irradiation continued for an additional 48 h. The sulfuric acid solution was quenched in 250 g of ice and extracted with ether. Analysis of the extract and isolation of the principal photoproduct **13** was by GLC using column A.

Spectral data: IR (CCl_4) 3470, 2990 (v w sh) 2952, 2920 (sh), 2887, 2860 (sh), 1742, 1715 (sh), 1480, 1452, 1402, 1380, 1261, 1177, 1160, 1130, 1103, 1062, 1025, 955, 910, and 840 cm^{-1}. ^1H NMR ($CDCl_3$, 90 M Hz) δ 2.40 (s, 2H); 2.3–2.0 (m, 3H); 1.7–1.4 (unresolved m, 8H cyclopentane CH_2); 1.02 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 22.6 M Hz) δ (rel. intensity) 219.2 (45), 54.1 (47), 50.2 (42), 43.6 (81), 41.9 (70), 40.4 (88), 37.8 (82), 31.5 (83), 25.5 (83), 24.8 (100), 14.4 (74). Mass spectrum *m/e* (rel. intensity): perhydro species 164 (M^+, 5), 149 (13), 136 (10), 123 (14), 122 (18), 109 (30), 107 (20), 96 (42) 93 (30), 91 (22), 81 (100), 67 (68); deuterated species 168 (M^+, 8), 153 (16), 140 (15), 127 (22), 124 (18), 113 (22), 112 (26), 110 (20), 109 (22), 100 (58), 95 (32), 93 (28), 85 (72), 81 (100), 69 (52).

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Registry No.—**1**, 826-56-2; **6**, 22960-97-0; **13**, 63076-57-3.

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Stereoselectivity of the Retro-Ene Reaction of 2-Vinylcyclohexanols[1]

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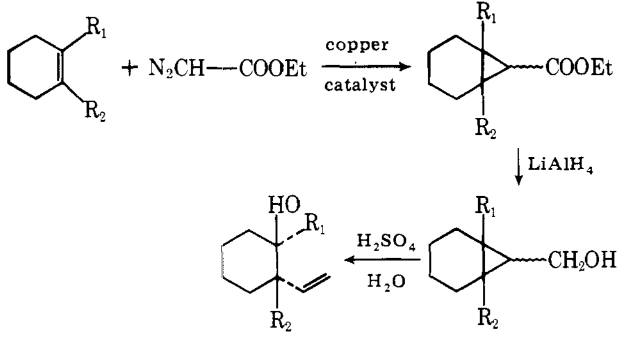
The retro-ene reaction of a 2-vinylcyclohexanol occurs readily in the vapor phase at 400–450 °C giving an unsaturated carbonyl compound in good yield. For the reactant the terms cis and trans refer to the hydroxyl and vinyl groups, R_1 refers to the other group on C_1, and R_2 to that at C_2. The numbers listed refer to percent *E*, percent *Z*, percent unidentified materials, and overall yield of product. Vapor phase reaction of the following examples was carried out: trans, 1 H, 2 H, 96, 0, 4, 95; cis, 1 H, 2 H, 59, 36, 5, 97; trans, 1 Me, 2 H, 92, 0, 8, 98; cis, 1 Me, 2 H, 52, 44, 4, 93; mixture trans (53), cis (47), 1 H, 2 Me, 81, 14, 5, 92; mixture trans (90) cis (10), 1 Me, 2 Me, 92, 0, 8, 96. The results suggest that the reaction is concerted and the products are kinetically determined. The reaction constitutes a useful stereoselective procedure for the synthesis of trisubstituted olefins.

The last decade has seen a great enhancement of interest in the stereoselective syntheses of double bonds of known configuration. Problems associated with the widespread dispersal of persistent insecticides in the environment and the discovery of insect pheremones have focussed attention particularly on the preparation of trisubstituted double bonds.[3] Many concerted thermal rearrangements exhibit a high degree of stereoselectivity, and numerous examples of their use for the synthesis of such alkenes have been reported.[4] Though the retro-ene reaction has not been used for this purpose, Arnold and Smolinsky[5] have established that rearrangement of *trans*-2-(alk-1-enyl)cycloalkanols leads to unsaturated aldehydes in high yield and apparently with high stereoselectivity. They examined cycloalkanols of varying ring size from cyclopentanols to cycloheptanols. In all cases the double bonds formed were disubstituted, and only the trans isomers were found. These results suggested that the retro-ene reaction might be useful for the stereoselective synthesis of more highly substituted alkenes. However, in view of the known sensitivity of the ene reaction to steric effects,[6] the stereoselectivity observed for disubstituted alkenes cannot a priori be extrapolated to more hindered systems. Therefore to ascertain the

Scheme I



1t, $R_1 = R_2 = H$
2t, $R_1 = Me$; $R_2 = H$
4t, $R_1 = R_2 = Me$

potential of the retro-ene reaction for the synthesis of alkenes of known configuration we have prepared and pyrolyzed a series of stereoisomeric 2-vinylcyclohexanols.

