(13) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).
(14) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).
(15) Since completion of this work the results of the work of Johnson and coworkers[12] became available. This evidence suggests the possibility that the yield of the isomer **17** in the cyclization stage of the present scheme could be improved.
(16) Melting points labeled (vacuum) were taken in evacuated capillaries on a Hoover capillary melting point apparatus, while all others were determined on a Kofler micro hot stage melting point apparatus. All melting points and boiling points are uncorrected. Infrared (ir) spectra were determined on a Perkin-Elmer 237B grating infrared spectrometer, and nuclear magnetic resonance (NMR) spectra were recorded using either a Varian A-60A or T-60 spectrometer. Chemical shifts are reported as δ values in parts per million relative to TMS (δ_{TMS} 0.0 ppm) as an internal standard.

Gas–liquid phase chromatographic (GLC) analyses were determined on either a Hewlett-Packard 5750 or F & M 810 research chromatograph using helium carrier gas at a flow rate of 60 ml/min. Unless otherwise noted, all analytical GLC was conducted on a 6 ft × 0.125 in. column packed with 4% SE-30 on 60–80 mesh Chromosorb W -DMCS.

Preparative thin layer chromatography (preparative TLC) was carried out on 20 × 20 × 0.2 cm glass plates coated with silica gel $PF_{254+266}$ (Brinkman Instruments Co.). Analytical thin layer chromatography (TLC) was conducted on 1 × 3 in. microscope slides coated with a 0.5-mm layer of silica gel G or $PF_{254+266}$.

Alumina used for column chromatography refers to the grade I, neutral variety manufactured by M. Woelm, Eschwege, Germany, and made up to grade II or III as indicated by the addition of 3 or 6% water prior to use. Silica gel columns used the 0.05–0.2-mm silica gel manufactured "for column chromatography" by E. Merck & Co., Darmstadt, Germany. Preparative medium-pressure column chromatography was performed using 0.5 × 20 in. or 2 × 20 in. glass columns with fittings supplied by Chromatronix, Inc., Berkeley, Calif., and an instrument minipump supplied by Milton Roy Co., St. Petersburg, Fla. (instrumentation designed by R. H. Mueller, these laboratories, and copies are available on request). The columns were packed with silica gel H "for TLC acc. to Stahl" (10–40 μ manufactured by E. Merck & Co., Darmstadt, Germany). Solvents were degassed under water aspirator vacuum prior to use.

"Dry" solvents were dried immediately prior to use. Ether, benzene, tetrahydrofuran, dioxane, and dimethoxyethane were distilled from lithium aluminum hydride; *tert*-butyl alcohol, dimethyl sulfoxide, pyridine, and hexamethylphosphoramide (HMPA) were distilled from calcium hydride; dichloromethane, carbon tetrachloride, diodomethane, and methyl iodide were distilled from phosphorus pentoxide; ammonia was distilled from the tank and then from a blue lithium or sodium solution; acetone was analytical reagent grade distilled from potassium permanganate; formic acid was distilled from boric anhydride. "Petroleum ether" refers to the "Analyzed Reagent" grade hydrocarbon fraction, bp 30–60°, which is supplied by J. T. Baker Co., Phillipsburg, N.J., and was not further purified.

Reactions described as run under nitrogen or argon employed a mercury bubbler arranged so that the system could be alternately evacuated and filled with the inert gas and left under a positive pressure.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.
(17) In cases where products were isolated "by solvent extraction," the procedure generally followed was to extract the aqueous layer with several portions of the indicated solvent; then the organic layers were combined and washed with water, followed by saturated brine. The organic layer was dried over anhydrous sodium or magnesium sulfate, then filtered, and the solvent was evaporated from the filtrate under reduced pressure (water aspirator) using a rotary evaporator. The use of the terms "base wash" or "acid wash" indicate washing the combined organic layers with saturated aqueous sodium bicarbonate solution or with dilute aqueous hydrochloric acid, respectively, prior to the aforementioned washing with water.
(18) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, *39* (1946); see also C. Djerassi, R. R. Engle, and A. Bowers, fiJ. Org. Chem., **21**, 1547 (1956).
(19) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).
(20) F. G. Mann and M. J. Pragnell, *Chem. Ind. (London)*, 1386 (1964).
(21) E. Crunden and F. Hudson, *J. Chem. Soc.*, 3591 (1962); H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. Wilding, and S. J. Woodcock, ibid., 2921 (1949).

Experiments Directed toward the Total Synthesis of Terpenes. XXII. A Polyene Cyclization Approach to Tetradecahydropicene Derivatives for Pentacyclic Triterpene Synthesis[1]

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The syntheses of two trienols through the ketones **8** and **9** are described, and the results of the stannic chloride catalyzed cyclizations of these materials is presented. The product variation as a result of solvent changes in the cyclization of the trienol from the ketone **8** revealed the formation of significant amounts of solvent-trapped products. The synthesis of the trienol from the ketone **25** follows the same pattern as the above models, but the yield of the olefin **26** in the stannic chloride cyclization is significantly lower than in the model series. Attempts to convert the olefin **26** to a known intermediate in a previous alnusenone (**1**) total synthesis were unsuccessful. The X-ray structural analysis of the ketone **27** is presented.

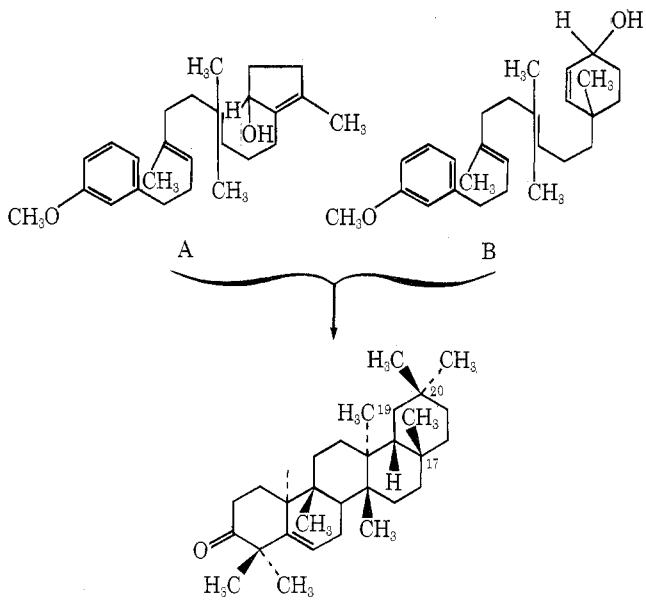
In the preceding paper[4] in this series the results of a program designed to construct intermediates for the total synthesis of alnusenone (**1**) via the acid-catalyzed cyclization of the 3-methyl-2-cyclopentenol A were discussed. At the inception of this synthetic scheme two possible cyclic allylic alcohol systems were considered useful candidates for the initiation of the cyclization step.[5] In addition to the 3-methyl-2-cyclopentenol system A, the 4-methyl-2-cyclohexenol system B has significant potential. In principle cyclization of this molecule will establish a pentacyclic intermediate in which the E ring is already six-membered and bears the desired C-17[1] methyl group at a cis D/E ring fusion. Addition of the *gem*-dimethyl grouping at C-20[1] through the agency of the C-19–C-20[1] double bond that results from cyclization would then complete the construction of the triterpenoid E ring. The advantages of this concept are apparent, for it avoids not only the selective lithium–ammonia reduction of the A,E-diaromatic pentacyclic intermediate used in the initial approach[6] but also the necessity for the subsequent incorporation of the C-17[1] angular methyl group that is inherent in both preceding syntheses.[4,6] While these two operations did not pose significant problems in fact, the advantages of this proposed scheme were great enough to warrant a concurrent investigation. The results of both a model study and the cyclization of the alcohol B are presented here.

