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Stereoselective cyclo-addition reactions of azomethine ylides catalysed by *in situ* generated Ag(I)/bisphosphine complexes

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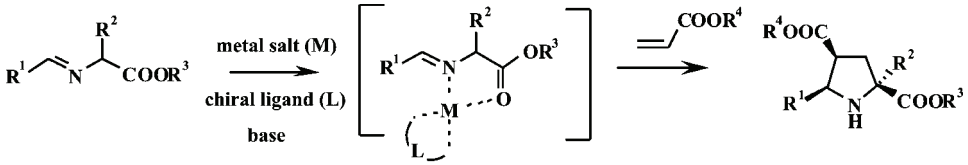
Abstract: Stereoselective cyclo-addition reactions of azomethine ylides promoted by *in situ* generated Ag(I)/bisphosphine complexes were studied. Under the optimised conditions, the pyrrolidine products were isolated in up to 84 % yield and with up to 71 % *e.e.* The effects of various reaction variables on the stereoselectivity were also investigated.

Keywords: azomethine ylides; stereoselectivity; chiral phosphine; Ag(I).

INTRODUCTION

1,3-Dipolar cyclo-addition reactions of metallo-azomethine ylides to electron deficient alkenes constitute a powerful tool for the preparation of substituted pyrrolidine derivatives.[1] If the metallo-ylide is generated in the presence of a chiral ligand, the pyrrolidine product can be obtained in a stereoselective manner, Scheme 1.



Scheme 1. Metal catalysed cycloaddition reactions of azomethine ylides.

Pioneering studies of stereoselective cyclo-additions of these ylides employed the stoichiometric amount of chiral cobalt complexes[2a] or a chiral auxilia-

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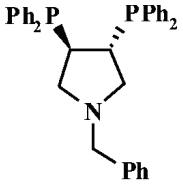
ry.[1a,b,d,2b–j] Recently, more efficient metal[3a–p] and organo-catalytic[3q,r] variations of this transformation have been developed. Various metal salts have been employed, such as Co (II),[2a] Mn(II),[2a] Ag(I),[3a–e] Cu(I/II),[3g–l] Au(I),[3m] Zn(II),[3n] Ca(II),[3o] Ni(II)[3p] in conjunction with a range of chiral ligands.

Of particular interest are the Ag(I)-based methods, which afford pyrrolidines with a high level of enantioselectivity and in good yield, invariably *via* an *endo* transition state. Under the standard conditions (Scheme 1), the use of base is necessary in order to generate the azomethine ylide, but this may be avoided by employing AgOAc as a Lewis acid.[4] In addition, the selection of a ligand in conjunction with an Ag(I) salt provides access to both enantiomeric pyrrolidine products.[5] In recent years, the development of Cu(I)/Cu(II) methods provided additional valuable synthetic methods, which is reflected in the high level of enantioselectivity[3g–l] and the potential to rationally control *exo/endo* selectivity.[3h]

RESULTS AND DISCUSSION

In this paper, initial results obtained in Ag(I)-promoted, stereoselective cyclo-addition reactions of metallo-azomethine ylides employing the bisphosphine ligand **1**:



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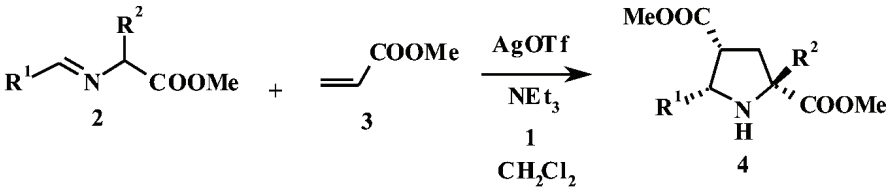
easily accessible from tartaric acid,[6] are discussed.