Reactants, Synthesis, and Stereochemistry

Arnold[5] prepared *trans*-2-alkenylcyclohexanols by treating cyclohexene oxide with an acetylide. This method suffers from poor yields and cannot be applied in general to substituted oxides. Both *cis*- and *trans*-2-vinylcyclohexanols have been prepared by Crandall.[7] He based his configurational assignment on the reasonable assumption that vinyllithium reacts with cyclohexene oxide to open the ring in the *trans* manner. For our studies it was advantageous to use a route with greater general utility for the preparation of substituted vinylcyclohexanols. This route is shown in Scheme I. In the first step the use of an activated copper catalyst rather than a soluble ionic copper coordination compound[8] gave better yields and no C–H insertion products. Reduction of the ester and formation of the homoallylic alcohol proceeded routinely. Though formation of the homoallylic product from a cyclopropylcarbinyl reactant is attributed to thermodynamic control, the homoallylic cation apparently reacts with water almost exclusively on the axial side. We obtained appreciable amounts of cis isomers only when the alcohol formed was tertiary. It is not clear whether the cis isomer[9] arises by ring inversion at the cation stage or via equilibration of the tertiary alcohol after its formation. It is obvious, however, that the major product results from kinetic control in the trapping step.

Acid catalyzed reaction of 7-hydroxymethylbicyclo[4.1.0]heptane gave only **1t**, with no discernible **1c** present. Collins' oxidation of **1t** gave 2-vinylcyclohexanone,[10] and reduction of this ketone with lithium aluminum hydride permitted a correlation between our assignments and those of Crandall.[7] When 2-vinylcyclohexanone was reduced with lithium tri-*s*-butylborohydride, **1c** was obtained in better than 95% purity. Reaction of 1-methyl-7-hydroxymethylbicyclo[4.1.0]heptane gave a mixture of two isomeric tertiary alcohols in 83:17 ratio. The major product was assigned the structure **2t** with vinyl and hydroxyl groups trans,[9] partially by analogy with the first example. This assignment was confirmed by a study of the reaction between 2-vinylcyclohexanone and methylmagnesium iodide. Two products were obtained in a 75:25 ratio. In this case the major isomer should be the cis product **2c** because the Grignard reagents generally enter equatorially.[11] As expected the major product of the ring opening corresponds to the minor isomer from the Grignard reaction. Opening of the cyclopropane ring of 1,6-dimethyl-7-hydroxymethylbicyclo[4.1.0]heptane produced a mixture of **4t** and **4c** in 86:14 ratio. Thus both reactions which lead to tertiary alcohols give very similar ratios of isomers. Assignment in this last case was based purely on analogy with the earlier reactions.

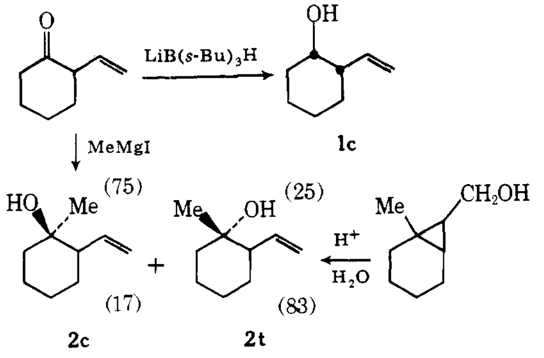
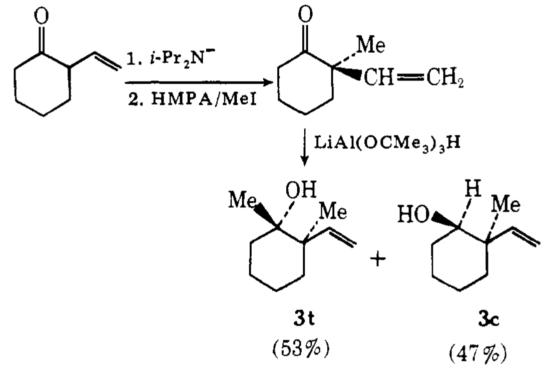


Table I. Stereoselectivity of the Retro-Ene Reaction of Substituted Vinylcyclohexanols

Reactant	% *E*	% *Z*	Yield[a]	% Other products
1t	100	0	95	4
1c	62	38	97	5
2t	100	0	98	8
2c	54	46	93	4
3t + **3c** (53:47)	85	15	92	5
4t + **4c** (90:10)	100 (−5 + 0)	0 (+5 − 0)	96	8

[a] Yields given are of total isolated material including byproducts.

The final pair of isomers, **3t** and **3c**, was obtained by methylation of 2-vinylcyclohexanone followed by reduction of the methylation product. Alkylation caused unexpected problems, principally because we failed to recognize just how lethargic the S_N2 reaction of this enolate is. Reaction of the carbanion with methyl iodide must be carried out at elevated temperatures, even in the presence of HMPA. Reduction of 2-methyl-2-vinylcyclohexanone is not expected to show any great degree of selectivity because the methyl and vinyl groups have similar size requirements. This expectation was borne out since a mixture containing 53% of **3t** and 47% of **3c** was obtained. Separation of the mixture was not attempted, and the more abundant isomer was assigned the **3t** structure, primarily because the resonance of methyl group in that isomer was further downfield (1.13 ppm) than that of the other isomer (0.98 ppm).[12]