Of initial concern in this work was the development of procedures for the conversion of the dienol **24** (Chart III) to the desired cyclization substrate B. The efficient synthesis already described[7] for the dienol **24** dictated its use in the synthesis of both allylic alcohols A[4] and B, but different subsequent schemes were required in each case. In addition a model series designed to test the efficiency of the cyclization step was deemed advisable. Even though this stage of the scheme is based on the principles that have been developed in the Johnson laboratories,[5,8] the presently proposed

Table I
Variation in Product Composition with Solvent on Cyclization of 4-Methyl-4-(3′-methyl-(*E*)-3,7-octadienyl)-2-cyclohexenol

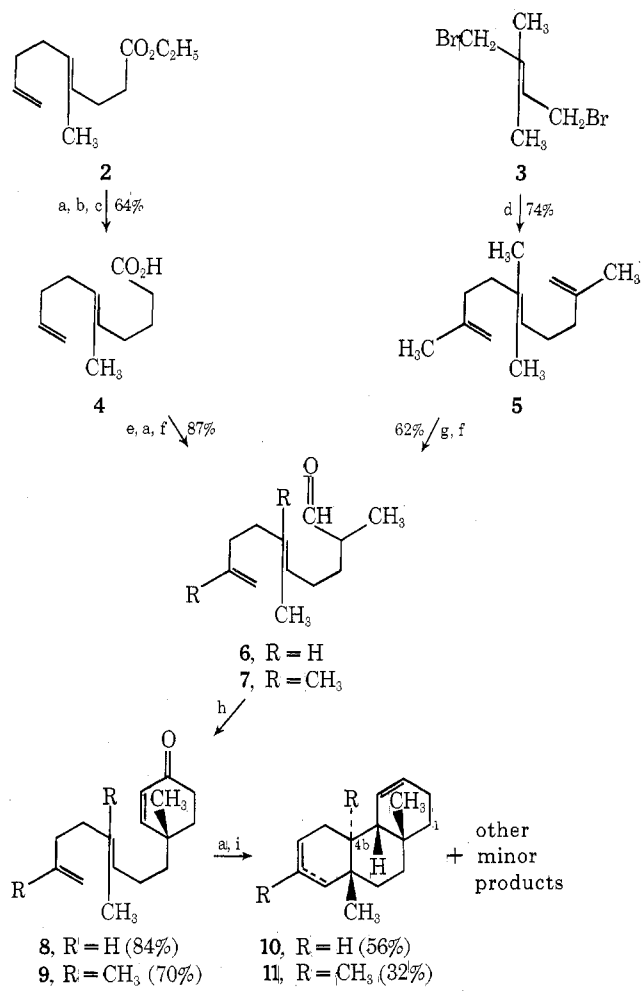
Expt	Solvent	Molar ratio SnCl/alc	Temp, °C	Reaction time	Products (% isolated yield)
1	CH_3NO_2	1.5	−28	1.5 min	**10** (25%)
2	CH_2Cl_2–$CO(OCH_2)_2$	6	25	1 hr	**10** (56%), **20** (4%)
3	C_6H_6	6	5	1.5 hr	**10** (22%), **19** (28%)
4	CH_2Cl_2	1.5	25	4 min	**10** (14%), **19** (35%)
5	CF_3CH_2OH	3	0	3 hr	**10** (20%), **21** (16%)
6	$C_6H_5OCH_3$	3	−10	15 min	**10** (12%), **20** (25%), **22** (20%), **23** (28%)
7	$C_6H_5CO_2CH_3$	3	then 25	5 hr	**10** (35%), **20** (3%)

substrate B differs in subtle but significant ways from those employed by Johnson. Thus, a 4-methyl-2-cyclohexenol is proposed here in contrast to the 1- and 3-methyl-2-cyclohexenols[8a,b] used by Johnson, and it seemed reasonable to test the stereochemical outcome of the cyclization with this system in a less complex model series before the dienol **24** was used. The synthesis and cyclization of two such model systems—the alcohols derived from the ketones **8** and **9**—were investigated.



An obvious route for the formation of the required allylic alcohols was through hydride reduction of the enones **8** and **9** (Chart I). Annelation of the enamines[9] derived from the aldehydes **6** and **7** with methyl vinyl ketone provided ready access to these enones **8** and **9.** For the construction of the aldehyde **7** in the series with the tetrasubstituted double bond, it was a simple matter to hydroborate[10] and then oxidize[11] the symmetrical diene **5** obtained from the coupling reaction[12] between methallylmagnesium bromide and the dibromide **3.**[13] However, since a polyene system like **5** was *not* intermediate in the established synthesis of the dienol **24,** another route to a 2-methylaldehyde similar to **7** was sought that required the introduction of the methyl group at this site. Such a system was the aldehyde **6,** which was available through direct methylation of the acid **4** and then a reduction–oxidation[11] sequence. The choice of this system **6** that contained the trisubstituted rather than the tetrasubstituted double bond was predicated on its ease of access through the ester **2,**[14] and the expectation that cyclization of the alcohol derived from the resulting enone **8** would be efficient.[8] That the structure and stereochemistry of the resulting tricyclic products would be more readily amenable to definition than in the tetrasubstituted double bond series was also considered.

Chart I
Hydrophenanthrene Formation via Polyene Cyclization[a]

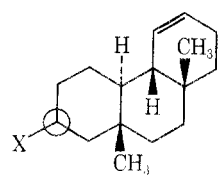


[a] a, $LiAlH_4$, Et_2O; b, Ph_3P, CCl_4; c, Mg, THF, CO_2; d, $CH_2{=}C(CH_3)CH_2MgBr$, THF; e, $LiN(i\text{-}Pr)_2$, THF, CH_3I; f, $CrO_3 \cdot 2Py$, CH_2Cl_2; g, Sia_2BH, THF, H_2O_2, aq NaOH; h, C_4H_9N,C_6H_6, $CH_3COCH{=}CH_2$, NaOAc, aq HOAc; i, $SnCl_4$, $(CH_2O)_2CO$, CH_2Cl_2.

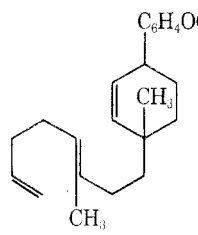
In fact, cyclization of the alcohol derived from the ketone **8** wth stannic chloride in dichloromethane–ethylene carbonate solution[15] led to a mixture of the dienes **10** in 56% yield. In addition it was possible to identify a minor component of the product mixture as the cholorocarbon **20** that resulted from solvent trapping of the tricyclic cation. This interesting observation led to the consideration of the effect of the solvent on the product distribution from the cy-

clization (Table I). It is interesting to note that in benzene, a common solvent for such reactions,[5] the *major* isolated product arises from attack of the tricyclic cation by the benzene solvent. Even the poorly nucleophilic solvent trifluoroethanol[16] successfully competed with proton abstraction and produced significant amounts of the ether **21.** Comparison of experiments 2 and 4 reveals the effect of the addition of ethylene carbonate to the reaction mixture. This reagent has been used[15] to trap the vinyl cation generated during cyclizations that terminate at an acetylenic linkage. In the present case, where a saturated cationic center is generated by cyclization, ethylene carbonate behaves as a base and promotes proton abstraction.

