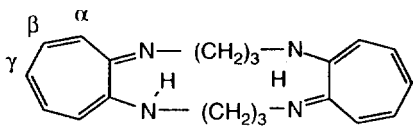
Table 1. ^{1}H NMR Data for ligand **4**, **6** and its Ni(II) complex

Compound	α	β	γ	C1	C2 (ppm)
4	6.29	6.66	6.16	4.75	3.96
5	5.77	6.47	6.04	2.83	3.79 (*trans*)
					3.86 (*cis*)
Trop (**6**)	6.24	6.78	6.12		
NiTrop	6.31	6.83	6.16		

of the macrocycle.[9]



6

Interestingly, as shown in the Table 1, the shielding effect of Ni on the hydrogen resonances of the cycloheptatriene ring is related to the distance from the Ni atom showing the large upfield shift of α hydrogen of **5**. In the case of hydrogens on C1 and C2 carbons, the effect on C1 hydrogen is quite significant when compared to C2 hydrogens, suggesting that the distances from Ni to C1 and C2 may not be equal and the Ni atom is more tightly bounded to two nitrogen site than two oxygen site. The square planar structure of the complex can also be confirmed from the inequivalent resonances of two geminal C2 hydrogens which are identical in the non metallated ligand. The two hydrogen resonances, *cis* and *trans* to phenyl group at C1 are distinguishable based on coupling constants.[13]

The NiPGAT (**5**) showed a complexation with amino acids in solution. In U-tube comprising three layers of water (phenylalanine)/chloroform (NiPGAT)/water, the NiPGAT in $CHCl_3$ actively transfers phenylalanine from one water layer to another water layer. We are currently investigating the selective transfer of D- or L-form of amino acid through NiPGAT in chloroform which can be applied in the separation of D- and L-form of amino acids from a racemic mixtures.

In conclusion, we have prepared a new chiral aminotroponeimine ligand (**4**) and its nickel complex (**5**). The ligand and metal complex were identified based on various spectroscopic data. Their applications to asymmetric reactions are being under study in our laboratory.

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10. Spectral data of PGAT (**4**): UV-VIS (EtOH): λ_{max} (log ε) 242 (4.14), 348 (3.84), 359 (3.83), 400 (3.74) nm; IR (KBr): 3300 (broad), 3028, 2864, 1678, 1590, 1274, 1040, 730, 700 cm^{-1}; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 3.52-3.46 (3H, s, broad), 3.96 (4H, d, J=4.4 Hz), 4.75 (2H, t, J=5.6 Hz), 6.16 (1H, t, J=10.4 Hz), 6.29 (2H, d, J=10.1 Hz), 6.66 (2H, t, J=10.2 Hz), 7.26-7.60 (10H, m) ppm; ^{13}C NMR ($CDCl_3$): δ 62.3, 67.3, 126.8, 127.3, 127.7, 128.6, 128.8, 132.0, 153.5 ppm; MS (EI) m/z (%) 360 (28, M$^+$), 329 (100), 223 (30), 209 (100), 165 (15), 131 (55), 116 (29), 103 (53), 91 (45), 79 (23), 77 (22); HRMS calcd for $C_{23}H_{24}N_2O_2$ 360.1838, found 360.1830.
11. Spectral data of NiPGAT (**5**): UV-VIS ($CHCl_3$): λ_{max} (log ε) 505 (3.72), 438 (3.81), 312 (3.97), 270 (4.29) nm; IR (KBr): 724, 1132, 1229, 1516, 1581, 2871, 3022, 3400 cm^{-1}; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.83 (2H, d, J=9.6 Hz), 3.79 (2H, dd, J=9.6 & 5.6 Hz), 3.86 (2H, d, J=4.8 Hz), 5.77 (2H, d, J=11.2 Hz), 6.04 (1H, t, J=9.6 Hz), 6.47 (2H, dd, 9.6 & 11.2 Hz), 7.27 (2H, t, J=7.2 Hz), 7.40 (4H, t, J=7.2 Hz), 7.25-7.41 (1H, br.), 7.79 (4H, d, J=7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 63.9, 75.6, 114.3, 118.3, 126.9, 128.5, 131.6, 141.1, 164.0 ppm; Anal. Calcd for $C_{23}H_{22}N_2O_2Ni$: C, 66.23; H, 5.32; N, 6.72. Found: C, 65.18; H, 5.21; N, 6.47.
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Oxidative Demercuration of Cyclohexylmercury Cyanides

