Characteristic ^1H NMR peaks for **9d** are as follows: 5.68 (br, 1, H_2), 2.17 (d, 3, J = 1.4, C_3-*Me*).

Characteristic ^1H NMR peaks for **9e** are as follows: 5.68 (br, 1, H_2), 1.89 (d, 3, J = 1.3, C_3-*Me*).

Compounds **30**, **9d**, and **10d** had the following GC data: t_R 3.3, 3.4, or 3.6 min. It was not possible to correlate the peaks to the compounds.

Attempted Preparation of Methyl [2-(2-Propenyl)cyclohexylidene]acetate. A 10:1 mixture of (*E*)- and (*Z*)-[2-(2-propenyl)cyclohexylidene]acetic acid (**19b** and **20b**) (136 mg, 0.76 mmol) was converted to a mixture of acid chlorides in the normal manner. The resulting 4:1 mixture of **19c** and **20c** in benzene (1 mL) was added dropwise to a solution of Et_3N (106 mg, 1.05 mmol) and methanol (39 mg, 1.21 mmol) in benzene (0.5 mL) at 0 °C. The solution was stirred for 1 h at 0 °C. Normal workup gave 88.7 mg of a ca. 4:1 mixture of **19d** and **20d** as determined by analysis of the 300-MHz ^1H and ^{13}C NMR spectra. The data given below were obtained from that mixture.

The spectral data for methyl (*E*)-[2-(2-propenyl)cyclohexylidene]acetate (**19d**) are as follows: ^1H NMR δ 5.7 (m, 1), 5.61 (d, 1, J = 1.2), 5.0 (m, 2), 3.68 (s, 3), 3.0 (m, 1), 2.7 (m, 1), 2.5–1.3 (m, 8); ^{13}C NMR δ 171.7, 166.0, 136.1, 116.5, 111.3, 50.7, 45.5, 36.4, 33.6, 28.4, 28.3, 23.5.

Characteristic peaks for methyl (*Z*)-[2-(2-propenyl)cyclohexylidene]acetate (**20d**) are as follows: ^1H NMR δ 5.7 (m, 1), 5.59 (br, 1), 5.0 (m, 2), 4.0 (m, 1), 3.67 (s, 3); ^{13}C NMR δ 136.3, 115.9, 113.5, 51.6, 36.2, 35.7, 33.4, 30.1, 28.1, 20.2, 2 carbons were not observed.

Preparation of *tert*-Butyl [6-(2-Propenyl)cyclohex-1-enyl]acetate (31). A ca. 3:1 mixture of (*E*)- and (*Z*)-[2-(2-propenyl)cyclohexylidene]acetic acid (**19b** and **20b**) (220 mg, 1.2 mmol) was converted to the acid chloride in the normal manner. The resulting 3:1 mixture of **19c** and **20c** was treated with Et_3N (152.5 mg, 1.51 mmol) and *t*-BuOH (125.8 mg, 1.7 mmol) at 0 °C for 1 h. Normal workup gave 147.7 mg (55%) of crude product, which consisted of a chromatographically inseparable 15:3:1 mixture of *tert*-butyl [6-(2-propenyl)cyclohexenyl]acetate (**31**), *tert*-butyl (*E*)-[2-(2-propenyl)cyclohexylidene]acetate (**19e**), and *tert*-butyl [2-(2-propenyl)cyclohexenyl]acetate (**32**) as determined by ^1H and ^{13}C NMR spectral analysis.

The spectral data for **31** are as follows: ^1H NMR δ 5.75 (dddd, 1, J = 17.5, 9.9, 7.5, 6.0), 5.58 (dddd, 1, J = 3.8, 3.8, 2.3, 1.5, H_2), 5.0 (m, 2), 3.01 (ddddd, 1, J = 15.2, 2.2, 2.2, 1.3, 0.9, CH_2CO_2R), 2.83 (ddddd, 1, $J \approx$ 15.2, 0.7, 0.7, 0.7, 0.7, CH_2CO_2R), 2.4–2.1 (m, 5), 2.0 (br m, 4), 1.45 (s, 9); ^{13}C NMR δ 171.6, 137.4 (CH), 134.3 (C), 126.9 (CH), 115.9 (CH_2), 80.2, 42.5, 37.0, 36.4 (C_6), 28.0 (3 C), 27.1, 25.5, 19.0.

Characteristic peaks for **19e** are as follows: ^1H NMR δ 5.61 (ddd, J = 0.9, 0.9, 0.9, =$CHCO_2R$); ^{13}C NMR δ 171.8, 162.2 (C_1), 111.3 (=$CHCO_2R$).

Characteristic peaks for **32** are as follows: ^1H NMR δ 3.04 (br d, 1, J = 13.3, CH_2CO_2R), 2.87 (dd, 1, J = 13.3, 0.8, CH_2CO_2R); ^{13}C NMR δ 171.8, 136.1.

Acknowledgment. We thank the National Institutes of Health for financial support.

Stereochemical Studies of Type-II Intramolecular Ene Reactions of δ,ε-Unsaturated Aldehydes

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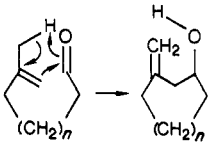
Received May 12, 1987

Intramolecular Lewis acid catalyzed ene reaction of aldehyde **3** gives the (*E*)-ene adduct **18** with 85–90% selectivity. Intramolecular ene reactions of aldehydes **6**, **10**, and **13** proceed with 88–100% selectivity for the isomer with an equatorial methyl group and an axial hydroxyl group. Intramolecular type-II ene reaction of allenic aldehyde **17** occurs either thermally or with Lewis acid catalysis to give a mixture of the expected ene adduct, bis exocyclic diene **26**, and diene **27**.

