Hexafluoroacetone (12 g, 0.072 mol) and 20.4 g (0.06 mol) of triphenylphosphine selenide were sealed in a glass tube and heated at 150 °C for 5 h. The mixture was steam distilled and the pale yellow diselenetane was filtered from the distillate and recrystallized from pentane to give 10.0 g (73%): mp 59.2–60 °C; mp 60 °C, bp 138 °C, by differential thermal analysis; ^{19}F NMR (CCl_4) −70.5 ppm (s); mass spectrum, m/z 459.8142 (parent), other peaks corresponding to $C_6F_{11}Se_2$, $C_5F_9Se_2$, C_3F_6Se, C_3F_5Se, C_2F_3Se, C_2F_2Se, CF_3. The compound is very volatile, and some escapes with boiling pentane.

Anal. Calcd for $C_6F_{12}Se_2$: C, 15.73; Se, 34.47; M_r, 458. Found: C, 15.67; Se, 34.24; M_r 467 (cryoscopic in benzene).

2,4-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-diselenetane (5). Bis(trifluoromethyl)ketene[11] (14 g, 0.08 mol), 24 g (0.07 mol) of triphenylphosphine selenide, and 20 mL of dichloromethane were heated in a sealed glass tube at 100 °C for 15 h. The product was steam distilled and taken up in additional dichloromethane. After being dried ($MgSO_4$), the solution was concentrated to crystallization and 2.67 g (15.8%) of the diselenetane was filtered off: mp 88–89 °C; mp 89 °C, bp 186 °C, by differential thermal analysis; IR 1595, 1626 (d, C=C) cm^{-1}; ^{19}F NMR (CCl_4) −59.6 ppm (s).

Anal. Calcd for $C_8F_{12}Se_2$: C, 19.93; Se, 32.77; M_r 482. Found: C, 20.25; Se, 32.22; M_r 490 (cryoscopic in benzene).

The yields were about the same when the reaction was carried out in benzene at 150 °C and without solvent at 200 °C.

Registry No. 4, 36827-57-3; 5, 74036-94-5; triphenylphosphine selenide, 3878-44-2; hexafluoroacetone, 684-16-2; bis(trifluoromethyl)ketene, 684-22-0.

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Dissymmetric Chromophores. 5.[1] Synthesis and Circular Dichroism of Chiral 3-Methylenebicyclo[2.2.1]heptan-2-ones

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Chiral α,β-unsaturated ketones which exhibit skew-dependent Cotton effects[2,3] in their optical rotatory dispersion spectra were classified in 1962[2] as inherently dissymmetric chromophores.[4] Subsequently, there appeared various empirically derived modified octant[5] and chirality rules[5,6] which attempted to provide predictive correlations between Cotton effect (CE) signs associated with the erstwhile $\pi-\pi^*$ and $n-\pi^*$ (K and R band) electronic transitions and relevant aspects of molecular geometry.[7,8] Thus, the CE sign of the long wavelength $n-\pi^*$ (R band) transition is thought to be determined largely by the inherent chirality of the skewed enone chromophore,[7,9] but the sign-determining criteria for the short wavelength CEs are less well understood. It was first postulated that the $\pi-\pi^*$ (K band) transition CE was determined by the inherent chirality of a transoid enone.[2] That notion was marshalled later[7,9] and extended to cisoid enones.[7,10] Simultaneously it was shown that allylic and homoallylic axial bond contributions can control the CE sign of the short wavelength transition;[6,8,10] however, the relative importance of those contributions depends critically on whether the enone assumes a transoid or a cisoid configuration.[7,8,11] Only a small number of cisoid α,β-unsaturated ketones have been studied, and those are limited to steroids[5-8,12] with only a few exceptions, e.g., (+)-methylenecamphor[10,13,14] and 3-ethylidenecamphor.[10] The latter compounds are of special interest because they appear to have an essentially planar enone chromophore. We surmise, therefore, that they should be good systems to aid in educing the nature and importance of allylic and homoallylic bond chirality effects on the sign and magnitude of the CE. In this work we present the syntheses and circular dichroism (CD) data for simple, structurally rigid cisoid α,β-unsaturated ketones: (1*R*)-3-methylenenorcamphor (**1**), (1*R*)-3-methylene-α-fenchocamphorone (**2**), (1*R*)-3-methylenecamphor (**3**), (1*R*)-2-methyleneepicamphor (**4**), and (1*R*)-3-isopropylidenecamphor (**9**).

