Pergamon

Tetrahedron Vol. 50, No. 15, pp. 4519-4528, 1994

0040-4020/94 $6.00+0.00

0040-4020(94)E0086-9

Enantioselective Intramolecular Cyclopropanation of *N*-Allylic- and *N*-Homoallylic Diazoacetamides Catalyzed by Chiral Dirhodium(II) Catalysts

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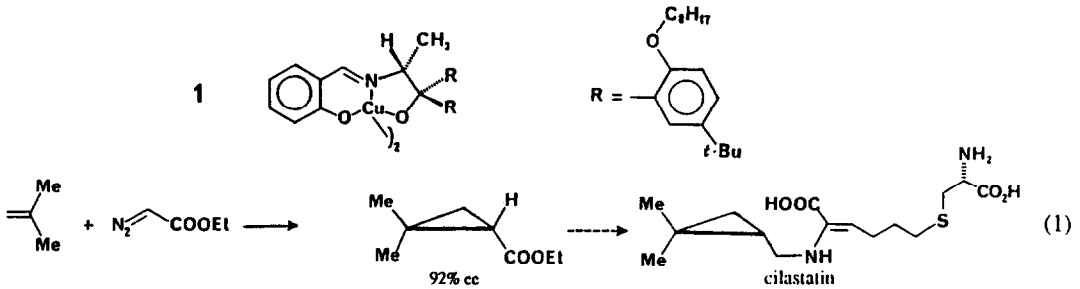
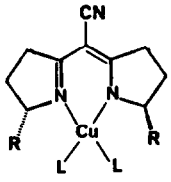
Abstract Diazodecomposition of *N*-(*tert*-butyl)-*N*-(3-buten-1-yl)diazoacetamides catalyzed by dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*S*)-carboxylate], $Rh_2(5S\text{-MEPY})_4$, and tetrakis[methyl 2-oxazolidinone-4(*S*)-carboxylate], $Rh_2(4S\text{-MEOX})_4$, forms products from intramolecular cyclopropanation in good yields with enantiomeric excesses ranging from 60-90%. Intramolecular cyclopropanation with *N*,*N*-diallyldiazoacetamide (72% ee) is competitive with intramolecular [3+2] dipolar cycloaddition.

Highly enantioselective addition of electrophilic metal carbenes to alkenes has been of considerable interest and importance since the development of the "Sumitomo process" for asymmetric cyclopropanation.[1] Copper(II) chelate complexes possessing chiral salicyclaldimine ligands, originally reported by Nozaki and Noyori,[2] were evolved into highly enantioselective catalysts (**1**) for intermolecular cyclopropanation by Aratani and coworkers.[3-6] Enantioselectivities exceeding 90% were achieved in select cases that included the synthesis of the 2,2-dimethylcyclopropanecarboxylate precursor to cilastatin, an *in vitro* stabilizer of the antibiotic imipenem (eq 1).



(1)

More recently, Pfaltz and coworkers have reported the synthesis of chiral (semicorrinato)copper complexes and their applications for intermolecular cyclopropanation reactions of diazocarbonyl compounds.[7-9] The stable crystalline bis(semicorrinato)copper(II) complex is the precursor to the active catalyst that is presumed to be a mono(semicorrinato)copper(I) complex (**2**, R = Me_2COH) formed in situ by reduction with the diazo compound or with phenylhydrazine. Enantiomeric excesses (ee's) greater than those from applications with the Aratani catalysts were obtained with selected monosubstituted alkenes and dienes, but trisubstituted alkenes were not amenable to the high yields and selectivities that characterized uses of the Aratani catalysts. Analogous C_2-symmetric bis-oxazoline ligated copper complexes (**3**, R = *tert*-Bu), developed by Masamune,[10,11] Evans,[12,13] and Pfaltz,[14] have provided similar enantiocontrol for intermolecular cyclopropanation reactions, and enantio-



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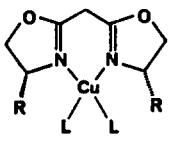

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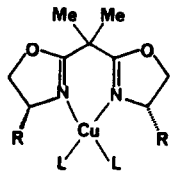

