8-ft 15% SE-30 on Chromosorb W column (70 °C isothermal). ^{1}H NMR (C_6D_6) δ 1.42 (s, 4 H), 1.64 (s, 6 H) (no SiH was found); IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (s), 2140 (vw) (residual SiH), 1560 (vs) (SiD), 1445 (m), 1175 (s), 765 (s), 735 (s), 680 (vs) cm^{-1} (the very weak band at 2140 cm^{-1} indicates only a trace of SiH); MS *m/e* (% relative intensity) (10.3 eV, Kratos MS-50, neat sample) 116 (3.8), 115 (11.9), 114 (100.0), 113 (3.6), 112 (1.0). Mass spectral measurements (Kratos MS-50, neat samples) and calculation[6] indicated **10** was ≥95% d_2.

Flow Pyrolysis of 10-d_2 in Excess 2,3-Dimethyl-1,3-butadiene. A solution of 0.2075 g of **10**-d_2 (1.82 mmol) dissolved in 1.5990 g (19.5 mmol) of 2,3-dimethyl-1,3-butadiene was slowly added dropwise via syringe drive to a vertical quartz-packed pyrolysis tube at 535 °C swept with a N_2 flow of 35 mL/min. The products were collected at −78 °C with a 67% mass recovery. The major components of the pyrolysate were recovered **10**-d_2 (18% GC yield) and dimethylbutadiene. Preparative GC of the recovered **10** (8-ft 15% SE-30 on Chromosorb W column, 70 °C isothermal) afforded a sample whose spectral characteristics were little changed from those of unpyrolyzed **10**-d_2: ^{1}H NMR (C_6D_6) δ 1.42 (s, 4 H), 1.64 (s, 6 H); ^{2}H NMR (C_6H_6) δ 4.0 (s) (no other signals were found); IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (m), 2140 (w) (SiH), 1560 (vs) (SiD), 1175 (s), 765 (s), 735 (s), 680 (vs) cm^{-1} (the band at 2140 cm^{-1} has increased somewhat in intensity relative to unpyrolyzed **10**-d_2). The mass spectra (10.3 eV, Kratos MS-50, neat samples) are given in Table IV.

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Induction of Asymmetry by a Remote Chiral Center in the Amide Acetal Claisen Rearrangement

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Abstract: The room-temperature preparation of *N,O*- and *N,S*-ketene acetals, which undergo facile sigmatropic rearrangement, from amides and thioamides has made possible the use of a remote chiral auxiliary to induce relative asymmetry in the rearrangement. *N*-Propionylprolinol and *N*-thiopropionylprolinol derivatives were converted into ketene acetals. Amide acetal Claisen rearrangements formed products with relative and internal induction of asymmetry. Products were formed in 50–70% isolated yields with average relative asymmetric induction of 4.7 to 1. The sense of asymmetric induction was opposite when the products of the amides were compared with those of the thioamides.

N-Propionylproline derivatives, **1**, have been used to prepare asymmetric *N,O*-ketene acetals, which can be employed in room-temperature amide acetal sigmatropic rearrangements.[1] This is the first report of an ambient-temperature amide acetal Claisen rearrangement where relative asymmetry[2] was induced by a remote asymmetric center not immediately adjacent to the rearranging framework.

Asymmetric syntheses employing Claisen rearrangements (Table I), widely used for the stereoselective construction of acyclic systems,[3] have often required an enantiomerically pure alcohol component for the transmission of asymmetry along the allylic array. Relative asymmetric induction by remotely placed substituents has been much less frequently employed. Chiral centers placed in rigid adjacent cyclic systems such as steroids,[4] terpenes,[5] butyrolactones,[6] and oxazolines[7] have effectively induced asymmetry. Where chelation is possible, as in ester enolate Claisen rearrangements, asymmetric β-carbons bearing a hydroxyl have induced relative asymmetry.[3e,8] Chiral substituents at either carbon 1[9] or carbon 6[10] of the network undergoing a 2,3- or 3,3-sigmatropic rearrangement have also induced relative asymmetry.