Synthesis and Stereochemistry. The synthesis of **1** proceeded smoothly in two steps from the known,[15] chiral (−)-(1*R*)-bicyclo[2.2.1]heptan-2-one (**5**) [44.5% enantiomeric excess (e.e.)] by the method of Adams and Vaughan,[16] who reacted (±)-norcamphor with formaldehyde/piperidine hydrochloride and then pyrolyzed the resultant 3-(piperidinomethyl)norcamphor hydrochloride. The enone (**1**) produced presumably retains the same (44.5%) e.e. as its precursor **5**. Enone **2** was prepared by reaction of α-fenchocamphorone[17] (**6**) with lithium diisopropylamide and treatment of the resulting lithium enolate with chloromethyl ether followed by base-catalyzed elimination of methoxide. Since **6** was prepared stereospecifically from (+)-camphor (**7**), we assume it has the same (100%) e.e. The synthesis of **3** or **4** could be achieved from **7** or **8**, respectively, in the same manner as the conversion of **6** to **2**. Alternatively, **3** was prepared from the 3-hydroxymethylene derivative of **7**, and **8** was prepared by SeO_2 oxidation of the methylene Wittig product of **7**. Isopropylidene derivative **9** was prepared first by quenching camphor zinc enolate with acetone followed by $SOCl_2$–pyridine catalyzed elimination of the alcohol. Since **3**, **4**, and **9** originate from (100% e.e.) **7**, we assume that they too have the same (100%) e.e.

Molecular Structure, Nuclear Magnetic Resonance, and Circular Dichroism Spectra. The ^{13}C NMR spectra of α,β-unsaturated ketones **1-4**, **9**, and pulegone and those of the parent bicyclic ketones (**5–8**) and

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Table I. ^{13}C Nuclear Magnetic Resonance Chemical Shifts[a] and Assignments for α,β-Unsaturated Ketones and Related Bicyclic Ketones and Their Derivatives

carbon	1	2	3	4[b]	5, X = O;[c] X = CH_2[c]	6, X = O;[c] X = CH_2[c,d]	7, X = O;[c] X = CH_2[c,d]	8[b]	9	pulegone[e,f]
1	49.1	58.3	57.7	58.9	49.7	58.1	57.5	60.2	58.6	50.7
2	205.7	204.1	207.3	205.3	217.4	156.2	218.7	216.7	207.8	199.1
3	150.0	150.9	150.3	154.0	45.1	37.7	43.2	49.2	136.9	131.7
4	42.5	51.4	51.4	51.3	35.3	45.2	43.1	45.6	49.4	28.5
5	28.1	27.6	26.9	(22.3)	27.1	(29.0)	27.1	34.2[g]	(25.3)	32.8
6	23.6	(23.7)	29.9	(34.1)	24.2	(28.7)	29.9	21.7	(30.4)	31.5
7	36.8	44.2	45.6	45.5	37.6	46.2	46.6	46.1	45.7	21.7
8	111.6	119.4	112.2	110.4	101.8	103.4	101.6		141.3	141.5
a		20.0	18.1	17.2		20.7	19.1	17.2	18.6	
b		(23.6)	20.5	20.3		21.6	19.8	19.1	20.2	
c			9.2	11.8		21.8	9.2	14.5	9.5	
d									20.2	22.0
e									22.8[h]	22.9

[a] Measured in $CDCl_3$, and reported in parts per million downfield from tetramethylsilane. [b] Measurements were performed on the enantiomer of the structure drawn. [c] Data and assignments from J. B. Stothers, C. T. Tan, and K. C. Teo, *Can. J. Chem.*, **51**, 2893 (1973). [d] Dioxane solvent. [e] Data and assignments from L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, 1972, no. 399. [f] Numbering system adjusted to correspond to that of other enones in this table. [g] In the spectrum of α-*exo*-deuterioepicamphor, this signal is broadened relative to that of C-6, and it is broader than that of C-5 in **8**. [h] This quartet becomes a singlet and its signal is enhanced (NOE) when the ^1H NMR signal at δ 2.10 (CH_3) is irradiated.