The cyclo-addition reactions of azomethine ylides generated from imines were performed using equimolar amounts of imine, dipolarophile, AgOTf and the ligand **1** in CH_2Cl_2 as the solvent in the presence of NEt_3 as a base, Scheme 2 and Table I. The products were isolated by flash chromatography and the *e.e.* was determined by ^{1}H-NMR spectroscopy using the chiral shift reagent, (+)-tris[(3--heptafluoropropylhydroxymethylene)camphorato]europium(III).[7]



Scheme 2. Ag(I)/**1** catalysed cyclo-addition reactions of azomethyne ylides.

Most of the reactions afforded the products in good yields (Table I), with reaction times of 3–4 h, suggesting that presence of the ligand did not significantly affect either the yield or the reaction time. The reaction employing the *S*-methylcysteine-derived imine, Table I, entry e, surprisingly, resulted in the recovery of the starting materials only. This may be the result of Ag(I) coordination by the thioether moiety, forming a complex which excluded either N or O coordination of the metal centre.[8] Chelate formation involving the iminoester functionality (see Scheme 1) is essential for lowering the pK_a of the α-C–H bond and the generation of the ylide,[1a] a process potentially disrupted by a competitive coordination of Ag(I) by an additional donor atom. Interestingly, when the thioether containing imine **2f** was used, the expected product was isolated in good yield. This may suggest that the aromatic thioether is a weaker coordinating agent than the aliphatic one, allowing equilibrium between different species, including those leading to the ylide.

TABLE I. Stereoselective Ag(I) catalysed 1,3-dipolar cycloaddition reactions

Entry	R (imine **2**)	R (product **4**)	*e.e.*, %[a]	Yield, %[b]
a	**2a**: R^1 = 2-naphthyl R^2 = H	**4a**: R^1 = 2-naphthyl R^2 = H	49	69
b	**2b**: R^1 = 2-naphthyl R^2 = CH_3	**4b**: R^1 = 2-naphthyl R^2 = CH_3	66	80
c	**2c**: R^1 = 2-naphthyl R^2 = benzyl	**4c**: R^1 = 2-naphthyl R^2 = benzyl	64	72
d	**2d**: R^1 = 2-naphthyl R^2 = 3-indolylmethyl	**4d**: R^1 = 2-naphthyl R^2 = 3-indolylmethyl	67	84
e	**2e**: R^1 = 2-naphthyl R^2 = methylthiomethyl	**4e**: R^1 = 2-naphthyl R^2 = methylthiomethyl	–	–
f	**2f**: R^1 = 2-(methylthio)phenyl R^2 = CH_3	**4f** : R^1 = 2-(methylthio)phenyl R^2 = CH_3	61	74

[a]Assigned by ^{1}H-NMR using chiral shift reagent; [b]isolated yield

The observed enantioselectivity ranged from 49 to 67 %. Although the enantioselectivity was lower for the glycine imine **2a** compared to the other substituted imines, **2b**, **2c**, **2d** and **2f**, there was no significant difference in the *e.e.* between the later ones. This puzzling result could be due to the Thorpe–Ingold effect which decreases the =N–C–CO angle and increases the steric congestion in the transition state.[9]

The absolute stereochemistry of product **4a** (2*R*, 4*R*, 5*S*) was established by comparison of its optical rotation ($[\alpha]_D$ –11.3°) with the optical rotation of (2*R*, 4*R*, 5*S*)-dimethyl 5-(2-naphthyl)pyrrolidine-2,4-dicarboxylate ($[\alpha]_D$ –19.5°) synthesized by a different method.[10] Based on all these results, a transition state was proposed, Fig. 1. It was assumed that the Ag(I) complex has a 4-coordinate square planar geometry. The donor atoms comprise the two phosphorus atoms from the

ligand and the nitrogen and the oxygen atoms from the imine. The approach of the dipolarophile to the *re* face of the imine *via* an *endo* transition state is less favoured due to steric interactions between the pseudo-axial phenyl group on the phosphorus and the ester group of the dipolarophile. The *si* face of the imine is less shielded due to pseudo-equatorial orientation of the phenyl substituent and, therefore, the approach of the dipolarophile from this side leads to the observed product.