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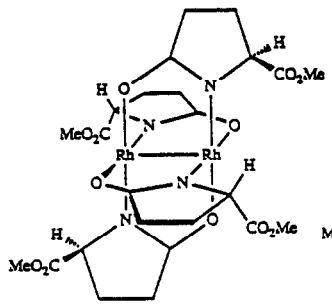
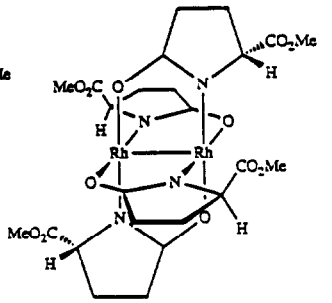
selectivities equal to or greater than 99% have been reached in several cases with the dimethyl bis-oxazoline copper(I) complexes (**4**).[12] Steric control from the use of 4-methyl-2,6-di-*tert*-butylphenyl diazoacetate[15] has been used to achieve high trans/cis cyclopropane product ratios in these reactions,[12] but highly enantioselective cis selectivity has not been developed.

Dirhodium(II) catalysts that possess four chiral pyrrolidone or oxazolidinone ligands have been prepared by ligand substitution of acetate from dirhodium(II) tetraacetate.[16] In their design, two oxygen and two nitrogen donor atoms from the ligands are bonded to each octahedral rhodium in a cis configuration. The asymmetric center of the chiral pyrrolidone or oxazolidinone ligand is the sp^3-hybridized carbon atom bonded to the nitrogen donor atom, and this structural design, exemplified with Rh_2(5*S*-MEPY)$_4$ (**5S**) and Rh_2(5*R*-MEPY)$_4$ (**5R**),[17] places the ring attachment (COOMe for **5**) over the carbene carbon in the intermediate metal carbene. This architecture is designed to provide electronic and/or steric control to the approach of the reacting substrate and thereby effect enantioselection in metal carbene reactions.

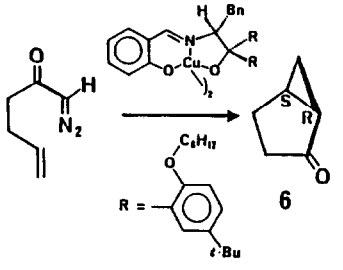


5S



5R

The uses of these chiral catalysts for enantioselective intramolecular cyclopropanation reactions have not been as vigorously pursued as their intermolecular counterparts. Dauben reported the use of an Aratani catalyst for intramolecular cyclopropanation of 1-diazo-5-hexen-2-one (eq 2) and its homolog (eq 3).[18] The best results (77% ee for eq 2, 34% ee for eq 3) were obtained after pretreatment of the catalyst with 0.25 equiv. of DIBAH.



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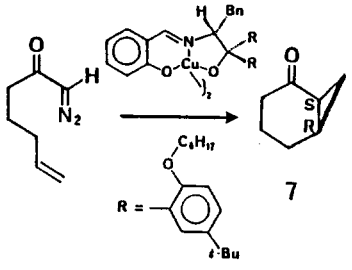
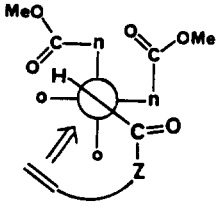


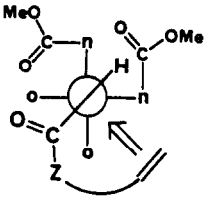
(3)

Pfaltz has revealed that when (semicorrinato)-copper catalysts were employed for these same cyclopropanation reactions,[7] enantiomeric excesses of 75-92% could be obtained; surprisingly, higher % ee's occurred for **7** than **6**.[19]

The design of $Rh_2(5R\text{-MEPY})_4$ and its enantiomer, $Rh_2(5S\text{-MEPY})_4$, both readily accessible from the corresponding methyl 2-pyrrolidone-5-carboxylates, is especially advantageous for asymmetric induction in intramolecular reactions. The directional orientation of chiral ligand attachments on the catalyst establishes relatively unimpeded pathways for intramolecular cyclization whose preferred route is determined by the relative energies for clockwise or counterclockwise atomic movements resulting in bond formation (**8A** and **8B**, axial