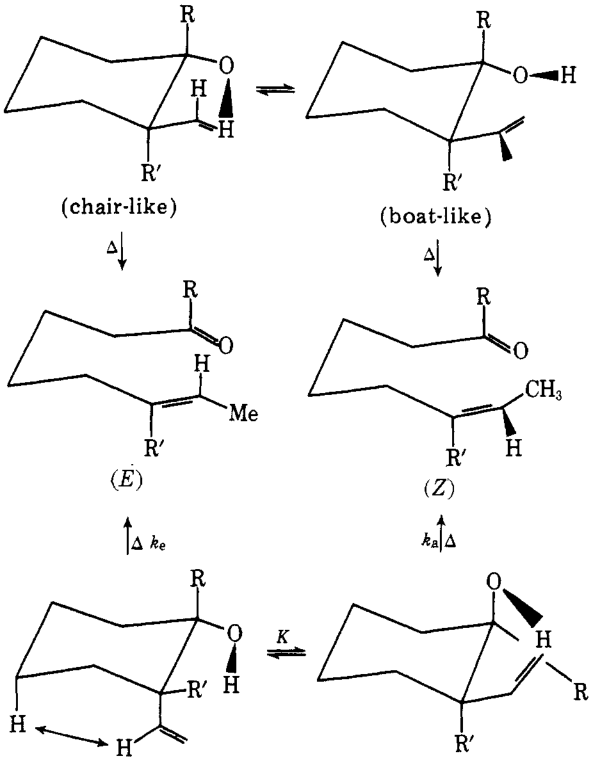
Results and Discussion

The vinylcyclohexanols were pyrolyzed in a flow reactor using nitrogen as a carrier gas. No attempt was made to optimize contact times or temperatures, but recovery was excellent in all cases, and the reaction was extremely clean. Aside from the retro-ene product only traces (4–8%) of other products were found, and no attempt was made to separate and identify these minor products. The results are listed in Table I. Before considering the significance of these data, we will discuss the structural assignments for the products. Products from both isomers of 1 and 2 have disubstituted double bonds, and the presence or absence of the out-of-plane C–H bending band at 970 ± 5 cm^{-1} was used to determine the double bond geometry. Coupling constants for the olefinic protons could not be obtained from the NMR spectra. Interestingly, this assignment was supported in both cases by the appearance of virtual coupling[13] in the resonance of the allylic methyl groups of both trans isomers, and its absence in the cis isomers.

The initial product from **3t** + **3c** was inseparable on all GLC columns we tried, but the NMR spectrum showed that it was a mixture since two cleanly separated resonances appeared for the aldehydic proton with an intensity ratio ca. 5:1. The aldehyde was reduced to an alcohol, and the alcohols were separated by GLC giving a ratio of the two isomers of 85:15. The assignment of configurations to the stereoisomers of trisubstituted double bonds of the general type RC(Me)=CHR′ has generally been based on the chemical shift of the methyl group and the coupling constant between the methyl and the olefinic proton.[14] Two problems complicated application of this procedure to the products from **3t** + **3c**. First the difference between the chemical shifts for the methyl groups was smaller than normal, thus lending a measure of uncertainty to the assignment. Second the R′ group in our case is a methyl, and its doublet pattern could not be cleanly identified. As a result the apparent splitting of the internal methyl resonance in the spectrum of the isomer assigned the *E* configuration could not be attributed with confidence to that coupling. Both indicators, however, lead to the same assignment for the *E* isomer, and this assignment is in agreement with expections based on the first four examples and on theory. This internal consistency engenders confidence in the assignment. The final example **4t** + **4c** gave a product which was not separable on any column we tried; however, the NMR spectrum of the product showed one sharp singlet at 2.02. Since the aldehydic proton of 6-methyl-6-octenal showed peaks for the *E* and *Z* isomers separated by 15 Hz, we expected some small separation of the methyl resonances for the *E* and *Z* isomers of 7-methyl-7-nonen-2-one. However, even if some separation were present, about 5% of a second isomer would not be identified. The *E* assignment in this case was based purely on analogy.

The most obvious conclusion reached from our data is that the reaction of the trans isomers **1t** and **2t** (presumably also **3t** and **4t**) is highly stereoselective. Tests using mixtures of *E* and *Z* products from **1t** and **1c** showed that 0.1% of the *Z* isomer could be identified in the *E*. Thus stereoselectivity is at least 99.9% for **1t**. From this we conclude that the product is kinetically determined, and that stereomutation of the double bond does not occur. The stereoelectronic requirements for the ene reaction demand a parallel alignment of the O–H and C–C σ bond orbitals with the p orbitals of the π bond.[6] As Scheme II shows, this requirement can be quite adequately met by a chair-like arrangement in the (ee) conformer of the trans isomer. This gives the *E* isomer in the product. A boat-like arrangement which would give the *Z* isomer cannot meet the stereoelectronic requirement, and our results indicate this transition state must be at least 10 kcal/mol above the chair-like state. It is also very clear from our results that the cis reactant is much less stereoselective. To treat this case we assume that conformational interconversions of the cyclohexane ring are fast compared to the retro-ene reaction, and the Curtin–Hammett principle applies. Transition states of the chair-like type having the OH either equatorial or axial (k_e and k_a of Scheme II, respectively) are attainable. The k_e state meets the stereoelectronic requirement better than the k_a state, but the k_e state introduces some steric interaction between the vinyl hydrogen and an axial hydrogen on the ring. While it is difficult to make any clear predictions, one certainly expects that (a) stereoselectivity will be reduced in comparison with trans reactants, and (b) stereoselectivity will be a function of the substituents R and R′.