For the successful induction of internal and relative asymmetry, rearrangement at low temperature of a reactive, asymmetric allylic *N,O*-ketene acetal was required. 1-[(2*S*)-(Hydroxymethyl)-pyrrolid-1-yl]propionic acid[11] (**1a**) was protected as its *O*-benzyl ether. Treatment of 1-(methoxypropylidene)-2(*S*)-[(benzyloxy)methyl]pyrrolidinium trifluoromethanesulfonate (**2b**), formed by alkylation of **1b** with methyl trifluoromethanesulfonate, with 3 equiv of the lithium salt of (*E*)- or (*Z*)-2-buten-1-ol led directly to formation of the amides **3b** and **4b** or **5b** and **6b**, respectively, as the major products of the rearrangement.

Both internal and relative asymmetric induction were only modest.[12] The *tert*-butyldimethylsilyl ether, **1c**, was subjected

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(12) Amides from the rearrangement of **1b**, **3b**/**4b**, and **5b**/**6b** were formed in a ratio of 2:1 from the reaction of the *E* alcohol and in a ratio of 1:3 from the *Z* alcohol. For reactions of the *E* alcohol, **3b** and **4b** were formed as a 2.3:1 mixture, whereas **5b** and **6b** were formed from the *Z* alcohol as a 1.9:1 mixture. Amides from the rearrangement of **1c**, **3c**/**4c**, and **5c**/**6c** were formed in a ratio of 2:1 for the reaction of the *E* alcohol and in a ratio of 1:2.8 from the *Z* alcohol. For reactions of the *E* alcohol, **3** and **4** were formed as a 2.2:1 mixture, whereas **5** and **6** were formed from the *Z* alcohol as a 1.8:1 mixture.

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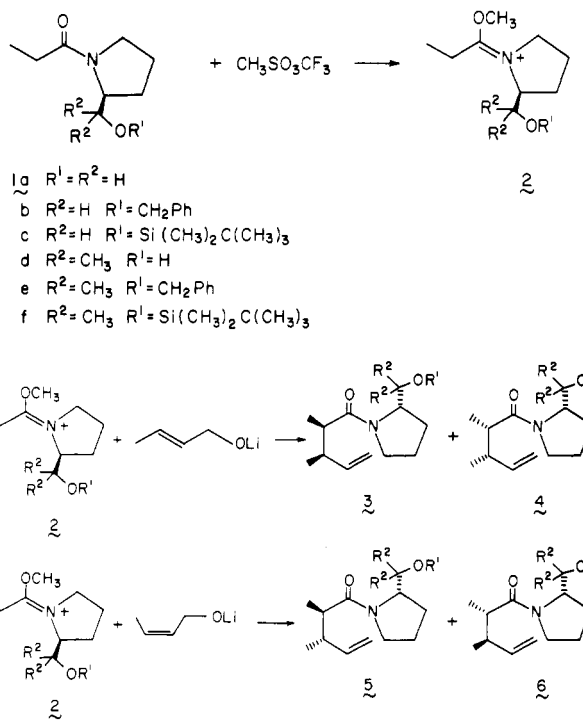
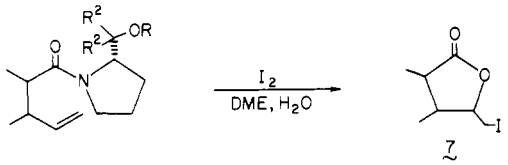


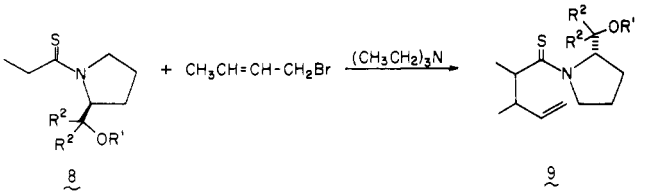
to the reaction conditions, but this simple change of the protecting group had little effect on the asymmetric induction. The rearranged amides were treated with iodine to form the 3,4-dimethyl-5-(iodomethyl)tetrahydrofuranones, **7**.[13] The relative



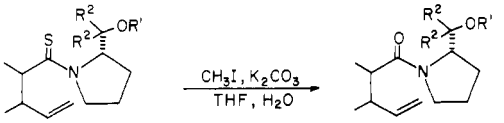
asymmetric induction was determined by NMR spectroscopy on the lactones derived from **3/4** and **5/6** employing both tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]praseodymium and -europium complexes.[14]