Particularly interesting, in view of the past[4] and proposed use of the anisole ring in the cyclization substrates, is the result (expt 6) when the cyclization was conducted in anisole. Even though the anisole solvent was quite nucleophilic and trapped both the initial **23** and tricyclic **22** cations effectively, it was not nucleophilic enough to prevent the formation of the dienes **10** and even allowed the tricyclic cation to be trapped by chloride from the catalyst. In addition the observed formation of *both* the ortho- and para-substitution products **22** and **23** corroborates previous experience[4,8c,17] in which both substitution patterns resulted when substrates that contained the anisole ring were used.



19, X = C_6H_5
20, X = Cl
21, X = CF_3CH_2O
22, X = *o*- and *p*-$CH_3OC_6H_4$



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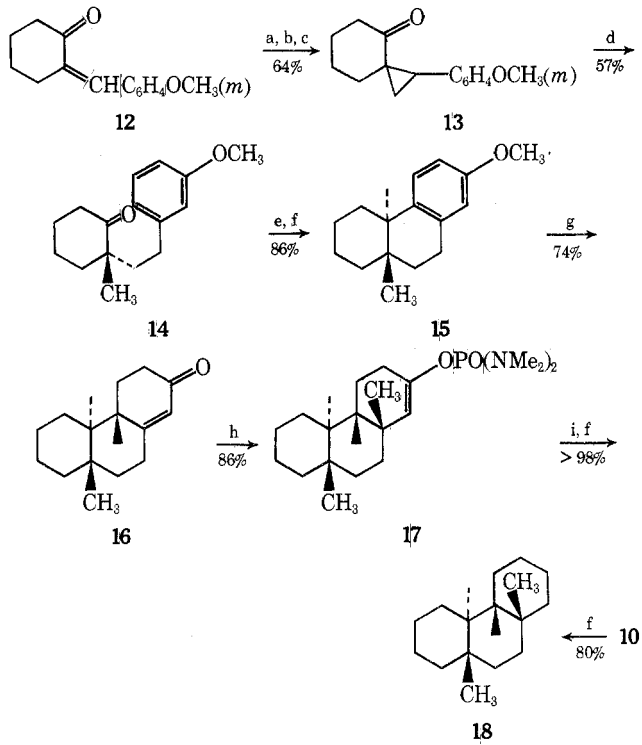
In order to provide the structure and stereochemistry of the tricyclic products from this cyclization, an alternate, stereorational synthesis of the system was developed (Chart II). A new route to the key substance in this sequence—the ketone **14**—was developed from *m*-methoxybenzylindenecyclohexanone (**12**)[18] via methylenation[19,20] to the cyclopropyl ketone **13** and then reductive methylation[21] to form the desired intermediate **14.** This sequence avoids the low yield anticipated from the more obvious alkylation of 2-methylcyclohexanone with β-(*m*-methoxyphenyl)ethyl bromide and should prove to be of general utility for the construction of systems such as the ketone **14.**

For comparison purposes the hydrocarbon **18** was prepared from the ketone **14** as outlined in Chart II. Strong precedence[22] as well as experimental evidence[23] exists for the stereochemical outcome at each stage, and the identity of the samples of the hydrocarbon **18** prepared by this route and by hydrogenation of the dienes **10** was established by spectra and GLC comparison. At least for a trisubstituted central double bond, this identity establishes that the cyclization of the 4-methyl-2-cyclohexenol bearing system gives the same trans-anti-trans stereochemical result as that observed by Johnson[8] in the 1- and 3-methyl cases.

Attention was now turned to the cyclization of the alcohol derived from the ketone **9** in order to test the effect of the central tetrasubstituted double bond on the outcome. Cyclization of this material with stannic chloride in dichloromethane again resulted in the formation of a complex mixture of products from which the major isolated component was taken to be the diene **11.** Although no detailed structure proof was undertaken, the spectral properties of this material as well as the analogy to the preceding cyclization serve to substantiate this structural assignment. The significant difference between the present cyclization experiment and the preceding one is the lower yield and more complex product mixture. Under the conditions used the more basic tetrasubstituted double bond may interfere through competitive interaction with the catalyst, but probably more significant is the severe congestion that develops during cyclization between the C-1[1] methylene and the C-4bα[1] angular methyl group. This interaction was lacking in the preceding trisubstituted double bond case and may add sufficient energy to the cyclization transition state to allow alternative reaction pathways to compete more effectively.

Chart II
Synthesis of the Hydrocarbon 18[a]



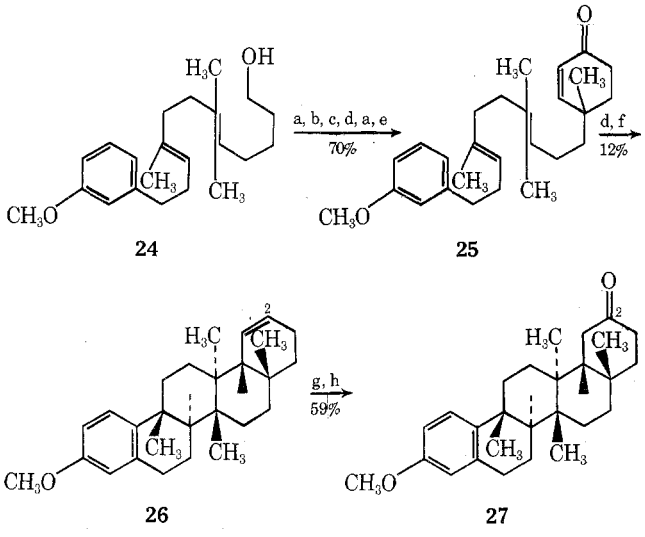
[a] a, $NaBH_4$, CH_3OH; b, Zn(Cu), CH_2I_2, Et_2O; c, 8 *N* aq H_2CrO_4, acetone; d, Li, NH_3, $(CH_3OCH_2)_2$, *t*-BuOH, HMPA, CH_3I; e, PPA; f, 10% Pd/C, EtOH or C_6H_{14},H_2; g, Li, NH_3, THF, *t*-BuOH; 5 *N* aq HCl, CH_3OH; h, $LiCu(CH_3)_2$, Et_2O, HMPA, $ClPO(NMe_2)_2$; i, Li, $EtNH_2$, THF, *t*-BuOH.

In spite of this nascent trend toward lower yields in the cyclization step as the system becomes more similar to the desired substrate B for the pentacyclic synthesis, the advantages of this approach in terms of structural and stereochemical control encouraged the continuation of the effort toward its desired conclusion.

Conversion of the dienol **24**[7] to the enone **25** (Chart III) followed the procedure already tested in the formation of the enone **8** from the acid **4** (Chart I), and the overall yield was equally as satisfactory. Cyclization of the alcohol obtained on hydride reduction of the enone **25** was accomplished with stannic chloride in dichloromethane–ethylene carbonate.[15] Again a complex mixture of products resulted, but one product predominated enough to permit its isolation and purification after repeated chromatography. The spectral properties of this material were consistent with those expected of the desired olefin **26.** Unfortunately, the unsatisfactorily low yield in which the olefin **26** was formed

in this cyclization could not be increased by experimentation with several alternate reaction conditions.