Table II. Reduced Rotatory Strengths and Circular Dichroism Transition Maxima for α,β-Unsaturated and Parent Ketones Measured in Methylcyclohexane at 22 °C

compd	λ, nm	$[R]^a$	compd	λ, nm	$[R]^a$
1	346	+3.94	5	305	+1.35
	228	+12.3			
	195	−1.41			
2	346	+3.81	6	304	+6.76
	230	+11.4			
	194	−1.59			
3	344	+2.69	7	302	+4.97
	228	+11.0			
	196	−1.63			
4	346	−3.44	8	307	−4.83
	228	−11.9			
	196	+1.18			
9	340	+1.48			
	247	+17.8			
	205	−1.73			

[a] Reduced rotatory strength values are corrected to 100% e.e. and were determined by graphical integration.

their exomethylene derivatives are presented in Table I. Conjugation produces the expected effect of shifting the $^{13}C{=}O$ resonances to higher field, whereas the α and β carbons of the conjugated enone are similarly shifted to higher and lower fields, respectively, as has been noted in related examples. The $^{13}C{=}O$ resonances of **1**–**4** and **9** are all very similar with the nearly identical values (δ 207.3 and 207.8 for **3** and **9**, respectively) appearing somewhat more downfield than those of **1**, **2**, and **4** due to the presence of a methyl group (c) at C-1. We believe that the strongly coincident $^{13}C{=}O$ resonances are consistent with an essentially coplanar cisoid enone chromophore in each case. This is an especially interesting conclusion to reach for **9** which exhibits considerable steric crowding of the syn (e) CH_3 and C=O groups. Apparently the bicyclic skeleton is too inflexible to permit the expected distortion consequent with relief of the (e) CH_3 and C=O steric compression. Consistent with such crowding in **9** are the ^{13}C and ^1H NMR chemical-shift differences between the isopropylidene CH_3 groups of **9**: C(e) δ 22.8 and C(d) δ 20.2 and CH_3(e) δ 2.10 and CH_3(d) δ 1.76. The ^{13}C(e) and CH_3(e) resonances of pulegone are similarly shifted and probably represent the time-average values associated with facile torsional isomerization about the C_2–C_3 bond. The syn (e) CH_3 group protrudes into a strong C=O deshielding area. Similarly, the *exo*-methylene protons of **1**–**4** are well-separated in the ^1H NMR by entry of the syn hydrogen into the C=O deshielding area: (**1**) δ 5.48 vs. 5.02, (**2**) δ 5.65 vs. 5.05, (**3**) δ 5.68 vs. 5.02, (**4**) δ 5.72 vs. 4.91.

Circular dichroism spectra of **1**–**4** are presented in Figure 1; structures and rotatory strength [*R*] data are found in Table II. As noted in Table II, the magnitudes of *R* for **1**–**4** are of the order of 10^{-40}, values more consistent with those of inherently symmetric chromophores[3] than with those of inherently dissymmetric chromophores ($R \sim 10^{-38}$ cgs).[3] This is true even for the more sterically crowded isopropylidene derivative **9**, which exhibits qualitatively

