Lewis Acid Catalyzed Ene Reactions of α,β-Unsaturated N-Acyloxazolidinones

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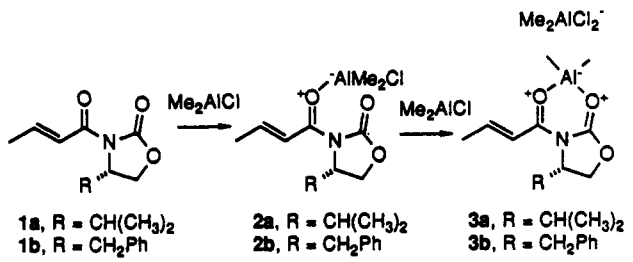
Chiral α,β-unsaturated *N*-acyloxazolidinones undergo a variety of Lewis acid catalyzed addition reactions to alkenes with modest to excellent asymmetric induction. The nature of the reaction is a function of alkene structure and reaction conditions. *N*-Crotonyloxazolidinone **1b** undergoes Me_2AlCl-catalyzed ene reactions with methylenecyclopentane and allyltrimethylsilane to give **6** (67% de) and **18** (33% de), respectively, as the major products. (Trimethylsilyl)cyclopentane **20** is formed stereospecifically as one of eight possible isomers as a minor product. Isobutylene undergoes an enantiospecific Me_2AlCl-catalyzed hetero-Diels–Alder reaction with **1b** to afford, after hydrolysis, lactone **10**. 2-Ethyl-1-butene undergoes ene reaction slowly with **1b** at −30 °C with modest asymmetric induction. The ene adducts **6** and **11** undergo Me_2AlCl-catalyzed Friedel–Crafts acylation at 0 °C to give cyclohexenones **16** and **13**. *N*-Acryloyloxazolidinones **21** and **26** undergo Me_2AlCl-catalyzed ene reactions with 1,1-di- and trisubstituted alkenes to give ene adducts in excellent yield. However, asymmetric induction with ethylidenecyclohexane is poor, since ene reaction can occur by exo or endo transition states and by abstraction of syn or anti hydrogens. Ene reaction of **26** with (*E*)-3,4,4-trimethyl-2-pentene proceeds selectively through the exo transition state to give **28** with 80% de.

Introduction

The Lewis acid catalyzed ene reaction of acrylate esters provides an efficient method for the functionalization of alkenes.[1-3] $EtAlCl_2$-catalyzed ene reactions of methyl acrylate and α-substituted acrylate esters with 1,1-di-, tri-, and tetrasubstituted and *trans*-1,2-disubstituted alkenes proceed in good yield. This reaction is restricted to β-unsubstituted acrylate esters.[4] The steric and electron-donating effects of the methyl group of methyl crotonate prevent Lewis acid catalyzed ene reaction. Although, intermolecular asymmetric ene reactions of carbonyl compounds have been extensively explored,[2] intermolecular asymmetric ene reactions using alkenes as enophiles are virtually unknown.[3,5]

Evans has developed asymmetric Lewis acid catalyzed Diels–Alder reactions of chiral α,β-unsaturated *N*-acyloxazolidinones.[6] Reaction of *N*-crotonyloxazolidinone **1a** with 1 equiv of Me_2AlCl gives complex **2a** that reacts with cyclopentadiene to give a 20:1 mixture of endo and exo adducts with a relative rate of 1 and modest asymmetric induction. Reaction of **1a** with 1.4 equiv of Me_2AlCl gives salt **3a** that reacts with cyclopentadiene to give a 60:1 mixture of endo and exo adducts with a relative rate of 100 and >90% asymmetric induction from the less hindered top face opposite to the isopropyl group. Salt **3** is much more reactive than complex **2** since it is a free cation. Furthermore, binding of aluminum to both oxygens in **3** locks the conformation about the C–N bond leading to higher asymmetric induction.

Complexes of type **3** are much more reactive than methyl crotonate, which does not form 1:2 complexes with Me_2AlCl, in Diels–Alder reactions. We had previously observed that β-substituted α,β-unsaturated ketones and



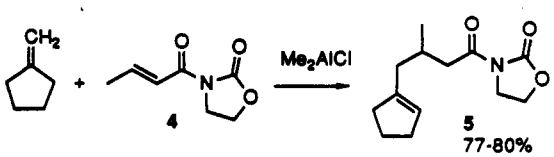
1a, R = $CH(CH_3)_2$ **2a**, R = $CH(CH_3)_2$ **3a**, R = $CH(CH_3)_2$
1b, R = CH_2Ph **2b**, R = CH_2Ph **3b**, R = CH_2Ph

aldehydes form similar 1:2 salts with $EtAlCl_2$, which react cleanly with a variety of alkenes to give zwitterions which undergo 1,2-hydride and alkyl shifts.[7]

We therefore decided to investigate the Lewis acid catalyzed ene reactions of α,β-unsaturated *N*-acyloxazolidinones with alkenes.[5] We anticipated that ene reactions would succeed with *N*-crotonyl-, as well as, *N*-acryloyloxazolidinones and that use of chiral oxazolidinones would result in efficient asymmetric induction.

Results and Discussion

Initially, we examined the reactions of oxazolidinone **4** with alkenes to determine the suitability of crotonyl derivatives as enophiles. Methylenecyclopentane reacts with **4** in the presence of 0.4 equiv of Me_2AlCl in CH_2Cl_2 for 20 h at 25 °C to give 77% of ene adduct **5**. Reaction with 2.0 equiv of Me_2AlCl for 20 h at −30 °C affords 80% of **5**. Unfortunately, *N*-crotonyloxazolidinone **4** undergoes ene reactions in high yield only with the most nucleophilic, least hindered alkenes. Complex mixtures are obtained from mono- and trisubstituted alkenes.



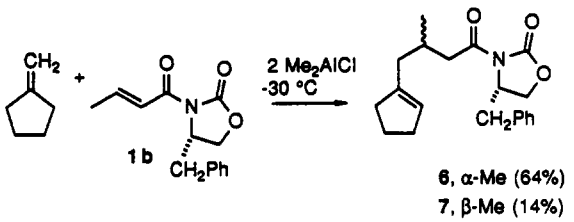
4 **5** 77-80%

N-Crotonyloxazolidinone **1b** derived from phenylalaninol was chosen for studies of asymmetric induction since Evans has shown that optimal results are obtained in Diels–Alder reactions with this reagent.[6] Reaction of **1b**, methylenecyclopentane, and 2.0 equiv of Me_2AlCl in