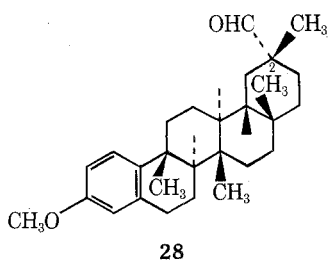
Chart III
Formation of Pentacyclic Olefin 26 via Polyene Cyclization[a]



[a] a, $CrO_3 \cdot 2Py$, CH_2Cl_2; b, $AgNO_3$, aq NaOH, EtOH; c, LiN(*i*-Pr)$_2$, THF, HMPA, CH_3I; d, $LiAlH_4$, Et_2O; e, C_4H_9N,C_6H_6, $CH_3COCH{=}CH_2$, NAOAc, aq HOAc; f, $SnCl_4$, $(CH_2O)_2CO$, CH_2Cl_2; g, $BH_3 \cdot THF$, THF, H_2O_2, aq NaOH; h, 8 *N* aq H_2CrO_4, acetone.

All that remained to connect the thread of the present synthetic scheme with that of the previously successful total synthesis[6] of alnusenone (1) was the conversion of the olefin **26** to the pentacyclic system that had a *gem*-dimethyl grouping at C-2.[1]

As a first step in this operation, hydroboration[10] and then oxidation[24] of the olefin **26** gave the ketone **27**, the point at which the synthetic effort came to a halt. The steric congestion about substituents at C-2[1] as a result of the cis D/E ring fusion and the subsequent proximity of the C-14aα[1] methyl group thwarted several attempts to develop means for this transformation. While the severely limited supply of the olefin **26** did not allow extensive experimentation, treatment with trimethylaluminum–benzene at 200°[25] and methylenetriphenylphosphorane in dimethyl sulfoxide[26] were found to be ineffectual. Formation of the C-2 oxirane by the method of Coates and Johnson[27] was possible and subsequent rearrangement of this oxirane to the C-2 aldehyde and then methylation led to material which had spectral properties (ir and NMR) consistent with the aldehyde **28**. Again limited supplies owing to low



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yields did not allow complete purification of this material, and it could not be freed from minor components that resulted from side reactions at each stage. Material of sufficient purity for combustion analysis was therefore not obtained. As might be expected, reduction of this aldehyde **28** to the desired C-2 *gem*-dimethyl system was not possible. Even after reduction with hydride to what was presumed to be the primary alcohol, the severe steric hindrance thwarted the formation of a phosphorodiamidate[28] derivative. These observations, as well as the bulk of precedence,[29] suggest the stereochemistry shown at C-2[1] in the aldehyde **28.** The aldehyde function in this configuration is effectively blocked toward intermolecular reactions by the C-14aα methyl group. This same steric situation exists in alnusenone (1) itself and is in part responsible for the ease of the acid-catalyzed rearrangement[30] of that carbon skeleton to the more familiar B-amyrin structure.

Table II
Crystal Data

Molecule trans-anti-trans-anti-cis ketone 27
Formula $C_{27}H_{38}O_2$
Formula wt 394.6
Space group $C2/c$
Systematic absences
hkl, $h + k = 2n + 1$
no l $l = 2n + 1$
a 50.1255 (16)
b 7.5886 (3)
c 11.4010 (4)
β 90.504 (2)
Z 8
F_{000} 1728
λ Co Kα 1.7902 Å
D_c 1.21 g cm^{-3}
D_m 1.23 ± 0.02 g cm^{-3}
μ 8.8 cm^{-1}
V 4336 Å^3
Background time 30 sec
Scan rate 2°/min
No. of reflections 2505
Nonzero reflections 2319
Final R index [a] 0.168
Standard deviation in C,O bond lengths 0.01 Å
Standard deviation in C,O bond angle 0.7°

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

In view of these observations and the very limited supplies of the olefin **26,** no further efforts were undertaken to effect the introduction of the *gem*-dimethyl grouping at C-2. In order to confirm the proposed structures and thereby establish that the formation of the olefin **26** in the cyclization reaction had taken the expected course, a single-crystal X-ray structural analysis was undertaken on the ketone **27.** The X-ray data were collected with iron-filtered Co Kα radiation to a spacing of 0.97 Å. The structure was solved by direct methods and refined by full-matrix least-squares refinement with isotropic temperature factors of all heavier atoms. The R index is 0.168 (Table II). A stereoplot of the molecule (Figure 1) confirms the structure assigned on the earlier spectral data and graphically illustrates the steric situation in the C/D/E rings that prevented the conversion of this ketone **27** to the desired hexamethyl system.

This work and that reported in the preceding paper demonstrate that the polyene cyclization sequence[5] is a valid means for the construction of polycyclic systems from polyolefinic substrates that make no attempt to simulate natural intermediates. The results of the cyclizations in anisole (Table I) and with those systems that incorporate the anisole ring in the polyene leave much to be desired in our hands.[8c] This should not, however, detract from the efficiency of the scheme, as demonstrated by the good yields obtained in the model aliphatic systems investigated. The

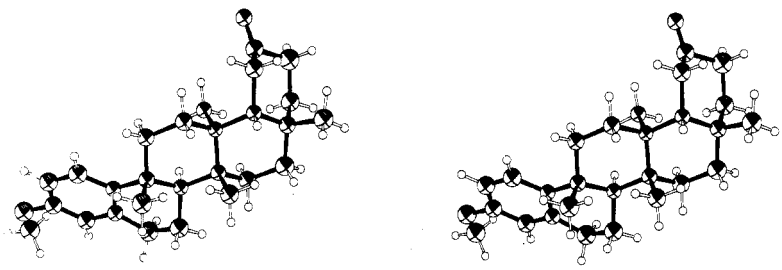

Figure 1. Stereoplot of the ketone **27.**

present work serves to underscore the effect of steric congestion on both the cyclization stage and the subsequent, more standard transformations.

Experimental Section[31]

4-Methyl-(*E*)-4,8-nonadienol. A solution of 4.63 g (23.6 mmol) of the ester **2**[14] in 30 ml of dry ether was added over 1 hr to a mixture of 0.90 g (23.6 mmol) of lithium aluminum hydride in 30 ml of dry ether, and the mixture was stirred at room temperature for 12 hr. After decomposition of the excess hydride with water and aqueous base, 3.58 g (99%) of the corresponding alcohol was isolated by ether extraction.[32] Bulb-to-bulb distillation (72°, 0.5 mm) of a portion of this material afforded analytically pure material: ir ($CHCl_3$) 3630 (OH), 1673 (C-4 C=C), 1645, 1010, and 920 cm^{-1} (C-8 C=C); NMR ($CDCl_3$) δ 1.56 (s, 1, OH), 1.63 (s, 3, C-4 CH_3), 3.63 (t, 2, J = 6 Hz, C-1 H_2), 4.8–5.3 (m, 3, C-5 H and C-9 H_2), and 5.6–6.3 (m, 1, C-8 H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.96; H, 11.79.

1-Chloro-4-methyl-(*E*)-4,8-nonadiene. A solution of 2.038 g (13.2 mmol) of the alcohol above and 3.80 g (14.5 mmol) of triphenylphosphine in 10 ml of dry carbon tetrachloride was heated at reflux for 33 hr, during which time approximately 10 ml of volatile distillate was removed. After cooling, the mixture was diluted with 20 ml of petroleum ether, and filtered to remove precipitated triphenylphosphine oxide, and then the crude chloride (2.7 g) was isolated by evaporation of the filtrate at atmospheric pressure. Purification of this material by chromatography on 75 g of silica gel (580 ml of petroleum ether eluent) and then bulb-to-bulb distillation at 75° and 1.75 mm gave 1.688 g (74%) of the corresponding chloride as a colorless liquid which showed one volatile component on GLC (100°): ir ($CHCl_3$) 1670 [CH=C(CH_3)], 1640, 995, and 920 cm^{-1} (CH=CH_2); NMR ($CDCl_3$) δ 1.61 (s, 3, C-4 CH_3), 3.56 (t, 2, J = 6 Hz, C-1 H_2), 4.8–5.3 (m, 3, C-5 H and C-9 H_2), and 5.6–6.3 (m, 1, C-8 H).

