the other explanations which might be considered are (1) vibrational effects; (2) separate contributions from planar and nonplanar conformers;[12] (3) mixing of a singlet state with a nearby triplet state; and (4) complex mixing with low-lying singlet states. Clearly, further work is required; however, some support for low-lying states can be found in the electron impact excitation spectrum of cycloheptatriene recently reported by Oosterhoff.[14] It should be noted that the ratio $B/D = 9.9 \times 10^{-5}\ \beta_M/\mathrm{cm}^{-1}$, although distinctly larger than the mean of the diene values, was determined by moment analysis[7f] and has significance only if the complex MCD is of vibrational rather than electronic origin.

In conclusion, our results support the current theoretical treatment of the Faraday effect and provide additional spectroscopic evidence for the prediction[11] of but a single electronic transition in the 200–300 nm region of conjugated dienes. Furthermore, these results provide the basis, and indeed the impetus, for further measurements in the vacuum ultraviolet. Although MCD in the 200–300 nm region has no distinct advantage over absorption spectroscopy for the structural identification of different diene systems, further work in this region on triene systems is definitely warranted.

Experimental Section

The synthesis and photochemical transformations of these compounds will be described in a future publication.

MCD measurements were made using a Japan Spectroscopic Company spectropolarimeter (Durrum-JASCO Model ORD/UV/CD-5) modified to accept a Lockheed Palo Alto Research Laboratories superconducting magnet (Model OSCM-103). The directions of the light beam and the positive sense of the magnetic field are coincident. All measurements were made at 21° in a magnetic field of 49.5 kG. The solvent was Spectrograde hexane.

Registry No.—**1**, 513-81-5; **2**, 33482-80-3; **3**, 33482-81-4; **4a**, 13376-06-2; **4b**, 33482-83-6; **5**, 33482-84-7; **6**, 33482-85-8; **7**, 33482-86-9; **8**, 33482-87-0; **9**, 4054-38-0; **10**, 3806-59-5; **11**, 33495-82-8; **12**, 31351-58-3; **13**, 544-25-2.

Acknowledgment.—The excellent technical assistance provided by Ruth Records, Gordon H. Scott, and Angus M. Babcock is gratefully appreciated.

(13) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).

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Stereospecific Introduction of Functionalized Angular Methyl Groups *via* the Claisen Rearrangement. The Octalin and Hydrindenyl Ring Systems[1,2]

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The one-step Claisen rearrangement using ethyl vinyl ether, *N,N*-dimethylacetamide dimethyl acetal, or triethyl orthoacetate provides a useful method for the preparation of octalin systems with functionalized angular methyl groups from octalols. This method fails with the hydrindenyl ring system. However, preparation and purification of vinyl ethers followed by thermolysis lead to functionalized methyl groups in both ring systems. The use of decalin as solvent in the thermolysis increases the amount of Claisen product in the hydrindenyl system. When the temperature is lowered, the rate of rearrangement is decreased and the amount of elimination increased.

In the synthesis of polycyclic sesqui- and diterpenes, the need often has arisen for a general stereospecific preparation of fused ring systems with functionalized angular methyl groups. Such a group has usually been introduced into the ring systems by a conjugated addition of hydrocyanic acid[3] or by functionalizing[4] an already present angular group. Previous studies[5] in this laboratory with regard to the stereospecific introduction of an angular methyl group *via* cyclopropanation of an allylic alcohol called attention to this latter system as a potential starting point for other stereospecific syntheses. Indeed, such a system has been utilized by conversion to a vinyl ether followed by a Claisen rearrangement to a γ,δ-unsaturated aldehyde.[6] The reports in the recent literature[7-9] of three different one-step methods (eq 1–3) for bringing about this conversion made this an attractive pathway to evaluate.

These three reaction sequences were studied using the allylic alcohols **1** and **4**, ring systems which typify those found in natural products. It wasf ound that, when the one-step method using ethyl vinyl ether (eq 1) with the recommended trace of phosphoric acid as a catalyst was employed, the sole products of the reac-

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(1) This work was supported by Grant GP-8700, National Science Foundation.

(2) In this paper the term hydrindenyl is used to describe the tetrahydroindan system represented by structures such as **4** and **5**.

(3) W. Nagata, M. Yoshioka, T. Okumura, and M. Murakami, *J. Chem. Soc. C*, 2355 (1970), and references cited therein.

(4) For a recent review of the Barton reaction see (a) R. H. Hesse in "Advances in Free Radical Chemistry," Vol. 3, G. H. Williams, Ed., Academic Press, New York, N. Y., 1969, pp 83–137. See also (b) A. Bowers, R. Villotti, J. A. Edwards, E. Denst, and O. Halpern, *J. Amer. Chem. Soc.*, **84**, 3204 (1962); (c) A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 35 (1962); (d) K. Hensler and J. Kalvoda, *Angew. Chem., Int. Ed. Engl.*, **3**, 525 (1964); (e) M. Aktar in "Advances in Photochemistry," Vol. 2, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience, New York, N. Y., 1964, pp 263–303.

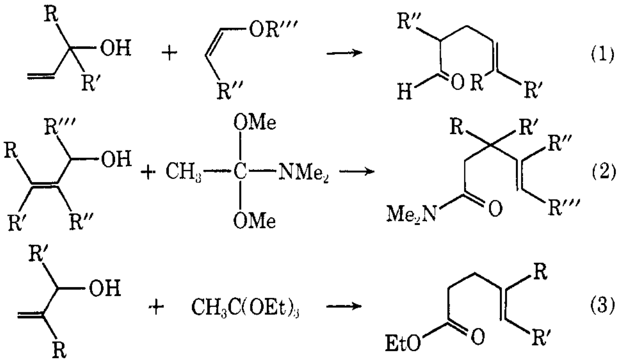
(5) (a) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963); (b) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966); (c) W. G. Dauben and D. S. Fullerton, *ibid.*, **36**, 3277 (1971).