Introduction

Oppolzer and Snieckus have classified intramolecular ene reactions into three types based on the connectivity of the ene and enophile.[1] Type-II reactions, which produce alkylidene cycloalkanes, proceed through a highly ordered bridged bicyclic transition state with considerable potential for control of stereochemistry (see eq 1). These



(1)

n = 1,2

reactions have been much less studied than type-I ene reactions and stereochemical constraints are less well understood. The majority of studies have involved Lewis acid catalyzed ene reactions with either aldehydes or ketones as enophiles.[2-5] These reactions, which can be considered to be intramolecular Prins reactions, can only be used to produce cyclohexanols or cycloheptanols.[2i] Cyclohexanols are produced exclusively with an axial alcohol group as expected from either a concerted reaction or stepwise re-

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(5) Transannular ring closure of cyclodecenones occurs thermally to give exomethylenedecalols. (a) Wender, P. A.; Letendre, L. J. *J. Org. Chem.* **1980**, *45*, 367. (b) Wender, P. A.; Hubbs, J. C. *J. Org. Chem.* **1980**, *45*, 365. (c) Williams, J. R.; Callahan, J. F. *J. Org. Chem.* **1980**, *45*, 4479.

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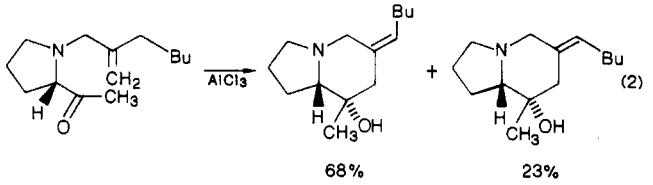
action with an intramolecular 1,5-proton transfer.

The suitability of this reaction for the synthesis of 3-methylenecyclohexanols has never been explored. All examples reported to date involve the annulation of a second ring to form a bicyclic or spirocyclic system. More remarkably, the stereochemistry of the exocyclic double bond has not been examined, with the exception of three examples reported by Overman and Lesuisse while this work was in progress[4] (see eq 2). All other examples report

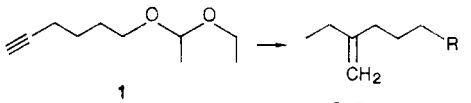


the synthesis of adducts containing a methylenecycloalkane. We therefore decided to explore the ene reactions of the δ,ϵ-unsaturated aldehydes **3**, **6**, **10**, and **13** to determine the stereochemistry of the products in unconstrained systems.

Bertrand and co-workers have reported extensive studies of type-I intramolecular ene reactions of allenic aldehydes which lead to 2-alkenyl-2-cyclohexenols.[6] Type-II intramolecular ene reactions of allenic aldehydes have not been examined. We decided to examine the type-II intramolecular ene reaction of allenic aldehyde **17**, which should give 2,3-dimethylenecyclohexanol (**26**), a useful diene for Diels–Alder reactions.

Results and Discussion

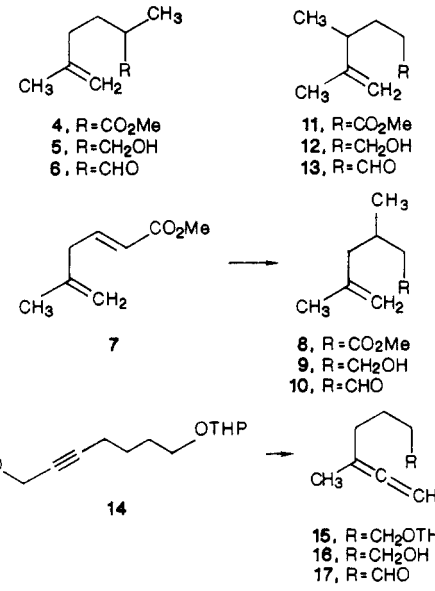
Preparation of Aldehydes. Addition of ethylcopper to **1** by the procedure of Normant et al.[7] followed by acidic hydrolysis of the ethoxyethyl ether gave alcohol **2** in 54% yield. Oxidation of **2** with Collins reagent generated in situ[8] gave aldehyde **3** in 82% yield.



1

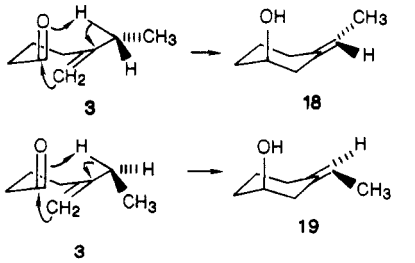
2, R=CH_2OH
3, R=CHO

Lewis acid catalyzed ene reactions provided efficient approaches to aldehydes **6**, **10**, and **13**. $EtAlCl_2$-catalyzed ene reaction[9] of methyl methacrylate with isobutylene gave ester **4** in 56% yield. Reduction of **4** with LAH gave alcohol **5** in 97% yield, which was oxidized as described above to give aldehyde **6** in 74% yield. $EtAlCl_2$-catalyzed ene reaction of methyl propiolate with isobutylene gave ester **7**.[10] Addition of lithium dimethylcuprate to **7** gave the saturated ester **8** in an unoptimized yield of 32%. Reduction with LAH gave alcohol **9** in 94% yield, which was oxidized as described above to give **10** in 81% yield. $EtAlCl_2$-catalyzed ene reaction of methyl acrylate with 2-methyl-2-butene gave ester **11**[11] in 12% yield. Although the yield of **11** is poor, the purification is straightforward, and adequate quantities of **11** can easily be obtained. Although this reaction has been reported to proceed in 37% yield in 1:1 ethylene chloride–nitromethane using $AlCl_3$ as catalyst,[11b] we were unable to obtain **11** by this procedure. Reduction of **11** with LAH gave **12** in 92% yield. Oxidation as described above gave **13** in 75% yield.



Alkylation of the lithium salt of 3-methoxypropyne[12] with 2-(4-bromobutoxy)tetrahydropyran[13] gave **14** in 88% yield which was treated with methylmagnesium bromide and a catalytic amount of cuprous bromide[14] to give **15**, which was hydrolyzed[15] to give **16** in 43% yield from **14**. Oxidation of **16** as described above gave aldehyde **17** in 92% yield.