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.55; H, 9.92; Cl, 20.52. Found: C, 69.63; H, 9.94; Cl, 20.47.

5-Methyl-(*E*)-5,9-decadienoic Acid (4). The Grignard reagent prepared from 7.55 g (43.7 mmol) of the above chloride and 7.2 g (0.3 g-atom) of magnesium in 60 ml of dry tetrahydrofuran was poured into a slurry of 300 g of Dry Ice in 100 ml of ether, and then the mixture was acidified to pH 2 with 6 N aqueous hydrochloric acid. The mixture was extracted with 2 × 10 ml of ether, and the combined ethereal extracts in turn were extracted with 3 × 100 ml of 10% aqueous sodium hydroxide solution. After acidification of the basic extracts to pH 2 and isolation of the crude product by ether extraction,[32] bulb-to-bulb distillation of the residue at 98–101° and 0.15 mm gave 6.96 g (88%) of the acid **4** as a colorless oil that consisted of a single volatile component on GLC (160°): ir ($CHCl_3$) 3400–2750 (bonded OH and CH), 1702 (C=O), 1635, 990, and 910 cm^{-1} (CH=CH_2); NMR ($CDCl_3$) δ 1.60 (s, 3, C-5 CH_3), 4.8–5.3 (m, 3, C-6 H and C-10 H_2), 5.6–6.3 (m, 1, C-9 H), and 10.81 (br s, 1, CO_2H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.57, H, 10.00.

2,5-Dimethyl-(*E*)-5,9-decadienoic Acid. To a solution of lithium diisopropylamide, prepared from 13.4 ml (9.64 g, 0.095 mol) of diisopropylamine and 28 ml (0.088 mol) of a 3.13 M hexane solution of n-butyllithium in 63 ml of dry tetrahydrofuran, was added with stirring under an argon atmosphere at 0° a solution of 6.94 g (0.038 mol) of the acid **4** in 30 ml of dry tetrahydrofuran. After the reaction solution had stirred for 15 min, 17.2 ml (17.09 g, 0.096 mol) of hexamethylphosphoramide, followed by 3.57 ml (8.16 g, 0.057 mol) of methyl iodide, were added at 0°, and then the mixture was stirred for 2 hr at room temperature. After acidification to pH 2, the organic layer was separated and washed with 5 × 75 ml of 10% aqueous hydrochloric acid solution and then extracted with 4 × 50 ml of 1:1 10% aqueous sodium hydroxide solution and saturated brine. After acidification of the basic extracts and isolation of the product by petroleum ether extraction,[32] purification of the crude product by bulb-to-bulb distillation at 111° and 0.18 mm afforded 7.06 g (95%) of the methylated acid which consisted of a single volatile component on GLC (160°): ir ($CHCl_3$) 3400–2750 (OH and CH), 1700 (C=O), 1640, 990, and 915 cm^{-1} (C=C and CH=CH_2); NMR ($CDCl_3$) δ 1.18 (d, 3, J = 6.5 Hz, C-2 CH_3), 1.61 (s, 3, C-5 CH_3), 4.8–5.3 (m, 3, C-6 H and C-10 H_2), 5.5–6.2 (m, 1, C-9 H), and 11.30 (br s, 1, CO_2H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.40; H, 10.26.

2,5-Dimethyl-(*E*)-5,9-decadienal (6). Reduction of 11.68 g (0.06 mol) of the above methylated acid was accomplished with 3.42 g (0.09 mol) of lithium aluminum hydride in 190 ml of dry ether at room temperature for 10 hr. After decomposition of the excess hydride with 8.5 ml of water, followed by the addition of 5 g of magnesium sulfate, filtration of the suspension, and then evaporation of the ether from the filtrate at reduced pressure afforded a colorless liquid which on bulb-to-bulb distillation at 84° and 0.3 mm gave 10.63 g (98%) of the corresponding alcohol: ir ($CHCl_3$) 3620 (OH), 1665 (C=C), 1635, 995, 910 (CH=CH_2), and 1025 cm^{-1} (C–O); NMR ($CDCl_3$) δ 0.92 (d, 3, J = 7 Hz, C-2 CH_3), 160 (s, 3, C-5 CH_3), 3.48 (br d, 2, J = 5 Hz, C-1 H_2), 4.8–5.3 (m, 3, C-6 H and C-10 H_2), and 5.5–6.2 (m, 1, C-9 H).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.15; H, 12.26.

Oxidation[11] of 1.83 g (0.01 mol) of the above alcohol was accomplished with a suspension formed from 6.00 g (0.06 mol) of chromium trioxide and 9.49 g (0.12 mol) of pyridine in 50 ml of dry dichloromethane. After 20 min at room temperature, the mixture was filtered through 25 g of Florisil with the aid of 75 ml of ether, and then the filtrate was concentrated by distillation of most of the solvents through a 12-in. Vigreux column on the steam bath. The aldehyde **6**, isolated from this concentrate by ether extraction[32] and then bulb-to-bulb distillation of the crude product at 80° and 0.75 mm, amounted to 1.68 g (93%) of a colorless liquid which consisted of a single volatile component on GLC (120°): ir ($CHCl_3$) 2720 (CHO), 1720 (C=O), 1655 (C=C), 1640, 995, and 915 cm^{-1} (CH=CH_2); NMR ($CDCl_3$) δ 1.09 (d, 3, J = 7 Hz, C-2 CH_3), 1.61 (s, 3, C-5 CH_3), 4.8–5.4 (m, 3, C-6 H and C-10 H_2), 5.5–6.3 (m, 1, C-9 H), and 9.63 (d, 1, J = 2 Hz, C-1 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.93; H, 11.04.

The aldehyde **6** was further characterized as the 2,4-dinitrophenylhydrazone, mp 64–65.5° (from ethanol).

Anal. Calcd for $C_{18}H_{24}N_4O_4$: C, 59.99; H, 6.71; N, 15.55. Found: C, 59.98; H, 6.70; N, 15.62.

2,5,6,9-Tetramethyl-1,(*E*)-5,9-decatriene (5). To a filtered solution of α-methallylmagnesium bromide, prepared from 39 ml (36.2 g, 0.4 mol) of α-methallyl bromide and 38.4 g (1.6 g-atoms) of magnesium in 340 ml of dry tetrahydrofuran, was added over a 5-hr period a solution of 24.2 g (0.1 mol) of the dibromide **3**[13] in 75 ml of dry tetrahydrofuran while the temperature was maintained at 30–35°, and then the mixture was allowed to stir at room temperature for an additional 4 hr. After the addition of 125 ml of a saturated aqueous ammonium chloride solution and then 125 ml of saturated brine, isolation of the crude product by ether extraction[32] afforded a yellow liquid which consisted of two volatile components in a ratio 15:85 by GLC (100°). Distillation of this material through a 6-in. Vigreux column afforded 14.2 g (74%) of the triene **5**, bp 40–46° (0.15 mm), which consisted of >91% of a single volatile component on GLC (100°). The analytical sample, obtained by redistillation of this material through an 18-in. spinning

column, boiled at 64° at 0.85 mm [99% one volatile component on GLC (100°)]: ir ($CHCl_3$) 1645 and 885 cm^{-1} ($CH{=}CH_2$); NMR ($CDCl_3$) δ 1.67 (s, 3, C-5 and C-6 CH_3), 1.77 (s, 3, C-2 and C-9 CH_3), 2.10 (s, 4, C-3 and C-4 H_2), 4.72 (br S, 2, C-1 and C-10 H_2).