(6) (a) A. W. Burgstahler and I. C. Nordin, *J. Amer. Chem. Soc.*, **81**, 3151 (1959); A. W. Burgstahler and I. C. Nordin, *ibid.*, **83**, 198 (1961); (b) R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, **31**, 2526 (1966); (c) D. J. Dawson and R. E. Ireland, *Tetrahedron Lett.*, 1899 (1968).

(7) (a) R. Marbet and G. Saucy, *Helv. Chim. Acta*, **50**, 1158 (1967); (b) R. Marbet and G. Saucy, *ibid.*, **50**, 2091 (1967); (c) R. Marbet and G. Saucy, *ibid.*, **50**, 2095 (1967).

(8) (a) A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *ibid.*, **47**, 2425 (1964); (b) D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *ibid.*, **52**, 1030 (1969).

(9) (a) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, **92**, 741 (1970); (b) W. S. Johnson, T. J. Brocksom, P. Loew, B. H. Rich, L. Werthemann, R. A. Arnold, T. Li, and D. J. Faulkner, *ibid.*, **92**, 4463 (1970).



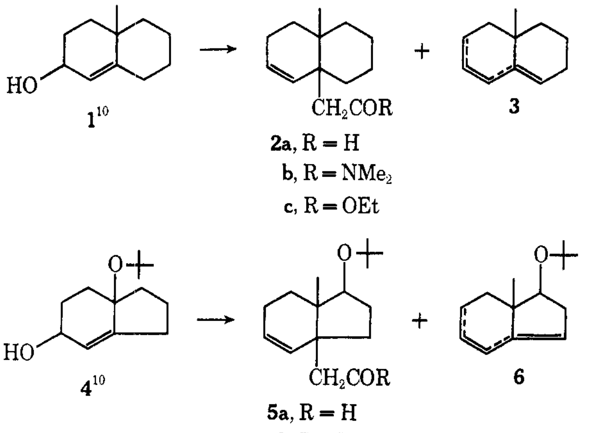
tions were the dienes **3** and **6**; no aldehydes **2a** and **5a** could be detected. An alternate procedure using mercuric acetate as the catalyst was tried and the results are recorded in Table I. This method works quite well for the octalin system **1**,[10] but with the hydrindenyl system **4** twice as much elimination as rearrangement resulted.

TABLE I

RESULTS OF ONE-STEP CLAISEN REARRANGEMENTS

Alcohol	Reaction	Reaction time, hr	Products,[a] %: Starting material	Claisen product	Dienes
1	$CH_3CH_2OCH{=}CH_2$, 200°	12	0	85 (**2a**)	15 (**3**)
4	$CH_3CH_2OCH{=}CH_2$, 200°	12	0	40 (**5a**)	60 (**6**)
1	$CH_3C(OMe)_2NMe_2$, 138°	24	50	50 (**2b**)	0 (**3**)
4	$CH_3C(OMe)_2NMe_2$, 138°	40	0	0 (**5b**)	100 (**6**)
1	$CH_3(OEt)_3$, 137°	24	40	60 (**2c**)	0 (**3**)
4	$CH_3(OEt)_3$, 137°	24	50	Trace (**5c**)	50 (**6**)

[a] Determined by nmr and/or glpc, and normalized.



1[10]

2a, R = H
b, R = NMe_2
c, R = OEt

3

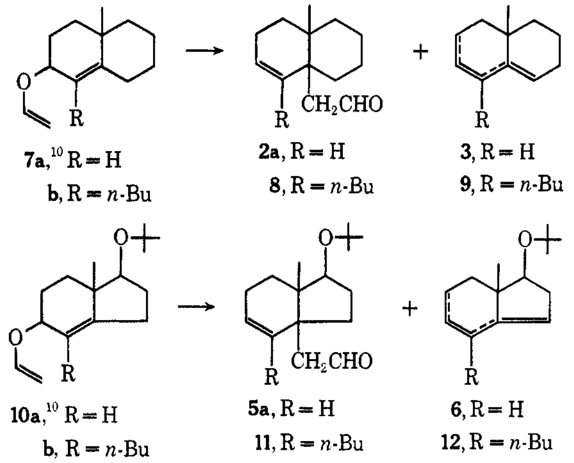
4[10]

5a, R = H
b, R = NMe_2
c, R = OEt

6

The dimethyl amide method (eq 2) was next studied. This process has been previously used on a system[6c] related to **1** and, indeed, the amide **2b** was found in high yield as reported in Table I. However, the products obtained from the hydrindenyl alcohol **4** were only the dienes **6**. Using the triethyl orthoacetate procedure (eq 3), similar results were obtained. A good yield of the ester **2c** resulted (Table I) but the hydrindenyl alcohol **4** gave only a trace of ester **5c** and a high yield of dienes **6**.

Thus, the one-step processes are excellent procedures for introducing various functionalized angular methyl groups in an octalin ring system but not in the hydrindenyl system. In view of the partial success of the modified vinyl ether approach with this latter system, the original two-step procedure of Burgstahler[6a] involving preparation of pure vinyl ether was studied in order to give some ideas as to where the one-step procedure met with difficulty.