Intramolecular Ene Reaction of 3. Treatment of aldehyde **3** in CH_2Cl_2 with 1 equiv of Me_2AlCl at −78 °C for 30 min gave a 63% yield of an 88:12 mixture of **18** and **19**. Acetylation of this mixture gave a mixture of acetates whose ^1H and ^{13}C NMR spectral data correspond closely to those previously described.[16] Me_2AlCl was chosen as Lewis acid since we have previously shown that this is a very effective catalyst for the intramolecular ene reactions of unsaturated aldehydes because it is both a strong Lewis acid and a Brønsted base.[17]



3

We have tried to optimize conditions for the selective formation of the *E* isomer **18**. Comparable results were obtained at −95 °C in CH_2Cl_2 and $CHFCl_2$ and at −126 °C

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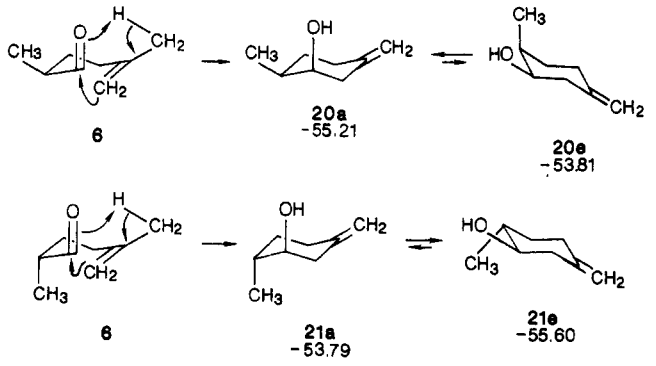
in CF_2Br_2. Lowering the temperature below −78 °C does not improve the selectivity. Use of Me_3Al or Et_2AlCl as catalyst gave lower yields of more complex mixtures of products.

Decreasing the reactivity of the catalyst should and did improve selectivity. Reaction of **3** with Me_2AlOPh[18] for 3 h at 0 °C gave a 56% yield of a 90:10 mixture of **18** and **19**. Use of the more hindered Lewis acid Me_2AlOPh-2,6-t-Bu_2-4-Me led to extensive reduction of the aldehyde to the primary alcohol **2** without improving selectivity in the ene reaction.

Thermal intramolecular ene reactions of aldehydes are often not practical since ΔH for these reactions is less exothermic than for their all carbon counterparts due to the strength of the carbonyl double bond. At elevated temperatures the unsaturated aldehyde is often more stable than the ene adduct due to entropic considerations.[17] Flash vacuum pyrolysis of **3** at 500 °C led mainly to recovered starting material. Ene reaction did occur on heating **3** in C_6D_6 in a sealed tube at 155 °C. The reaction was ≈50% complete after 20 h. The selectivity for **18** was lower, and other products were also formed. Further reaction did not improve the yield of ene adducts.

Lewis acid catalyzed ene reactions can be used to produce 3-alkylidenecyclohexanols with ≈90% selectivity for the *E* isomer. This selectivity results exclusively from a kinetic preference. There is little thermodynamic preference for either isomer. Slightly higher stereoselectivity is observed in the ene reaction of **3** than in the example explored by Overman[7] (see eq 2).

Intramolecular Ene Reaction of 6. Treatment of aldehyde **6** in CH_2Cl_2 with 1 equiv of Me_2AlCl at −78 °C for 30 min gave a 65% yield of a 90:10 mixture of **20** and **21**. The selective formation of the less stable cis isomer **20** indicates that the methyl group selectively adopted the equatorial conformation in the transition state since the ene adducts must be formed in the conformation with an axial hydroxyl group.



To our surprise, treatment of **6** with 1 equiv of Me_2AlOPh in CH_2Cl_2 for 1.5 h at 0 °C led to a 40:37:23 mixture of **20**, **21**, and the reduction product **5**. In this case selectivity is markedly decreased by the use of the weaker Lewis acid. We believe that the ene reaction of these aldehydes is readily reversible and is driven by the irreversible deprotonation of the Lewis acid–alcohol complex to give an aluminum alkoxide, which is reconverted to the alcohol on workup.[17] The retro-ene reaction is favored by higher temperature. The rate of deprotonation with Me_2AlCl at −78 °C should be much faster than retro-ene reaction. The weaker Lewis acid Me_2AlOPh does not catalyze the reaction below 0 °C. At this temperature, the retro-ene reaction can compete with deprotonation.

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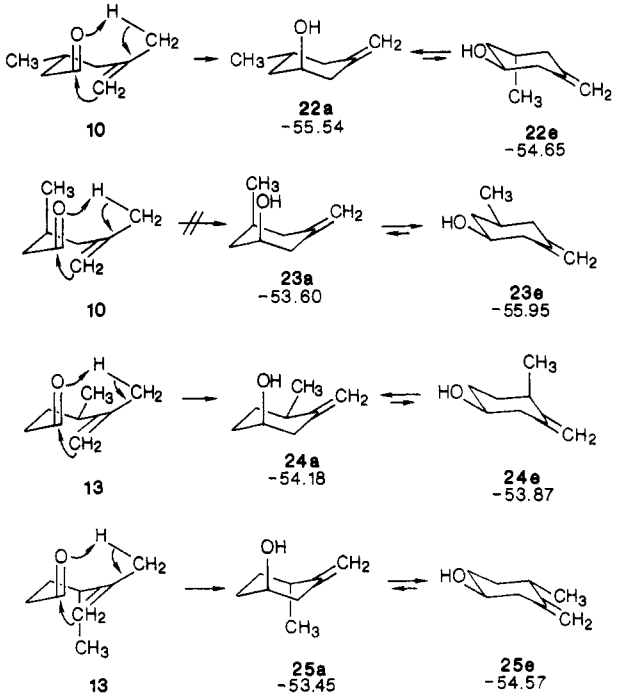
Two features favor improved selectivity for the formation of **18** but decreased selectivity for the formation of **20** with Me_2AlOPh. First, the double bond of **18** is trisubstituted, while that of **20** is disubstituted. This makes the ene reaction of **3** to give **18** and **19** thermodynamically more favored by ≈1 kcal/mol than the ene reaction of **6** to give **20** and **21** and therefore decreases the likelihood of reversal of the ene reaction prior to deprotonation. Second, ene adducts **18** and **19** are similar in energy. Molecular mechanics calculations[19] indicate that they are within 0.05 kcal/mol of each other. On the other hand, alcohol **20** is less stable than alcohol **21** by ≈0.8 kcal/mol. Therefore reversibility of the ene reaction should favor the formation of **21** but not the formation of **19**.