For efficient relative asymmetric induction, the pyrrolidine ring must have a single preferred conformation in the *N,O*-ketene acetal intermediate. The presence of two sets of resonances for each carbon in the ^{13}C NMR of the amides **1a**, **1b**, and **1c** indicated two isomers differing in the C–N amide bond geometry had been formed at this earlier step in the reaction. 1-[2-(Dimethylhydroxymethyl)pyrrolid-1-yl]propionic acid[11] (**1d**), prepared to maximize the population of a single ketene acetal conformer, did not exhibit these multiple resonances in the ^{13}C NMR. Formed by alkylation of the benzyl ether **1e** with methyl trifluoromethanesulfonate, **2e** was allowed to react with the lithium salt of (*E*)- or (*Z*)-2-buten-1-ol. The relative asymmetric induction was significantly improved. In addition, the internal asymmetric induction in the reaction of the *E* allylic alkoxides also improved; however, that observed for reaction of the *Z* allylic alkoxide remained modest.[15] Substitution of the benzyl group by the *tert*-butyldimethylsilyl protecting group had little effect on the stereochemistry of the rearrangement. Heating to 60 °C, to accelerate the rearrangement, diminished the asymmetric induction.

In order to explore the generality of proline-derived chiral auxiliaries in inducing relative asymmetry in amide acetal Claisen rearrangement, the amides **1b**, **1c**, **1e**, and **1f** were converted to the corresponding thioamides, **8**, by treatment with Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide.[16] The thioamides were treated with (*E*)- and



(*Z*)-1-bromobut-2-ene[17] followed by triethylamine. After 10–12 h at room temperature the products of the thioamide acetal Claisen rearrangement, **9**, were isolated. This procedure is in contrast to previously reported thioamide acetal Claisen rearrangements, which required alkylation of the lithium thioenolate followed by heating.[18] The rearranged thioamides were hydrolyzed to the amides[18a] and the amides treated with iodine; the relative asymmetric induction was determined by spectroscopic methods.



It was evident from the spectra that the sense of relative asymmetric induction had been reversed. The sense of the internal asymmetric induction was unchanged although the thioamides were generally less selective than the amides. Interestingly, the ^{13}C NMR spectra of the thioamides **8e** and **8f** both exhibited two sets of resonances for each carbon, suggesting that, in the case of the thioamides, even when the steric demand of the amide was increased, it was still possible to have two amide C–N isomers. Internal asymmetric induction seems to correlate with selectivity in formation of a single amide isomer; that is, under those conditions when apparently a single isomer was formed, the highest internal and relative asymmetric induction was observed.

Further studies of the steric effects on the efficiency of the chiral auxiliary, as well as preparation of new chiral auxiliaries, are in progress.

General Experimental Procedures

Thin-layer chromatography was performed with silica gel F_{254} (Merck) as the adsorbent on 0.2-mm-thick, plastic- or foil-backed plates. The chromatograms were visualized under UV, by staining with iodine or by spraying the plates with a solution of 5% phosphomolybdic acid in ethanol and then heating in an oven for 4–5 min at 140 °C. Column chromatography was performed as follows: Method A, flash chromatography, refers to the procedure of W. C. Still,[19] using either silica gel 60, 230–400 mesh (Merck), or Davisil, grade 633, 200–425 mesh. Method B refers to gravity chromatography with use of silica gel 60, 70–230 mesh (Merck), or Davisil, grade 62, 600–200 mesh. Bulb-to-bulb distillation refers to distillation with use of a Kugelrohr apparatus where the boiling point reported is the oven temperature.