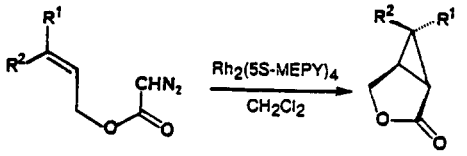


8A



8B

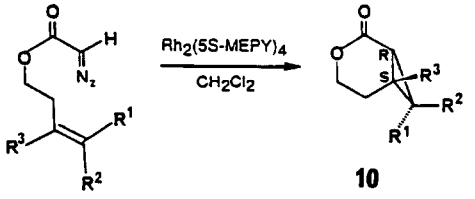
view of the carbene bonded to rhodium in $Rh_2(5S\text{-MEPY})_4$). The exceptional capabilities of these catalysts for enantiocontrol are evident in results obtained with a series of allyl diazoacetates (eq 4).[20,21] For $R^1 = R^2 = H$, the



(4)

9

bicyclic lactone product (**9**) has been obtained in 95% ee (74% yield), and with $R^1 = R^2 = CH_3$, the cyclopropane product is formed in 84% isolated yield with 98% ee.[16] With cis disubstituted double bonds ($R^1 = H$, R^2 = Ph, Et, CH_2Ph, and $Sn(n\text{-}Bu)_3$), enantiocontrol for intramolecular cyclopropanation is virtually complete (≥ 94% ee). Martin and coworkers have reported similarly high enantioselectivities for intramolecular cyclopropanation of homoallylic diazoacetates catalyzed by $Rh_2(5S\text{-MEPY})_4$ (eq 5, 71-90% ee).[22] The absolute configuration of the



(5)

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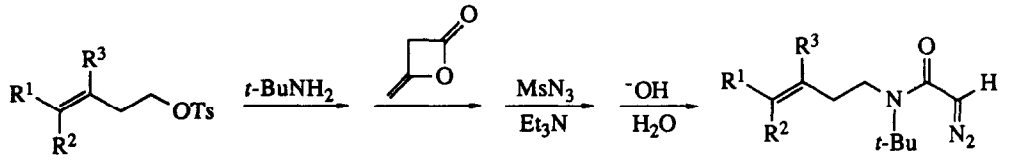
cyclopropane products (**9** and **10**) are those described in the equations; use of $Rh_2(5R\text{-MEPY})_4$ gives the mirror image structures with the same optical purities. The use of a soluble polyethylene-bound 2-pyrrolidone-5(*S*)-carboxylate as a ligand for $Rh_2(5S\text{-MEPY})_4$ produced a recoverable dirhodium(II) catalyst whose effectiveness was demonstrated by intramolecular cyclopropanation of 3-methyl-2-buten-1-yl diazoacetate (eq 4, 98% ee at 80°C).[23]

Diazodecomposition of the amide analogs of allylic and homoallylic diazoacetates have not been previously

investigated. Since there are significant differences in enantiocontrol for dirhodium(II) catalyzed intramolecular carbon-hydrogen insertion between alkyl diazoacetates[24] and *N*-alkyldiazoacetamides,[25] the latter undergoing cyclization with lower enantioselectivities, we have undertaken this investigation to ascertain the feasibility of highly enantioselective cyclopropanation as a synthetic entry to bicyclic amides. *N-tert*-Butyl derivatives were prepared because of our prior experience with these compounds[26] and the synthetic difficulties in forming *N*-monosubstituted diazoacetamides.[27]

RESULTS

Homoallylic diazoacetamides **12a-e** were prepared in four steps from the corresponding homoallylic tosylates (eq 6) in good yield. These compounds were stable at 40°C and were subjected to catalytic diazo-

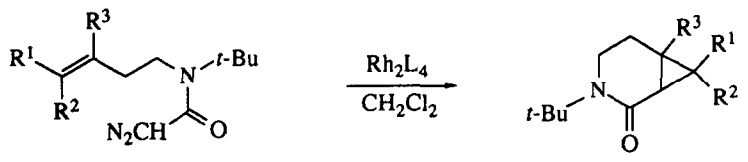


(6)