Intramolecular Ene Reaction of 10. Treatment of aldehyde **10** in CH_2Cl_2 with 1 equiv of Me_2AlCl at −78 °C for 30 min gave a 64% yield of the trans isomer **22**; the cis isomer **23** was not formed. Similar results were obtained with Me_2AlOPh at 0 °C. The stereoselective formation of **22** is strongly favored by severe steric interactions between the methyl group and oxygen in the transition state leading to **23**.



Intramolecular Ene Reaction of 13. Treatment of aldehyde **13** in CH_2Cl_2 with 1 equiv of Me_2AlCl at −78 °C for 30 min gave a 65% yield of a 96:4 mixture of **24** and **25**. As in the ene reaction of **6**, the selective formation of the less stable cis isomer **24** indicates that the methyl group selectively adopted the equatorial conformation in the transition state. Treatment of **13** with 1 equiv of Me_2AlOPh in CH_2Cl_2 for 1.5 h at 0 °C gave a 9:1 mixture of **24** and **25**. The decreased selectivity for **24** in the ene reaction of **13** with Me_2AlOPh as catalyst results from the same factors discussed above for the ene reaction of **6**. With either catalyst the ene reaction of **13** is more selective than the ene reaction of **6**.

Stereochemical Assignment of Ene Adducts 20–25. Assignment of stereochemistry to the ene adducts **20–25** requires a careful analysis of the conformation of these

(19) MMPM was used on an IBM PC and MMX was used on a VAX. Both were obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401. Updated versions of MODEL obtained from Prof. Midland, University of California, Riverside, and Prof. Steliou, University of Montreal, were used for structure input and analysis.

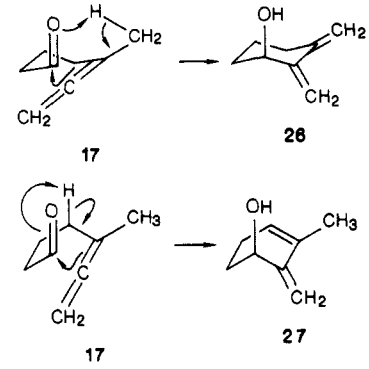
adducts. These cyclohexanols must be formed exclusively in the conformation with an axial alcohol group (**20a–25a**) since either a concerted reaction or stepwise reaction with an intramolecular 1,5-proton transfer will lead initially to the axial alcohol. Interconversion among the two chair conformers of these adducts will be facile; the adducts will exist as an equilibrium mixture of isomers. Molecular mechanics calculations[19] were carried out to determine the relative energies of the conformers with an axial hydroxyl group (**20a–25a**) and with an equatorial hydroxyl group (**20e–25e**). *The calculated heats of formation are shown under the structures.* In all cases the conformer with an equatorial methyl group was calculated to be more stable, although the amount varied from 2.35 kcal/mol in the case of **23** to only 0.3 kcal/mol in the case of **24**.

Alcohol **20** is expected to exist largely as the conformer with an axial alcohol (**20a**), which is calculated to be more stable than **20e** by 1.4 kcal/mol. Alcohol **21** is expected to exist as the diequatorial conformer (**21e**), which is calculated to be more stable than **21a** by 1.8 kcal/mol. On the basis of this analysis, the ^{1}H NMR spectra permit assignment of structure **20** to the major product and **21** to the minor product. The proton on the oxygen-bearing carbon of the major product **20** absorbs at δ 3.80 as a broad peak with $w_{1/2}$ = 13 Hz. Both the shape and chemical shift are characteristic of equatorial protons of axial alcohols. The proton on the oxygen-bearing carbon of the minor product **21** absorbs at δ 3.18 as a ddd (9.7, 9.7, 4.4 Hz). Both the chemical shift and coupling constants are characteristic of axial protons of equatorial alcohols. In addition, several peaks in the aliphatic region of the ^{13}C NMR spectrum of **20** are shifted upfield substantially from those in the ^{13}C NMR spectrum of **21** as expected for the isomer which has an axial and equatorial rather than two equatorial substituents.

Alcohol **22** is expected to exist largely as the conformer with an axial alcohol (**22a**), which is calculated to be more stable than **22e** by 0.9 kcal/mol. Alcohol **23** is expected to exist as the diequatorial conformer (**23e**), which is calculated to be more stable than **23a** by 2.35 kcal/mol. The single product formed in this reaction is undoubtedly **22** since the proton on the oxygen-bearing carbon absorbs as a broad peak at δ 4.07 with $w_{1/2}$ = 13.7 Hz, strongly suggesting that the hydroxyl group is axial and the proton is equatorial.

Alcohol **24** is expected to exist as a mixture of conformers since the conformer with an axial alcohol (**24a**) is calculated to be more stable than **24e** by only 0.3 kcal/mol. Alcohol **25** is expected to exist as the diequatorial conformer (**25e**), which is calculated to be more stable than **25a** by 1.1 kcal/mol. On the basis of this analysis, the ^{1}H NMR spectra permit assignment of structure **24** to the major product. The proton on the oxygen-bearing carbon of **25** absorbs at δ 3.60 as a dddd (10.5, 10.5, 4.2, 4.2 Hz) as expected for an axial proton of an equatorial alcohol. The proton on the oxygen-bearing carbon of **24** absorbs further downfield at δ 4.00 as a dddd ($\approx$4, 4, 4, 4 Hz) as expected for a mixture of equatorial and axial conformers.

Intramolecular Ene Reaction of 17. Intramolecular type-II ene reactions of allenic aldehydes have not been previously examined. Heating a solution of **17** in C_6D_6 at 155 °C gave a 1:1 mixture of ene adducts **26** and **27** with a half-life of $\approx$30 h. Flash vacuum pyrolysis of **17** at 10^{-1} Torr gave a 2:1 mixture of **26** and **27** with 5%, $\approx$25%, $\approx$50%, and 90% conversion at 350, 400, 450, and 550 °C, respectively. Treatment of **17** with 1 equiv of Me_2AlCl in dichloromethane at 25 °C for 1 h led to a 70% yield of a 1:3 mixture of **26** and **27**. Separation of the unstable



dienols could only be accomplished by analytical HPLC.