1-[2(*S*)-[(Benzyloxy)methyl]pyrrolid-1-yl]propanoic Acid (1b). To a dry 100-mL, three-necked round-bottomed flask under an inert atmosphere was added 0.24 g (0.0098 mol) of sodium hydride (50% dispersion in mineral oil). After the sodium hydride was washed with pentane (3

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(14) For determination of relative asymmetric induction, a mixture of 0.001 mol of the amides **3–6** were converted to the iodo lactones according to ref 16. Separation by chromatography afforded the lactones derived from **3/4** or **5/6**. To a clean, dry NMR tube, containing 0.005–0.007 g (0.02–0.03 mmol) of the iodo lactones was added 0.5 mL of a $CDCl_3$ solution of either tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]praseodymium or -europium (0.010–0.012 g/mL) so that the concentration of the shift reagent was about 15–25 mol%. After the solution was shaken well, the relative asymmetric induction of the rearrangement was determined by integrating and comparing the signals assigned to the resolved pair of lactones **3** and **4** or **5** and **6**. In all cases the pair of lactones, which was derived from the major products of the rearrangement, was analyzed.

(15) Molecular mechanics with C. Still's MODEL package, version 2.7 by K. Steliou, clearly indicate that the *N,O*-ketone acetal geometry is strongly affected by the remote asymmetric center. Further studies on the effect of the asymmetric center on the transition-state geometry are in progress.

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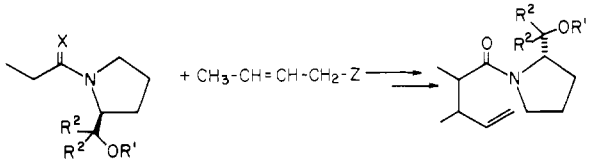
Table I. Asymmetric Induction in the Amide Acetal Claisen Rearrangement



R^1	R^2	X	Z	olefin geometry	int asym induction[a]	rel asym induction[b]
CH_2Ph	CH_3	OCH_3	OLi	*E*	15.5:1	6.4:1
CH_2Ph	CH_3	OCH_3	OLi	*Z*	1:3.0	4.7:1
$(CH_3)_3C(CH_3)_2Si$	CH_3	OCH_3	OLi	*E*	13.8:1	4.0:1
$(CH_3)_3C(CH_3)_2Si$	CH_3	OCH_3	OLi	*Z*	1:2.7	5.5:1
$(CH_3)_3C(CH_3)_2Si$	H	S	Br	*Z*	1:5.28	1:5.3
CH_2Ph	CH_3	S	Br	*E*	1.5:1	1:3.1
CH_2Ph	CH_3	S	Br	*Z*	1:4.7	1:5.6
$(CH_3)_3C(CH_3)_2Si$	CH_3	S	Br	*E*	1.7:1	1:2.5
$(CH_3)_3C(CH_3)_2Si$	CH_3	S	Br	*Z*	1:4.1	1:8.1

[a] Determined by gas chromatography, 25 m × 0.25 mm, OV-101 at 220 °C. [b] Determined by ^1H NMR spectroscopy on the lactones prepared from **3** and **4** or **5** and **6**, the major products of the rearrangement as shown under internal asymmetric induction.

× 3 mL), 20 mL of anhydrous THF was added and the suspension was cooled to 0 °C. The hydroxy amide **1a**,[11] 1.50 g (0.0096 mol) in 5 mL of anhydrous THF, was added dropwise at 0 °C followed by 0.35 g (0.000 96 mol) of tetrabutylammonium iodide and 1.2 mL (0.0097 mol) of benzyl bromide. The reaction mixture was stirred at room temperature for 3 h. Florisil, 2.0 g, was added, and the THF was removed in vacuo. The residue was extracted several times with pentane or hexanes. Concentration of hexanes yielded the crude product, which showed three spots on TLC (ethyl acetate); R_f 0.8, 0.4, and source. Chromatography (method A, ethyl acetate) afforded 1.85 g (79%) of pure **1b** as a pale yellow oil: R_f 0.38 (ethyl acetate); $[\alpha]^{23}_D$ −76.22° (*c* 4.6, CH_2Cl_2), $[\alpha]^{23}_D$ −88.10° (*c* 4.6, $CHCl_3$).

1-[2(*S*)-[[(*tert*-Butyldimethylsilyl)oxy]methyl]pyrrolid-1-yl]propanoic acid (1c): prepared after ref 11; $[\alpha]^{23}_D$ −59.05° (*c* 4.0, CH_2Cl_2) [lit.[11] $[\alpha]^{23}_D$ −63.40° (*c* 9.26, $CHCl_3$)].