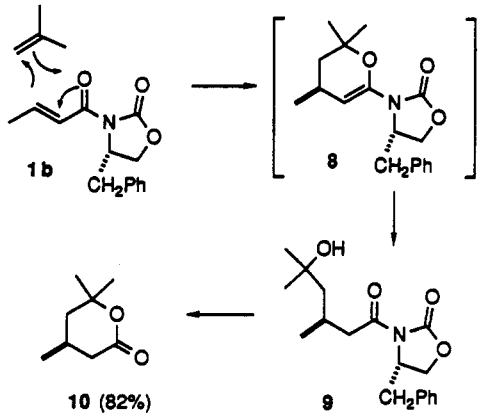
(1) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. Snider, B. B. In *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer: Dordrecht, 1989; pp 147–167.
(2) Snider, B. B. In *Comprehensive Organic Synthesis, Vol. 2*; Pergamon: Oxford, 1991; in press.
(3) Snider, B. B. In *Comprehensive Organic Synthesis, Vol. 5*; Pergamon: Oxford, 1991; in press.
(4) Duncia, J. V.; Lansbury, P. T., Jr.; Miller, T.; Snider, B. B. *J. Am. Chem. Soc.* **1982**, *104*, 1930.
(5) Asymmetric intramolecular ene reactions of α,β-unsaturated *N*-acyloxazolidinones catalyzed by chiral titanium alkoxides have been described. Narasaka, K.; Hayashi, Y.; Shimada, S. *Chem. Lett.* **1988**, 1609.
(6) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1984**, *106*, 4261; **1988**, *110*, 1238.
(7) Snider, B. B.; Rodini, D. J.; van Straten, J. *J. Am. Chem. Soc.* **1980**, *102*, 5872.

0022-3263/91/1956-4908$02.50/0

CH_2Cl_2 for 20 h at −30 °C affords 83% of **6** and **7** as a 5:1 mixture of diastereomers. Reaction with 0.4 equiv of Me_2AlCl in CH_2Cl_2 for 16 h at 25 °C affords 83% of a 2:1 mixture of **6** and **7**. Higher diastereomeric excess is obtained from complex **3b** at −30 °C (67%) than from complex **2b** at 25 °C (33%). Reaction at lower temperatures is very slow. The temperature difference is at least partially responsible for the difference in de from **2b** and **3b** as discussed below in the formation of **16**. The structure of the major isomer **6** is assigned as shown based on the expected addition to the less hindered top face of complex **3b**. The stereochemistry of **6** could not be assigned unambiguously by comparison to known materials.

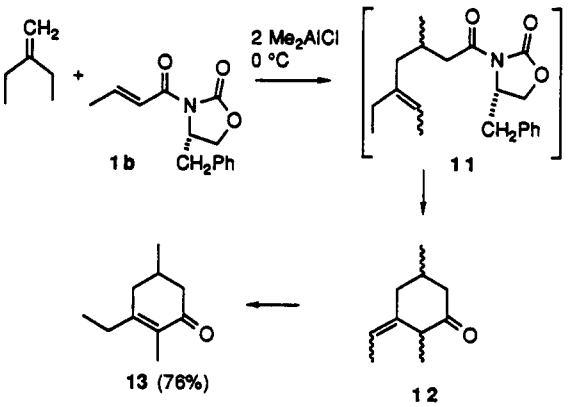


We therefore examined the reaction of **1b** with isobutylene since the ene adduct could be easily converted by hydrolysis and hydrogenation to 3,5-dimethylhexanoic acid whose absolute stereochemistry is known.[8] To our surprise, reaction of **1b**, isobutylene, and 2.0 equiv of Me_2AlCl for 40 h at −30 °C in CH_2Cl_2 provides 68% of alcohol **9** and 14% of lactone **10**. Treatment of this mixture with sodium carbonate in methanol gives lactone **10** in quantitative yield. Alcohol **9** is presumably formed by hydrolysis of hetero-Diels–Alder adduct **8**. Similar Diels–Alder reactions have been observed as side products in intramolecular ene reactions.[5] In the reaction with isobutylene, hetero-Diels–Alder reaction occurs to the complete exclusion of the ene reaction.

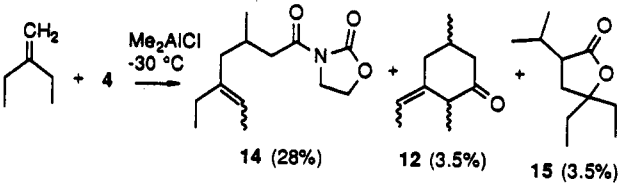


The $[\alpha]_D$ of lactone **10** is −45.9°. The reported $[\alpha]_D$ of the *R* isomer is +45.5°.[9] Therefore hetero-Diels–Alder reaction occurs from the less hindered top face of **3b** with very high asymmetric induction. The Diels–Alder reaction presumably is more stereoselective than the ene reaction since a bond is formed to both Cα and Cβ of **3b** in the transition state.

The hetero-Diels–Alder reaction is more sensitive to steric hindrance than the ene reaction. With the small methyl substituents of isobutylene, hetero-Diels–Alder reaction occurs exclusively. With larger substituents, ene reaction occurs exclusively. The two ethyl groups of 2-ethyl-1-butene are large enough to prevent the hetero-Diels–Alder reaction. Reaction of **1b**, 2-ethyl-1-butene and 2.0 equiv of Me_2AlCl for 20 h at 0 °C affords a mixture of **12** and **13**, which is converted to 76% of **13** on chromatography. Complex **3b** is formed and reacts with 2-ethyl-1-butene to give ene adduct **11**, which then undergoes an intramolecular Friedel–Crafts acylation to give a mixture of **12** and **13**. We have previously observed related tandem ene reactions with methyl vinyl ketone and acrolein,[2] and Wolinsky has reported related tandem ene and Friedel–Crafts acylation with acryloyl chloride.[10] Analogous mixtures of cyclohexenones are obtained in the reaction of **1b** with 2-methyl-1-butene, indicating that the hetero-Diels–Alder reaction does not occur with one methyl and one ethyl group on the double bond and is therefore restricted to isobutylene.



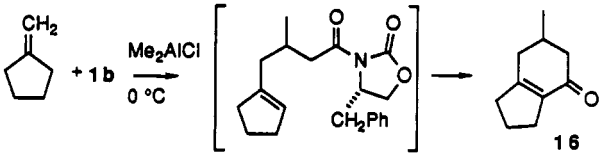
The Friedel–Crafts acrylation following the ene reaction of **1b** with 2-ethyl-1-butene, but not with methylenecyclopentane, results primarily from the difference in reaction temperature required for the initial ene reaction. Friedel–Crafts acylation occurs at 0 °C but not at −30 °C. Ene adduct can be obtained in good yield from methylenecyclopentane which reacts completely with **1b** in 20 h at −30 °C, but not from the less reactive 2-ethyl-1-butene, which reacts very slowly with **1b** at −30 °C. Reaction of 2-ethyl-1-butene, **4**, and 2.0 equiv of Me_2AlCl at −30 °C for 24 h gives 65% recovered **4**, 28% of ene adduct **14** as a 2:1 *E*/*Z* mixture, 3.5% of **12**, and 3.5% of **15**. The conversion is low at −30 °C, but Friedel–Crafts acylation is a minor side reaction. Similarly, ene adducts **6** and **7** can be converted to indenone **16** by running the reaction at 0 °C. Reaction of methylenecyclopentane with **1b** and 2.0 equiv of Me_2AlCl at 0 °C, rather than −30 °C, gives a mixture of indenones, which are converted to 75% of **16**,[11] $[\alpha]_D$ +63.1°, on treatment with basic alumina.[12]