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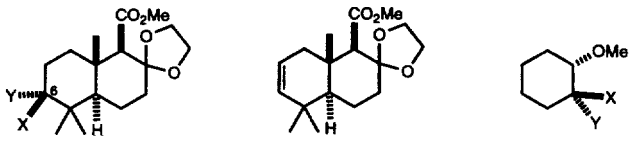
Introduction of various nucleophiles to carbon-carbon double bond using soft acid is an important tool for functionali-



1 X=HgCl,Y=H
2 X=HgCN,Y=H
3 X=H,Y=OH
4 X=OH,Y=H
5 X=H,Y=OAc
6 X=OAc,Y=H

7

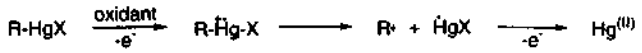
8 X=HgCl,Y=H
9 X=HgCN,Y=H
10 X=OH,Y=H
11 X=H,Y=OH
12 X=OAc,Y=H
13 X=H,Y=OAc
14 X=Ph,Y=H

Figure 1.

zation of alkene.[1] In particular, mercury(II)-initiated stereoselective polyene cyclizations have been extensively utilized for the synthesis of cyclic terpenoids.[2] These reactions depend primarily upon the replacement of mercury halide with oxygen functionality by reduction of sodium borohydride or tri-n-butyltin hydride followed by the capture of the molecular oxygen by the radical intermediate in a nonstereoselective manner.[3] Ozone and chromium trioxide oxidize secondary organomercury halides to ketones but they are also reactive with other functional groups present in the molecule.[4] Although organomercury halides are relatively stable toward mild oxidants, the reactivity may be sufficiently enhanced if the halides were replaced by other stronger nucleophile, so that oxidative cleavage of the carbon-mercury bond may possible under mild condition.

In this work, we have prepared the derivatives of cyclohexylmercury cyanides, carried out the oxidation reaction and analyzed the stereochemical results of the oxygenated products. Mercury chloride **1**, prepared from geranyl bromide using a known three-step sequence, was treated with aqueous sodium cyanide to provide stable mercury cyanide **2** in quantitative yield.[2] The chemical shift of the C(H)-Hg proton changed slightly upfield from δ 2.66 for chloride **1** to δ 2.37 for cyanide **2** in ^{1}H NMR spectrum, indicating the increase of electron density on mercury.[5] The cyanide **2** was heated at reflux with *m*-chloroperoxybenzoic acid in 1,2-dichloroethane to provide a 4 : 1 mixture of alcohol **3** and **4** in 70% yield.[6] On the other hand, when mercury chloride **1** was subjected to the same reaction condition, the yield decreased to 35%. The reaction of **2** with one equivalent of lead tetraacetate in refluxing benzene gave 13 : 1 mixture of **5** and **6** in 37% yield together with 56% of elimination product **7**. In contrast, mercury chloride **1** did not react under this condition. Stereochemical outcome of **3-6** apparently results from the preferential axial attack of the nucleophile to conformationally fixed cyclohexyl carbocation.[7]

Mercury cyanide **9**, prepared from **8** in 95% yield, could also be oxidized readily with *m*-CPBA and $Pb(OAc)_4$. Oxidation of **9** by *m*-CPBA provided 2 : 1 mixture of **10** and **11** in 58% yield. Treatment with lead tetraacetate in benzene furnished 7 : 1 mixture of **12** and **13** in 63% yield together with 10% of **14**, which must have been produced by the trapping of the carbocationic intermediate by the solvent molecule.[8]



Scheme 1.