7a,[10] R = H
b, R = *n*-Bu

2a, R = H
8, R = *n*-Bu

3, R = H
9, R = *n*-Bu

10a,[10] R = H
b, R = *n*-Bu

5a, R = H
11, R = *n*-Bu

6, R = H
12, R = *n*-Bu

The vinyl ethers (**7a,b** and **10a,b**) could be prepared in good yield (75–90%) from ethyl vinyl ether in the presence of mercuric acetate.[11] Unless special care was taken to obtain pure ether, larger amounts of diene were formed in the thermal rearrangement. The most efficient purification procedure was found to be chromatography on Florisil. The results of the vinyl ether thermolyses are given in Table II; the use of decalin as a solvent had been reported by Burgstahler.[6a] It is seen that, with the unsubstituted components **7a** and **10a**, the reaction proceeded very well and the use of decalin noticeably increased the yield of aldehyde **5a**. The presence of a substituent as in **7b** and **10b** had a small effect (~10% decrease) on the yield in the octalin system but in the hydrindenyl system the yield was

TABLE II

RESULTS OF VINYL ETHER THERMOLYSES[a]

Vinyl ether	Phase	Products,[b] %: Aldehyde	Diene
7a	Neat	90 (**2a**)	10 (**3**)
7a	Decalin	90 (**2a**)	10 (**3**)
10a	Neat	70 (**5a**)	30 (**6**)
10a	Decalin	90 (**5a**)	10 (**6**)
7b	Neat	80 (**8**)	20 (**9**)
7b	Decalin	80 (**8**)	20 (**9**)
10b	Neat	45 (**11**)	55 (**12**)
10b	Decalin	65 (**11**)	35 (**12**)

[a] The thermolyses were run at 195–200° for 3–5 hr. [b] Determined by nmr and glpc, and normalized.

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[10] Structure **1** represents a mixture of 87% β isomer and 13% α isomer by glpc analysis. Nmr analysis of compounds represented by structures **2a–c**, **7a**, **13**, and **14** consist of a mixture with approximately the same isomer ratio. Structure **4** represents a mixture of 95% β isomer and 5% α isomer by glpc analysis. Nmr analysis of compounds represented by structures **5a**, **5c**, and **10a** indicates no more than 5% isomer.

The alcohol from which **7b** is formed consists of a mixture of 80% β isomer and 20% α isomer by glpc. Though it is impossible to determine by nmr analysis the isomer ratio for **7b** and **8**, it is assumed, by analogy with the unsubstituted octalin **1**, to be the same as the alcohol precursor. The alcohol precursor for **10b** shows only β isomer.

[11] W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **79**, 2828 (1957).

greatly affected. The use of decalin as solvent in this latter case brought the yield of aldehyde **11** back to 65%.

Although Claisen rearrangements have been run over a wide range of temperatures (100–425°), there is lacking a study of the effect of temperature on the side reactions. Table III shows the effect of temperature on the product distribution from the thermolysis of **10a**. At higher temperature (160° and above) the aldehyde to diene ratio remained the same. At 139° not only did the aldehyde to diene ratio drop but the rate of reaction was slowed down appreciably. Indeed, at 116° the rate of reaction was too slow to be of any synthetic value. The only study on the octalin system **7a** at 139° showed similar results in that the rate of the reaction slowed down and the aldehyde to diene ratio dropped off slightly.

TABLE III

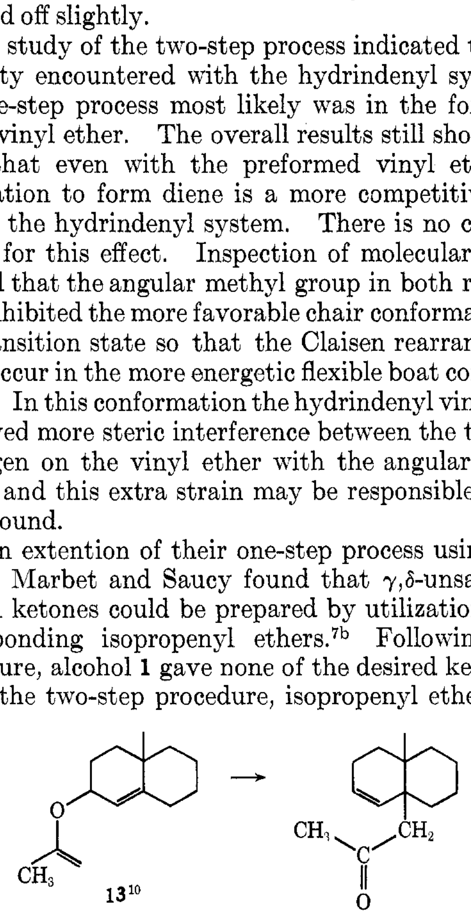
THE EFFECT OF TEMPERATURE ON VINYL ETHER THERMOLYSES

Vinyl ether	Temp, °C	Reaction time, hr	% Reaction	Products,[a] % Starting material	Aldehyde	Diene
10a	229	2.5	100	0	70 (**5a**)	30 (**6**)
10a	193	4	100	0	70	30
10a	160	23	100	0	70	30
10a	139	23	55	45	30	25
10a	116	23	<5	>95	Trace	Trace
7a	193	4	100	0	90 (**2a**)	10 (**3**)
7a	139	23	60	40	40	20

[a] Determined by nmr and normalized.

