenyl)-4-methyl-4,5-dihydroisoxazole-5-carboxylate (7) and methyl 3-(4-trifluoro-methylphenyl)-5-methyl-4,5-dihydroisoxazole-4-carboxylate (8). These compounds were obtained as colorless oils. Regioisomer-5: ir (neat) CO 1741, phenyl 1619, 1482, 847, CF_3 1324 cm^{-1}; ^1H nmr ($CDCl_3$, 200 MHz) δ 7.97 (d, J = 8.1 Hz, 2H, 5'-H, 3'-H), 7.68 (d, J = 8.1 Hz, 2H, 6'-H, 2'-H), 4.84 (d, J = 4.2 Hz, 1H, 5-H), 4.02 (dq, J = 7.3; 4.2 Hz, 4-H), 3.81 (s, 3H, CH_3O), 1.43 (d, J = 7.3 Hz, 3H, CH_3-CH-). *Anal*. Calcd. For $C_{13}H_{12}F_3NO_3$: C, 54.36; H, 4.21. Found: C, 54.48; H, 4.01. Regioisomer-4: ir (neat) CO 1742, phenyl 1620, 849, 1325 (CF_3) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.82 (d, J = 8.6 Hz, 2H, 5'-H, 3'-H), 7.65 (d, J = 8.6 Hz, 2H, 6'-H, 2'-H), 5.15 (quintuplet, J = 6.3 Hz, 1H, 5-H), 4.11 (d, J = 6.3 Hz, 4-H), 3.73 (s, 3H, CH_3O), 1.49 (d, J = 6.3 Hz, 3H, CH_3CH). *Anal*. Calcd. for $C_{13}H_{12}F_3NO_3$: C, 54.36; H, 4.21. Found: C, 54.59; H, 4.17.

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