11 **12**

a: $R^1 = R^2 = R^3 = H$
b: $R^1 = R^2 = Me$, $R^3 = H$
c: $R^1 = R^2 = H$, $R^3 = Me$
d: $R^1 = Et$, $R^2 = R^3 = H$
e: $R^1 = R^3 = H$, $R^2 = Et$

decomposition in refluxing dichloromethane without undue complications. With the simplest substrate in the series, **12a**, treatment with $Rh_2(5S\text{-MEPY})_4$ produced the product from intramolecular cyclopropanation (**13a**, eq 7) that, following distillation, was isolated in 60% yield. Gas chromatographic analysis of **13a** on a Chiraldex

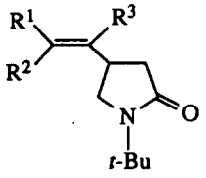


(7)

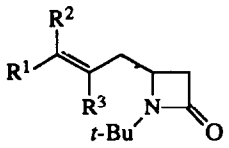
12 **13**

G-TA column provided enantiomer separation with baseline resolution, from which the enantiomeric excess was calculated to be 62%. Treatment of this same diazo compound with dirhodium(II) tetrakis[methyl 2-oxazolidinone-4(*S*)-carboxylate], $Rh_2(4S\text{-MEOX})_4$, the oxazolidinone analog of $Rh_2(5S\text{-MEPY})_4$, formed **13a** in 54% yield after distillation with 65% ee.

Analysis of the reaction mixtures prior to distillation revealed minor amounts of products from carbene dimerization as well as the product from insertion into the allylic C-H bond (**14a**). With $Rh_2(5S\text{-MEPY})_4$ this C-H insertion product was formed in 11% relative yield, whereas with $Rh_2(4S\text{-MEOX})_4$ the **13a**:**14a** ratio was 81:19. Products from insertion into a methylene C-H bond α to nitrogen (**15**) or into a methyl C-H bond of the *tert*-butyl group were not observed.



14



15

Results from catalytic diazodecomposition of **12a-e** with $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(5S\text{-MEOX})_4$ are presented in Table 1. Overall product yields are moderate to high, and enantiomeric excesses for **13a-e** range

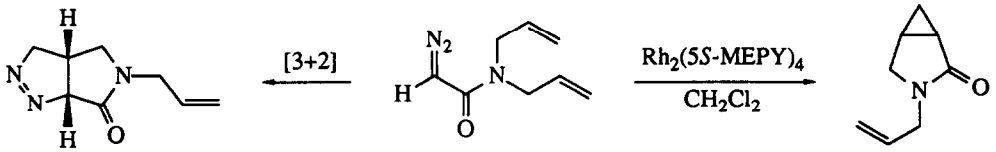
Table 1. Intramolecular Cyclization Reactions of Homoallylic Diazoacetamides Catalyzed by $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(4S\text{-MEOX})_4$[a]

diazo compound	R^1	R^2	R^3	catalyst	yield,[b] %	**13**, % ee	**13**:**14**
12a	H	H	H	$Rh_2(5S\text{-MEPY})_4$	60	60	90:11
				$Rh_2(4S\text{-MEOX})_4$	54	65	81:19
12b	Me	Me	H	$Rh_2(5S\text{-MEPY})_4$	75	75	92:8
				$Rh_2(4S\text{-MEOX})_4$	80	72	84:16
12c	H	H	Me	$Rh_2(5S\text{-MEPY})_4$	87	78	98:2
				$Rh_2(4S\text{-MEOX})_4$	90	76	96:4
12d	Et	H	H	$Rh_2(5S\text{-MEPY})_4$	62	67	71:29
				$Rh_2(4S\text{-MEOX})_4$	84	60	63:37
12e	H	Et	H	$Rh_2(5S\text{-MEPY})_4$	94	90	99:1
				$Rh_2(4S\text{-MEOX})_4$	73	83	94:6

[a]Reactions performed in refluxing CH_2Cl_2 with 1.0 mol % of catalyst. [b]Yield of **14** following distillation, except **a** and **d** which include **13** and **14**.