Analysis of the CD of indenone **16** provides an alternative approach to assigning the absolute stereochemistry of ene adduct **6**. The Snatzke rule for cyclohexenones with planar chromophores indicates that the *S* isomer of indenone **16**, with an α-methyl group, should have a positive

(8) Rice, K. C. *J. Org. Chem.* **1982**, *47*, 3617.
(9) (a) Ahlquist, L.; Asselineau, J.; Asselineau, C.; Serck-Hanssen, K.; Stallberg-Stenhagen, S.; Stenhagen, E. *Arkiv Kemi* **1959**, *14*, 171. (b) Bardili, B.; Marschall-Weyerstahl, H.; Weyerstahl, P. *Liebigs Ann. Chem.* **1985**, 275.
(10) Moore, L.; Gooding, D.; Wolinsky, J. *J. Org. Chem.* **1983**, *48*, 3750.
(11) Ballester, P.; Garcia-Raso, A.; Mestres, R. *Synthesis* **1985**, 802.
(12) Piers, E.; Banville, J.; Lau, C.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 2965.

Cotton effect.[13] The observed positive Cotton effect for **16** confirms the assignment of **6** as the major ene adduct. With ene adducts **6** and **7**, determination of the extent of asymmetric induction is straightforward. We cannot determine the ee in **16** since chiral shift reagents were ineffectual. We therefore carried out the initial ene reaction at −30 °C, which we know gives a 5:1 mixture of **6** and **7**, and then stirred the solution for 35 h at 0 °C to effect Friedel–Crafts acylation. After isomerization with basic alumina we obtained 82% of **16**, $[\alpha]_D$ +86.7°, which should be a 5:1 mixture of enantiomers (67% ee). Since the $[\alpha]_D$ of **16** is +63.1° (48% ee) when the ene reaction is carried out at 0 °C, a 2.9:1 mixture of ene adducts **6** and **7** must be formed.

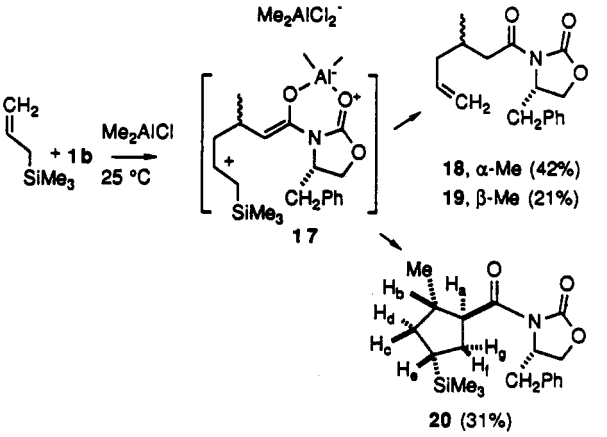


6, α-Me
7, β-Me

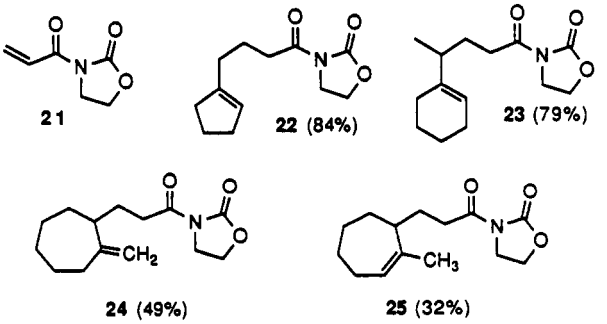
The formation of traces of **15** is puzzling. Although the structure of **15** has been unambiguously assigned by spectral analysis, the mechanism of its formation is not clear since a two-electron oxidation has taken place. The first step is almost definitely the conjugate addition of a methyl group.[14] The resulting aluminum enolate should not add to an alkene. Oxidation of the enolate would give the enol radical that could add to the alkene to give a tertiary radical, which could be oxidized to a cation that would cyclize to form the lactone. It is possible that Al(III) or traces of oxygen are responsible for the oxidation. Epoxides have been obtained by addition of oxygen to dialkylaluminum alkenoxides.[15] The epoxide of 2-ethyl-1-butene would react with the aluminum enolate to give **15**.

Although monosubstituted alkenes do not react with **1b**, allyltrimethylsilane is more nucleophilic and therefore should react cleanly. Reaction of **1b**, allyltrimethylsilane, and 2.0 equiv of Me_2AlCl at 25 °C for 12 h affords 63% of a 2:1 mixture of **18** and **19** and 31% of **20**. Reaction of **1b** with 3.5 equiv of $TiCl_4$ at −78 °C for 35 h in CH_2Cl_2 affords 72% of a 3:1 mixture of **18** and **19** and 20% recovered **1b**. Addition of allyltrimethylsilane to **3b** affords intermediate **17**, which can lose the trimethylsilyl group to give **18** and **19**. A 1,2-trimethylsilyl shift followed by ring closure will give **20**. Similar Lewis acid catalyzed reactions of enones with allenylsilanes have been extensively studied by Danheiser,[16] and related Lewis acid catalyzed reactions of enones with allylsilanes and stannanes have recently been reported.[17-19]

Cyclopentane **20** is formed as only one of eight possible stereoisomers. The relative stereochemistry of the three cyclopentane ring centers can be assigned based on analysis of the coupling constants and NOE. The coupling constants between all seven ring protons fit very closely with those calculated for the minimum energy geometry calculated by MM2.[20] Irradiation of H_a at δ 3.45 leads to NOE of H_g and the methyl group. Irradiation of H_b at δ 2.50 leads to enhancement of H_c, H_e and the methyl group. The NOE between H_b and H_e establishes the relative stereochemistry of the methyl and trimethylsilyl groups. The trans relationship of the carbonyl and trimethylsilyl groups corresponds to that observed in related additions of enones to allyltrimethylsilane.[17,18] The trans stereochemistry of the methyl and carbonyl groups, which is expected based on mechanistic considerations, follows from the NOE between H_a and the methyl group and the absence of an NOE between H_a and H_b. The absolute stereochemistry of the three cyclopentane ring centers is assigned based on mechanistic considerations. Intermediate **17** should to be formed as a ≈3.5:1 mixture of diastereomers. The major isomer with an α-methyl group, resulting from attack to the top face, can give **18** or **20**. The minor isomer can only give **19** since ring closure cannot occur from the bottom face due to steric hindrance from the benzyl group.



We next turned our attention to the more reactive *N*-acryloyloxazolidinone (**21**), which undergoes ene reactions with 1,1-di- and trisubstituted alkenes. Reaction of **21** with methylenecyclopentane and 0.3 equiv of Me_2AlCl at 25 °C affords 84% of **22**. Similarly, reaction with 1-methylcycloheptene gives 81% of a 60:40 mixture of **24** and **25**. Finally, reaction with ethylidenecyclohexane and 0.8 equiv of Me_2AlCl at −40 °C provides 79% of ene adduct **23**. New chiral centers are formed only in the reaction of **21** with trisubstituted alkenes.