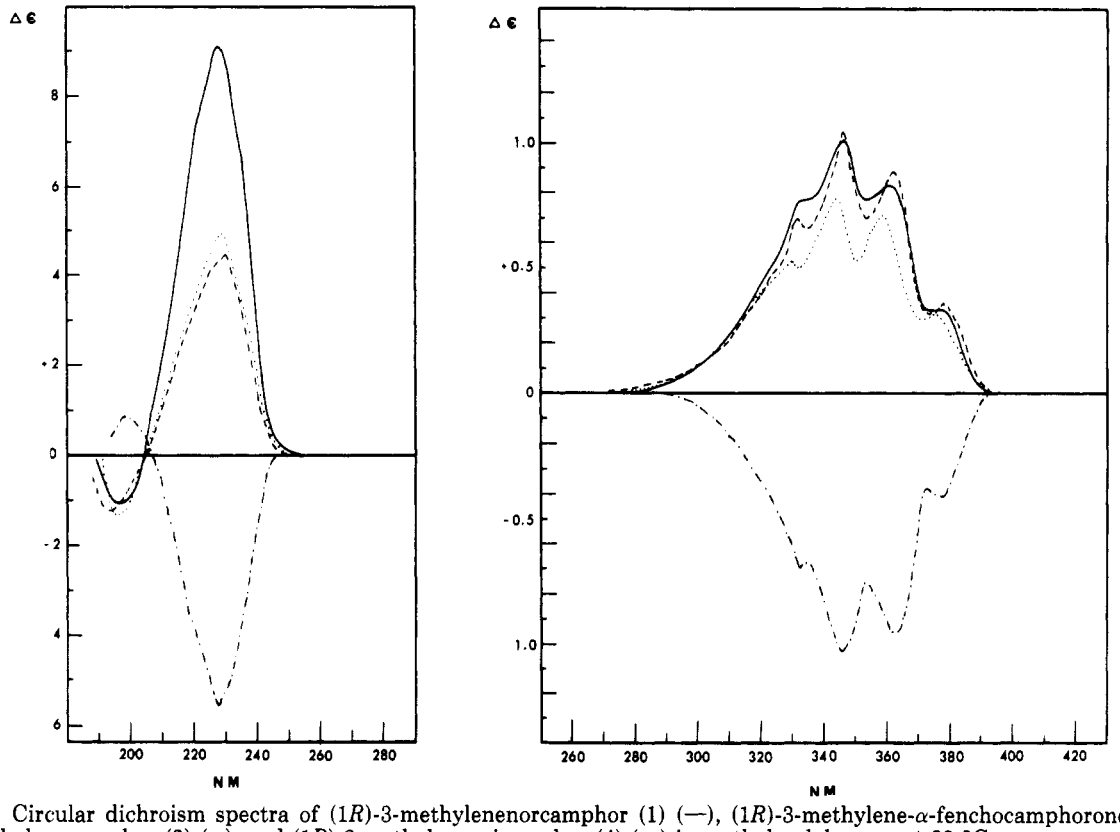

Figure 1. Circular dichroism spectra of (1*R*)-3-methylenenorcamphor (1) (—), (1*R*)-3-methylene-α-fenchocamphorone (2) (---), (1*R*)-3-methylenecamphor (3) (···), and (1*R*)-2-methyleneepicamphor (4) (-·-) in methylcyclohexane at 22 °C.

similar CD data. Thus, any contributions from skewed chirality are necessarily of the order of those emanating from extrachromophoric perturbers. Comparison of the long wavelength (R band) CD transitions of **1–4** and **9** to the corresponding n–π* transitions of parent ketones **5–8** is especially revealing: the CE signs are correspondingly the same and the magnitudes are rather similar. Differences in the magnitudes of the long wavelength CEs between the parent ketone and its α,β-unsaturated analogue may reflect contributions from the skewed chiral chromophore and/or differences between octant[18] and axial allylic bond contributions.

If one assumes that the C=C and C=O groups are essentially coplanar, the observed CEs must arise from extrachromophoric perturbations. By comparing the R and K band CEs of **1** and **2**, it is tempting to conclude that the *gem*-dimethyl group makes only a small negative (~–0.1) contribution to the reduced rotatory strength of the R band but a much larger negative (~–1) contribution to the K band. Curiously the *gem*-dimethyl group has a large (+) influence on the n–π* CE of saturated alkyl analogues, cf. **5** and **6**. It is as yet unclear whether the major source of perturbation in either case arises from the syn or the anti CH_3. An estimate of the contribution of the nearly in plane C_{10}–CH_3 group can be made by comparing the [*R*] values of **2–4**. When α to the C=O, the C_{10}–CH_3 appears to make a negative contribution (~–1.1) to the R band, and when it is α to the C=C, it makes a smaller positive contribution (~+0.4). A parallel behavior is exhibited on the n–π* CEs of **6–8**. Contributions to the reduced rotatory strength of the K band are also small and depend on location. When the CH_3 group is α to the C=O, it makes a small (–) contribution (~–0.4), but when it is α to the C=C, it makes a positive (~+0.5) contribution. Thus, the extrachromophoric CH_3 groups in α,β-unsaturated ketones **2–4** behave in a way qualitatively similar to those of saturated ketones **6–8**. We assume that the ring carbons do likewise since the long wavelength CE signs correlate one-for-one with the pairs of skeletally equivalent ketones, e.g., **1** and **5**, **2** and **4**.

In conclusion, it would appear that the R band CE of planar cisoid α,β-unsaturated ketones **1–4** is governed largely by ring-atom contributions, probably of the axial allylic type suggested by Burgstahler and Naik,[10] with C_4–C_5 bond contributions dominating. The R band also displays a curious sensitivity toward the extrachromophoric CH_3 lying in the plane of the C=C and C=O groups and a surprising insensitivity toward out of plane homoallylic groups (*gem*-dimethyl). The R band of **9** presumably is also governed by these factors in addition to the expected allylic CH contributions from the isopropylidene group. Application of the octant rule[4,17] would have predicted the observed CE sign. The K band is largely insensitive to extrachromophoric CH_3 perturbers lying outside the ring skeleton, and its CE sign is probably also determined by axial allylic bond contributions, as noted above.