Scheme II. Conformational Effects on the Retro-Ene Reaction of 2-Vinylcyclohexanols



These ideas can be compared with our experimental results if we assume that the trans reactants are 100% stereoselective in all cases, and that the cis isomers with the equatorial hydroxyl give exclusively *E* products while those with axial hydroxyls lead only to *Z* products. Thus for **1c** $k_e/k_a = 1.6$; for **2c**, 1.2; for **3c**, 2.2; and no information can be obtained for **4c**. The values for k_e/k_a obtained seem quite reasonable in terms of the transition states. Clearly, addition of a methyl at C_1(R = Me) should increase the energy of the transition state for k_e (Me is axial), but the full 1.7 kcal/mol of the $\Delta G_{\text{conf.}}$ for methyl is not effective. The vinyl–methyl skew interaction in the k_a transition state could account for some increase in energy in that state. A $\Delta\Delta G^{\ddagger}$ of ca. 0.5 kcal/mol favoring k_a would account for the effect of changing R = H to R = Me. For the change R′ = H to R′ = Me, i.e., **1c** to **3c**, the methyl should show the opposite effect and a $\Delta\Delta G^{\ddagger}$ of 0.5 kcal/mol favoring k_e would give $k_e/k_a = 2.2$ for **3c**. The agreement is better than this simplistic approach deserves.

Experimental Section

7-Carbethoxybicyclo[4.1.0]heptane. A mixture of 82.0 g (1.0 mol) of cyclohexene, 2.9 g of benzoyl peroxide, and 222 mg of (trimethyl phosphite)copper(I) chloride[8] was heated until a green solution was obtained. To this was added a mixture containing 82 g of cyclohexene and 23 g (0.2 mol) of ethyl diazoacetate. The solution was heated to reflux overnight, and the cold mixture was filtered. Excess cyclohexene was removed by distillation, and the residual product was distilled with a 45-cm spinning band column giving 26 g (77%) of 7-carbethyoxybicyclo[4.1.0]heptane: bp 41 °C (1.9 mm) [lit.[15] bp 110 °C (18 mm)]; NMR (CCl_4) δ 1.13 (t, 3H, J = 7 Hz), 1.1–1.5 (broad m, 6H), 1.8 (broad m, 4H), 4.04 (q, 2H, J = 7 Hz).

1-Methyl-7-carbethoxybicyclo[4.1.0]heptane. A 13 g sample (0.14 mol) of 1-methylcyclohexene was treated with 6.9 g (0.06 mol) of ethyl diazoacetate according to the procedure described above. Distillation gave 4.4 g (40%) of 1-methyl-7-carbethoxybicyclo[4.1.0]-heptane: bp 125–130 °C (25 mm); NMR (CCl_4) δ 1.05 (s, 3H), 1.15 (t, 3H, J = 7 Hz), 1.1–1.3 (broad m, 5H), 1.6 (broad m, 4H), 4.04 (q, 2H, J = 7 Hz) [lit.[17] bp 110 °C (18 mm)].

Copper Catalyst. A solution containing 60 g of copper sulfate in 400 mL of water was mixed with 10 g of 20 mesh zinc, and the mixture was stirred for 2 h at 100 °C. The precipitate was removed by filtration and was treated for 30 min with 100 mL of a solution containing 2 g of iodine in 100 mL of acetone. The catalyst was isolated by filtration and was washed with a 1:1 mixture of acetone and hydrochloric acid. After having been dried in vacuo at 66 °C for 2 h, 6.6 g of catalyst was obtained.

1,6-Dimethyl-7-carbethoxybicyclo[4.1.0]heptane. A mixture containing 300 mg of the copper catalyst and 6.0 g (55 mmol) of 1,2-dimethylcyclohexene was heated to reflux and 6.3 g (55 mmol) of ethyl diazoacetate was added dropwise. The mixture was heated at reflux overnight, and the product was isolated as described above. Distillation gave 3.6 g (51%) of 1,6-dimethyl-7-carbethoxybicyclo[4.1.0]heptane: bp 133–135 °C (13 mm); NMR (CCl_4) δ 1.17 (t, 3H, J = 7 Hz), 1.1–1.3 (broad m, 4H), 1.23 (s, 6H), 1.6 (broad m, 4H), 4.02 (q, 2H, J = 7 Hz) [lit.[18] bp 105–125 °C (20 mm)].