Since ethylidenecyclohexane gives a single ene adduct, we investigated its reaction with chiral *N*-acryloyloxazolidinone **26**. Reaction with 1.5 equiv of Me_2AlCl at

(13) Legrand, M.; Rougier, M. J. In *Stereochemistry, Volume 2*; Kagan, H. B.; Ed.; Thieme: Stuttgart, 1977; pp 123–128. Snatzke, G.; Snatzke, F. In *Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism*; Ciardelli, F., Salvadori, P., Eds.; Heyden & Son: London, 1973; pp 109–125. Barrieux, J. J.; Gore, J.; Subit, M. *Tetrahedron Lett.* **1975**, 1835. Suga, T.; Imamura, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2060. Agami, C.; Platzer, N.; Sevestre, H. *Bull. Soc. Chim. Fr. II* **1987**, 358.
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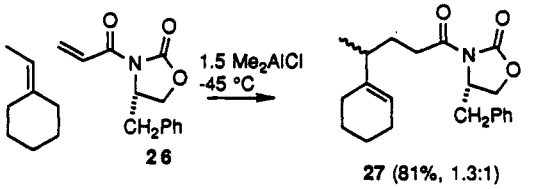
(17) Danheiser, R. L., private communication 1990.
(18) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Syn. Lett.* **1990**, 429.
(20) Herndon, J. W.; Wu, C. *Syn. Lett.* **1990**, 411.
MODEL version 2.95, obtained from Kosta Steliou, University of Montreal, was used.

−45 °C affords 81% of a 1.3:1 mixture of diastereomers of **27**. Not surprisingly, much lower asymmetric induction is obtained with **26** than in the addition of mono- and 1,1-disubstituted alkenes to **1b**. Asymmetric induction in addition to **1b** depends only on the face of the conjugated double bond to which the alkene adds. Asymmetric induction in the formation of **27** from **26** requires control of the stereochemistry of the ene reaction (endo or exo), control of regiochemistry of the ene reaction (hydrogen abstraction from the methylene syn or anti to the methyl group) in addition to selective reaction from the top face of **26**. Not surprisingly, there is poor control of stereochemistry.

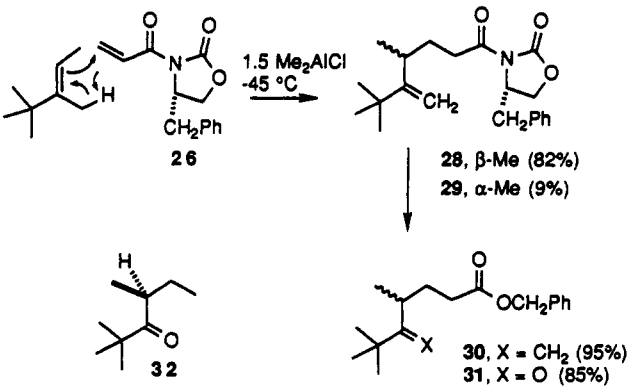


26 **27** (81%, 1.3:1)

We therefore investigated the reaction of **26** with (*E*)-3,4,4-trimethyl-2-pentene.[21] This alkene only has allylic hydrogens syn to the methyl group. Furthermore, the large *tert*-butyl group should favor exo addition at the expense of endo addition. Exo ene reaction from the less hindered top face of **26** will give **28**. Endo ene reaction from the top face of **26** or exo ene reaction from the bottom face of **26** will give **29**. As expected, ene reaction with 1.5 equiv of Me_2AlCl at −45 °C affords 91% of a 9:1 mixture of **28** and **29**. We planned to establish the stereochemistry of the major isomer by converting the mixture to 2-methylglutaric acid whose stereochemistry is known.[22] The benzyl ester **30** is prepared by treatment with $LiOCH_2Ph$;[6] ozonolysis[23] gives ketone **31**. Unfortunately, we were unable to carry out a Baeyer–Villiger oxidation on the hindered ketone of **31** even with pertrifluoroacetic acid. We therefore turned our attention to the chiroptical properties of ketone **31**, which showed a positive Cotton effect, $[\theta]$ + 397° at 285 nm. This value suggested that **31** was *S* based on a similar Cotton effect for (*S*)-*sec*-butyl methyl ketone.[24] This assignment was confirmed by preparing **32**, $[\theta]$ +280° at 308 nm, by the reaction of *tert*-butyllithium with (*S*)-2-methylbutyric acid.[25] Although **31** has both a benzyl ester and a ketone, the Cotton effect at 285 nm should be due almost entirely to the n to π* transition of the ketone. The absolute stereochemistry of **31** and **32** are the same since they are structurally identical in the region of the ketone and both have a positive Cotton effect.

Conclusion

Chiral α,β-unsaturated *N*-acyloxazolidinones undergo a variety of Lewis acid catalyzed addition reactions to alkenes with modest to excellent asymmetric induction. The nature of the reaction is a function of alkene structure and reaction conditions. *N*-Crotonyloxazolidinone **1b** undergoes Me_2AlCl-catalyzed ene reactions with methylenecyclopentane and allyltrimethylsilane to give **6** (67% de) and **18** (33% de) as the major products. (Trimethylsilyl)cyclopentane **20** is formed stereospecifically as one of eight possible isomers as a minor product. Isobutylene undergoes an enantiospecific Me_2AlCl-catalyzed hetero-Diels–Alder reaction with **1b** to afford, after hydrolysis, lactone **10**. 2-Ethyl-1-butene undergoes ene reaction slowly with **1b** at −30 °C with modest asymmetric induction. The ene adducts **6** and **11** undergo Me_2AlCl-catalyzed Friedel–Crafts acylation at 0 °C to give cyclohexenones **16** and **13**. *N*-Acryloyloxazolidinones **21** and **26** undergo Me_2AlCl-catalyzed ene reactions with 1,1-di- and trisubstituted alkenes to give ene adducts in excellent yield. However, asymmetric induction with ethylidenecyclohexane is poor, since ene reaction can occur by exo or endo transition states and by abstraction of syn or anti hydrogens. Ene reaction of **26** with (*E*)-3,4,4-trimethyl-2-pentene proceeds selectively through the exo transition state to give **28** with 80% de.



26 **32**

Experimental Section

Preparation of Starting Materials. Oxazolidinones **1b**, **4**, **21**, and **26** were prepared by the literature procedure.[6,26] (*E*)-3,4,4-Trimethyl-2-pentene[21] was purchased from Wiley Organics.

General Protocol for the Reaction of Alkenes and 2-Oxazolidinones. Me_2AlCl (1.93 M in hexane, Texas Alkyls) was added via syringe to a solution of alkene and **1b**, **4**, **21**, or **26** in 15 mL of anhydrous CH_2Cl_2 in a flame-dried flask under N_2. The solution was stirred and quenched by dilution with CH_2Cl_2 and slow addition of water until gas evolution ceased. The organic layer was separated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to afford the desired product.