Presence of radical intermediate in the oxidation of **2** by *m*-CPBA was demonstrated by the strong rate retardation in the presence of a radical inhibitor. Thus addition of 2 mole percent of 3-*t*-butyl-4-hydroxy-5-methylphenylsulfide completely inhibited the reaction.[9] A plausible mechanism for this oxidation process is as follows.

The organomercury compound is oxidized by the oxidant to form a radical cation. The radical cation would then decompose to carbocation and HgX, which would in turn react with the nucleophile to afford the oxygenated products. The radical inhibitor would have inhibited the radical chain process forming the radical cation. The presence of carbocation intermediate is strongly supported by the formation of elimination product **7** and substitution product **14**. The observation that electron rich cyanide **2** oxidized faster than the corresponding chloide **1** is also consistent with this mechanism.

In summary, oxidation of organomercury cyanides provided direct replacement of mercury with oxygen nucleophile through carbocationic intermediate and the mechanism of this oxidative process is proposed. Synthetic potential of this approach to incorporate two nucleophiles at each carbon end of double bond is currently under investigation.

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5. **2**: mp 220-221 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.20-1.64 (m, 8H), 1.77 (ddd, J=14, 7, 4 Hz, 1H), 1.86 (dt, J=10, 3 Hz, 1H), 2.05 (dg, J=13, 3 Hz, 1H), 2.37 (dd, J=14, 4 Hz, 1H, CHHg), 2.46 (s, 1H, $CHCO_2$), 3.36 (s, 3H, CO_2CH_3), 3.73-4.07 (m, 4H, $2CH_2O$); IR ($CHCl_3$, cm^{-1}) 1735, 1150, 1070.
6. The ratio of **3** and **4** was determined by integration of $CHCO_2$ signals at δ 2.60 and δ 2.47, respectively, in the ^{1}H NMR spectrum.
7. The assignment of stereochemistry of **5** and **6** was made

with the coupling constants of equatorial C(6)-H of **5** (t, J=8 Hz) at δ 4.76 and axial C(6)-H of **6** (dd, J=12, 4 Hz) at δ 4.50. This assignment was further verified by comparing the ^{1}H NMR spectrum after acetylation of **3** and **4** mixture (Ac_2O, DMAP, pyridine).

8. The relative stereochemistry of **10-13** was verified by comparing the ^{1}H NMR spectra of the compounds prepared from solvolysis of cyclohexene oxide in methanol followed by acetylation.
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Synthesis of Thiazole Derivatives *via* Lewis Acid Promoted Reactions of Diazopyruvate with Thioamides

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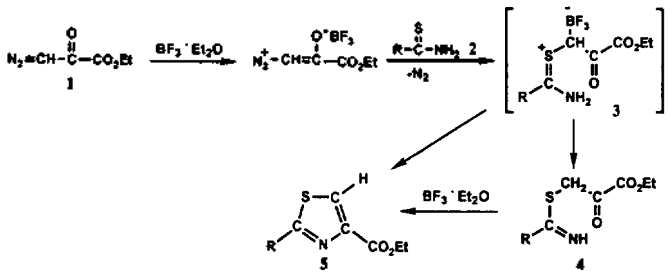
The thiazole derivatives are found as sub-unit of many biologically important and structurally complex natural products such as theonezolide,[1] leinamycin,[2] and bleomycin.[3] It has been well documented that bithiazole derivatives cleave duplex DNA either in the presence of oxygen and ferrous ion[4] or irradiation.[5] Consequently the development of new, efficient, and general methods for the synthesis of thiazoles continues to be an attractive objective. Several different synthetic approaches to thiazoles have been developed.[6]

Thiocarbonyl ylides have been the subject of much interest in recent years due to their potential roles as intermediates in a variety of reactions, including the five-membered ring sulfur heterocycles.[7] The carbene approach to sulfur ylide formation by thermal, photochemical, and transition metal catalyzed reaction has been extensively explored.[8] However, the Lewis acid catalyzed ylide formation of α-diazocarbonyl compounds has received little attention.

In continuation of our work on the use of α-diazocarbonyl compounds for the synthesis of heterocycles such as β-furoic acid,[9] γ-pyrone,[10] and oxazole,[11] we have attempted to develop a new route to thiazoles based on cyclization of thiocarbonyl ylide, which generated from the Lewis acid-promoted reaction of α-diazocarbonyl compounds with thioamide.