This study of the two-step process indicated that the difficulty encountered with the hydrindenyl system in the one-step process most likely was in the formation of the vinyl ether. The overall results still show, however, that even with the preformed vinyl ether the elimination to form diene is a more competitive reaction in the hydrindenyl system. There is no clear-cut reason for this effect. Inspection of molecular models showed that the angular methyl group in both ring systems inhibited the more favorable chair conformation for the transition state so that the Claisen rearrangement must occur in the more energetic flexible boat conformation.[12] In this conformation the hydrindenyl vinyl ether displayed more steric interference between the terminal hydrogen on the vinyl ether with the angular methyl group, and this extra strain may be responsible for the effect found.

In an extention of their one-step process using vinyl ethers, Marbet and Saucy found that γ,δ-unsaturated methyl ketones could be prepared by utilization of the corresponding isopropenyl ethers.[7b] Following their procedure, alcohol **1** gave none of the desired ketone **14**. Using the two-step procedure, isopropenyl ethers from



13[10] → **14**[10]

1 and **4** could be prepared in low yield (10–20%). Thermolysis of ether **13** gave methyl ketone **14** in 35% yield plus 65% diene; reaction of the related hydrindenyl ether **15** gave only diene.

The alcohols (**1** and **4**) prepared by LiAlH$_4$ reduction gave a mixture of epimer which consisted of approximately 85–95% of the β alcohol, as could be determined by analytical glpc or nmr analysis.[10] In this study the preparation of vinyl ethers and their thermolyses showed no preference as to stereochemistry and nmr analysis showed the same relative amounts of epimers. Burgstahler[6a] reported that, though the 3α-cholestenyl vinyl ether underwent thermolysis with ease, the formation of the α-vinyl ether went in only 5% yield as compared to the β-vinyl ether (65%). The higher flexibility of the more simple compounds may be responsible for this difference.

Experimental Section

Melting points were determined on a Büchi Schmelzpunktbestimmungsapporat and are uncorrected, as are boiling points. Reactions were monitored and product mixtures were analyzed by gas–liquid phase chromatography (glpc) on a Varian Aerograph A-90-P using a 10-ft column, 5% SE-30 on Chromosorb W, unless otherwise stated. Infrared (ir) spectra were measured on a Perkin-Elmer 137 spectrophotometer with carbon tetrachloride as solvent. Nuclear magnetic resonance (nmr) spectra were obtained as carbon tetrachloride solutions with a Varian T-60 spectrometer, and peak positions are given in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were recorded on Consolidated Electrodynamics Corp. type 21-103C and Varian M-66 spectrometers. Elemental analyses were conducted by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

10-Methyl-$\Delta^{1(9)}$-2-octalol (**1**).—To a suspension of lithium aluminum hydride (3.8 g, 0.100 mol) in 100 ml of dry ether was added, dropwise, 10-methyl-Δ-$^{1(9)}$-2-octalone (16.4 g, 0.100 mol) in 100 ml of dry ether. The mixture was refluxed overnight. Water was added until a white, flocculent material formed, and the ether was filtered, dried (MgSO$_4$), and rotary evaporated. Distillation in a short-path still gave 14.3 g (86%) of **1**: bp 89–90° (0.5 mm) [lit.[13] bp 73.5–76° (0.2 mm)]; ir 3350, 1050 cm^{-1}; nmr δ 5.4 (d, J = 4.5 Hz, vinyl proton, α alcohol), 5.2 (s, vinyl proton, β alcohol, total 1 H), 4.0 (m, 1, carbinol H), 1.1 (s, angular methyl, β alcohol) and 1.0 (s, angular methyl, α alcohol, total 3 H). Glpc analysis[14] showed 87% β alcohol and 13% α alcohol.[15]

9-Formylmethyl-10-methyl-Δ^1-octalin (**2a**).—The allylic alcohol **1** (0.3 g, 1.80 mmol), mercuric acetate (0.2 g), and 1.5 ml of ethyl vinyl ether were sealed in a Carius tube and heated for 12 hr at 200°. Glpc and nmr analyses showed 85% of the aldehyde **2a** and 15% of the dienes **3** (collected by preparative glpc): mass spectrum (70 eV) *m/e* 133 (base peak), 148 (molecular ion). The aldehyde **2a** was collected for spectral analysis by preparative glpc: ir 2720, 1720 cm^{-1}; nmr δ 9.8 (m, 1, two overlapping triplets from α- and β-formylmethyl groups), 5.7 (m, 2, vinyl), 1.0 (s, angular methyl, α aldehyde) and 0.9 (s, angular methyl, β aldehyde) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 149 (base peak), 192 (molecular ion).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.23; H, 10.67.

9-(N,N-Dimethyl)formamidomethyl-10-methyl-Δ^1-octalin (**2b**).—The allylic alcohol **1** (1.66 g, 0.010 mol) and N,N-dimethylacetamide dimethyl acetal[16] (2.0 g, 0.015 mol) were stirred in refluxing xylene for 24 hr. The excess acetal and xylene were rotary evaporated to give 1.9 g of crude material which by nmr was found to be a 50:50 mixture of starting material **1** and amide **2b**. The amide was collected for spectral analysis by preparative glpc: ir 1660 and 1640 cm^{-1}; nmr δ 5.52 (s, 2, vinyl), 2.95 and 2.85

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(12) The need for high temperature might also be indicative of the involvement of a higher energy pathway.

(13) H. B. Henbest and J. McEntee, *J. Chem. Soc.*, 4478 (1961).

(14) 5 ft, 5% KOH, 5% Carbowax on Chromosorb G.