Experimental Section

Circular dichroism (CD) spectra were obtained on a JASCO J-40 automatic recording spectropolarimeter equipped with a photoelastic modulator and PAR lock-in amplifier. ^1H nuclear magnetic resonance spectra and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer and are presented in Table I along with assignments. All NMR spectra (^1H and ^{13}C) are recorded in $CDCl_3$, unless otherwise indicated, in δ units (parts per million from an internal standard tetramethylsilane). Infrared (IR) spectra were recorded in CCl_4 unless otherwise indicated on a Perkin-Elmer Model 599 instrument. Ultraviolet (UV) spectra were collected on either a Cary Model 219 or a Beckman Model 25 spectrophotometer. Rotations were run in $CHCl_3$ unless otherwise specified on a Perkin-Elmer Model 141 polarimeter. Mass spectral data were collected on a JEOL JMS-07 mass spectrometer. Preparative gas chromatography was performed

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on a Varian Aerograph Series 1700 T/C instrument, using column A ($^3/_8$ in. × 6 ft 15% Carbowax 20M on Chromosorb W, AW-DMCS), column B ($^3/_8$ in. × 6 ft 10% SE-30 on Chromosorb W, AW-DMCS), or column C ($^3/_8$ in. × 9 ft 14% TCEP on Chromosorb P). Analytical gas chromatography was performed on a Varian Aerograph Series 2400 F/I instrument with column D ($^1/_8$ in. × 6 ft 5% SE-30 on Chromosorb W, AW-DMCS). Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Combustion microanalysis were determined by Chemalytics (Tempe, AZ). All solvents for UV and CD measurements were Eastman spectro-grade. Dry tetrahydrofuran and diethyl ether were obtained by first distilling from CaH_2 and redistilling from lithium aluminum hydride (LAH). Dry dimethyl sulfoxide was obtained by distillation from CaH_2. Column chromatography was carried out with neutral alumina (Woelm, Eschwege).

(+)-α-Methylenenorcamphor (1). In a 50-mL round-bottom flask equipped with a reflux condenser, 5 g (45 mmol) of (−)-norcamphor,[15] $[\alpha]^{22}_D$ −15.8° (*c* 0.10), was combined with 2.5 g (31 mmol) of piperidine (Aldrich) and 6 mL of a 37% aqueous formaldehyde solution. To the rapidly stirred solution was added 4.6 mL of concentrated HCl dropwise and the resulting solution stirred for 22 h at reflux. The solution was then cooled and extracted with diethyl ether (2 × 25 mL). The aqueous phase was concentrated in vacuo until crystals were deposited. The crystalline material was collected by suction filtration and recrystallized from isopropyl alcohol to give 2.15 g (20%) of a white solid, mp 210 °C [lit.[16] mp 198–199 °C]. The solid was pyrolyzed at 260 °C in a Woods metal bath with concomitant distillation of a brown oil. The oil was collected in 50 mL of diethyl ether, washed with 2% aqueous H_2SO_4 (2 × 5 mL), saturated aqueous $NaHCO_3$ (2 × 5 mL), and H_2O (2 × 5 mL), and dried over $MgSO_4$, and the ether was evaporated. Preparative gas chromatography on column A provided 800 mg (74%) of pure 1: $[\alpha]^{22}_D$ +143° (*c* 0.74); ^1H NMR δ 5.48 (s, 1 H), 5.02 (s, 1 H), 3.1 (s, 1 H), 1.63 (m, 6 H); IR ν 2988, 2893, 1740, 1654 cm^{-1}; mass spectrum, *m/e* (relative intensity) 122 (81% M^+), 93 (93%), 91 (21%), 79 (100%), 77 (35%); UV (methylcyclohexane) ϵ_{347} = 40, ϵ_{235} = 9074; CD (methylcyclohexane) $\Delta\epsilon_{346}$ = +1.05, $\Delta\epsilon_{228}$ = +9.09, $\Delta\epsilon_{195}$ = −1.23.