from 60 to 90%. Generally, higher % ee values are obtained with $Rh_2(5S\text{-MEPY})_4$ than with $Rh_2(4S\text{-MEOX})_4$. Competition from C-H insertion is of minor importance except in reactions with the trans-disubstituted olefinic compound **12d**. Enantiocontrol for the formation of γ-lactam **14d** is moderate: 64% ee with $Rh_2(5S\text{-MEPY})_4$ and 78% with $Rh_2(4S\text{-MEOX})_4$. Similar selectivities are observed for γ-lactam **14a**: 62% ee with $Rh_2(5S\text{-MEPY})_4$ and 74% with $Rh_2(4S\text{-MEOX})_4$.

Efforts to prepare allylic analogs of **12** were frustrated by an unexpectedly facile intramolecular [3+2] cycloaddition to pyrazolines. However, the *N,N*-diallyl-α-diazoacetaide (**16**) was prepared[28] and catalytically decomposed to form the intramolecular cyclopropanation product (**17**) under conditions in which [3+2] cycloaddition was competitive (eq 8). After chromatographic separation, **17** was obtained in 50% yield with an

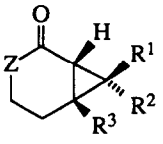


18 **16** **17** (8)

enantiomeric excess of 72%. Although **18** undergoes thermal decomposition, the product formed is the conjugated 2-pyrazoline[29] rather than **17** even when heated neat at 100°C in the presence of $Rh_2(5S\text{-MEPY})_4$.

DISCUSSION

Enantioselectivities for intramolecular cyclopropanation of homoallylic diazoacetamides **12** with $Rh_2(5S\text{-MEPY})_4$ are comparable to those for intramolecular cyclopropanation of homoallylic diazoacetates reported by Martin and coworkers:[22]



		% ee Z = N(*t*-Bu)	% ee Z = O
a:	$R^1 = R^2 = R^3 = H$	60	71
b:	$R^1 = R^2 = Me$, $R^3 = H$	75	77
c:	$R^1 = R^2 = H$, $R^3 = Me$	78	79
d:	$R^1 = Et$, $R^2 = R^3 = H$	67	82
e:	$R^1 = R^3 = H$, $R^2 = Et$	90	90

Apparently the functional group Z does not play a major role in enantioselection. However, whereas the homoallylic diazoacetates do not produce carbon-hydrogen insertion products, competitive insertion at the allylic C-H bond does take place with the homoallylic diazoacetamides. The relative yield of insertion product is higher from $Rh_2(4S\text{-MEOX})_4$ catalyzed reactions than from $Rh_2(5S\text{-MEPY})_4$ catalyzed reactions (Table 1) and, consistent with our recent report of C-H insertion reactions with *N*-alkyldiazoacetamides,[25] enantioselectivities of C-H insertion products are also higher with the use of $Rh_2(4S\text{-MEOX})_4$.

Comparison of results from diazodecomposition of **12d** and **12e** show two noteworthy differences. Enantioselectivity for intramolecular cyclopropanation is higher for the cis-disubstituted olefin than for its trans isomer. In addition, the relative yield of C-H insertion product from **12d** is significant, corresponding to a rate which is one-half that for intramolecular cyclopropanation, whereas that from **12e** is negligible. We believe that these two characteristics, higher relative yield and % ee for **13e**, lower relative yield and % ee for **13d**, are linked through steric effects that are encountered in bringing the reacting bond into close proximity with the electrophilic carbene center.[30]

The enantioselectivity for intramolecular cyclopropanation of allylic diazoacetamide **16** is lower than that of its allylic diazoacetate counterpart.[20] However, further evaluation of these compounds could not be productively undertaken because of the competitive [3+2] dipolar cycloaddition process (eq 8).

The construction of **13** in moderate to high enantiomeric excesses is an attractive synthetic methodology that provides potential entry into a variety of heterocyclic products, including azepines and piperidines, by common chemical transformations.[31] Pyrethroid analogs are possible synthetic derivatives.[32] Replacement of the *N*-

tert-butyl group by a more easily removable nitrogen attachment will add synthetic versatility to the overall transformation.