(4*S*)-3-(4-(1-Cyclopentenyl)-3-methyl-1-oxobutyl)-4-(phenylmethyl)-2-oxazolidinone (6 and 7). Reaction of methylenecyclopentane (0.087 mL, 0.83 mmol), **1b** (100 mg, 0.41 mmol), and Me_2AlCl (0.42 mL, 0.81 mmol) at −30 °C for 20 h gave 153 mg (115%) of crude **6** and **7**. Flash chromatography (12:1 hexane–EtOAc) gave 111 mg (83%) of an inseparable 5:1 mixture of **6** and **7**: ^1H NMR ($CDCl_3$) δ 7.21–7.35 (m, 5), 5.38–5.39 (m, 1), 4.68 (m, 1, CHN), 4.18 (ddd, 1, *J* = 0.5, 6.5, 9.1, CHHO), 4.14 (dd, 1, *J* = 3.5, 9.0, CHHO), 3.31 (dd, 1, *J* = 3.1, 13.4, CHHPh, **6**), 3.30 (dd, 1, *J* = 3.1, 13.4, CHHPh, **7**), 2.96 (dd, 1, *J* = 5.1, 16.6, CHHCO), 2.86 (dd, 1, *J* = 9.9, 13.4, CHHPh, **7**), 2.74 (dd, 1, *J* = 8.3, 16.5, CHHCO), 2.74 (dd, 1, *J* = 9.9, 13.4, CHHPh, **6**), 1.82–2.32 (m, 9), 0.99 (d, 3, *J* = 7.1, CH_3, **7**), 0.96 (d, 3, *J* = 6.6, CH_3, **6**); ^{13}C NMR ($CDCl_3$) δ 172.8, 153.4, 142.70 (**7**), 142.64 (**6**), 135.3, 129.3, 128.9, 127.3, 125.6, 66.05 (**6**), 65.99 (**7**), 55.1, 42.2 (**6**), 42.0 (**7**), 38.62 (**6**), 38.57 (**7**), 37.9, 34.90 (**6**), 34.86 (**7**), 32.4, 28.03 (**7**), 27.92 (**6**), 23.5, 20.12 (**7**), 20.01 (**6**); IR 1790, 1700 cm^{-1}; $[\alpha]_D$ +107.6° (*c* 0.276, $CHCl_3$). Anal. Calcd for $C_{20}H_{25}O_3N$: C, 73.37; H, 7.70. Found: C, 73.06; H, 7.74.

The same reaction catalyzed by 0.4 equiv of Me_2AlCl at 25 °C for 16 h gave 83% of a 2:1 mixture of **6** and **7**. The same reaction catalyzed by 1.5 equiv of Me_2AlCl at 25 °C for 20 h in toluene gave 86% of a 2:1 mixture of **6** and **7**.

(4*S*)-3-(5-Hydroxy-3,5-dimethyl-1-oxohexyl)-4-(phenylmethyl)-2-oxazolidinone (9). Reaction of isobutylene (420 mg,

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7.5 mmol), **1b** (600 mg, 2.45 mmol), and Me_2AlCl (2.5 mL, 4.8 mmol) at −30 °C for 40 h gave 896 mg of crude **9**, **10**, and **1b** as a yellow oil. Flash chromatography (8:1 hexane–EtOAc) gave 48 mg (14%) of **10**, 413 mg (68%) of **9**, and 128 mg (20% recovered) of starting material (**1b**).

The data for **9**: ^1H NMR ($CDCl_3$) δ 7.20–7.40 (m, 5), 4.69 (dddd, 1, J = 3.3, 3.4, 7.0, 9.8, CHN), 4.17 (dd, 1, J = 7.0, 9.1, CHHO), 4.15 (dd, 1, J = 3.4, 9.1, CHHO), 3.31 (dd, 1, J = 3.3, 13.3, CHHPh), 3.16 (dd, 1, J = 6.5, 16.5, CHHCO), 2.76 (dd, 1, J = 7.0, 16.5, CHHCO), 2.75 (dd, 1, J = 9.8, 13.3, CHHPh), 2.28–2.38 (m, 1, $CHCH_3$), 2.23 (s, 1, OH), 1.60 (dd, 1, J = 5.1, 14.4, CHH), 1.44 (dd, 1, J = 6.0, 14.4, CHH), 1.264 (s, 3, CH_3), 1.258 (s, 3, CH_3), 1.08 (d, 3, J = 6.7, CH_3); ^{13}C NMR ($CDCl_3$) δ 173.0, 153.4, 135.3, 129.3, 128.9, 127.3, 70.97, 66.2, 55.1, 50.0, 43.8, 38.0, 30.8, 29.0, 25.6, 22.4; IR (neat) 3520, 1780, 1700 cm^{-1}; $[\alpha]_D$ +101.0° (c 0.347, MeOH). Anal. Calcd for $C_{18}H_{25}O_4N$: C, 67.69; H, 7.89. Found: C, 67.84; H, 7.92.

(4*S*)-4,6,6-Trimethyl-3,4,5,6-tetrahydro-2*H*-pyran-2-one (10). Alcohol **9** (95 mg, 0.30 mmol) was added to a solution of 5 mL of MeOH and 5 mL of saturated Na_2CO_3 at 25 °C and stirred for 1.5 h, acidified with 15% HCl until the solution was slightly acidic, and extracted with ether. The ether extract was left at 25 °C for 2.5 h to allow relactonization of any hydroxy acid present.[9] The solution was dried ($MgSO_4$) and evaporated to give 96.8 mg (102%) of crude **10** and benzyloxazolidinone. Flash chromatography (14:1 hexane–EtOAc) gave 42.4 mg (100%) of pure **10**: ^1H NMR ($CDCl_3$) δ 2.64 (ddd, 1, J = 2.2, 5.1, 17.6, CHHCO), 2.08–2.18 (m, 1, $CHCH_3$), 1.94 (dd, 1, J = 11.9, 17.6, CHHCO), 1.81 (ddd, 1, J = 2.2, 3.3, 13.8, CHH), 1.43 (s, 3, CH_3), 1.40 (dd, 1, J = 12.0, 13.8, CHH), 1.38 (s, 3, CH_3), 1.05 (d, 3, J = 6.4, CH_3); ^{13}C NMR ($CDCl_3$) 171.3, 82.1, 42.8, 37.8, 30.7, 27.7, 24.0, 21.4; IR (neat) 1730 cm^{-1}; $[\alpha]_D$ −45.9° (c 0.195, $CHCl_3$); $[\alpha]_D$ +45.4° for the *R* enantiomer.[9]

3-Ethyl-2,5-dimethyl-2-cyclohexenone (13). Reaction of 2-ethyl-1-butene (0.20 mL, 1.6 mmol), **1b** (200 mg, 0.82 mmol), and Me_2AlCl (0.85 mL, 1.6 mmol) at 0 °C for 24 h gave 281 mg of crude **12** and **13**. Flash chromatography (35:1 hexane–EtOAc) of 250 mg of crude product on silica gel converted **12** to **13**, affording 84 mg (76%) of pure **13**: ^1H NMR ($CDCl_3$) δ 2.47 (br d, 1, J = 14.0, CHHCO), 2.36 (br d, 1, J = 14.0, CHHCO), 2.272 (dq, 1, J = 12.3, 7.4, $CHHCH_3$), 2.238 (dq, 1, J = 12.3, 7.4, $CHHCH_3$), 1.99–2.11 (m, 3), 1.76 (s, 3), 1.07 (t, 3, J = 7.6), 1.03 (d, 3, J = 6.0); ^{13}C NMR ($CDCl_3$) δ 199.8, 159.5, 129.8, 45.8, 38.7, 29.7, 28.1, 21.2, 11.6, 10.2; IR (neat) 1670, 1635 cm^{-1}; $[\alpha]_D$ +139.0° (c 0.330, CH_3Cl_2). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.73; H, 10.38.