(+)-α-Methylene-α-fenchocamphorone (2). In an oven-dried 25-mL round-bottom flask fitted with a rubber stopper were placed 5 mL of dry THF and 0.66 mL (5.0 mmol) of diisopropylamine under N_2. The magnetically stirred solution was cooled to 0 °C in an ice bath and 1.96 mL of a 2.4 M solution of *n*-BuLi in hexane (MCB) was added dropwise by syringe. The solution was then allowed to stir for 10 min at 0 °C, and then 0.5 g (3.8 mmol) of α-fenchocamphorone (**6**,[17] $[\alpha]^{22}_D$ +67.5° (*c* 0.021, EtOH)) was added as a solution in 2 mL of dry THF. The mixture was cooled to −78 °C and 0.55 mL of chloromethyl ether was added, after which the cooling bath was removed and the mixture stirred 1.5 h at room temperature. The solution was then poured into 10 mL of saturated aqueous NH_4Cl and extracted with pentane (2 × 20 mL). The pentane solution was washed with distilled water (1 × 5 mL), dried over $MgSO_4$, and evaporated under reduced pressure to give a clear oil. The oil was taken up in 2 mL of methanol and stirred with 0.2 g of KOH for 1 h. The methanol solution was diluted with 10 mL of distilled water and extracted with pentane. The pentane was washed with distilled water (3 × 20 mL), dried over $MgSO_4$, and evaporated. An analytical sample was prepared by preparative gas chromatography (column A): $[\alpha]^{23}_D$ +170° (*c* 0.09); ^1H NMR δ 5.65 (s, 1 H), 5.05 (s, 1 H), 2.50 (m, 1 H), 1.1 (s, 3 H), 1.05 (s, 3 H); IR ν 3091, 2980, 2894, 1743, 1655, 1479, 1455, 1250, 1085, 930 cm^{-1}; mass spectrum, *m/e* (relative intensity) 150 (100%, M^+), 135 (50%), 108 (50%), 107 (82%), 93 (40%), 91 (32%), 81 (64%), 79 (79%); UV (methylcyclohexane) ϵ_{344} = 40, ϵ_{227} = 12 300; CD (methylcyclohexane) $\Delta\epsilon_{347}$ = +1.14, $\Delta\epsilon_{230}$ = +4.52, $\Delta\epsilon_{194}$ = −1.21.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.94; H, 9.39. Found: C, 80.08; H, 9.17.

(+)-(1*R*,4*S*)-1,7,7-Trimethyl-3-methylenebicyclo[2.2.1]heptan-2-one (α-Methylenecamphor) (3). This substance was prepared from (+)-*d*-camphor (J. T. Baker), $[\alpha]_D$ +41.3° (*c* 0.081), according to the published procedure.[13] It was >99.9% pure by analytical GC (column D): $[\alpha]_D$ +104.6° (*c* 3.54); ^1H NMR δ 5.68 (s, 1 H), 5.02 (s, 1 H), 2.53 (m, 1 H), 0.95 (s, 6 H), 0.80 (s, 3 H); IR ν 2989, 1730, 1652, 1480, 1455, 1010, 939 cm^{-1}; mass spectrum, *m/e* (relative intensity) 164 (68%, M^+), 149 (45%), 136 (13%), 135 (12%), 121 (100%), 106 (41%), 95 (52%); UV (methylcyclohexane) ϵ_{344} = 40, ϵ_{227} = 9115; CD (methylcyclohexane) $\Delta\epsilon_{344}$ = +0.81, $\Delta\epsilon_{228}$ = +4.99, $\Delta\epsilon_{196}$ = −1.47.

(−)-(1*S*,4*R*)-4,7,7-Trimethyl-3-methylenebicyclo[2.2.1]heptan-2-one (α-Methyleneepicamphor) (4). 2-Methylenebornane[19] was prepared from (+)-camphor (J. T. Baker, $[\alpha]_D$ +41.3° (*c* 0.081)) in 54% yield (sublimed, 65 °C) and used in the following reaction. 2-Methylenebornane (1 g, 6 mmol) prepared above was dissolved in 12 mL of acetic anhydride and magnetically stirred with 1.6 g (14 mmol) of SeO_2 (J. T. Baker) at reflux for 16 h. The solution was cooled and selenium precipitated by addition of 50 mL of diethyl ether. The ether solution was removed by pipet, transferred to a 250-mL beaker, and magnetically stirred while small portions of saturated aqueous $NaHCO_3$ solution were added until all acidic material was quenched. The ether solution was separated, washed with H_2O (3 × 25 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The crude material was subjected to a rough sublimation to remove high molecular weight organoselenium compounds and purified by preparative gas chromatography (column B). White crystalline material (122 mg) was obtained which contained an anomalous UV band at 280 nm. The material was adsorbed on 10 g of activity I neutral alumina and eluted with 1:9 chloroform–pentane to give 100 mg of pure **4**: $[\alpha]_D$ −102° (*c* 8.8); ^1H NMR δ 5.72 (s, 1 H), 4.91 (s, 1 H), 2.5 (d, 1 H), 1.09 (s, 3 H), 0.95 (s, 3 H), 0.86 (s, 3 H); IR ν 2985, 2889, 1737, 1653, 1472, 1455, 1395, 1160, 930 cm^{-1}; mass spectrum, *m/e* (relative intensity) 164 (59%, M^+), 149 (43%), 121 (100%), 107 (42%), 95 (63%), 83 (37%), 79 (48%); UV (methylcyclohexane) ϵ_{346} = 36, ϵ_{227} = 6651; CD (methylcyclohexane) $\Delta\epsilon_{346}$ = −1.04, $\Delta\epsilon_{228}$ = −5.54, $\Delta\epsilon_{196}$ = +0.92.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.76. Found: C, 80.09; H, 9.50.