EXPERIMENTAL SECTION

Preparation of Homoallylic Diazoacetamides (12). The *p*-toluenesulfonates of homoallylic alcohols (**11**) were prepared from *p*-toluenesulfonyl chloride in pyridine at 0°C, and tosylate displacement by *tert*-butylamine was carried out in DMF containing 2 equiv K_2CO_3 at 65°C. Diazoacetamides were prepared by amine condensation with diketene in THF, diazo transfer using methanesulfonyl azide and triethylamine in acetonitrile, and deacetylation with $LiOH{\cdot}H_2O$ (3 equiv) in acetonitrile.[26a]

***N*-(*tert*-Butyl)-*N*-(3-buten-1-yl)diazoacetamide (12a).** Yellow oil, 41% yield from **11a**. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.75 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.15-5.07 (m, 2H), 4.99 (s, 1H), 3.19-3.13 (m, 2H), 2.33-2.27 (m, 2H), 1.48 (s, 9H). Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.54; H, 8.72; N, 21.54. Found: C, 61.51; H, 8.72; N, 21.50.

***N*-(*tert*-Butyl)-*N*-(4-methyl-3-penten-1-yl)diazoacetamide (12b).** Yellow oil, 57% yield from **11b**. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.03 (t, *J* = 6.7 Hz, 1H), 4.98 (s, 1H), 3.08-3.01 (m, 2H), 2.27-2.20 (m, 2H), 1.72 (s, 3H), 1.66 (s, 3H), 1.48 (s, 9H). Anal. Calcd for $C_{12}H_{21}N_3O$: C, 64.57; H, 9.42; N, 18.83. Found: C, 64.61; H, 9.46; N, 18.87.

***N*-(*tert*-Butyl)-*N*-(3-methyl-3-buten-1-yl)diazoacetamide (12c).** Yellow solid, mp 42-43°C, 45% yield from **11c**. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.90 (s, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 3.15-3.08 (m, 2H), 2.20-2.12 (m, 2H), 1.68 (s, 3H), 1.40 (s, 9H). Anal. Calcd for $C_{11}H_{19}N_3O$: C, 63.18; H, 9.09; N, 20.10. Found: C, 63.25; H, 9.12; N, 20.16.

***N*-(*tert*-Butyl)-*N*-(*trans*-3-hexen-1-yl)diazoacetamide (12d).** Yellow oil, 62% yield from **11d**. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.56 (dt, *J* = 15.3, 6.2 Hz, 1H), 5.31 (dt, *J* = 15.3, 6.8 Hz, 1H), 4.98 (s, 1H), 3.12-3.06 (m, 2H), 2.26-2.18 (m, 2H), 2.02 (quin, *J* = 7.2 Hz, 2H), 1.47 (s, 9H), 0.98 (t, *J* = 7.2 Hz, 3H). Anal. Calcd for $C_{12}H_{21}N_3O$: C, 64.57; H, 9.42; N, 18.83. Found: C, 64.53; H, 9.46; N, 18.80.

***N*-(*tert*-Butyl)-*N*-(*cis*-3-hexen-1-yl)diazoacetamide (12e).** Yellow oil, 60% yield from **11e**. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.56-5.44 (m, 1H), 5.29-5.17 (m, 1H), 4.98 (s, 1H), 3.12-3.03 (m, 2H), 2.33-2.23 (m, 2H), 2.07 (quin, *J* = 7.4 Hz, 2H), 1.49 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H). Anal. Calcd for $C_{12}H_{23}N_3O$: C, 64.57; H, 9.42; N, 18.83. Found: C, 64.53; H, 9.48; N, 18.81.