1,2,3,5,6,7-Hexahydro-6-methyl-4*H*-inden-4-one (16). Reaction of methylenecyclopentane (0.086 mL, 0.82 mmol), **1b** (100 mg, 0.41 mmol), and Me_2AlCl (0.42 mL, 0.81 mmol) at 0 °C for 24 h gave 192 mg of a crude mixture of **16** and unconjugated indenones. A CH_2Cl_2 solution of indenones containing basic alumina was stirred overnight to bring the double bond into conjugation.[12] Flash chromatography (30:1 hexane–EtOAc) afforded 46 mg (75%) of pure **16**: $[\alpha]_D$ +63.1° (c 0.218, CH_2Cl_2); $[\theta]$ +1490° at 326 nm (CH_2Cl_2); $[\theta]$ +1024° at 325 nm (EtOH); $[\theta]$ +416° at 327 nm, +502° at 340 nm, +446° at 354 nm, and +186° at 371 nm (2,2,4-trimethylpentane). The ^1H and ^{13}C NMR and IR spectral data are identical with those previously described.[11]

A similar reaction was carried out at −30 °C for 20 h to give a mixture of **6** and **7** as shown by TLC analysis. This solution was then stirred at 0 °C for 35 h, worked up, conjugated, and purified as described above to give 82% of pure **16**: $[\alpha]_D$ +86.7° (c 0.170, CH_2Cl_2).

(4*S*)-3-(3-Methyl-1-oxo-5-hexenyl)-4-(phenylmethyl)-2-oxazolidinone (18 and 19) and (4*S*)-3-((1*S*,2*S*,4*R*)-2-Methyl-4-(((trimethylsilyl)cyclopentyl)carbonyl)-4-(phenylmethyl)-2-oxazolidinone (20). Reaction of allyltrimethylsilane (0.20 mL, 1.26 mmol), **1b** (100 mg, 0.41 mmol), and Me_2AlCl (0.42 mL, 0.81 mmol) at 25 °C for 12 h gave 135 mg of a mixture of **18**, **19**, and **20**. Flash chromatography (20:1 hexane–EtOAc) gave 45.5 mg (31%) of pure **20** and 74 mg (63%) of a 2:1 mixture of **18** and **19**.

The data for **20**: ^1H NMR ($CDCl_3$) δ 7.14–7.42 (m, 5), 4.70 (dddd, 1, J = 3.1, 3.2, 7.4, 9.6, CHN), 4.21 (dd, 1, J = 7.4, 9.1, CHHO), 4.16 (dd, 1, J = 3.2, 9.1, CHHO), 3.45 (ddd, 1, J = 6.4, 8.9, 10.2, H_a), 3.28 (dd, 1, J = 3.1, 13.4, CHHPh), 2.77 (dd, 1 H, J = 9.6, 13.4, CHHPh), 2.50 (dddq, 1, J = 6.3, 10.4, 8.9, 6.6, H_b), 2.12 (ddd, 1, J = 9.9, 10.2, 13.1, H_g), 1.99 (ddd, 1, J = 6.3, 6.5, 11.6, H_c), 1.81 (dddd, 1, J = 0.8, 6.4, 9.1, 13.1, H_f), 1.21 (dddd, 1, J = 6.5, 9.1, 9.9, 12.6, H_e), 1.05 (ddd, 1, J = 10.5, 11.6, 12.6, H_d), 1.03 (d, 3 H, J = 6.6, CH_3); ^{13}C NMR ($CDCl_3$) δ 176.2, 153.2, 135.4, 129.4, 128.9, 127.3, 66.0, 55.4, 51.3, 39.6, 38.0, 37.7, 32.9, 25.7, 18.9, −3.1; IR (neat) 1780, 1695 cm^{-1}; $[\alpha]_D$ +101.8° (c 0.358, $CHCl_3$). Anal. Calcd for $C_{20}H_{29}O_3NSi$: C, 66.81; H, 8.13. Found: C, 66.59; H, 7.96.

NOE of **20** showed that irradiation of H_b at δ 2.50 gave 3–5% NOE at δ 1.99, 1.21, and the methyl group at δ 1.03. Irradiation of H_a at δ 3.45 gave 3–5% NOE at δ 2.12 and the methyl group at δ 1.03.

The data for **18** and **19**: ^1H NMR ($CDCl_3$) δ 7.20–7.39 (m, 5, Ph), 5.72–5.88 (m, 1, =CH), 5.01–5.09 (m, 2, =CHH), 4.68 (dddd, 1, J = 3.1, 3.4, 7.0, 9.7, CHN), 4.19 (dd, 1, J = 7.0, 9.1, CHHO), 4.15 (dd, 1, J = 3.4, 9.1, CHHO), 3.32 (dd, 1, J = 3.1, 13.2, CHHPh), 3.01 (dd, 1, J = 5.5, 16.6, CHHCO, **18**), 2.88 (dd, 1, J = 6.6, 16.6, CHHCO, **19**), 2.73 (dd, 1, J = 9.7, 13.2, CHHPh), 2.73 (dd, 1, J = 7.9, 16.5, CHHCO), 2.01–2.67 (m, 3, CH, CH_2), 1.04 (d, 3, J = 6.6, CH_3, **19**), 1.02 (d, 3, J = 6.6, CH_3, **18**); ^{13}C NMR ($CDCl_3$) δ 172.6, 153.4, 136.5, 135.3, 129.4, 128.9, 127.3, 116.57 (**18**), 116.51 (**19**), 66.08 (**18**), 66.06 (**19**), 55.2, 41.76 (**18**), 41.67 (**19**), 41.03 (**18**), 40.94 (**19**), 37.9, 29.40 (**19**), 29.30 (**18**), 19.67 (**19**), 19.63 (**18**); IR (neat) 1785, 1700 cm^{-1}; $[\alpha]_D$ +68.9° (c 0.232, $CHCl_3$). Anal. Calcd for $C_{17}H_{21}O_3N$: C, 71.06; H, 7.37. Found: C, 71.28; H, 7.21.