1-[2(*S*)-(Dimethylhydroxymethyl)pyrrolid-1-yl]propanoic Acid (1d). To 17.3 g (0.066 mol) of *N*-propionylproline benzyl ester[11] in 600 mL of anhydrous THF was added 28.22 g (0.17 mol) of methylmagnesium iodide in 70 mL of anhydrous ether. The resulting mixture was stirred at room temperature for 3 h and then was quenched with saturated aqueous ammonium chloride. The mixture was partitioned between methylene chloride and water. The organics were dried over anhydrous $MgSO_4$ and concentrated in vacuo. Chromatography (method A, ethyl acetate) afforded 4.22 g (35%) of **1d** as a pale yellow oil, R_f 0.30 (ethyl acetate).

1-[2(*S*)-[Dimethyl(benzyloxy)methyl]pyrrolid-1-yl] Propanoic Acid (1e). To a dry 100-mL three-necked round-bottomed flask under an inert atmosphere was added 0.19 g (0.008 mol) of sodium hydride (50% dispersion in mineral oil). After it was washed with pentane, the sodium hydride was suspended in 50 mL of anhydrous THF. The mixture was cooled to 0 °C, and the hydroxy amide **1d**, 1.0 g (0.0054 mol), in 10 mL of anhydrous THF was added dropwise, followed by 0.02 g (0.000 054 mol) of tetrabutylammonium iodide and 0.96 mL (0.0081 mol) of benzyl bromide. The reaction mixture was heated under reflux for 7 days and then was cooled to room temperature. Florisil, 2.0 g, was added, and THF was removed in vacuo. The residue was extracted several times with methylene chloride. Concentration of methylene chloride in vacuo yielded 1.88 g of crude product, which showed three spots on TLC (ethyl acetate); R_f 0.76, 0.50, and 0.28. Purification by chromatography (method B, ethyl acetate) yielded 0.75 g (83%, based on recovered hydroxy amide) of **1e**: R_f 0.48 (ethyl acetate); $[\alpha]^{23}$ D −63.75° (*c* 4.0, CH_2Cl_2).

1-[2(*S*)-[Dimethyl[(*tert*-butyldimethylsilyl)oxy]methyl]pyrrolid-1-yl]-propanoic acid (1f): prepared after ref. 11; $[\alpha]^{23}_D$ −50.77° (*c* 5.2, CH_2Cl_2).

General Method for the Preparation of 2. To 0.001 mol of **1b**, **1c**, **1e**, or **1f** at room temperature was added dropwise with stirring 0.14 mL (0.0012 mol) of methyl triflate. The mixture was allowed to stir at room temperature for 30 min and washed with pentane (3 × 3 mL). The pentane layer was decanted from the reaction flask with the aid of a disposable pipet. The last traces of pentane were removed in vacuo to obtain the crude salts in quantitative yield.

Typical Procedure for Amide Acetal Claisen Rearrangement. To 10 mL of anhydrous THF containing 0.0035 mol of methyllithium (1.55 M in diethyl ether) and 0.003 mol of (*E*)- or (*Z*)-2-buten-1-ol under an inert atmosphere was added **2** (0.001 mol) in 5 mL of THF. The mixture was allowed to stir at room temperature until there was no change in the ratio of products to starting amide as determined by gas chromatography. The products **3e**, **4e**, **5e**, and **6e**, as well as **3f**, **4f**, **5f**, and **6f**, were separable by gas chromatography (220 °C) and were formed in a ratio in agreement with the optical purity as determined in ref 14. The reaction mixture was diluted with 20 mL of methylene chloride, was washed with saturated aqueous sodium bicarbonate (3 × 20 mL) and 20 mL of brine, was dried over anhydrous magnesium sulfate, and was concentrated in vacuo to yield the crude product.

General Methods for the Preparation of Thioamides 8. A mixture of 0.01 mol of the amide and 0.005 mol of 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent, Aldrich) in 10 mL of anhydrous toluene (dried over sodium) was kept at 100 °C for 12–16 h. The toluene was removed in vacuo and the residue extracted several times with hexane–ether (1:1). The crude product, obtained by concentration of the hexane–ether phase in vacuo, was purified by chromatography (method B, methylene chloride).