7-Hydroxymethylbicyclo[4.1.0]heptane. A solution containing 5.6 g (33 mmoles) of 7-carbethoxybicyclo[4.1.0]heptane in 25 mL of anhydrous ether was added dropwise to a mixture of 1.25 g (32 mmol) of lithium aluminum hydride and 25 mL of ether. The reaction mixture was treated cautiously with 1 mL of water followed by 40 mL of 10% sulfuric acid. The product was taken up in ether and dried ($MgSO_4$), and the ether was removed giving 3.8 g (90%) of 7-hydroxymethylbicyclo[4.1.0]heptane: NMR (CCl_4) δ 0.70 (broad s, 2H), 1.1–1.2 (broad m, 5H), 1.73 (broad s, 4H), 3.33 (d, 3/2 H, J = 6 Hz), 3.59 (d, 1/2 H, J = 6 Hz) 4.4 (OH). This spectrum matches that of an authentic sample.[16]

1-Methyl-7-hydroxymethylbicyclo[4.1.0]heptane. A 4.4 g sample (24 mmol) of 1-methyl-7-carbethoxybicyclo[4.1.0]heptane was reduced as described above. There was obtained 3.3 g (97%) of a liquid: NMR (CCl_4) δ 0.70 (m, 1H), 1.11 (s, 3H), 1.1–1.3 (broad m, 5H), 1.7 (broad m, 4H), 3.59 (m, 2H), 3.97 (OH). This crude material was not purified but was used directly in the next step.

1,6-Dimethyl-7-hydroxymethylbicyclo[4.1.0]heptane. A sample of 1,6-dimethyl-7-carbethoxybicyclo[4.1.0]heptane was reduced as above, and the crude alcohol was isolated in 85% yield, 2.1 g: NMR (CCl_4) δ 1.04 (s, 3H), 1.16 (s, 3H), 1.1–1.3 (broad m, 5H), 1.6 (broad m, 4H), 3.54 and 3.68 (two d, 2H, J = 7 Hz), 4.08 (OH). The crude product was used directly in the next step.

***trans*-2-Vinylcyclohexanol (1t).** A mixture of 3.4 g (26 mmol) of 7-hydroxymethylbicyclo[4.1.0]heptane and 25 mL of 10% sulfuric acid was stirred at room temperature overnight. The product was taken up in ether, and the ether solution was washed with sodium bicarbonate solution and then with saturated sodium chloride solution. The solution was dried (Na_2SO_4), the ether was evaporated and the crude product, 3.2 g (94%), was distilled giving 1.2 g, bp 41 °C (1.9 mm) [lit.[7] bp 44 °C (2 mm)]. GLC analysis on a 5% FFAP column at 150 °C showed the product was a single substance: NMR (CCl_4) δ 1.2 (m, 4H), 1.78 (m, 5H), 2.42 (OH), 3.18 (apparent sextet, spacing 4 Hz, probable d of t, J_{aa} ~8, J_{ae} ~ 4 Hz), 5.05, 5.75 (ABM part of ABMX, 3H, J_{AB} ~ 2, $J_{AM} + J_{BM}$ = 28, J_{MX} = 6 Hz); IR (neat) 3400, 1640, 995, 910 cm^{-1}.

***trans*-1-Methyl-2-vinylcyclohexanol (2t).** Reaction of 1-methyl-7-hydroxymethylbicyclo[4.1.0]heptane, 3.1 g (22 mmol), with 25 mL of 10% sulfuric acid and isolation of the product as described above gave 1.0 g (32%) of a mixture of isomers after distillation. GLC analysis on a 5% FFAP column at 155 °C showed the mixture to contain 83% **2t** and 17% **2c**. Preparative GLC separation permitted isolation of 300 mg of pure **2t**: NMR (CCl_4) δ 1.02 (s, 3H), 1.0–2.2 (broad m, 9H), 2.3 (OH), 5.05, 5.88 (ABM of ABMX, 3H, J_{MX} = 7.5, $J_{AM} + J_{BM}$ = 27 Hz); IR (neat) 3500, 1640, 970, 910 cm^{-1}. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.82; H, 11.49.

***trans*-1,2-Dimethyl-2-vinylcyclohexanol (4t).** A 2.1 g (13.6 mmol) sample of 1,6-dimethyl-7-hydroxymethylbicyclo[4.1.0]heptane was stirred with 25 mL of 10% sulfuric acid and worked up according to the procedure above. The distilled product was obtained in 76% yield (1.6 g) and GLC analysis on a 5% FFAP column at 160 °C showed the product contained 86% **4t** and 14% **4c**: NMR (CCl_4) δ 1.02 (s, 3H), 1.08 (s, 3H), 1.5 (m, 8H), 4.92, 5.04, 6.12 (ABX, J_{AB} = 1.8, J_{AX} = 18, J_{BX} = 10 Hz). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.97; H, 11.83.

2-Vinylcyclohexanone. A solution containing 2.0 g (16 mmol) of 2-vinylcyclohexanol was added in one portion to a solution containing 24 g (0.10 mol) of Collin's reagent[12] in 315 mL of methylene chloride. This mixture was stirred at room temperature for 2 h, and the solution was decanted from a gummy precipitate. The precipitate was extracted with methylene chloride and the combined extracts and supernatant solution was washed with 5% sodium hydroxide, then 5% hydrochloric acid. The solution was concentrated to ca. 50 mL, dried ($MgSO_4$), and the solvent removed, giving 1.82 g (92%) of crude ketone. Distillation, bp 95–96 °C (35 mm) [lit.[7] bp 35 °C (0.3 mm)], gave 1.67 g (85%) of 2-vinylcyclohexanone: NMR (CCl_4) δ 1.5–2.1 (broad m, 6H), 2.2–2.5 (m, 2H), 2.95 (m, 1H), 5.1 and 6.0 (ABM of ABMX, J_{AB} ~ 1.5, $J_{AM} + J_{BM}$ = 28, J_{MX} = 6.5).