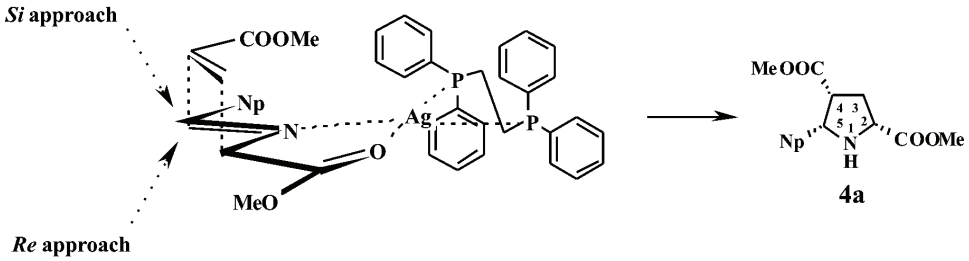


Fig. 1. Proposed transition state for the Ag(I)/**1** catalysed cycloaddition reactions (the pyrrolidine ring of the ligand omitted for clarity).

After these initial results, the effects of various reaction parameters on the enantioselectivity were investigated. Performing the reaction of imine **2b** and acrylate **3** at a lower temperature, Table II, entry a, slightly improved the *e.e.* without influencing the reaction yield. At –78 °C, Table II, entry b, the reaction was very slow and it is likely that the major part of the reaction occurred as the reaction mixture was gradually warmed up.

TABLE II. The effect of temperature on enantioselectivity

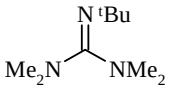
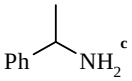
Entry	Imine	Product	*t* / °C	*e.e.*, %[a]	Yield, %[b]
a	**2b**	**4b**	–20	71	78
b	**2b**	**4b**	–78 to r.t.	71	78

[a]Assigned by ^{1}H-NMR using chiral shift reagent; [b]isolated yield

Variation of the base gave some unexpected results, Table III. When (*R*)- or *(S)-N,N,α*-trimethylbenzylamine or pyridine (Table III, entries d and e) were used instead of triethylamine, no cyclo-adduct was obtained. The ^{1}H-NMR spectrum of the crude reaction mixture indicated the presence of starting materials only. This may suggest that the formation of Ag(I) complexes containing these bases as ligands prevented the coordination of the imine and subsequent formation of the ylide. Ag(I)/pyridine complexes are known and their stability depends on the coordination number.[11] On the other hand, the benzylamine derivatives may act as bidentate ligands. The 1:1 complexes of Ag(I) with 2-allylpyridine and vinyldiphenylphosphine, as well as related complexes, have been reported in the literature.[12] When stronger bases than triethylamine were used, such as DBU,

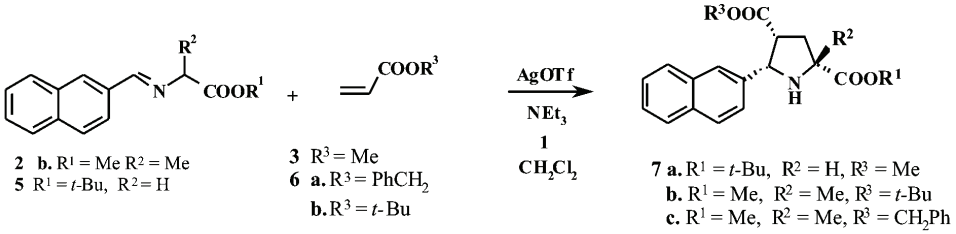
sparteine and tetramethyl-*t*-butylguanidine, Table III, entries a–c, the reaction times were shorter but, unfortunately, the *e.e.* slightly decreased. This might indicate that apart from the phosphine/Ag(I) complex catalysed reaction, a reaction promoted by the base/Ag(I) complex occurred as well. Although steric factors play an important role in the stability of amine/Ag(I) complexes, increased amine bulk may stabilise the complex and, therefore, promote the competitive non-stereoselective process.[11c,13]

TABLE III. The effect of base on enantioselectivity

Entry	Imine	Product	Base	e.e., %[a]	Yield, %[b]
a	**2b**	**4b**	DBU	57	87
b	**2b**	**4b**	Sparteine	57	80
c	**2b**	**4b**		49	88
d	**2b**	**4b**		–	–
e	**2b**	**4b**	Pyridine	–	–