Initial studies on the Lewis acid-promoted reactions of α-diazocarbonyl compounds with thioamides were carried out with ethyl diazopyruvate. Reaction of diazopyruvate **1** with thiobenzamide **2a** (R=Ph) in the presence of Lewis acid (*e.g.*, BF_3·Et_2O, $AlCl_3$, $FeCl_3$) at room temperature, after aqueous work-up, resulted in S-alkylisothiobenzamide **4a** in good to excellent yields.[12] Use of 2 equiv of Lewis acids to the 1 : 1 mixture of **1** and thiobenzamide **2a** afforded the following yields of isothiobenzamide **4a**, BF_3·Et_2O (97%), $AlCl_3$ (54%), $FeCl_3$ (30%).



Scheme 1.

Table 1. Lewis Acid Promoted Reactions of Diazopyruvate **1** with Thioamides

Thioamide (2) R	Reagent	Reaction[a] conditions	Product	Yield (%)[b]	mp (℃)
2a C_6H_5	BF_3·Et_2O	A	**4a**	97	109-110
2a C_6H_5	$AlCl_3$	A	**4a**	54	109-110
2a C_6H_5	$FeCl_3$	A	**4a**	30	109-110
2a C_6H_5	BF_3·Et_2O	B	**5a**	82	48-49
2a C_6H_5	$AlCl_3$	B	**5a**	79	48-49
2a C_6H_5	$FeCl_3$	B	**5a**	20	48-49
2b 4-O_2N-C_6H_4	BF_3·Et_2O	A	**4b**	60[c]	150-152
2b 4-O_2N-C_6H_4	BF_3·Et_2O	B	**5b**	72	152-154
2c 4-CH_3O-C_6H_4	BF_3·Et_2O	B	**5c**	89	97-98
2d 2-CH_3O-C_6H_4	BF_3·Et_2O	B	**5d**	87	86-87
2e 4-CH_3-C_6H_4	BF_3·Et_2O	B	**5e**	97	44.5-45
2f 4-CH_3O_2C-C_6H_4	BF_3·Et_2O	B	**5f**	51	121.5-122
2g 4-Cl-C_6H_4	BF_3·Et_2O	B	**5g**	68	100-100.5
2h 2-C_5H_4N	BF_3·Et_2O	B	**5h**	41	70.5-71
2i CH_3	BF_3·Et_2O	B	**5i**	57	57-57.5
2j $C_6H_5CH_2$	BF_3·Et_2O	B	**5j**	49	77-78
2k $C_6H_5CH_2CH_2$	BF_3·Et_2O	B	**5k**	75	51

[a]Method A: Ethyl diazopyruvate (1 mmol) in ether (5 mL) was added to the mixture of thioamide (1 mmol)-Lewis acid (2 mmol) in ether (5 mL) for 2 h under Ar at 0 ℃ and then the reaction mixture was stirred for 3-7 h at room temperature. Method B: Ethyl diazopyruvate (1 mmol) in DME (5 mL) was added to the mixture of thioamide (1 mmol)-Lewis acid (2 mmol) in DME (5 mL) for 2 h under Ar at 0 ℃ and then the reaction mixture was refluxed for 3-7 h. [b]Isolated yield. [c]Also thiazole **5b** was obtained in 17% yield.

Treatment of 4-nitrothiobenzamide **2b** with **1** in 2 equiv of boron trifluoride at room temperature gave rise to a mixture of the corresponding isothiobenzamide **4b** and thiazole **5b** in the yields of 60 and 17%, respectively. This result suggests that diazopyruvate **1** under the Lewis acid condition generate initially thiocarbonyl ylide **3** which yield **5** by the loss of water as shown in Scheme 1.

We have found that boron trifluoride promoted reactions of diazopyruvate with thioamides at room temperature produce the corresponding S-alkylisothioamide derivatives **4** in preparatively useful yield.

Treatment of the isothiobenzamide **4a** with 1 equiv of bo-