The bis exocyclic diene **26** is the expected product of a type-II ene reaction. The formation of adduct **27** was surprising since adducts with endocyclic double bonds have not been previously obtained in type-II intramolecular ene reactions of unsaturated aldehydes except in those cases where the exocyclic double bond of the initially formed ene adduct is isomerized to the more stable endocyclic double bond. The formation of **26** and **27** in constant ratio in flash vacuum pyrolysis at varying temperatures suggests that **27** is a primary product of the ene reaction. Examination of models indicates that both **26** and **27** can be formed by concerted ene reactions. The additional double bond of the allene apparently perturbs the reaction allowing the formation of **27** to occur a rate comparable to the formation of **26**.

Conclusion. These results indicate that type-II intramolecular ene reactions can be used for the construction of 3-alkylidenecyclohexanols. They delineate in a systematic fashion the factors responsible for stereocontrol in these reactions and the extent to which modification of reaction conditions can be used to optimize control.

Experimental Section

General. NMR spectra were recorded on Varian EM-390 and XL-300 spectrometers in $CDCl_3$ unless otherwise specified. Chemical shifts are reported in δ; coupling constants are reported in Hz. Reverse-phase high-performance liquid chromatography (HPLC) was performed on an Altex 10 mm × 25 cm Ultrasphere octadecylsilane column.

Dichloromethane was dried by distillation from calcium hydride. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl. Me_2AlCl was obtained from Texas Alkyls Inc. as a solution in hexane. Me_3Al was obtained from Alfa Products as a solution in hexane. Mg turnings were obtained from Reade Mfg. Co. sealed under an inert atmosphere in Mylar bags. Me_2AlOPh was prepared by the method of Mole,[18] except that CH_2Cl_2 was used as solvent and the products were not distilled but diluted to a known volume.

All air-sensitive reactions were run under nitrogen in flame-dried glassware with magnetic stirring. Reagents were added via dry syringes through septa. Thermal ene reactions were carried out in degassed C_6D_6 solution in sealed NMR tubes by heating the tube at the indicated temperature in an oil bath. The progress of the reaction was monitored at intervals by NMR spectroscopy.

5-Ethyl-5-hexen-1-ol (2) was prepared by a modification of the literature procedure.[7] A mixture of cuprous bromide–dimethyl sulfide complex (2.0 g, 9.74 mmol) in 9 mL of ether and 10 mL of dimethyl sulfide was stirred until the solution became homogeneous. The solution was cooled to −45 °C and treated with EtMgBr (3.25 mL of 3.0 M in ether, 9.75 mmol) over 10 min. The solution was stirred for 2 h at −45 °C and treated with 1.18 g (6.96 mmol) of **1**. The reaction mixture was stirred for 2 h at −45 °C, warmed to 0 °C, and quenched by addition of saturated ammonium chloride solution. Normal workup gave 1.44 g of crude product, which was hydrolyzed without purification. A solution of crude product (1.314 g) in 10 mL of acetone, 4.5 mL of water, and 2 drops of concentrated sulfuric acid was heated at reflux

for 2 h. The acetone was evaporated in vacuo, and 12 mL of water was added. The aqueous layer was extracted with three portions of CH_2Cl_2, which were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to give 0.72 g of crude **2**. Flash chromatography on silica gel (3:1 hexane–EtOAc) gave 0.456 g (54%) of pure **2**: ^{1}H NMR 4.71 (m, 2), 3.62 (t, 2, J = 6.4), 2.28 (br, 1, OH), 1.9–2.1 (m, 4), 1.4–1.6 (m, 4), 1.02 (t, 3, J = 7.4); ^{13}C NMR 151.2, 107.6, 62.6, 35.9, 32.3, 28.6, 23.8, 12.3. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.41; H, 12.71.

Preparation of 5-Ethyl-5-hexenal (3). A mixture of CrO_3 (1.97 g, 19.7 mmol), pyridine (3.18 mL, 39.3 mmol), and CH_2Cl_2 (45 mL) was stirred for 5 min at 0 °C and allowed to warm to 25 °C. Celite and alcohol **2** (420 mg, 3.28 mmol) in 10 mL of CH_2Cl_2 were then added. The solution was stirred 2–4 h at 25 °C. The solution was decanted and the residue washed with three portions of ether. The combined organic layers were washed sequentially with 5% aqueous NaOH, 5% hydrochloric acid, saturated $CuSO_4$, water, and saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo to give 340 mg (82%) of **3**, which was used without purification: ^{1}H NMR 9.78 (t, 1, J = 1.5), 4.76 (br s, 1), 4.71 (br s, 1), 2.44 (dt, 2, J = 1.5, 7.3), 1.9–2.1 (m, 4), 1.7–1.9 (m, 2), 1.03 (t, 3, J = 7.2); ^{13}C NMR 202.5, 150.1, 108.4, 43.2, 35.3, 28.4, 20.0, 12.2.

Preparation of Methyl 2,5-Dimethyl-5-hexenoate (4). Isobutylene (0.53 mL, 5.5 mmol) was added to a solution of methyl methacrylate (0.54 mL, 5.0 mmol) and $EtAlCl_2$ (3.2 mL of 1.4 M in hexane, 4.5 mmol) in 5 mL of benzene in a sealable tube at −78 °C. The tube was sealed, and the resulting mixture was heated for 6 days at 50 °C. Workup as previously described[9] gave 806 mg of crude product. Flash chromatography on silica gel (6:1 hexane–EtOAc) gave 443 mg (56%) of pure **4**: ^{1}H NMR 4.72 (br s, 1), 4.68 (br s, 1), 3.67 (s, 3), 2.45 (ddq, 1, J = 7, 7, 7), 1.8–2.1 (m, 3), 1.71 (s, 3), 1.5–1.6 (m, 1), 1.17 (d, 3, J = 7.0); ^{13}C NMR 177.0, 144.9, 110.2, 51.4, 38.9, 35.2, 31.2, 22.2, 17.0.