[a]Assigned by ^{1}H-NMR using chiral shift reagent; [b]isolated yield; [c]both (*R*)- and (*S*)- enantiomers were surveyed

The proposed transition state model, Fig. 1, suggests that the approach of the dipolarophile to the dipole is controlled by steric interactions involving the phenyl substituent on the phosphorus and the ester group on the dipolarophile. This prompted evaluation of bulkier ester functionalities of both the dipole and the dipolarophile, Scheme 3, Table IV. When imine *t*-butyl ester **5** was used (Table IV, entry a), the *e.e.* was similar to that observed for imine methyl ester **2a** (Scheme 2, Table I, entry a). This may indicate that the imine ester group does not play a crucial role in inducing the stereoselectivity, which would be expected based on the proposed transition state. On the other hand, *t*-butyl acrylate **6b** (Table IV, entry b) was shown to be ineffective in this reaction, affording the product in only 28 % yield after 4 days. The use of benzyl ester **6a** resulted in a slightly lower *e.e.* (Table IV, entry c).



Scheme 3. Ag(I)/**1** catalysed cycloaddition reactions of azomethine ylides.

In conclusion, the effect of chiral bisphosphine **1** in stereoselective cyclo-addition reactions of metallo-azomethine ylides generated in the presence of AgOTf was studied. Under the optimized conditions, pyrrolidine products were obtained in good yields with up to 71 % *e.e.*

TABLE IV. Effect of steric factors on the *e.e.*

Entry	Imine	Acrylate	Product	*e.e.*, %[a]	Yield, %[b]
a	**5**	**3**	**7a**	48	91
b	**2b**	**6b**	**7b**	–	28[c]
c	**2b**	**6a**	**7c**	57	67

[a]Assigned by ^{1}H-NMR using chiral shift reagent; [b]isolated yield; [c]reaction time: 4 days

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba Elemental Analyser MOD 1106. Mass spectral data were recorded using a VG-AutiSpec spectrometer operating at 70 eV. Nuclear magnetic resonance spectra were recorded at 300 MHz using a General Electric QE300 instrument and at 400 MHz using a Bruker WP400 instrument. Chemical shift are given in parts per million (δ) downfield from tetramethylsilane as the internal standard. Unless otherwise specified, deuterochloroform was used as the solvent. Silica gel 60 (230–400mesh) was employed for flash chromatography.

Of the prepared compounds, the imines **2a**,[14a] **2b**,[14b] **2c**[14c] and **2d**[14c] and pyrrolidines **4a**–**d**[14c] are reported in the literature. Some analytical and spectral data of the newly synthesised compounds are given below.

All *e.e.* values reported in this study were established by ^{1}H-NMR spectroscopy using the chiral shift reagent tris[(3-heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III). The reagent was added in small portions (2–3 mg) to the $CDCl_3$ solution (NMR tube) of the product until a good baseline separation of the enantiomeric signals for the methyl

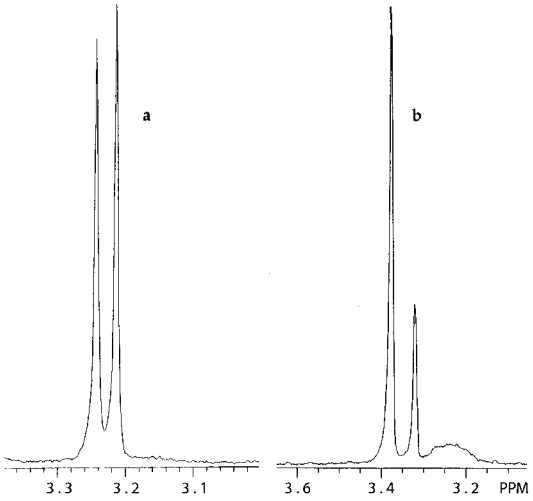


Fig. 2. Separation of the enantiomeric signals.

protons of the ester was observed. The experiment was performed using the products discussed above and the corresponding racemic mixtures. A typical example, Fig. 2, shows the separation of the COOMe signals for the racemic **4a** (Fig. 2a) and the same product obtained with 49 % *e.e.* (Fig. 2b).