(15) A. C. Ashcraft, Jr., Dissertation, University of California, Berkeley, 1963.

(16) Fluka A. G., stabilized with 5–10% methanol.

(two s, 6, *N*,*N*-dimethyl), 1.0 (s, angular methyl, α amide) and 0.92 (s, angular methyl, β amide) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 87 (base peak), 235 (molecular ion).

Anal. Calcd for $C_{15}H_{25}ON$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.46; H, 10.70; N, 5.76.

9-Carbethoxymethyl-10-methyl-Δ^1-octalin (2c).—The allylic alcohol **1** (1.66 g, 0.010 mol), triethyl orthoacetate (16.2 g, 0.1 mol), and propionic acid (0.037 g, 0.5 mmol) were heated for 24 hr at 137° under conditions for distillative removal of ethanol. The nmr of the reaction mixture showed 40% of starting material **1** and 60% of ester **2c**. The ester was collected for spectral analysis by preparative glpc; ir 1730 cm^{-1}; nmr δ 5.55 (s, 2, vinyl), 4.0 (q, 2, J = 7 Hz, ester CH_2O), 2.25 (s, 2, carbethoxy methylene), 1.2 (t, 3, J = 7 Hz, ester CH_3), 1.0 (s, angular methyl, α ester) and 0.9 (s, angular methyl, β ester) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 149 (base peak), 148 (98% of base peak), 236 (molecular ion).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.49; H, 10.38.

1β-*tert*-Butoxy-5,6,7,7a-tetrahydro-7aβ-methyl-5-indanol (4).—The ketone, 1β-*tert*-butoxy-7,7a-dihydro-7aβ-methyl-5(6*H*)-indanone[17] (22.2 g, 0.100 mol) was reduced with $LiAlH_4$ (3.8 g, 0.100 mol) in the standard fashion (as for **1**) to yield 21.2 g of crude product **4**. Glpc analysis[18] showed 95% β alcohol and 5% α alcohol. A small sample was recrystallized from ice-cold petroleum ether (bp 30–60°) to give a white, granular powder: mp 67–68°; ir 3400 cm^{-1}; nmr δ 5.23 (broad s, 1, vinyl), 4.03 (m, 1, carbinol H), 3.3 (m, 1, *tert*-butyl–OCH), 1.1 (s, 9, *tert*-butyl), 0.94 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 150 (base peak), no molecular ion.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.18; H, 10.95.

1β-*tert*-Butoxy-3a-formylmethyl-3a,6,7,7a-tetrahydro-7aβ-methylindan (5a).—The allylic alcohol **4** (0.3 g, 1.30 mmol), mercuric acetate (0.2 g), and 1.5 ml of ethyl vinyl ether were sealed in a Carius tube and heated for 12 hr at 200°. Glpc and nmr analyses showed 40% of aldehyde **5a** and 60% of dienes **6**. The dienes were collected by preparative glpc: ir 3030 cm^{-1}; nmr δ 5.7 (m, 3, vinyl), 3.7 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 0.83 and 0.85 (two s, 3 H, angular methyls); mass spectrum (70 eV) *m/e* 206 (molecular ion).

Anal. Calcd for $C_{14}H_{24}O$: C, 81.50; H, 10.75. Found: C, 81.30; H, 10.72.

The aldehyde **5a** was collected for spectral analysis by preparative glpc: ir 2720, 1725 cm^{-1}; nmr δ 9.77 (t, 1, J = 3 Hz), 5.55 (s, 2, vinyl), 3.8 (m, 1, *tert*-butyl–OCH), 2.35 (d, 2, J = 3 Hz, formylmethylene), 1.15 (s, 9, *tert*-butyl), 0.9 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 150 (base peak), no molecular ion.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.49; H, 10.52.

Reaction of 4 with *N*,*N*-Dimethylacetamide Dimethyl Acetal.—The allylic alcohol **4** (0.33 g, 1.50 mmol) and *N*,*N*-dimethylacetamide dimethyl acetal (0.23 g, 2.00 mmol) were stirred in refluxing xylene for 40 hr. The excess acetal and xylene were rotary evaporated to leave 0.2 g of crude product which by nmr and ir proved to be the dienes **6**.

Reaction of 4 with Triethyl Orthoacetate.—The allylic alcohol **4** (2.24 g, 0.010 mol), triethyl orthoacetate (16.2 g, 0.100 mol), and propionic acid (0.037 g, 0.5 mmol) were heated for 24 hr at 137° under conditions for distillative removal of ethanol. The reaction mixture was subjected to analytical glpc analysis which revealed starting material **4** and dienes **6** in a 1:1 ratio and a trace of material which was collected by preparative glpc and shown by spectral analysis to be the ester **5c**: ir 1730 cm^{-1}; nmr δ 5.45 (s, 2, vinyl), 4.1 (q, 2, J = 7 Hz, ester CH_2O), 3.8 (m, 1, *tert*-butyl–OCH), 1.3 (t, 3, J = J Hz, ester CH_3), 1.2 (s, 9, *tert*-butyl), 0.8 (s, 3, angular methyl).