***cis*-2-Vinylcyclohexanol (1c).** A solution of 1.08 g (8.7 mmol) of 2-vinylcyclohexanone in 25 mL of anhydrous THF was cooled in an ice bath under nitrogen, and 8.9 mL (8.9 mmol) of a 1 M solution of lithium tri-*s*-butylborohydride in THF was added dropwise. The solution was stirred at 0 °C for 6 h, and then 1 mL of water was added to the mixture. After 25 mL of ether had been added the solution was extracted with saturated ammonium chloride, water, and saturated sodium chloride. The ether solution was dried ($MgSO_4$) and the ether was removed by evaporation. The residue was mixed with 5 mL of acetic acid, the acid was neutralized with dilute sodium hydroxide, and the organic material was taken up in 10 mL of ether. To this was added 10 mL of 1.5 N sodium hydroxide and the mixture was cooled in an ice bath while 4 mL of 50% hydrogen peroxide was added. This mixture was stirred at room temperature for 12 h, and the layers were separated. The aqueous layer was extracted with ether; the ether solutions were combined and dried ($MgSO_4$). The ether was removed and the residue distilled giving 0.66 g (60%) of a liquid which GLC analysis showed was at least 95% **1c**, bp 68–70 °C (4 mm). Preparative GLC on a 3% DEGS column at 165 °C gave 200 mg of pure **1c**: NMR (CCl_4) δ 1.1–2.0 (broad m, 9H), 2.18 (b, OH), 3.80 (broad s, $W_{1/2}$ = 11 Hz, 1H), 5.1 and 5.9 (ABM of ABMX, J_{MX} = 6.5, $J_{AM} + J_{BM}$ = 28, J_{AB} ~1.5 Hz); IR (CCl_4) 3650, 3100, 1640, 1010, 920 cm^{-1}.

***cis*-1-Methyl-2-vinylcyclohexanol (2c).** A Grignard reagent was prepared from 15.6 mmol of methyl iodide, and a solution containing 1.8 g (14.5 mmol) of 2-vinylcyclohexanone in 20 mL of anhydrous ether was added dropwise. The reaction mixture was treated with saturated ammonium chloride solution and the ether layer was separated and dried ($MgSO_4$). The ether was evaporated and 2.0 g (93%) of crude alcohol was obtained. GLC analysis showed this contained 75% **2c** and 25% **2t**. A sample of **2c** was separated by preparative GLC on a 5% FFAP column at 135 °C: NMR (CCl_4) δ 1.13 (s, 3H), 1.2–2.0 (broad m, 10H), 5.0 and 5.9 (ABM of ABMX, J_{AB} = 2, J_{MX} = 8, $J_{AM} + J_{BM}$ = 27 Hz); IR (neat) 3500, 1640, 1000, 910 cm^{-1}. Anal. Calcd for $C_9H_{16}O$: C, 77.09, H, 11.50. Found: C, 76.97; H, 11.51.

2-Methyl-2-vinylcyclohexanone. A solution containing 1 mmol of lithium diisopropylamide in 25 mL of THF was prepared at −60 °C under nitrogen using butyllithium as a base. To this solution at −60 °C was added a solution of 11 mg (0.89 mmol) of 2-vinylcyclohexanone in 2 mL of THF. This solution was allowed to warm to room temperature and it was heated then to 30 °C for 30 min. After 0.2 mL of HMPT had been added, 0.3 g (2.1 mmol) of methyl iodide was added and the solution was heated at 40 °C for 2 h. The solution was mixed with 25 mL of ether, and the mixture was washed with saturated ammonium chloride, water, and then saturated sodium chloride. The ether layer was dried ($MgSO_4$) and the solvent was removed, giving 110 mg (90%) of 2-methyl-2-vinylcyclohexanone: NMR (CCl_4) δ 1.09 (s, 3H), 1.5–2.1 (broad m, 6H), 2.32 (m, 2H), 5.0 and 5.95 (ABX, 3H, J_{AB} ~1.5, $J_{AX} + J_{BX}$ = 27 Hz); IR (CCl_4) 1725, 1000, 910 cm^{-1}.

***cis*- and *trans*-2-Methyl-2-vinylcyclohexanols (3t and 3c).** Lithium tri-*tert*-butoxyaluminum hydride[13] was prepared under nitrogen in THF from 1.22 g (33 mmol) of lithium aluminum hydride and 7.26 g (98 mmol) of *tert*-butyl alcohol. A solution containing 946 mg (6.9 mmol) of 2-methyl-2-vinylcyclohexanol in 6 mL of THF was added dropwise at 0 °C. The mixture was stirred 22 h at room temperature, and then 10 mL of a 1:1 mixture of THF/H_2O was added, followed by 30 mL of 10% sulfuric acid and 50 mL of ether. The ether layer was washed with water, saturated sodium bicarbonate, and finally saturated sodium chloride solution. The ether solution was dried ($MgSO_4$), and the ether was evaporated to give 782 mg (75%) of product. GLC analysis on a 5% FFAP column at 150 °C showed 53% of **3t** and 47% of **3c**: NMR (CCl_4) δ 0.98 and 1.13 (2s, 3H), 1.2–2.0 (broad m, 8H and OH), 3.24 (broad m, 1H), 5.1 and 5.9 (two overlapping ABX, $J_{AX} + J_{BX}$ = 28 for both); IR (neat) 3400, 1640, 990, 915 cm^{-1}.