Diazodecomposition of Homoallylic Diazoacetamides (12). To a light blue solution of Rh_2(5*S*-MEPY)$_4$(CH_3CN)(*i*-PrOH)[16] or Rh_2(4*S*-MEOX)$_4$(CH_3CN)$_2$[25] (0.010 mmol) in 15 mL of refluxing anhydrous CH_2Cl_2 and under nitrogen was added **12** (1.00 mmol) in 5 mL of CH_2Cl_2 through a syringe pump at a rate of 0.4 mL/h. After addition was complete, the blue reaction solution was filtered through a 1-cm silica plug, and the plug was eluted with an additional 20 mL of CH_2Cl_2. The resulting dichloromethane solution was evaporated under reduced pressure to produce a residue whose relative composition was determined on a methylsilicone GC column. Kugelrohr distillation gave a colorless liquid whose identity was determined by ^1H NMR analysis and whose % ee values were obtained by GC with baseline resolution on a Chiraldex γ-cyclodextrin trifluoroacetate column. Racemic mixtures were produced by $Rh_2(OAc)_4$ catalyzed reactions. Analyses for % ee before and after distillation provided the same values. The identities of **14b,c,e** were determined in the reaction mixtures from their characteristic proton and mass spectra, but they were not isolated

and purified as were **14a,d**.

***N*-(*tert*-Butyl)-3-azabicyclo[4.1.0]heptan-2-one (13a).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.38 (dddd, *J* = 12.8, 5.6, 2.3, 1.2 Hz, 1H), 2.87 (dt, *J* = 12.8, 4.3 Hz, 1H), 2.08-1.83 (m, 2H), 1.70 (dt, *J* = 8.9, 4.3 Hz, 1H), 1.58-1.48 (m, 1H), 1.41 (s, 9H), 1.08 (q, *J* = 5.0 Hz, 1H), 0.89-0.80 (m, 1H). Mass spectrum, *m/e* (rel abundance): 168 (M+1, 6), 167 (M, 52), 153 (10), 152 (100), 124 (70), 112 (42), 111 (21), 110 (23), 96 (29), 95 (21), 94 (23), 83 (26), 70 (28), 68 (30), 67 (47), 57 (40). Anal. Calcd for $C_{10}H_{17}NO$: C, 71.86; H, 10.18; N, 8.38. Found: C, 72.01; H, 10.22; N, 8.36.

***N*-(*tert*-Butyl)-4-vinyl-2-pyrrolidone (14a).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.19-5.07 (m, 2H), 3.61 (dd, *J* = 9.5, 7.9 Hz, 1H), 3.19 (dd, *J* = 9.5, 7.5 Hz, 1H), 2.53 (dd, *J* = 16.5, 8.6 Hz, 1H), 2.25 (dd, *J* = 16.5, 8.9 Hz, 1H), 2.02-1.90 (m, 1H), 1.40 (s, 9H). Mass spectrum, *m/e* (rel abundance): 168 (M+1, 1.4), 167 (M, 9.8), 153 (10), 152 (100), 124 (22), 112 (22), 67 (22), 58 (23), 57 (22). Anal. Calcd for $C_{10}H_{17}NO$: C, 71.86; H, 10.18; N, 8.38. Found: C, 71.94; H, 10.25; N, 8.34.

***N*-(*tert*-Butyl)-7,7-dimethyl-3-azabicyclo[4.1.0]heptan-2-one (13b).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.36-3.18 (m, 2H), 2.05-1.93 (m, 1H), 1.76-1.63 (m, 1H), 1.40 (s, 9H), 1.35-1.22 (m, 2H), 1.130 (s, 3H), 1.127 (s, 3H). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.85; H, 10.77; N, 7.18. found: C, 73.80; H, 10.72; N, 7.23.

***N*-(*tert*-Butyl)-4-methyl-3-azabicyclo[4.1.0]heptan-2-one (13c).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.38 (ddd, *J* = 13.1, 5.8, 2.1 Hz, 1H), 2.89 (dt, *J* = 13.1, 4.2 Hz, 1H), 1.94-1.87 (m, 1H), 1.75 (dt, *J* = 13.1, 5.8 Hz, 1H), 1.49 (ddd, *J* = 9.2, 4.2, 1.2 Hz, 1H), 1.40 (s, 9H), 1.24 (t, *J* = 4.7 Hz), 1.20 (s, 3H), 0.70 (ddd, *J* = 9.2, 5.3, 0.9 Hz, 1H). Anal. Calcd for $C_{11}H_{19}NO$: C, 72.93; H, 10.50; N, 7.73. Found: C, 72.84; H, 10.55; N, 7.71.