General procedure for the preparation of imines

A mixture of aldehyde (0.010 mol), amino ester hydrochloride (0.012 mol), triethylamine (0.018 mol) and anhydrous $MgSO_4$ (3–4 g) in dichloromethane (30 mL) was stirred for 12 h. The obtained solid was separated by filtration and the filtrate washed with water (2×20 mL). The organic layer was then dried ($MgSO_4$) and the solvent evaporated under reduced pressure. When possible, the imines were further purified by distillation or crystallisation. The imines **2f** and **5**, obtained as colourless oils, were used without further purification.

Methyl N-*[2-(methylthio)benzylidene]alaninate (**2f**)*. ^{1}H-NMR ($CDCl_3$, δ / ppm): 1.58 (3H, *d*, *J* = 7.9 Hz, CCH_3), 2.47 (3H, *s*, SCH_3), 3.77 (3H, *s*, $COOCH_3$), 4.22 (1H, *q*, *J* = 7.8 Hz, CH), 7.20–7.42 (3H, *m*, ArH), 7.98 (1H, *d*, ArH), 8.82 (1H, *s*, N=CH). MS (EI) (*m*/*z* (%)): 236, M^+–1 (1), 205 (8), 182 (26), 167 (33), 141 (11), 128 (22), 119 (28), 98 (59), 85 (63), 72 (33), 55 (79), 43 (100).

t-*Butyl* N-*(2-naphthalenylmethylene)glycinate (**5**)*. ^{1}H-NMR ($CDCl_3$, δ / ppm): 1.52 (9H, *s*, *t*-Bu), 4.38 (2H, *s*, CH_2), 7.51 (2H, *m*, ArH), 7.83 (3H, *m*, ArH), 8.25 (2H, *m*, ArH) 8.40 (1H, *s*, N=CH). MS (EI) (*m*/*z* (%)): 269, M^+ (8), 212 (28), 168 (100), 154 (21), 141 (83), 127 (22), 115 (19), 84 (6), 57 (71), 41 (56).

*General procedure for the cyclo-addition reactions in the presence of AgOTf/phosphine **1***

AgOTf (0.10 mmol) was added to a stirred solution of phosphine **1** (0.10 mmol) and imine (0.10 mmol) in dry CH_2Cl_2 (5.0 mL). The reaction mixture was stirred at room temperature for 20 min. Methyl acrylate (0.2–0.3 mmol) was then added followed by base (0.15–0.2 mmol) and the mixture was stirred at room temperature until thin layer chromatography indicated the absence of the starting material. The reaction mixture was then filtered through celite, the filtrate washed with water (2×), dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, petroleum ether/ /diethyl ether) to afford the product. The enantiomeric excess was determined by ^{1}H-NMR spectroscopy using tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium (III) as the chiral shift reagent.

*Dimethyl 2-methyl-5-[2-(methylthio)phenyl]pyrrolidine-2,4-dicarboxylate (**4f**)*. Flash chromatography (SiO_2, 1:1 v/v petroleum ether–diethyl ether) afforded the product in 74 % yield as a pale yellow oil, which solidified upon standing; m.p. 76–80 °C. Anal. Calcd. for $C_{16}H_{21}NO_4S$: C, 59.45; H, 6.50; N, 4.35 %. Found: C, 59.65; H, 6.60; N, 4.2 %. ^{1}H-NMR ($CDCl_3$, δ / ppm): 1.58 (3H, *s*, SCH_3), 2.10 (1H, *dd*, *J* = 13.8 and 7.5 Hz, 3-H), 2.49 (3H, *s*, CH_3C), 2.77 (1H, *dd*, *J* = 13.7 and 3.0 Hz, 3-H), 3.12 (3H, *s*, $COOCH_3$), 3.51 (1H, *m*, 4-H), 3.83 (3H, *s*, $COOCH_3$), 5.01 (1H, *d*, *J* = 7.8 Hz, 5-H), 7.20 (3H, *m*, ArH), 7.41 (1H, *d*, *J* = 7.6 Hz, ArH). MS (EI) (*m*/*z* (%)): 323, M^+ (5), 264 (100), 237 (24), 223 (18), 204 (22), 188 (11), 162 (53), 150 (15), 121 (10), 91 (7), 77 (8).