Thermolysis Apparatus. All thermolyses described below were carried out in a vertical quartz column packed with cut pieces of quartz tubing and heated externally by a electric oven. Temperatures were monitored continuously near the top, at the center and near the bottom of the column. The column was surmounted by a short preheater section wrapped with heating tape and equipped with a nitrogen inlet and a septum for injection of the sample. The preheater was kept at 200–215 °C, while the column was maintained at 440 °C. The nitrogen flow rate was about 50–75 mL/min, which equates to contact times between 1.5 and 2.2 min. Products were collected in a series of three traps cooled in dry ice–acetone.

***trans*-6-Octenal.** A total of 78 mg (0.62 mmol) of **1t** was pyrolyzed with a contact time of 1.46 min, and 74.2 mg of product (95%) was collected. The product was separated on a 5% FFAP column, and it contained 96% *trans*-6-octenal: NMR (CCl_4) δ 1.65 (m, 3H), 1.2–1.8 (broad m, 4H), 2.0 (m, 2H), 2.36 (d of t, $J = 6.8$, $J = 1.8$, 2H), 5.38 (m, 2H), 9.13 (t, 1H, $J = 1.8$ Hz); IR (neat) 2725, 1725 (s), 965 (s) cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.72; H, 11.23.

***cis*-6-Octenal.** Pure *cis*-2-vinylcyclohexanol, 80 mg (0.64 mmole), was pyrolyzed with a contact time of 1.41 min, and 78 mg (97%) of crude product was collected. GLC analysis on a 5% OV-17 column at 150 °C showed the product contained 59% *trans*-6-octenal, 36% *cis*-6-octenal, and 5% unidentified material. A sample of *cis*-6-octenal was collected from the GLC column: NMR (CCl_4) δ, 1.62 (d, 3H, $J = 5$ Hz), 1.2–1.9 (broad m, 4H), 2.0 (m, 2H), 2.35 (m, 2H), 5.38 (m, 2H), 9.15 (t, 1H, $J = 1.8$ Hz); IR (CCl_4), 1715, 905, 670 cm^{-1}.

***trans*-2-Nonen-8-one.** A 72 mg (0.52 mmol) sample of **2t** was pyrolyzed with a contact time of 1.5 min, and 70 mg (98%) of crude product was collected. GLC analysis on a column at 150 °C showed that the product contained 92% *trans*-2-nonen-8-one and 8% of unidentified products. A sample of *trans*-2-nonen-8-one collected from GLC showed an NMR spectrum (CCl_4) δ 1.65 (m, 3H), 1.2–1.8 (m, 4H), 1.95 (m, 2H), 2.04 (s, 3H), 2.33 (t, 2H, $J = 7$ Hz), 5.38 (m, 2H); IR (neat) 1730, 1360, 970 (s); mol wt 140, mass spectrum *m/e* (rel intens) 140 (2), 125 (4.4), 122 (3.6), 111 (7.5), 97 (9.4), 82 (29.7), 81 (11.0), 71 (35.3), 67 (39.6), 58 (20.9), 55 (34.2), 43 (100), 41 (23.4).

***cis*-2-Nonen-8-one.** A sample of **2c** (45 mg, 0.33 mmol) was pyrolyzed with contact time of 1.98 min, and 42 mg (93%) was recovered. The crude product was analyzed on a 3% DEGS column at 150 °C, and it contained 52% *trans*-2-nonen-8-one (GLC internal comparison), 44% *cis*-2-nonen-8-one and 4% by-products. Separation on a 16 ft × ¼ in. 3% DEGS column gave pure *cis*-2-nonen-8-one: NMR (CCl_4) δ 1.62 (d, 3H, $J = 5$ Hz), 1.2–1.85 (broad m, 4H), 1.98 (broad m, 2H), 2.05 (s, 3H), 2.35 (t, 2H, $J = 7$ Hz), 5.38 (m, 2H); IR (CCl_4) 1730 (s), 1340, 860 cm^{-1}; mol wt 140, mass spectrum *m/e* (rel intens) 140 (3.4), 125 (4.7), 122 (5.0), 111 (7.7), 97 (9.7), 82 (29.3), 81 (13.5), 71 (37.3), 67 (40.7), 58 (21.1), 55 (40.1), 43 (100), 41 (24.5).