(+)-(1*R*,4*S*)-1,7,7-Trimethyl-3-isopropylidenebicyclo[2.2.1]heptan-2-one (9).[20] To a solution of 0.85 mL (6 mmol) of diisopropylamine in 5 mL of dry THF containing a few milligrams of 2,2′-bipyridyl was added 2.5 mL of 2.4 M *n*-butyllithium in hexane under argon at −40 °C. To this solution was added a solution of 761 mg (5 mmol) of (+)-camphor, $[\alpha]_D$ +41.3° (*c* 0.081), in 2.5 mL of dry THF at −20 °C, followed by addition of 5 mL of 1.23 M anhydrous $ZnCl_2$ in dry THF at −10 °C and then 0.74 mL (10 mmol) of dry acetone at 0 °C. The solution was stirred at room temperature for 1.5 h and then extracted with Et_2O/pentane on saturated NH_4Cl/saturated NaCl. The extracts afforded 1.1 g of an oil which was distilled at 85–90 °C (1.6 mmHg) to remove unreacted camphor. The distillate (665 mg) was a mixture of exo/endo (ca. 9:1) aldol[20,21] product contaminated with some unreacted camphor, according to GC (column D). It solidified in the refrigerator.

A sample of the exo aldol[21] product, mp 87–88 °C, was obtained by crystallization from pentane (CMe_2OH signal appeared at δ 1.17 in CCl_4); GC rentention time 9.7 ± 0.1 min, column D. A solution of 605 mg of the aldol product in 5 mL of CH_2Cl_2 and 1 mL of dry pyridine was treated slowly with 0.3 mL of $SOCl_2$. After 0.5 h at room temperature, the mixture was extracted with pentane–saturated NaCl to give 548 mg of the crude product. This was purified by column chromatography on activity II silica gel. Elution with pentane–1% Et_2O gave 300 mg (31% overall yield) of the isopropylidene derivative (purity 98%+), followed by the mixture of mesityl oxide and 2-propene derivative of camphor (no camphor was eluted). Isopropylidenecamphor was further purified by preparative GC on column C: $[\alpha]^{22}_D$ +223° (CH_2Cl_2); ^1H NMR δ (CCl_4) 0.75 (s, 3 H), 0.86 (s, 3 H), 0.89 (s, 3 H), 1.76 (s, 3 H), 2.10 (s, 3 H), 2.57 (d, *J* = 3.6 Hz, 1 H); IR ν (neat) 1720, 1650 cm^{-1}; UV (methylcyclohexane) ϵ_{338} = 174, ϵ_{241} = 12 800; CD (methylcyclohexane) $\Delta\epsilon_{340}$ = +0.50, $\Delta\epsilon_{247}$ = +6.0, $\Delta\epsilon_{205}$ = −0.87.

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methylene)camphor, Dr. C. S. Pak for early determinations of CD spectra of 1 and 5–7, and Dr. F. S. Steinberg for establishing a modified synthesis of 1.

Registry No. 1, 74033-52-6; 2, 74033-53-7; 3, 16161-84-5; 5, 29583-35-5; 6, 40550-41-2; 7, 464-49-3; 8, 10292-98-5; 9, 25861-51-2; 2-methylenebornane, 5655-58-3.

A New Synthesis of Cyclic Allenic Esters[1]

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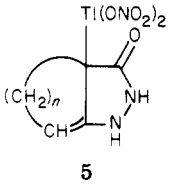
Previous studies[2,3] have demonstrated the generality of the conversion of 3,4-polymethylene-2-pyrazolin-5-ones to cycloalkene-1-carboxylic acids in two steps: first by conversion to the 4-halo-3,4-polymethylene-2-pyrazolin-5-one and then by a ring-opening reaction with aqueous sodium hydroxide. In related work, Taylor's group[4] has converted 3,4-dialkyl-2-pyrazolin-5-ones directly to acyclic allenic esters using thallium(III) nitrate and methanol, a reaction which simultaneously involved putting on the leaving groups in the 4-position of the pyrazolin-5-one and ring opening. There has been much interest in the synthesis[5] and reactions[6] of allenic acids and esters, and in this paper, we describe an extension of this reaction to the synthesis of the difficult-to-obtain 1-carbomethoxy cyclic allenic esters from the readily available cycloalkanones.