Preparation of Vinyl Ethers. 10-Methyl-$\Delta^{1(9)}$-2-octalyl Vinyl Ether (7a).—The vinyl ethers of the cyclic allylic alcohols were prepared using mercuric acetate as catalyst.[11] In a typical reaction 10-methyl-$\Delta^{1(9)}$-2-octalol (**1**, 2.96 g, 0.018 mol) and 1.0 g of freshly recrystallized mercuric acetate (from absolute ethanol containing 0.025% glacial acetic acid) were stirred in 200 ml of refluxing ethyl vinyl ether (distilled after reflux from sodium and stored over sodium) for 10 hr. Best results were obtained when an additional 0.5–1.0 g of mercuric acetate was added every 2 hr.[6a] After the final addition of mercuric acetate, the mixture was refluxed overnight. To the cooled mixture, 0.25 ml of glacial acetic acid was added and stirring was continued for 3 hr.[6b] The mixture was diluted with an equal volume of petroleum ether, washed with 50 ml of 5% aqueous potassium hydroxide, dried (K_2CO_3), and rotary evaporated. The residue was chromatographed on 100 g of Florisil (60–100 mesh) with petroleum ether as the eluent. Distillation in a short-path still gave 3.4 g (74%) of the vinyl ether **7a**: bp 51–55° (0.06 mm); ir 3105, 3025, 1625, 1600, 1175 cm^{-1}; nmr δ 6.25 (dd, 1, $J_{AX} = 7$, $J_{BX} = 14$ Hz), 5.3 (broad s, 1, vinyl), 4.13 (dd, 1, $J_{BX} = 14$, $J_{AB} = 1.5$ Hz), 3.87 (dd, 1, $J_{AX} = 7$, $J_{AB} = 1.5$ Hz), 4.2 (m, 1, carbinol H), 1.1 (s, angular methyl, β-vinyl ether) and 1.02 (s, angular methyl, α-vinyl ether) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 149 (base peak), 192 (molecular ion).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.96; H, 10.73.

Thermolysis of Vinyl Ethers. Thermolysis of 7a.—The vinyl ethers were sealed in a Carius tube under nitrogen, neat or in freshly distilled decalin,[6a] and heated for 3–5 hr at 195–200°. In a typical run a 150-mg portion of the 10-methyl-$\Delta^{1(9)}$-2-octalyl vinyl ether **7a** was sealed neat or sealed with 1.5 ml of decalin in two separate Carius tubes, and heated for 5 hr at 200°. Nmr and glpc analyses of the reaction material in both cases showed 90% of the aldehyde **2a** and 10% of the dienes **3**.

1-Butyl-10-methyl-$\Delta^{1(9)}$-2-octalyl Vinyl Ether (7b).—The precursor to the vinyl ether was prepared by alkylating 10-methyl-$\Delta^{1(9)}$-2-octalone.[19] Sodium hydride (3.3 g of a 55% dispersion in mineral oil, 0.075 mol), washed with pentane and dried under nitrogen, was stirred in 100 ml of DMSO for 1.5 hr at 65°, under nitrogen. To the cooled mixture, the octalone (10.9 g, 0.066 mol) in 100 ml of DMSO was added over several minutes and stirred for 3.5 hr. *n*-Butyl bromide (9.6 g, 0.070 mol) in 50 ml of DMSO was added and the mixture was stirred for 3 days at room temperature. A 300-ml portion of a saturated ammonium chloride solution was added and the mixture was extracted with four 100-ml portions of ether. The ether layer was washed with saturated sodium chloride, dried ($MgSO_4$), and rotary evaporated to leave a crude yellow oil which by spectral and glpc analyses contained, in addition to starting material, mono- and dialkylated material and O-alkylated material. The crude oil was stirred in 100 ml of glacial acetic acid and 15 ml of water for 4 hr at 65° and overnight at room temperature. The solution was cooled in an ice bath, neutralized to pH 9 with 10% sodium hydroxide, and extracted with ether. The solvent was evaporated and 9.5 g of a crude oil was chromatographed on 700 g of silica gel using 2% ethyl acetate in hexane as the eluent. The first eluate contained 1.0 g of dialkylated product: ir 1705 cm^{-1}; nmr δ 5.4 (m, 1, vinyl), 0.95 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 276 (molecular ion). The second eluate yielded 3.9 g (27%) of the monoalkylated product: ir 1660, 1620 cm^{-1}; nmr δ 1.2 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 163 (base peak), 220 (molecular ion). The final eluate yielded 2.8 g of the starting enone. The monoalkylated enone (3.63 g, 0.0165 mol) was reduced with $LiAlH_4$ (0.63 g, 0.0165 mol) in the standard fashion (as for **1**) to yield 3.44 g of crude product. A small amount of the material was bulb-to-bulb distilled: ir 3500 cm^{-1}; nmr δ 3.9 (m, 1, carbinol H), 1.1 (s, angular methyl, β alcohol) and 1.0 (s, angular methyl, α alcohol) (total 3 H); mass spectrum (70 eV) *m/e* 165 (base peak), 222 (molecular ion). Glpc analysis[18] showed 80% β alcohol and 20% α alcohol.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 8.10; H, 11.52.

To the alcohol (0.77 g, 3.50 mmol) in 100 ml of refluxing ethyl vinyl ether was added 1.0 g of mercuric acetate every 2 hr for 8 hr and reflux was continued overnight. Work-up as for **7a** provided 0.7 g (81%) of analytically pure vinyl ether **7b** after passing through 50 g of Florisil: ir 3105, 1625, 1600, 1175 cm^{-1}; nmr δ 6.25 (dd, 1, $J_{AX} = 7$, $J_{BX} = 14$ Hz), 4.19 (dd, 1, $J_{BX} = 14$, $J_{AB} = 2$ Hz), 3.82 (dd, 1, $J_{AX} = 7$, $J_{AB} = 2$ Hz), 4.2 (m, 1, carbinol H), 1.1 (s, angular methyl, β alcohol) and 1.0 (s, angular methyl, α alcohol) (total = 3 H, ratio assumed 80β:20α); mass spectrum (70 eV) *m/e* 248 (molecular ion).