Thermolysis of a Mixture of 3t and **3c.** A mixture containing 53% of **3t** and 47% of **3c** (244 mg, 2.6 mmol) was pyrolyzed with 2 min contact time. The recovered material amounted to 205 mg (92%), but the mixture which contained 5% by-products could not be separated successfully with 5% FFAP, 3% DEGS, or 5% OV-17 columns. The crude mixture showed NMR (CCl_4) δ 1.55 (m), 1.60 (s, 3H), 1.98 (apparent t, 2H, $J \sim 7$ Hz), 2.48 (d of t, 2H, $J = 7$ Hz, $J = 1$ Hz), 5.2 (m, 1H), 9.56 and 9.70 (2t, 1H, $J \sim 1$ Hz); IR (CCl_4) 1730 (s), 1370 cm^{-1}. Anal. Calcd for $C_9H_{16}O$: C, 77.09, H, 11.50. Found: C, 77.20, H, 11.49.

(*E*)- and (*Z*)-6-Methyl-6-octen-1-ols. The mixture of 6-methyl-6-octenals above (66.8 mg, 0.48 mmol) was added dropwise to 20 mg (0.52 mmol) of lithium aluminum hydride in 20 mL of ether. The mixture was stirred for 2 h and was then hydrolyzed with 10% sulfuric acid. The ether layer was separated and the aqueous layer was extracted with ether. The ether solutions were combined and dried ($MgSO_4$), and the ether was evaporated giving 65.5 mg (97%) of a mixture of 6-methyl-6-octen-1-ols. GLC analysis on a 3% DEGS column at 140 °C showed the mixture contained 85% of the *E* isomer and 15% of the *Z* isomer. The isomers were separated on the DEGS column: *E* isomer, NMR (CCl_4) δ 1.2–1.8 (broad m), 1.55 (partly resolved d, $J \sim 1$ Hz), 1.8–2.2 (m), 3.50 (m), 5.0–5.3 (broad m); *Z* isomer, NMR (CCl_4) δ 1.2–1.8 (broad m), 1.56 (s), 1.8–2.2 (m), 2.85 (s, OH), 3.2–3.7 (broad m), 5.0–5.3 (broad m).

(*E*)-7-Methyl-7-nonen-2-one. Three separate runs on mixtures containing respectively 88% **4t**/12% **4c**, 86% **4t**/14% **4c**, and 90% **4t**/10% **4c** were carried out under the same conditions, and the products were the same in all cases. Thus 75.3 mg (0.50 mmol) of the 86/14 mixture was pyrolyzed with a contact time of 2.2 min, and 72.1 mg (96%) was recovered. This product contained 92% of 7-methyl-7-nonen-2-one and 8% of unidentified material. No GLC evidence for separation of the ketone was found, and a pure sample showed NMR (CCl_4) δ 1.2–1.7 (broad m), 1.55 (s, CH_3), 1.8–2.1 (m), 2.02 (s, 3H), 2.32 (clean t, 2H, $J = 6.5$ Hz), 5.17 (m, 1H); IR (neat) 1730 s, 1380, 1372, 1360, 805 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.65, H, 11.80.

Registry No.—**1c,** 17807-20-4; **1t,** 6376-95-0; **2c,** 63196-52-1; **2t,** 63196-53-2; **3c,** 63196-54-3; **3t,** 63196-55-4; **4c,** 63196-56-5; **4t,** 63196-57-6; cyclohexene, 110-83-8; ethyl diazoacetate, 623-73-4; 7-carbethoxybicyclo[4.1.0]heptane, 52917-64-3; 1-methycyclohexane, 591-49-1; 1-methyl-7-carbethoxybicyclo[4.1.0]heptane, 63196-58-7; 1,6-dimethyl-7-carbethoxybicyclo[4.1.0]heptane, 63196-59-8; 7-hydroxymethylbiocyclo[4.1.0]heptane, 6226-39-7; 1-methyl-7-hydroxymethylbicyclo[4.1.0]heptane, 63196-60-1; 1,6-dimethyl-7-hydroxymethylbicyclo[4.1.0]heptane, 63196-61-2; 2-vinylcyclohexanone, 1122-24-3; 2-vinylcyclohexanol, 29108-24-5; methyl iodide, 74-88-4; 2-methyl-2-vinylcyclohexanone, 63196-62-3; *trans*-6-octenal, 63196-63-4; *cis*-6-octenal, 63196-64-5; *trans*-2-nonen-8-one, 25143-93-5; *cis*-2-nonen-8-one, 63196-65-6; (*E*)-6-methyl-6-octen-1-ol, 63196-66-7; (*Z*)-6-methyl-6-octen-1-ol, 63196-67-8; (*E*)-7-methyl-7-nonen-2-one, 63230-66-0.

References and Notes

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(3) See, for example, B. M. Trost, T. J. Dietsche, and T. J. Fullerton, *J. Org. Chem.*, **39,** 737 (1974); R. S. Lenox and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **95,** 957 (1973); B. M. Trost and T. J. Fullerton, *ibid.*, **95,** 292 (1973); S. B. Bowles, and J. A. Katzenellenbogen, *J. Org. Chem.*, **38,** 2733 (1973); M. P. Cooke, Jr., *Tetrahedron Lett.*, 1983 (1973); P. Grieco and R. S. Finkelhor, *J. Org. Chem.*, **38,** 2245 (1973).

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(9) Throughout this paper the designations cis and trans as applied to the variously substituted vinylcyclohexanols always refer to the relative positions of the vinyl and hydroxyl groups.

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