For purposes of clarity, the overall synthetic route is shown in Scheme I.

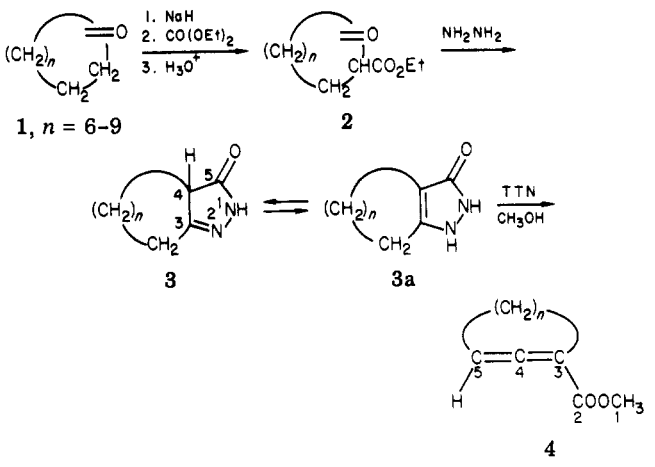
The first step in the synthesis invovled the conversion of the cycloalkanone 1 to the respective β-keto ester 2, which was readily accomplished by reaction of 1 with sodium hydride and diethyl carbonate. The second step involved reaction of 2 with hydrazine hydrate to form the corresponding 3,4-polymethylene-2-pyrazolin-5-one, 3. Compound 3 was converted to the cyclic allenic ester 4 by reaction with thallium(III) nitrate (TTN) and methanol.

The conversion of 3 to allenic esters[4] can be explained by electrophillic thallation of the enamine (3-pyrazolin-5-one) tautomer[7] 3a followed by loss of proton at the 3-substituted methylene position to give the cyclic alkylidene pyrazolidone 5. Subsequent oxidation of the hydrazo bond



5

Scheme I



of 5 by TTN and ring opening with methanol would give the cyclic allenic ester 4. Previous evidence that 5-pyrazolones undergo oxidation to oxopyrazoles[8] supports this explanation.

The structures of 4 (n = 6–9) were supported by spectral and analytical data. In general, the infrared spectra of the cyclic allenes showed a sharp absorption near 1960 cm^{-1}, corresponding to the allene linkage, and one around 1720 cm^{-1}, indicative of the carbonyl stretching frequency of the allenic ester. The proton magnetic resonance spectra of 4 showed a complex multiplet ranging from 0.90–2.50 ppm downfield from Me_4Si, assigned to the methylene hydrogens, a singlet of area 3 hydrogens near 3.70 ppm, and a multiplet or broad triplet of area 1 near 5.60 ppm, attributed to the methyl ester and vinyl hydrogens, respectively. ^{13}C nuclear magnetic resonance spectra of 4 exhibited an extreme downfield shift and weak absorption (small NOE) of the central allenic (C_4) carbon (208.5 to 211.1 ppm) which is consistent with data reported by Friedel and Retcofsky[9] and Stens and co-workers[10] for acylic allenes. The very low position of the central allenic carbon makes ^{13}C NMR an important tool for investigating molecular structures of this type. The cumulative olefinic resonances of the C_3 and C_5 carbons range from 96.25 to 101.19 ppm and 91.62 to 96.14 ppm, respectively, giving a total spread of the allenic carbons of 120 ppm as compared to 140 ppm for the acyclic case.[9] The methylene bridge carbons, the methyl ester carbon (C_1), and carbonyl ester carbon (C_2) all exhibit chemical shift values in expected areas.[11]

The preparation of 1-substituted cyclic allenes through the cyclic 5-pyrazolone appears to be most promising in that the method could be used as a general synthesis of lower or higher cyclic allene systems and utilizes readily available cycloalkanones as starting materials.

Experimental Section

All melting and boiling points were uncorrected. IR spectra were determined with a Perkin-Elmer Model 621 double-beam spectrophotometer and were calibrated vs. polystyrene. ^1H NMR spectra were recorded on a Perkin-Elmer 60-MHz R20A spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR

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