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.36; H, 11.35.

Thermolysis of 7b.—A 200-mg portion of the vinyl ether **7b**

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(17) A gift from Hoffmann-La Roche, Inc., Nutley, N. J.

(18) 5 ft, 10% KOH, 10% Carbowax on Chromosorb W.

(19) Z. G. Hajos, R. A. Micheli, D. R. Parrish, and E. P. Oliveto, *J. Org. Chem.*, **32**, 3008 (1967).

was sealed neat or sealed with 2 ml of decalin in two separate Carius tubes, and heated for 3 hr at 195°. Nmr and glpc analyses of the reaction material in both cases showed 80% of the aldehyde **8** and 20% of the dienes **9**. The dienes were collected by preparative glpc: nmr δ 5.6 (m, 2, vinyl), 0.95 and 0.9 (s, 3, angular methyls); mass spectrum (70 eV) *m/e* 204 (molecular ion).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.41; H, 11.74.

The aldehyde **8** was collected for spectral analysis by preparative glpc: ir 2720, 1725 cm^{-1}; nmr δ 9.7 (two overlapping t, 1, α and β formylmethyls), 5.55 (m, 1, vinyl), 1.0 (s, angular methyl); mass spectrum (70 eV) *m/e* 248 (molecular ion).

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.09; H, 11.33.

1β-*tert*-Butoxy-5,6,7,7a-tetrahydro-7αβ-methyl-5-indanyl Vinyl Ether (10a).—To the alcohol **4** (3.7 g, 0.0165 mol) in 250 ml of refluxing ethyl vinyl ether was added 1.0 g of mercuric acetate every 2 hr for 8 hr and reflux was continued overnight. Work-up as for **7a** provided 3.26 g (79%) of vinyl ether **10a**: bp 97–100° (0.1 mm); ir 3105, 1625, 1600, 1175 cm^{-1}; nmr δ 6.25 (dd, 1, $J_{AX} = 7$, $J_{BX} = 14$ Hz), 5.35 (s, 1, vinyl), 4.13 (dd, 1, $J_{BX} = 14$, $J_{AB} = 1.5$ Hz), 3.85 (dd, 1, $J_{AX} = 7$, $J_{AB} = 1.5$ Hz), 4.3 (m, 1, carbinol H), 3.35 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 1.0 (s, 3 H, angular methyl); mass spectrum (70 eV) *m/e* 151 (base peak), no molecular ion.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.80; H, 10.40.

Thermolysis of 10a.—A 200-mg portion of the vinyl ether was sealed neat or sealed with 1:5 ml of decalin in two separate Carius tubes and heated for 4 hr at 195°. Nmr and glpc analyses of the reaction material showed (i) neat, 70% aldehyde **5a** and 30% dienes **6**; (ii) decalin, 90% aldehyde **5a** and 10% dienes **6**.

1β-*tert*-Butoxy-4-*n*-butyl-5,6,7,7a-tetrahydro-7aβ-methyl-5-indanyl Vinyl Ether (10b).—Sodium hydride (5.0 g of a 55% suspension in mineral oil, 0.115 mol), washed with pentane and dried under nitrogen, was stirred in 100 ml of DMSO for 1.5 hr at 70° under nitrogen. To the cooled mixture 1β-*tert*-butoxy-7,7a-dihydro-7aβ-methyl-5(6*H*)-indanone[17] (22.2 g, 0.100 mol) in 100 ml of DMSO was added over several minutes and stirred for 2 hr. *n*-Butyl bromide (15.7 g, 0.115 mol) in 50 ml of DMSO was added and the mixture was stirred for 2 days at room temperature. Work-up and removal of O-alkylated material was carried out as in the preparation of **7b** to yield 27 g of crude oil. The oil was vacuum distilled to yield 13 g of a fraction containing 85% of monoalkylated material. This mixture was chromatographed on 700 g of silica gel with 2% ethyl acetate in hexane as the eluent to yield as first eluate 0.55 g of the dialkylated material: ir 1705 cm^{-1}; nmr δ 5.25 (m, 1, vinyl), 4.75 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 1.0 (s, 3, angular methyl). The second eluate yielded 3.5 g of a 2:1 mixture of mono- to dialkylated material. The third eluate yielded 8.13 g which was distilled to give 7.6 g of the monoalkylated material: bp 120–125° (0.1 nm); ir, 1660, 1605 cm^{-1}; nmr δ 3.5 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 1.05 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 222 (base peak), 278 (molecular ion).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.92; H, 10.65.

The monoalkylated enone (6.11 g, 0.022 mol) was reduced with $LiAlH_4$ (0.84 g, 0.022 mol) in the standard fashion (as for **1**) to yield 6.09 g of a white solid. A small amount of the alcohol was bulb-to-bulb distilled: ir 3400 cm^{-1}; nmr δ 4.0 (m, 1, carbinol H), 3.25 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 0.93 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 161 (base peak), no molecular ion. Glpc analysis[18] showed only the β alcohol.

Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.94; H, 11.49.