1-[2(*S*)-[(Benzyloxy)methyl]pyrrolid-1-yl]thiopropanoic Acid (8b). A mixture of 4.15 g (0.017 mol) of **1b** and 3.4 g (0.0084 mol) of Lawesson's reagent in 17 mL of anhydrous toluene gave on purification (method B, methylene chloride) 3.50 g (78%) of pure **8b** as a yellow oil, $[\alpha]^{23}_D$ −82.2° (*c* 4.0, CH_2Cl_2).

1-[2(*S*)-[[(*tert*-Butyldimethylsilyl)oxy]methyl]pyrrolid-1-yl]thiopropanoic Acid (8c). From the reaction between 2.71 g (0.01 mol) of the amide **1c** and 2.03 g (0.005 mol) of Lawesson's reagent, 1.75 g (61%) of pure thioamide **8c** was obtained on chromatography (method B, methylene chloride): R_f 0.44 (ethyl acetate–hexanes, 1:4); $[\alpha]^{23}_D$ −53.43° (*c* 4.2, CH_2Cl_2).

1-[2(*S*)-[Dimethyl(benzyloxy)methyl]pyrrolid-1-yl]thiopropanoic Acid (8e). Reaction between 4.13 g (0.015 mol) of amide **1e** and 3.04 (0.0075 mol) of Lawesson's reagent in 15 mL of dry toluene yielded after purification (method B, methylene chloride) 2.1 g (48%) of pure thioamide **8e** as a dark yellow oil: R_f 0.38 (ethyl acetate–hexanes, 1:4); $[\alpha]^{23}_D$ −58.50° (*c* 4.4, CH_2Cl_2).

1-[2(*S*)-[Dimethyl[[(*tert*-butyldimethylsilyl)oxy]methyl]pyrrolid-1-yl]thiopropanoic Acid (8f). Reaction between 1.5 g (0.005 mol) of **1f** and 1.01 g (0.0025 mol) of Lawesson's reagent in 5 mL of toluene gave on purification with methylene chloride (method B) 1.32 g (84%) of pure **8f** as a pale yellow oil: R_f 0.53 (ethyl acetate–hexanes, 1:4); $[\alpha]^{23}_D$ −40.71° (*c* 4.2, CH_2Cl_2).

General Method for the Preparation of S-Alkylated Thioamides. A mixture of 0.001 mol of the thioamide and 0.0011 mol of (*E*)- or (*Z*)-1-bromo-2-butene[17] was stirred at room temperature for 30 min for the (*Z*)-olefin to 1 h for the (*E*)-olefin. The excess bromoalkene was removed in vacuo to afford the S-alkylated product in quantitative yields.

Typical Procedure for Thioamide Acetal Claisen Rearrangement. To a solution of 0.001 mol of the S-alkylated thioamide in 10 mL of dry methylene chloride was added 0.21 mL (0.0015 mol) of dry triethylamine. The progress of the reaction was monitored by GC. When the ratio of the product to starting thioamide did not increase further, the reaction mixture was washed with 2% citric acid (2 × 10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give the crude product.

Typical Procedure for the Conversion of the Rearranged Thioamides to Amides.[18a] To a solution of 0.001 mol of the rearranged thioamides in 10 mL of 50% aqueous THF was added 1.42 g (0.01 mol) of iodomethane and 0.28 g (0.002 mol) of K_2CO_3. The mixture was stirred overnight at room temperature and was diluted with 20 mL of methylene chloride. The organic layer was washed with water (2 × 2 mL) and dried

over anhydrous $MgSO_4$. Concentration in vacuo afforded the crude amides, **3**/**4** and **5**/**6**.

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Supplementary Material Available: Complete spectral data for all new compounds (11 pages). Ordering information is given on any current masthead page.

Synthesis and Chiroptical Properties of γ-Substituted Rigid and Conformationally Flexible Systems Having 1,3-Diene and α,β-Unsaturated Carbonyl Chromophores. The Planar Diene Rule

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Abstract: The syntheses of chiral (*aS*)-(5-hydroxyadamantylidene)- and (*aS*)-(5-methyladamantylidene)acetaldehyde and the corresponding adamantylidenepropene (rigid system) as well as (*aS*)-(4-hydroxycyclohexylidene)acetaldehyde and (*aS*)-(4-hydroxycyclohexylidene)propene (flexible system) are described. The effects of the γ-hydroxy and γ-methyl substituents on the π–π* Cotton effects of both systems are discussed as is the application of the "planar diene rule" to these systems. The adamantyl system provides a means to directly determine $\delta(\Delta\epsilon)$ for an equatorial substituent, which in turn can be used to determine the contribution that an axial substituent makes to the $\Delta\epsilon$ of a conformationally mobile system.