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.52; H, 12.49.

2,5,6,9-Tetramethyl-(*E*)-5,9-decadienal (7). To a solution of 35 g (0.183 mol) of the triene **5** in 100 ml of dry tetrahydrofuran cooled to 0° was added 0.09 mol of a tetrahydrofuran solution of disiamylborane,[10] and then the mixture was allowed to warm to room temperature and stir for 15 hr. After the mixture was cooled at 0°, it was treated with a solution of 12 g of sodium hydroxide in 40 ml of water, and then with 35 ml of 30% aqueous hydrogen peroxide. Isolation of the crude product by ether extraction[32] and then purification of this material by chromatography on 1200 g of Florisil gave first 20 g (57% recovery) of the triene **5** with 500 ml of petroleum ether. Distillation of the material eluted with 2.5 l. of 40% ether–petroleum ether afforded 10.83 g (28%, 65% based on recovered triene **5**) of the corresponding monoalcohol, bp 111–114° (1.5 mm), which consisted of >95% of a single volatile component on GLC (140°). Evaporative distillation of a portion of this material at 100° and 2.0 mm gave the analytical sample: ir ($CHCl_3$) 3620, 3450, (OH), 1650, and 890 cm^{-1} ($CHCH_2$); NMR ($CDCl_3$) δ 0.93 (d, 3, J = 6 Hz, C-2 CH_3), 1.43 (s, 1, OH), 1.67 (s, 2 × 3, C-5 and C-6 CH_3), 1.75 (br s, 3, C-9 CH_3), 3.48 (d, 2, J = 5.5 Hz, C-1 H_2), and 4.72 (br s, 2, C-10 H_2).

Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.04; H, 12.51.

To a suspension[11] of 15.04 g (0.04 mol) of pyridinium dichromate in 200 ml of dry dichloromethane was added 1.05 g (0.005 mol) of the above alcohol in 20 ml of dry dichloromethane. After removal of the salts by filtration of the reaction mixture through 10 g of Florisil and concentration of the filtrate by distillation at atmospheric pressure on the steam bath, bulb-to-bulb distillation of the residue at 72–76° and 025 mm afforded 0.98 g (94%) of the aldehyde **7** as a colorless liquid that was >90% of a single volatile component on GLC[31] (140°). The analytical sample was obtained from material of similar purity from another experiment by evaporative distillation at 85° and 0.5 mm: ir ($CHCl_3$) 2720 (CHO), 1720 (C=O), 1650, and 890 cm^{-1} ($CH{=}CH_2$); NMR ($CDCl_3$) δ 1.11 (d, 3, J = 6.5 Hz, C-2 CH_3), 1.67 (s, 2 × 3, C-5 and C-6 CH_3), 1.75 (s, 3, C-9 CH_3), 4.72 (br s, 2, C-10 H_2), and 9.67 (d, 1, J = 2 Hz, C-1 H); GLC (140°) >98% single volatile component.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.62. Found: C, 80.65; H, 11.76.

The aldehyde **7** was further characterized as the 2,4-dinitrophenylhydrazone, mp 102–105° (from ethanol).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.92; H, 7.11; N, 14.49.

4-Methyl-4-(3′-methyl-(*E*)-3′,7′-octadienyl)-2-cyclohexenone (8). A solution of 4.6 g (0.026 mol) of the aldehyde **6** and 4.4 g (0.06 mol) of pyrrolidine in 175 ml of dry benzene was refluxed under an argon atmosphere under a Dean-Stark water separator for 4 hr, and then the benzene and excess pyrrolidine were removed at reduced pressure. The residue was dissolved in 200 ml of dry benzene under an argon atmosphere, and then 3.57 g (0.05 mol) of methyl vinyl ketone was added. After stirring at room temperature for 2 hr and then at reflux for 17 hr, the mixture was treated with a solution of 1.55 g of sodium acetate in 4.2 ml of glacial acetic acid and 5 ml of water. After 4 hr at reflux, this mixture was diluted with water, and the product was isolated by ether extraction.[32] Evaporative distillation of the residue at 112–115° and 0.15 mm afforded 4.97 g (84%) of the enone **8**. The analytical sample was obtained by a second evaporative distillation of a portion of this material under the same conditions: ir ($CHCl_3$) 1665 (C=O), 1610 (C=C), 995, and 910 cm^{-1} ($CH{=}CH_2$); uv (95% ethanol) 226 nm (ϵ 11,200); NMR ($CDCl_3$) δ 1.15 (s, 3, C-4 CH_3), 1.61 (s, 3, C-3 CH_3), 2.46 (t, 2, J = 6.5 Hz, C-6 H), 4.8–5.3 (m, 3, C-4′ H and C-8′ H_2), 5.5–6.2 (m, 1, C-7′ H), 5,86 (d, 1, J = 10 Hz, C-2 H), and 6.68 (d, 1, J = 10 Hz, C-3 H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.68; H, 10.43. Found: C, 82.59; H, 10.19.

4-Methyl-4-(3′,4′,7′-trimethyl-(*E*)-3′,7′-octadienyl)-2-cyclohexenone (9). By a similar procedure to that described above for the formation of the enone **8**, 1.40 g (7.7 mmol) of the aldehyde **7** was converted first to its enamine with 0.72 g (10 mmol) of pyrrolidine in 55 ml of benzene, and this enamine was then condensed with 0.91 g (13 mmol) of methyl vinyl ketone in 40 ml of dry benzene. After hydrolysis of the reaction mixture with 0.37 g of sodium acetate in 0.75 ml of glacial acetic acid and 0.75 ml of water and then ether extraction,[32] purification of the product was effected by chromatography of the residue on 100 g of silica gel. Elution with 2 l. of benzene afforded 1.36 g of material that consisted of >95% of a single volatile component on GLC (180°) and which on bulb-to-bulb distillation at 116–124° and 0.1 mm afforded 1.16 g (70%) of the enone **9** as a colorless liquid [>98% of a single volatile component on glpc (180°)]: ir ($CHCl_3$) 1665 (C=O), 1610 (C=C), and 885 cm^{-1} (C=CH_2); uv (CH_3OH) 224 nm (ϵ 10,900); NMR ($CDCl_3$), δ1.20 (s, 3, C-4 CH_3), 1.68 (s, 2 × 3, C-3′ and C-4′ CH_3), 1.77 (s, 3, C-7′ CH_3), 4.73 (br s, 2, C-8′ H_2), 5.91 (d, 1, J = 10 Hz, C-2 H), and 6.75 (d, 1, J = 10 Hz, C-3 H).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.95; H, 10.94.

The enone **9** was further characterized by formation of the semicarbazone, mp 136.5–138° (from 50% ethanol–water).

Anal. Calcd for $C_{19}H_{31}N_3O$: C, 71.88; H, 9.84; N, 13.24. Found: C, 71.85; H, 9.65; N, 13.26.