Preparation of 2,5-Dimethyl-5-hexen-1-ol (5). A solution of **4** (440 mg, 2.8 mmol) in 3 mL of ether was added to a solution of LAH (0.14 g, 3.8 mmol) in 5 mL of ether. The mixture was heated at reflux for 15 h, cooled to 0 °C, and quenched by the careful addition of water. Sulfuric acid (1 mL of 2.5 M) was then added, and the layers were separated. The aqueous layer was extracted with three portions of ether. The combined organic layers were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to give 349 mg of crude **5**. Evaporative distillation (45 °C, 2 Torr) gave 346 mg (97%) of pure **5**: ^{1}H NMR 4.69 (m, 2), 3.50 (dd, 1, J = 10.4, 5.8), 3.42 (dd, 1, J = 10.4, 5.8), 2.32 (br, 1), 1.9–2.1 (m, 2), 1.72 (br s, 3), 1.5–1.7 (m, 2), 1.2–1.3 (m, 1), 0.93 (d, 3, J = 6.5); ^{13}C NMR 146.0, 109.6, 68.0, 35.3, 35.1, 31.0, 22.3, 16.4. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.44; H, 13.02.

Preparation of 2,5-Dimethyl-5-hexenal (6). Oxidation of **5** (350 mg, 2.7 mmol) as described above for the preparation of **3** gave 250 mg (74%) of **6**,[20] which was used without purification: ^{1}H NMR 9.64 (d, 1, J = 2.0), 4.75 (br s, 1), 4.70 (br s, 1), 2.36 (dddq, 1, J = 6.8, 6.8, 6.8, 2.0), 1.8–2.1 (m, 3), 1.73 (s, 3), 1.4–1.6 (m, 1), 1.12 (d, 3, J = 6.8); ^{13}C NMR 204.8 144.7, 110.5, 45.6, 34.8, 28.2, 22.1, 13.1.

Preparation of Methyl 3,5-Dimethyl-5-hexenoate (8). MeLi (43 mL of 0.9 M in ether, 39 mmol) was added to a suspension of CuI (3.73 g, 19.6 mmol) in 45 mL of ether at 0 °C. The mixture was stirred for 20 min at 0 °C and treated with **7**[10] (2.29 g, 16.3 mmol) in 10 mL of ether over the course of 30 min. The solution was stirred for 1 h at 0 °C and poured into 100 mL of saturated NH_4Cl solution. The organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give 2.014 g of crude product. Flash chromatography on silica gel (4:1 hexane–EtOAc) gave 0.84 g (32%) of pure **8**: ^{1}H NMR 4.76 (br s, 1), 4.67 (br s, 1), 3.67 (s, 3), 2.34 (d, 1, J = 14.4, 4.9), 1.85–2.21 (m, 4), 1.71 (br s, 3), 0.93 (d, 3, J = 6.3); ^{13}C NMR 173.6, 143.7, 112.1, 51.2, 45.4, 41.0, 28.1, 22.0, 19.7.

Preparation of 3,5-Dimethyl-5-hexen-1-ol (9). Reduction of **8** (773 mg, 4.95 mmol) as described above for the preparation of **5** gave 593 mg (94%) of crude **9**. Flash chromatography on silica gel (3.5:1 hexane–EtOAc) gave 510 mg (81%) of pure **9**: ^{1}H NMR 4.74 (br s, 1), 4.67 (br s, 1), 3.70 (m, 2), 2.03 (dd, 1, J = 5.6, 12.9), 1.9 (br, 1, OH), 1.69 (br s, 3), 1.55–1.90 (m, 3), 1.35 (m, 1), 0.87 (d, 3, J = 6.4); ^{13}C NMR 144.4, 111.6, 60.9, 46.0, 39.6, 27.2, 22.1, 19.4. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found C, 74.91; H, 12.57.

Preparation of 3,5-Dimethyl-5-hexenal (10). Oxidation of **9** (435 mg, 3.39 mmol) as described above for the preparation of **6** gave 346 mg (81%) of **10**, which was used without purification: ^{1}H NMR 9.77 (dd, 1, J = 1.9, 2.4), 4.79 (br s, 1), 4.69 (br s, 1), 2.44 (ddd, 1, J = 1.9, 4.2, 15.4), 2.26 (m, 1), 2.20 (ddd, 1, J = 2.4, 8.2, 15.4), 2.01 (dd, 1, J = 6.5, 13.5), 1.96 (dd, 1, J = 7.5, 13.5), 1.71 (br s, 3), 0.95 (d, 3, J = 6.2); ^{13}C NMR 202.7, 143.6, 112.5, 50.5, 45.6, 26.0, 22.0, 20.1.

Preparation of Methyl 4,5-Dimethyl-5-hexenoate (11). Ester **11** was prepared in low yield by a modification of the literature procedure.[11b] $EtAlCl_2$ (9 mL of 1.44 M in hexane, 13 mmol, 0.65 equiv) was added to a solution of 2-methyl-2-butene (1.54 g, 22 mmol) and methyl acrylate (1.72 g, 20 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The solution was stirred for 4 days and worked up as described above to give 1.158 g of crude product containing some polymer. Evaporative distillation (40 °C, 1 Torr) gave 0.573 g, which was purified by flash chromatography on silica gel (30:1 hexane–EtOAc) to give 0.37 g (12%) of pure **11**: ^{1}H NMR 4.70 (m, 2), 3.66 (s, 3), 2.1–2.3 (m, 3), 1.60–1.75 (m, 2), 1.65 (br s, 3), 1.03 (d, 3, J = 6.8); ^{13}C NMR 174.3, 148.6, 110.3, 51.4, 40.6, 32.0, 29.6, 19.4, 18.6.

Preparation of 4,5-Dimethyl-5-hexen-1-ol (12). Reduction of **11** (370 mg, 2.37 mmol) as described above for the preparation of **5** gave 280 mg (92%) of pure **12**: ^{1}H NMR 4.69 (m, 2), 3.63 (t, 2, J = 6.3), 2.16 (m, 1), 1.66 (br s, 3), 1.40–1.51 (m, 4), 1.02 (d, 3, J = 6.8); ^{13}C NMR 149.8, 109.6, 63.1, 40.9, 30.9, 30.7, 18.8, 19.7.

Preparation of 4,5-Dimethyl-5-hexenal (13). Oxidation of **12** (225 mg, 1.76 mmol) as described above for the preparation of **6** gave 166 mg (75%) of **13**, which was used without purification: ^{1}H NMR 9.76 (t, 1, J = 1.7), 4.73 (br s, 1), 4.70 (br s, 1), 2.38 (dt, 2, J = 1.7, 7.5), 2.2 (m, 1), 1.65 (br s, 3), 1.5–1.8 (m, 2), 1.04 (d, 3, J =6.8); ^{13}C NMR 202.5, 148.5, 110.5, 41.9, 40.5, 26.7, 19.5, 18.5.