In recent papers from this laboratory the chiroptical properties of substituted cyclohexylidenepropenes and related trienes and α,β-unsaturated carbonyl compounds have been reported.[1] On the basis of experimental data a simple sector rule was proposed for the planar transoid diene chromophore attached to the cyclohexylidene moiety (Figure 1).

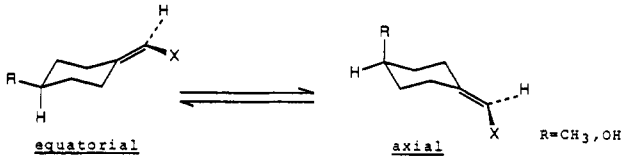
The "planar diene rule" was applied successfully to numerous methyl-substituted cyclohexylidenepropenes and structurally related α,β-unsaturated aldehydes.[1] This rule relates the sign of the long-wavelength π–π* transition in cyclohexylidene-substituted planar *s-trans*-butadienes and planar *s-trans*-acroleins with their absolute configuration.

The characteristic feature of these systems (Figure 1) is the presence of a transoid chromophore and a cyclohexane ring in a chair conformation, in which the 4-methyl (γ) substituent occupies (>95%) an equatorial position. As it is the methyl substituent which defines the chirality of the system, the following questions arise: (1) is the effect of the strong predominance of ring conformation with equatorial methyl substituent responsible for the observed rotatory power of the system (Scheme I) and (2) is the optical activity of the system influenced by the nature of the substituent in a cyclohexylidene ring?

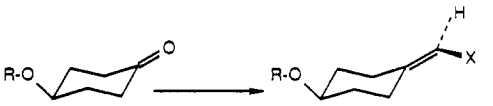
We have previously studied the conformationally flexible system substituted with a methyl group in the γ-position[1] and we have now selected, for comparison, the polar hydroxy group (R = OH) (Scheme I). Moreover, at equilibrium, the hydroxyl group has been shown to exist less in the equatorial position than the methyl group.[2] The standard free energy change, $\Delta G°_{25}$, for methylcyclohexane is 1.7 kcal/mol and for cyclohexanol it is 0.5 kcal/mol.[2,3] These values equate to approximately 95% equatorial for the methyl group and 70% for the hydroxyl group. The "flexible system" molecules that we have selected for investigation are the 4-hydroxycyclohexylidene derivatives **5**, **7**, **9**, and **11** (Scheme II).

In order to establish the nature of the effect displayed by the chirality-defining substituent (R in Figure 1), it was also necessary

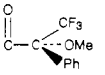
Scheme I



Scheme II



1, R = H
2, R = $SiMe_2$-*t*-Bu

no.	R	X	abs config
3	$SiMe_2$-*t*-Bu	COOH	(*aS*)-(+)
4	$SiMe_2$-*t*-Bu	COOMe	(*aS*)-(+)
5	H	COOMe	(*aS*)-(−)
6	$SiMe_2$-*t*-Bu	CHO	(*aS*)-(+)
7	H	CHO	(*aS*)-(−)
8	$SiMe_2$-*t*-Bu	$CH{=}CH_2$	(*aS*)-(−)
9	H	$CH{=}CH_2$	(*aS*)-(+)
10	$SiMe_2$-*t*-Bu	COMe	(*aS*)-(+)
11	H	COMe	(*aS*)-(−)
12		COOMe	

to obtain a conformationally rigid system with high symmetry for comparison. An interesting system which meets these criteria is the adamantane structure. This system has previously been explored by, inter alia, Djerassi,[4] Snatzke,[5] and Lightner[6] in their

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(3) Bushweller, C. H.; Beach, J. A.; O'Neil, J. W.; Rao, G. V. *J. Org. Chem.* **1970**, *35*, 2086.

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