***N*-(*tert*-Butyl)-*anti*-7-ethyl-3-azabicyclo[4.1.0]heptan-2-one (13d).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.42-3.33 (m, 1H), 2.89 (dt, *J* = 13.0, 4.3 Hz, 1H), 2.05-1.97 (m, 1H), 1.90-1.77 (m, 1H), 1.50-1.38 (m, 2H), 1.41 (s, 9H), 1.36-1.12 (m, 2H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.98-0.89 (m, 1H). Mass spectrum, *m/e* (rel abundance): 196 (M+1, 5.3), 195 (M, 53), 181 (12), 180 (98), 152 (100), 140 (26), 124 (25), 110 (89), 97 (29), 96 (27), 95 (31), 81 (62), 70 (61), 67 (33), 57 (87), 55 (50). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.85; H, 10.77; N, 7.18. Found: C, 73.56; H, 10.82; N, 7.03.

***N*-(*tert*-Butyl)-4-(*trans*-1-buten-1-yl)-2-pyrrolidone (14d).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.55 (dt, *J* = 15.2, 6.2 Hz, 1H), 5.36 (ddt, *J* = 15.2, 7.6, 1.2 Hz, 1H), 3.56 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.13. (dd, *J* = 9.5, 7.4 Hz, 1H), 2.82 (q, *J* = 7.8 Hz, 1H), 2.47 (dd, *J* = 16.5, 8.5 Hz, 1H), 2.19 (dd, *J* = 16.5, 8.9 Hz, 1H), 2.07-1.96 (m, 2H), 1.38 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H). Mass spectrum, *m/e* (rel abundance): 196 (M+1, 1.2), 195 (M, 9), 181 (13), 180 (100), 152 (25), 140 (7), 95 (14), 67 (18), 58 (19), 57 (23), 55 (20). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.85; H, 10.77; N, 7.18. Found: C, 73.92; H, 10.71; N, 7.23.

***N*-(*tert*-Butyl)-*syn*-7-ethyl-3-azabicyclo[4.1.0]-heptan-2-one (13e).** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.36-3.22 (m, 2H), 2.03-1.93 (m, 1H), 1.76-1.64 (m, 1H), 1.63-1.33 (m, 4H), 1.40 (s, 9H), 1.09 (quin, *J* = 8.8 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.85; H, 10.77; N, 7.18. Found: C, 73.79; H, 10.76; N, 7.23.

Diazodecomposition of *N,N*-Diallyldiazoacetamide (16). Reactions were performed with **16**[28] in the same manner as for **12**. Diazodecomposition in the presence of Rh_2(5S-MEPY)$_4$ was sluggish at room temperature, so reactions were performed in refluxing dichloromethane. The formation of **18** accounted for approximately half the total product mixture (**17**+**18**) independent of the rate of addition. When the reaction

between **16** and $Rh_2(5S\text{-MEPY})_4$ was performed in refluxing benzene, **17** was isolated in analytically pure form after column chromatography on silica in 56% yield (56% ee).

***N*-(2-Propen-1-yl)-3-azabicyclo[3.1.0]hexan-2-one (17).** ^1H NMR ($CDCl_3$, 300 MHz): δ 5.66 (ddt, *J* = 16.6, 10.5, 6.0 Hz, 1H), 5.20-5.10 (m, 2H), 3.85-3.68 (m, 2H), 3.48 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.26 (dd, *J* = 10.3, 1.5 Hz, 1H), 1.96-1.80 (m, 2H), 1.10 (dt, *J* = 8.2, 4.6 Hz, 1H), 0.60 (q, *J* = 4.2 Hz, 1H). IR (thin film): 1662 cm^{-1}. Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.88; H, 8.13; N, 10.18.

Acknowledgments

Support for this research by the National Science Foundation and the National Institutes of Health (GM 46503) is gratefully acknowledged. We also wish to express our gratitude to R. Noyori and K. B. Sharpless for their extraordinary insights and developments in asymmetric catalysis.

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(*Received in USA* 5 *October* 1993; *accepted* 24 *October* 1993)