The same reaction catalyzed by 3.5 equiv of $TiCl_4$ at −78 °C for 35 h gave, after chromatography, 91% of a 3:1 mixture of **18** and **19**.

(4*S*)-3-(4-(1-Cyclohexenyl)-1-oxopentyl)-4-(phenylmethyl)-2-oxazolidinone (27). Reaction of ethylidenecyclohexane (0.058 mL, 0.43 mmol), **26** (50 mg, 0.22 mmol), and Me_2AlCl (0.17 mL, 0.33 mmol) at −45 °C for 21 h gave 75 mg of a crude mixture of stereoisomers of **27**. Flash chromatography (15:1 hexane–EtOAc) gave 60 mg (81%) of a 1.3:1 mixture of stereoisomers of **27a** and **27b** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.19–7.37 (m, 5), 5.43–5.44 (m, 1), 4.62–4.70 (dddd, 1, J = 2.7, 3.6, 6.9, 9.6, CHN), 4.19 (dd, 1, J = 6.9, 9.1, CHHO), 4.15 (dd, 1, J = 3.6, 9.1, CHHO), 3.29 (dd, 1, J = 2.7, 13.2, CHHPh), 2.83–2.96 (m, 2, CH_2CO), 2.76 (dd, 1, J = 9.6, 13.3, CHHPh), 1.55–2.20 (m, 11), 1.20 (d, 3, J = 6.8, CH_3); ^{13}C NMR ($CDCl_3$) 173.68 (**27b**), 173.64 (**27a**), 153.7, 135.34 (**27b**), 135.32 (**27a**), 129.4, 128.9, 127.3, 121.32 (**27a**), 121.27 (**27b**), 66.09 (**27b**), 66.04 (**27a**), 55.18 (**27b**), 55.13 (**27a**), 40.90 (**27a**), 40.84 (**27b**), 37.93 (**27b**), 37.90 (**27a**), 33.70 (**27a**), 33.68 (**27b**), 29.3, 25.2, 24.63 (**27b**), 24.54 (**27a**), 23.0, 22.8, 19.5; IR (neat) 1780, 1700 cm^{-1}; $[\alpha]_D$ +66.9° (c 0.135, $CHCl_3$). Anal. Calcd for $C_{21}H_{27}O_3N$: C, 73.87; H, 7.79. Found: C, 73.94; H, 7.77.

(4*S*)-3-(4,6,6-Trimethyl-5-methylene-1-oxoheptyl)-4-(phenylmethyl)-2-oxazolidinone (28 and 29). Reaction of (*E*)-3,4,4-trimethyl-2-pentene (73 mg, 0.65 mmol), **26** (75 mg, 0.32 mmol), and Me_2AlCl (0.25 mL, 0.48 mmol) at −40 °C for 33 h gave 115 mg of crude product. Flash chromatography (10:1 hexane–EtOAc) of 80 mg gave 71 mg (92%) of a 9:1 mixture of **28** and **29**: ^1H NMR ($CDCl_3$) δ 7.20–7.37 (m, 5), 4.95 (s, 1, =CHH), 4.78 (s, 1, =CHH), 4.66 (dddd, 1, J = 3.2, 3.6, 6.6, 9.9, CHN), 4.18 (dd, 1, J = 6.6, 9.1, CHHO), 4.14 (dd, 1, J = 3.6, 9.1, CHHO), 3.31 (dd, 1, J = 3.2, 13.3, CHHPh), 2.98 (ddd, 1, J = 7.6, 7.9, 17.4, CHHCO), 2.87 (ddd, 1, J = 7.6, 7.4, 17.4, CHHCO), 2.72 (dd, 1, J = 9.9, 13.3, CHHPh), 2.32 (m, 1, $CHCH_3$), 1.80 (ddd, 2, J = 7.5, 7.6, 7.8, CH_2), 1.09 (d, 3, J = 6.7, CH_3), 1.07 (s, 9, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 173.5, 163.2, 153.4, 135.4, 129.4, 128.9, 127.3, 105.24 (**29**), 105.20 (**28**), 66.12 (**29**), 66.09 (**28**), 55.1, 37.9, 36.6, 34.2, 33.39 (**29**), 33.36, (**28**), 32.82 (**29**), 32.74 (**28**), 28.8, 23.73 (**28**), 23.61 (**29**); IR (neat) 1790, 1710 cm^{-1}; $[\alpha]_D$ +27.7° (c 0.271, $CHCl_3$). Anal. Calcd for $C_{21}H_{29}O_3N$: C, 73.44; H, 8.51. Found: C, 73.53; H, 8.50.

Benzyl 5-Methylene-4,6,6-trimethylheptanoate (30).[5] To a stirred solution of 2.0 equiv of benzyl alcohol in anhydrous THF (0.2 M) at −78 °C was added 1.5 equiv of *n*-BuLi. A solution of 70 mg (0.2 mmol) of a mixture of **28** and **29** in 1 mL of anhydrous THF was added, and the mixture was warmed to 0 °C. The solution was stirred at that temperature for 3 h, and the reaction was quenched with excess saturated aqueous ammonium chloride. The mixture was concentrated in vacuo, diluted with water, and extracted with CH_2Cl_2. The combined organic layers were dried

over magnesium sulfate, filtered, and concentrated in vacuo to give 120 mg of crude **30** and benzyloxazolidinone. Flash chromatography (50:1 hexane–EtOAc) gave 52 mg (95%) of pure **30**: ^{1}H NMR ($CDCl_3$) δ 7.29–7.39 (m, 5), 5.10 (s, 2, CH_2Ph), 4.92 (s, 1, =CHH), 4.74 (s, 1, =CHH), 2.34 (t, 2, J = 7.7, CH_2CO), 2.25 (m, 1, $CHCH_3$), 1.75 (ddt, 1, J = 7.3, 13.7, 7.6, C*H*HCH), 1.74 (ddt, 1, J = 7.4, 13.7, 7.6, CH*H*CH), 1.04 (d, 3, J = 6.8), 1.02 (s, 9); ^{13}C NMR ($CDCl_3$) δ 173.7, 163.1, 136.1, 128.5, 128.3, 128.2, 105.2, 66.1, 36.6, 33.4 (2 C), 32.7, 28.8, 23.6; IR (neat) 1740 cm^{-1}; $[\alpha]_D$ −16.6° (c 0.247, $CHCl_3$).