Preparation of 14. Butyllithium (48 mL, 2.6 mL in hexane, 125 mmol) was added over 40 min to a solution of methyl propargyl ether (9.29 g, 132 mmol) in 500 mL of anhydrous THF at 0 °C. The THP ether of 4-bromobutanol[13] (15.7 g, 66.3 mmol) was added via syringe over 5 min. The reaction mixture was heated at reflux for 4 days, cooled to 25 °C, and quenched by the addition of 100 mL of water. Most of the THF was removed in vacuo, and the residue was extracted with 5 × 50 mL of ether. The combined organic extracts were dried and evaporated to give 24.0 g of crude **14**. Evaporative distillation gave 13.2 g (88%) of pure **14**: ^{1}H NMR 4.48–4.53 (m, 1), 4.07 (t, 1, J = 2.1), 3.65–3.82 (m, 2), 3.35 (s, 3), 2.28 (tt, 2, J = 6.9, 2.1), 1.40–1.90 (m, 12); ^{13}C NMR 98.7, 86.7, 75.9, 66.8, 62.1, 60.1, 57.2, 30.6, 28.8, 25.4 (2 C), 19.5, 18.5.

5-Methyl-5,6-heptadien-1-ol (16). Methylmagnesium bromide (9.46 mL, 2.8 M in ether, 26.5 mmol) was added to a solution of **14** (4.00 g, 17.67 mmol) and cuprous bromide (1.52 g, 5.3 mmol) in 300 mL of anhydrous ether. The resulting black solution was heated at reflux for 60 h with vigorous mechanical stirring. The reaction was cooled, quenched with water, and worked up to give 4.14 g of crude **15**.

A solution of crude **15** (4.14 g) and pyridinium tosylate (600 mg, 2.4 mmol) in 180 mL of anhydrous EtOH was stirred for 24 h at 55 °C.[15] The solution was cooled and evaporated in vacuo to give 3.1 g of an orange oil. Flash chromatography on silica gel (3:1 hexane–EtOAc) gave 900 mg (43% from **14**) of pure **16**: ^{1}H NMR 4.50 (tq, 2, J = 3.4, 3.4), 3.59 (t, 2, J = 6.2), 2.65 (s, 1), 1.75–2.10 (m, 2), 1.67 (t, 3, J = 3.4), 1.35–1.65 (m, 4); ^{13}C NMR 206.0, 98.1, 74.0, 62.6, 33.1, 32.2, 23.5, 18.6; IR (neat) 3330, 2960, 2860, 1958, 1445, 1428, 1321, 1060, 850 cm^{-1}.

5-Methyl-5,6-octadienal (17). Oxidation of alcohol **16** (115 mg, 0.91 mmol) by the procedure reported above for the preparation of **6** gave 103.7 mg (92%) of crude **16** as a yellow oil: ^{1}H NMR 9.71 (t, 1, J = 1.8), 4.45–4.65 (m, 2), 2.42 (dt, 2, J = 1.8, 6.9), 1.50–2.10 (m, 4), 1.67 (t, 3, J = 3.4).

Preparation of (*E*)- and (*Z*)-3-Ethylidenecyclohexanol (18 and 19). Me_2AlCl (0.38 mL of 1.93 M in hexane, 0.73 mmol) was added to a solution of aldehyde **3** (93 mg, 0.74 mmol) in 2 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 30 min

(20) Tietze, L.-F.; Kinast, G.; Uzar, H. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 541.

at −78 °C and quenched by the addition of water. The mixture was stirred for 15 min to dissolve the precipitate. The layers were separated, and the aqueous layer was extracted with three portions of ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to give 85 mg (92%) of crude **18** and **19**. Flash chromatography of 76 mg on deactivated silica gel (4:1 hexane–EtOAc) gave 50 mg (63%) of an inseparable 88:12 mixture of **18** and **19**. **18**: ^{1}H NMR 5.23 (br q, 1, J = 6.7), 3.70 (m, 1), 2.42 (dd, 1, J = 12.7, 3.4), 2.24 (m, 1), 1.7–2.1 (m, 4), 1.5 (d, 3, J = 6.7), 1.3–1.6 (m, 2); ^{13}C NMR 136.1, 118.5, 70.1, 45.4, 34.8, 27.1, 23.2, 12.8. **19**: ^{1}H NMR 5.30 (q, 1, J = 6.7), 2.65 (dd, 1, J = 12.7, 3.6); ^{13}C NMR 118.4, 69.9, 37.0, 35.7, 35.1, 24.1, 12.8 [the quaternary carbon resonance was not detected]. The spectral data of the acetates of **18** and **19** correspond closely to those previously described.[16]

Preparation of *cis*-6-Methyl-3-methylenecyclohexanol (20). Me_2AlCl (0.87 mL of 1.93 M in hexane, 1.68 mmol) was added to a solution of aldehyde **6** (230 mg, 1.82 mmol) in 2.6 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 30 min at −78 °C and quenched by the addition of water. Normal workup gave 224 mg of crude adduct. Flash chromatography on deactivated silica gel (6:1 hexane–EtOAc) gave 132 mg of pure **20** followed by 6.2 mg of a 5:2 mixture of **20** and **21** and 10 mg of pure **21**. The total yield of **20** was 59%. The total yield of **21** was 6%.

The data for **20**: ^{1}H NMR 4.82 (br s, 1), 4.74 (br s, 1), 3.80 (m, 1, $w_{1/2}$ = 13.0 Hz), 2.2–2.4 (m, 3), 2.0–2.1 (m, 1), 1.35–1.75 (m, 3), 0.98 (d, 3, J = 6.8); ^{13}C NMR 144.8, 111.3, 71.7, 42.4, 35.9, 34.0, 29.8, 17.5.