4-Methyl-4-(3′-methyl-(*E*)-3′,7′-octadienyl)-2-cyclohexenol. The reduction of 3.87 g (16.5 mmol) of the enone **8** was accomplished with 0.314 g (8.2 mmol) of lithium aluminum hydride in 60 ml of dry ether at 0°. After decomposition of the excess hydride with 1.5 ml of water and then addition of 2 g of magnesium sulfate, the mixture was filtered and then the ether was removed from the filtrate at reduced pressure. Evaporative distillation of the residue at 110–112° and 0.1 mm afforded 3.82 g (98%) of the corresponding alcohol as a colorless liquid that consisted of two volatile components (epimeric at C-1) in the ratio of 2:1 on GLC (160°): ir ($CHCl_3$) 3600 (OH), 1640 (C=C), 990, 915 ($CH{=}CH_2$), and 1040 cm^{-1} (C–O); NMR ($CDCl_3$) δ 0.96 [s, 1, C-4 CH_3 (C-1 αOH)], 1.01 [s, 2, C-4 CH_3 (C-1 βOH)], 4.0–4.2 (br m, 1, C-1 H), and 4.8–6.4 (m, 6, olefinic H).

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.82; H, 11.20.

4-Methyl-4-(3′,4′,7′-trimethyl-(*E*)-3′,7′-octadienyl)-2-cyclohexenol. By the same procedure as that described above for the reduction of the enone **8**, 2.56 g (9.8 mmol) of the enone **9** was reduced at 0° with 190 mg (5 mmol) of lithium aluminum hydride in 55 ml of dry ether. After the same work-up and evaporative distillation of the residue at 110° and 0.1 mm, there was obtained 2.55 (99%) of the corresponding alcohol as a colorless liquid that also consisted of two volatile components in a ratio of 2:1 by GLC (180°): ir ($CHCl_3$) 3600 (OH), 1648, and 885 cm^{-1} (C=C and C=CH_2); NMR ($CDCl_3$) δ 0.96 [s, 1, C-4 CH_3 (C-1 αOH)], 1.01 [s, 2, C-4 CH_3 (C-1 βOH)], 1.63 (s, 2 × 3, C-3′ and C-4′ CH_3), 1.75 (s, 3, C-7′ CH_3), 4.10 (m, 1, $W_{1/2}$ = 12 Hz, C-1 H), 4.70 (s, 2, C-8′ H_2), and 5.63 (m, 2, C-2 H, C-3 H).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 83.20; H, 11.48.

Cyclization of 4-Methyl-4-(3′-methyl-(*E*)-3′,7′-octadienyl)-2-cyclohexenol. A. 8aβ,10aβ-Dimethyl-1,4,4aα,4bβ,7,8,8a,9,-10,10a-decahydrophenanthrene and 8aβ,10aβ-Dimethyl-3,4,4aα,4bβ,7,8,8a,9,10,10a-decahydrophenanthrene (10). To a solution of 117 mg (0.5 mmol) of the alcohol from ketone **8** and 6 ml of ethylene carbonate in 2 ml of dry dichloromethane was added 350 μl of stannic chloride, and the red mixture was stirred for 1 hr at 25°. The mixture was then poured into a solution of 25 g of potassium carbonate in 50 ml of methanol. After the color disappeared, sufficient methanol was added to form one phase, and then the solution was stirred at room temperature for 10 hr. After isolation of the product by ether extraction,[32] there was obtained 117 mg of a yellow oil, the GLC (150°) of which consisted of two overlapping peaks (corresponding to the tricyclic dienes **10**) that comprised ca. 75% of the volatile material. In addition to several less volatile components in minor amounts, a more volatile series of peaks that comprised ca. 15% of the volatile material corresponded to the chlorocarbon mixture **20**.

Purification of this crude mixture by chromatography on 25 g of silica gel afforded 61 mg (56%) of a mixture of the dienes **10** with 60 ml of petroleum ether eluent as a colorless oil that consisted of >99% of these two partially resolved components on GLC (150°). The analytical sample was obtained by evaporative distillation of this material at 60–64° and 0.3 mm: ir ($CHCl_3$) 1655 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.81, 0.91 (2 × s, 3 each, C-8a and C-10a CH_3), and 5.33–5.95 (m, 4, vinyl H).

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.76; H, 11.17.

Continued elution of the column with 20 ml of petroleum ether gave 5 mg (4%) of the epimeric chlorocarbons **20**. This material was identified by comparison of the ir, NMR, and GLC (150°) spectral data of this sample with those of an authentic sample prepared in

an alternate experiment (see Table I). Material from the latter procedure was used for analytical purposes after bulb-to-bulb distillation at 75° and 0.075 mm; ir ($CHCl_3$) 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.85, 0.90 (2 s, experiment (see Table I). Material from the latter procedure was used for analytical purposes after bulb-to-bulb distillation at 75° and 0.075 mm; ir ($CHCl_3$) 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.85, 0.90 (2 s, 3 each, C-8a and C-10a CH_3), 3.75–4.75 (br m, 1, CHCl), and 5.33–6.00 (m, 2, CH=CH).

Anal. Calcd for $C_{16}H_{25}Cl$: C, 76.00; H, 9.96; Cl, 14.02. Found: C, 75.84; H, 9.74; Cl, 13.96.

B. Variation of Product Composition with Solvent. In Table I are compiled the results of the cyclization of the alcohol from the ketone **8** in various solvents and conditions. The general procedure used was identical with that described in part A except for the variations noted in Table I. Identification of the solvent-trapped compounds isolated is presented below.

8aβ,10aβ-Dimethyl-7-phenyl-1,2,4aβ,4bα5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene (19): oil, evaporative distillation at 121–124° (0.1 mm); ir ($CHCl_3$) 1601 and 1495 cm^{-1} (C_6H_5); NMR (CCl_4) δ 0.90, 0.96 (2 s, 3 each, C-8a and C-10a CH_3), 2.46–2.93 (m, 1, C-7 H), 5.16–5.83 (m, 2, C-3 and C-4 H), and 7.08 (s, 5, ArH); MS (70 eV) *m/e* 294 (M^+).

Anal. Calcd for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.97; H, 10.20.

8aβ,10aβ-Dimethyl-7-(2',2',2'-trifluoroethoxy)-1,2,4aβ,4bα,-5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene (21): oil, evaporative distillation at 107° (0.075 mm); ir ($CHCl_3$) 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.83, 1.01 (2 s, 3 each, C-8a and C-10a CH_3), 3.83 (q, 2, J = 9 Hz, CH_2CF_3), 3.65 (m, 1, C-7 H), and 5.36–5.80 (m, 2, C-3 and C-4 H).

Anal. Calcd for $C_{18}H_{27}F_3O$: C, 68.32; H, 8.60; F, 18.01. Found: C, 68.45; H, 8.70; F, 18.09.

8aβ,10aβ-Dimethyl-7-(2'- and 4'-methoxyphenyl)-1,2,4aβ,-4bα,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene (22): oil, evaporative distillation at 145° (0.05 mm); ir ($CHCl_3$) 1580–1610 cm^{-1} ($ArOCH_3$); NMR ($CDCl_3$) δ 0.80–1.13 (br s, 6, angular CH_3), 3.76, 3.80 (2 s, 3, OCH_3), 5.36–6.03 (m, 2, C-3 and C-4 H), and 6.73–7.36 (m, 4, ArH); MS (70 eV) *m/e* 324 (M^+).

Anal. Calcd for $C_{23}H_{32}O$: C, 85.13; H, 9.94. Found: C, 85.11; H, 9.97.