Benzyl 5-Oxo-4,6,6-trimethylheptanoate (31).[23] A solution of 40 mg (0.14 mmol) of **30** in 3 mL of CH_2Cl_2 was cooled to −78 °C, and O_3 was passed through the solution for 1 min. The reaction was quenched by 1.4 equiv of dimethyl sulfide, and the solution was stirred at 25 °C for 30 min. The solution was diluted with 2 mL of water and extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 42 mg of crude **31**. Flash chromatography (50:1 hexane–EtOAc) gave 34 mg (85%) of pure **31**: ^{1}H NMR ($CDCl_3$) δ 7.30–7.39 (m, 5), 5.11 (s, 2, CH_2Ph), 3.05 (br sext, 1, J = 7.0, $CHCH_3$), 2.30 (t, 1, J = 7.5, CHHCO), 2.29 (t, 1, J = 7.3, CHHCO), 1.94 (dddd, 1, J = 7.3, 7.5, 7.1, 14.0, CHHCH), 1.68 (dddd, 1, J = 7.3, 7.5, 7.1, 14.0, CHHCH), 1.10 (s, 9), 1.04 (d, 3, J = 6.8); ^{13}C NMR ($CDCl_3$) δ 173.0, 135.8, 128.5, 128.3, 128.2, 66.2, 44.6, 38.4, 31.8, 28.8, 26.0, 18.2; IR (neat) 1740, 1705 cm^{-1}; $[\alpha]_D$ −18.8° (c 0.268, $CHCl_3$); $[\theta]$ +397° at 285 nm.

(*S*)-*sec*-Butyl *tert*-Butyl Ketone (32). *t*-BuLi (2.0 equiv) was added dropwise during 20 min to a solution of (*S*)-(+)-2-methylbutyric acid (0.5 mL, 4.5 mmol, 98% pure) in 10 mL of anhydrous ether at 0 °C. The mixture was stirred overnight, and the reaction mixture was hydrolyzed by pouring it slowly into 15 mL of water. The organic phase was separated, and the aqueous layer was extracted twice with 15 mL of ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 0.6 g of crude **32** as a clear yellow liquid. Distillation of the crude product at 20 Torr gave 0.35 g (45%) of ketone **32**, bp 60–65 °C: ^{1}H NMR δ 2.91 (br sext, 1, J = 7.0), 1.62 (m, 1), 1.33 (m, 1), 1.15 (s, 9), 1.03 (d, 3, J = 6.7), 0.84 (t, 3, J = 7.4); $[\alpha]_D$ +27.7° (c 0.132, $CHCl_3$); $[\alpha]_D$ −29.6° for the *R* enantiomer,[27] $[\theta]$ +280° at 308 nm.

Registry No. **1b**, 90719-30-5; **4**, 109299-92-5; **5**, 134178-33-9; **6**, 134178-34-0; **7**, 134178-35-1; **9**, 134178-36-2; **10**, 134178-37-3; **12**, 134178-38-4; **13**, 134178-39-5; **14** (isomer 1), 134178-40-8; **14** (isomer 2), 134178-41-9; **15**, 134178-42-0; **16**, 134178-43-1; **18**, 134178-44-2; **19**, 134178-45-3; **20**, 134178-46-4; **21**, 2043-21-2; **22**, 134178-47-5; **23**, 134178-48-6; **24**, 134178-49-7; **25**, 134178-50-0; **26**, 90719-27-0; **27a**, 134178-51-1; **27b**, 134178-52-2; **28**, 134178-53-3; **29**, 134178-54-4; **30**, 134178-55-5; **31**, 134178-56-6; **32**, 134178-57-7; Me_2AlCl, 1184-58-3; methylenecyclopentane, 1528-30-9; isobutylene, 115-11-7; 2-ethyl-1-butene, 760-21-4; allyltrimethylsilane, 762-72-1; ethylidenecyclohexane, 1003-64-1; (*E*)-3,4,4-trimethyl-2-pentene, 39761-57-4; 1-methylcycloheptene, 1453-25-4; (*S*)-(+)-2-methylbutyric acid, 1730-91-2.

Supplementary Material Available: Experimental details for the ene reactions of the achiral oxazolidinones **4** and **21** (3 pages). Ordering information is given on any current masthead page.

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Synthesis of Enantioenriched α-Hydroxy-α-allenylacetic Acids by [2,3] Wittig Rearrangement of α-(Propargyloxy)acetates

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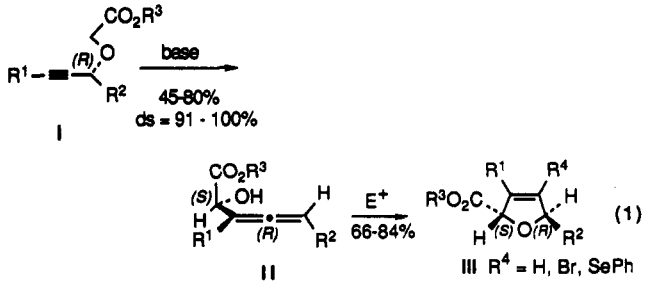
Optically active (*R*)-(propargyloxy)acetic esters **5**, available in ca. 90% ee through reduction of alkynones **2** with Chirald–$LiAlH_4$ followed by alkylation with chloroacetic acid and esterification with CH_2N_2, undergo highly stereoselective [2,3] rearrangement upon treatment with LDA in THF at −78 °C followed by Cp_2ZrCl_2 to afford α(*S*)-hydroxy-β(*R*)-allenic esters **7** with complete transfer of chirality and >90% diastereoselectivity. Upon treatment with TESOTf in Et_3N the (*R*)-(propargyloxy)acetic esters **5** afford the diastereomeric α-(*R*)-hydroxy-β-(*R*)-allenic esters **8** stereoselectively. Both hydroxy esters **7** and **8** cyclize stereospecifically to *trans*- and *cis*-2,5-dihydrofurans **13–15** and **17–19** upon treatment with $AgNO_3$–$CaCO_3$, PhSeCl, or NBS.

We recently showed that enantioenriched α-hydroxy-α-allenylacetic acids II can be readily prepared by [2,3] Wittig rearrangement of chiral α-(propargyloxy)acetates (eq 1).[1] The reaction proceeds with excellent diastereoselectivity, especially when Cp_2ZrCl_2 is added to chelate the ether and carboxylic groupings.[2] Cyclization of the allenyl alcohol products II is readily effected with $AgNO_3$, NBS, or PhSeCl to give the tri- or tetrasubstituted 2,5-dihydrofurans III stereospecifically.[3] Such furans are of interest as subunits of various natural products.[4]



(1)

Propargylic [2,3] rearrangements differ from their allylic counterparts in that the chiral sense of the sp^3 carbinyl center is faithfully transferred to the allenyl moiety of the product as a consequence of a rigid five-center transition state (A in Figure 1.)[1] In contrast, the stereogenicity of analogous allylic ether rearrangements, though generally high, depends upon conformational, and to some extent,

(1) Marshall, J. A.; Robinson, E. D.; Zapata, A. *J. Org. Chem.* **1989**, *54*, 5854.

(2) Cf: Kuroda, S.; Sakaguchi, S.; Ikegami, S.; Harramoto, T.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1988**, *29*, 4763. Uchikawa, M.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 4581.

(3) For a preliminary account, see: Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1990**, *55*, 2995.

(4) Cf: Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. Mulholland, R. L., Jr.; Chamberlin, A. R. *J. Org. Chem.* **1988**, *53*, 1082. Perron, F.; Albizati, K. F. *Chem. Rev.* **1989**, *89*, 1617.

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