The data for **21**: ^{1}H NMR 4.69 (br s, 2), 3.18 (ddd, 1, J = 9.7, 9.7, 4.4), 2.57 (ddd, 1, J = 12.7, 4.4, 1.5), 1.9–2.3 (m, 3), 1.4–1.7 (m, 3), 1.03 (d, 3, J = 6.7); ^{13}C NMR 146.7, 109.0, 76.4, 43.6, 39.4, 33.9, 33.1, 17.9.

Preparation of *trans*-5-Methyl-3-methylenecyclohexanol (22). Me_2AlCl (0.87 mL of 1.60 M in hexane, 1.39 mmol) was added to a solution of aldehyde **10** (190 mg, 1.50 mmol) in 4 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 30 min at −78 °C and quenched by the addition of water. Normal workup gave 188 mg of crude **22**. Flash chromatography on deactivated silica gel (4:1 hexane–EtOAc) gave 112 mg (64%) of pure **22**: ^{1}H NMR 4.82 (m, 1), 4.76 (m, 1), 4.07 (m, 1, $w_{1/2}$ = 13.7 Hz), 2.20–2.35 (m, 3), 1.63–1.95 (m, 3), 1.57 (br, 1, OH), 1.30 (ddd, 1, J = 13.4, 10.7, 2.7), 0.94 (d, 3, J = 6.7); ^{13}C NMR 144.7, 111.2, 67.5, 43.0, 42.3, 41.0, 28.6, 21.7. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.35; H, 11.23.

Preparation of *cis*-4-Methyl-3-methylenecyclohexanol (24). Me_2AlCl (0.46 mL of 1.93 M, 0.89 mmol) was added to a solution of aldehyde **13** (122 mg, 0.96 mmol) in 3 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 40 min at −78 °C and quenched by the addition of water. Normal workup gave 122 mg of crude adduct, which was purified by flash chromatography (silica gel, 4:1 hexane–EtOAc) to give 71 mg of pure **24** followed by 8 mg of a 7:2 mixture of **24** and **25** and 1.5 mg of a 1:6 mixture of **24** and **25**. The total yield of **24** was 63%. The total yield of **25** was 2.5%.

The data for **24**: ^{1}H NMR 4.79 (br s, 1), 4.77 (br s, 1), 4.00 (dddd, 1, $J \approx$ 4, 4, 4, 4), 2.35 (d, 2, J = 4), 2.14 (m, 1), 1.6–1.8 (m, 3), 1.30–1.45 (m, 1), 1.08 (d, 3, J = 6.5); ^{13}C NMR 149.4, 108.5, 68.5, 42.9, 37.0, 32.0, 30.8, 18.3. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.19; H, 11.27.

The data for **25**: ^{1}H NMR 4.74 (br s, 1), 4.67 (br s, 1), 3.62 (dddd, 1, J = 10.5, 10.5, 4.2, 4.2), 2.62 (ddd, 1, J = 2.2, 4.4, 12.2), 1.05 (d, 3, J = 6.6).

Cyclization of 17. Flash vacuum pyrolysis of **17** was carried out at 10^{-1} Torr by distilling the sample, which was cooled in a liquid nitrogen bath and allowed to warm slowly to room temperature as the liquid nitrogen evaporated, through a quartz tube at the indicated temperature into a U-tube cooled in liquid nitrogen. The sample recovery was nearly quantitative. At 550 °C a 60:30:10 mixture of **26**, **27**, and recovered **17** was obtained. Purification by reverse-phase high-performance liquid chromatography (7:3 water–acetonitrile for 2 min, increasing linearly to pure acetonitrile in 20 min; flow rate, 2.5 mL/min) gave pure **27** as a pale yellow oil and pure **26** as a viscous yellow oil.

The data for **27**: ^{1}H NMR 5.67 (br, 1, CH=C), 5.11 (s, 1, C*H*H=C), 5.02 (s, 1, CH*H*=C), 4.31 (br, 1, C*H*OH), 2.10–2.40 (m, 2), 1.60–1.90 (m, 2), 1.81 (br, 3, CH_3), 1.53 (br, 1, OH); ^{13}C NMR 147.3, 130.8, 127.4, 108.6, 70.6, 30.9, 22.7, 19.6; IR ($CDCl_3$) 3610, 3155, 3095, 2925, 1645, 1609, 1447, 1384, 1038 cm^{-1}; t_R 12.6 min.

The data for **26**: ^{1}H NMR 5.04 (dd, 1, J = 1.7, 1.7, CH*H*=CCHOH), 4.96 (br, 1, CH*H*=CCH_2), 4.94 (dd, 1, J = 1.7, 1.7, C*H*H=CCHOH), 4.75 (br, 1, C*H*H=CCH_2), 4.19 (br, 1, C*H*OH), 2.10–2.30 (m, 2), 1.80–2.00 (m, 2), 1.45–1.65 (m, 3); ^{13}C NMR 152.0, 147.5, 110.5, 107.8, 72.6, 34.8, 34.7, 22.4; IR ($CDCl_3$) 3615, 3155, 3090, 2935, 1635, 1458, 1383, 1046 cm^{-1}; t_R 13.1 min.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. We thank the National Institutes of Health for the partial support of this research.

Registry No. 1, 67448-61-7; **2**, 71097-17-1; **3**, 110774-36-2; **4**, 32852-53-2; **5**, 39892-55-2; **6**, 70576-23-7; **7**, 22070-63-9; **8**, 77290-93-8; **9**, 88295-59-4; **10**, 110774-37-3; **11**, 61549-51-7; **12**, 110774-38-4; **13**, 110774-39-5; **14**, 110774-40-8; **15**, 110774-41-9; **16**, 110774-42-0; **17**, 110774-43-1; **18**, 110774-44-2; **19**, 110774-45-3; *cis*-**20**, 110774-46-4; *trans*-**21**, 110774-47-5; *trans*-**22**, 110774-48-6; *cis*-**24**, 110774-49-7; *trans*-**25**, 110774-50-0; **26**, 110774-51-1; **27**, 110774-52-2; Me_2AlOPh, 6062-74-4; $Br(CH_2)_4OTHP$, 31608-22-7; H_2C=C(Me)CO_2Me, 80-62-6; H_3CC(Me)=CHMe, 513-35-9; H_2C=$CHCO_2Me$, 96-33-3; HC≡CCH_2OMe, 627-41-8; isobutylene, 115-11-7.