t-*Butyl 4-methoxycarbonyl-5-(2-naphthyl)pyrrolidine-2-carboxylate (**7a**)*. Flash chromatography (SiO_2, 1:1 v/v petroleum ether–diethyl ether) afforded the product in 91 % yield as a colourless oil which solidified upon standing; m.p. 67–69 °C. Anal. Calcd. for $C_{21}H_{25}NO_4$: C, 70.95; H, 7.05; N, 3.95 %. Found: C, 70.65; H, 7.15; N, 3.70 %. ^{1}H-NMR ($CDCl_3$, δ / ppm): 1.77 (9H, *s*, *t*-Bu), 2.45 (2H, *m*, 3-H), 2.67 (1H, *br s*, NH), 3.15 (3H, *s*, $COOCH_3$), 3.42 (1H, *q*, *J* = 7.5 Hz, 4-H), 3.93 (1H, *t*, *J* = 7.6 Hz, 2-H), 4.67 (1H, *d*, *J* = 7.6 Hz, 5-H), 7.45 (3H, *m*,

ArH), 7.82 (4H, *m*, ArH). MS (EI) (*m/z* (%)): 269, M^+ (8), 212 (28), 168 (100), 154 (21), 141 (83), 127 (22), 115 (19), 84 (6), 57 (71) 41 (56).

*Benzyl 2-methoxycarbonyl-2-methyl-5-(2-naphthyl)pyrrolidine-4-carboxylate (**7c**).* Flash chromatography (SiO_2, 3:7 v/v petroleum ether-ether) afforded the product in 74 % yield as a colourless oil which solidified upon standing; m.p. 85.5–87 °C. Anal. Calcd. for $C_{25}H_{25}NO_4$: C, 74.45; H, 6.20; N, 3.45 %. Found: C, 74.35; H, 6.1; N, 3.25 %. ^{1}H-NMR ($CDCl_3$, δ/ ppm): 1.56 (3H, *s*, CCH_3), 2.17 and 2.83 (2×1H, 2×*m*, 3-H), 3.35 (1H, *br s*, NH), 3.48 (1H, *br m*, 4-H), 3.83 (3H, *s*, $COOCH_3$), 4.39 and 4.61 (2×1H, 2×*d*, *J* = 12.0 Hz, C**H**$_2$Ph), 4.82 (1H, *d*, *J* = 6.6 Hz, 5-H), 6.65 (2H, *d*, ArH), 7.00 (2H, *t*, ArH), 7.15 (1H, *m*, ArH), 7.41 (1H, *d*, ArH), 7.47 (2H, *m*, ArH), 7.76 (4H, *m*, ArH). MS (EI) (*m/z* (%)): 404, M^++1 (4), 344 (100), 298 (11), 241 (65), 208 (36), 181 (70), 155 (11), 140 (20), 91 (97), 65 (12), 42 (20).

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И З В О Д

СТЕРЕОСЕЛЕКТИВНЕ ЦИКЛОАДИЦИОНЕ РЕАКЦИЈЕ АЗОМЕТИНСКИХ ИЛИДА КАТАЛИЗОВАНЕ *IN SITU* ГЕНЕРИСАНИМ Ag(I)/БИСФОСФИНСКИМ КОМПЛЕКСИМА

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Проучаване су стереоселективне циклоадиционе реакције азометинских илида катализоване комплексима сребра и бисфосфинског лиганда генерисаних *in situ*. Пиролидински деривати изоловани су у добрим приносима и са енантиоселективношћу до 71 %. Проучавани су такође и ефекти реакционих услова на стереоселективност ових реакција.

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