To the crude alcohol (2.8 g, 0.010 mol) in 100 ml of refluxing ethyl vinyl ether was added 1.0 g of mercuric acetate every 2 hr for 8 hr and reflux was continued overnight. Work-up as for **7a** provided 2.8 g (92%) of analytically pure vinyl ether **10b** after passing through 50 g of Florisil: ir 3105, 3125, 1625, 1600, 1175 cm^{-1}; nmr δ 6.25 (dd, 1, $J_{AX} = 7$, $J_{BX} = 14$ Hz), 4.19 (dd, 1, $J_{BX} = 14$, $J_{AB} = 1.5$ Hz), 3.85 (dd, 1, $J_{AX} = 7$, $J_{AB} = 1.5$ Hz), 4.2 (m, 1, carbinol H), 3.27 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 0.95 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 119 (base peak), no molecular ion.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.58; H, 11.23.

Thermolysis of 10b.—A 200-mg portion of the vinyl ether was sealed neat or sealed with 2 ml of decalin in two separate Carius tubes and heated for 3 hr at 195°. Nmr and glpc analyses of the reaction material showed (i) neat, 45% aldehyde **11** and 55% dienes **12**; (ii) decalin, 65% aldehyde **11** and 35% dienes **12**. The dienes were collected for spectral analyses by preparative glpc: ir 3030 cm^{-1}; nmr δ 5.4 (m, 2, vinyl), 3.65 (m, 1, *tert*-butyl–OCH), 1.15 (s, 9, *tert*-butyl), 0.83 and 0.80 (s, 3, angular methyls); mass spectrum (70 eV) *m/e* 119 (base peak), 262 (molecular ion).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.17; H, 11.47.

The aldehyde **11** was collected for spectral analyses by preparative glpc: ir 2720, 1725 cm^{-1}; nmr δ 9.65 (t, 1 H, $J = 3$ Hz), 5.5 (m, 1, vinyl), 3.7 (m, 1, *tert*-butyl–OCH), 2.4 (d, 2, $J = 3$ Hz, formylmethylene), 1.15 (s, 9, *tert*-butyl), 0.83 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 57 (base peak), no molecular ion.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.51; H, 11.24.

10-Methyl-$\Delta^{1(9)}$-2-octalyl Isopropenyl Ether (13).—To the alcohol **1** (1.5 g, 0.090 mol) in 100 ml of refluxing methyl isopropenyl ether[7b] was added 1.0 g of mercuric acetate every 2 hr for 8 hr and reflux was continued overnight. Work-up as for **7a** provided 200 mg of analytically pure vinyl ether **13**: ir 1650, 1610 cm^{-1}; nmr δ 5.33 (m, 1, vinyl), 4.32 (m, 1, carbinol H), 3.73 (s, 2, methylene), 1.70 (s, 3, vinyl methyl), 1.1 (s, angular methyl, β-vinyl ether) and 1.02 (s, angular methyl, α-vinyl ether) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 149 (base peak), 206 (molecular ion).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.38; H, 10.60.

Thermolyses of 13.—A 200-mg portion of the isopropenyl ether was sealed neat in a Carius tube and heated for 2.5 hr at 200°. Glpc analysis showed 65% of dienes **3** and 35% of methyl ketone **14**. The ketone was collected by preparative glpc: ir 1715 cm^{-1}; nmr δ 5.55 (s, 2 H, vinyl), 2.0 (s, 3, methyl ketone), 0.95 (s, angular methyl, β-methyl ketone) and 0.90 (s, angular methyl, α-methyl ketone) (total 3 H, ratio 85β:15α); mass spectrum (70 eV) *m/e* 58 (base peak), 57 (83% of base peak), 206 (molecular ion).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.35; H, 10.54.

1β-*tert*-Butoxy-5,6,7,7a-tetrahydro-7aβ-methyl-5-indanyl Isopropenyl Ether (15).—To the alcohol **4** (1.12 g, 5.00 mmol) in 30 ml of refluxing methyl isopropenyl ether[7b] was added 0.5 g of mercuric acetate every 2 hr for 8 hr and reflux was continued overnight. Work-up as for **7a** provided 200 mg of analytically pure vinyl ether **15**: ir 1650, 1610 cm^{-1}; nmr δ 5.4 (s, 1, vinyl), 4.4 (m, 1, carbinol H), 3.71 (s, 2, methylene) 3.4 (m, 1, *tert*-butyl–OCH), 1.74 (s, 3, vinyl methyl), 1.15 (s, 9, *tert*-butyl), 1.0 (s, 3, angular methyl); mass spectrum (70 eV) *m/e* 57 (base peak), 264 (molecular ion).

Anal. Calcd for $C_{17}H_{28}O_2$: C, 72.22; H, 10.67. Found: C, 77.18; H, 10.56.

Thermolysis of 15.—A 200-mg portion of the isopropenyl ether was sealed neat in a Carius tube and heated for 2.5 hr at 200°. Nmr and glpc analyses showed only the dienes **6**.

Registry No.—**1,** 26675-10-5; **2a,** 33834-80-9; **2b,** 33872-31-0; **2c,** 33834-81-0; **4,** 33835-35-7; **5a,** 33835-36-8; **5c,** 33835-37-9; **7a,** 33834-82-1; **7b,** 33890-39-0; **8,** 33834-83-2; **10a,** 33835-38-0; **10b,** 33835-39-1; **11,** 33834-84-3; **13,** 33834-85-4; **14,** 33834-86-5; **15,** 33872-32-1; alcoholic precursor of **7b,** 33834-87-6; monoalkylated enone (precursor of **10b**), 33835-40-4; alcoholic precursor of **10b,** 33835-41-5; ethyl vinyl ether, 109-92-2; *N,N*-dimethylacetamide dimethyl acetal, 18871-66-4; triethyl orthoacetate, 78-39-7; decalin, 91-17-8.