The dienes **23** were analyzed as their perhydro derivatives formed by hydrogenation of the mixture in hexane over 10% palladium on carbon. On preparative TLC (1:1 ether–benzene) of the saturated products, the mixture could be separated into two components that consisted of the *o*-methoxyphenyl derivatives (R_f 0.7) and the *p*-methoxyphenyl isomers (R_f 0.6).

***cis*- and *trans*-4-(2'-Methoxyphenyl)-1-methyl-1-(3'-methyloctyl)cyclohexane:** oil, evaporative distillation at 160° (0.06 mm); ir ($CHCl_3$) 1612 and 1585 cm^{-1} ($ArOCH_3$); NMR ($CDCl_3$) δ 0.80–1.13 (br s, 6, methyl groups), 3.83 (s, 3, OCH_3), and 6.73–7.06 (m, 4, ArH).

Anal. Calcd for $C_{23}H_{38}O$: C, 83.59; H, 11.59. Found: C, 83.56; H, 11.70.

***cis*- and *trans*-4-(4'-Methoxyphenyl)-1-methyl-1-(3'-methyloctyl)cyclohexane:** oil, evaporative distillation at 160° (0.06 mm); ir ($CHCl_3$) 1612 and 1585 cm^{-1} ($ArOCH_3$); NMR ($CDCl_3$) δ 0.80–1.13 (br s, 6, methyl groups), 3.80 (s, 3, OCH_3), 7.12 (d, 2, J = 8 Hz, C-3' and C-5' H), and 7.33 (d, 2, J = 8 Hz, C-2' and C-6' H).

Anal. Calcd for $C_{23}H_{38}O$: C, 83.59; H, 11.59. Found: C, 83.57; H, 11.62.

1-*m*-Methoxyphenyl-*trans*-spiro[2.5]octan-4-one (13). Reduction of 4.03 g (0.019 mol) of the unsaturated ketone **12**[18] was accomplished with 7.07 g (0.019 mol) of sodium borohydride in 175 ml of methanol, and after bulb-to-bulb distillation of the crude product at 123° and 0.1 mm, there was obtained 3.65 (90%) of the corresponding allylic alcohol as a colorless oil which was homogeneous by TLC ($CHCl_3$, R_f 0.08): ir (CCl_4) 3620 (OH) and 1665 cm^{-1} (C=C); NMR (CCl_4) δ 3.71 (s, 3, OCH_3), 410 (br m, 1, C-1 H), and 6.31–7.43 (m, 5, C=CH– and ArH).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.99; H, 8.22.

A solution of 3.75 g (0.017 mol) of the above allylic alcohol in 25 ml of dry ether was added to 250 ml of an ethereal solution of iodomethylzinc iodide[20] prepared from 22.3 ml (73.7 g, 0.275 mol) of diiodomethane and 18 g of zinc–copper couple,[20] and the mixture was stirred under an argon atmosphere for 4 hr. After the addition of 25 ml of saturated aqueous ammonium chloride solution, the product was isolated by ether extraction[32] and then chromatographed on 300 g of neutral alumina (activity III). After elution with 100 ml each of 2, 5, 10, 25, and 50% ether–petroleum ether, 500 ml of ether eluted 3.92 g (98%) of the cyclopropyl alcohol as a colorless oil which consisted of a single volatile component on GLC (200°). The analytical sample was obtained by evaporative distillation of a portion of this material at 110–114° and 0.1 mm: ir ($CHCl_3$) 3600 (OH) and 3050 cm^{-1} (cyclopropyl CH); NMR (CCl_4) δ 0.53–0.95 (m, 2, cyclopropyl CH_2), 1.91–2.25 (m, 1, cyclopropyl, benzyl CH), 3.21–3.48 (m, 1, CHOH), 3.75 (s, 3, OCH_3), and 6.45–7.31 (m, 4, ArH).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.42; H, 8.80.

Oxidation of this cyclopropyl alcohol was accomplished routinely on a small scale by titration of an acetone solution with 8 *N* aqueous chromic acid solution.[24] Thus, oxidation of 2.61 mg (1.12 mmol) of the alcohol in 15 ml of acetone afforded 186 mg (72%) of the ketone **13** as a colorless liquid [evaporative distillation at 104–108° (0.1 mm)] that consisted of a single volatile component on GLC (200°): ir (CCl_4) 3050 (cyclopropyl CH) and 1685 Cm^{-1} (C=O); NMR (CCl_4) δ 0.72–1.06 (m, 2, cyclopropyl CH_2), 2.16–2.76 (m, 3, cyclopropyl, benzyl CH, and CH_2CO), 3.76 (s, 3, OCH_3), and 6.51–7.35 (m, 4, ArH).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.37; H, 7.94.

2-(2'-*m*-Methoxyphenylethyl)-2-methylcyclohexanone (14). To a solution of 40 mg (5.7 mg-atom) of lithium in 15 ml of dry ammonia was added a solution of 178 mg (0.77 mmol) of the cyclopropyl ketone **13** and 94 μl (74 mg, 1 mmol) of dry *tert*-butyl alcohol in 5 ml of glyme. The mixture was stirred under a nitrogen atmosphere for 45 min and then 180 μl (179 mg, 1 mmol) of hexamethylphosphoramide was added. The ammonia was then evaporated in a stream of nitrogen, and then a solution of 1 ml of methyl iodide in 18 ml of dry glyme was added all at once with vigorous stirring. After stirring at room temperature for 1 hr, the mixture was treated with 80 ml of water, and the product was isolated by ether extraction,[32] including both an acid and base wash. Purification of the crude product (179 mg) by chromatography on 20 g of silica gel afforded 109 mg (57%) of the ketone **14** as a colorless oil by elution with 850 ml of 50% ether–benzene. The analytical sample was obtained by evaporative distillation of this material at 115–116° and 0.1 mm: ir (CCl_4) 1700 cm^{-1} (C=O); NMR (CCl_4) δ 1.08 (s, 3, C-2 CH_3), 3.73 (s, 3, OCH_3), and 6.46–7.26 (m, 4, ArH).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.11; H, 9.00.

2-Methoxy-8a-methyl-6,7,8,8a,9,10-hexahydrophenanthrene. To a solution of 246 mg (1 mmol) of the ketone **14** in 2.5 ml of dry benzene was added 75 ml of freshly prepared polyphosphoric acid,[33] and the mixture was heated at 50° for 1 hr. The reaction mixture was then poured onto 450 g of ice in water with stirring, and the product was isolated by benzene extraction,[32] including a base wash. Chromatography of the crude product on 25 g of silica gel afforded 208 mg (91%) of the tricyclic olefin, mp 63–65°, by elution with 500 ml of 1% ether–petroleum ether. The analytical sample, obtained by crystallization of a portion of this material from methanol, melted at 69–69.5°: ir ($CHCl_3$) 1635 cm^{-1} (C=C); NMR (CCl_4) δ 1.00 (s, 3, C-8a CH_3), 3.75 (s, 3, CH_3), 5.91 (br t, 1, J = 3.5 Hz, C-5 H), 6.16 (d, 1, $J_{1,3}$ = 2 Hz, C-1 H), 6.70 (d of d, 1, $J_{3,4}$ = $J_{1,3}$ = 2 Hz, C-3 H), 7.43 (d, 1, $J_{3,4}$ = 7 Hz, C-4 H).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.01; H, 8.80.

2-Methoxy-8aβ-methyl-4bα,5,6,7,8,8a,9,10-octahydrophenanthrene (15). A solution of 173 mg (0.75 mmol) of the tricyclic olefin above in 32 ml of hexane containing 50 mg of 10% palladium on carbon as stirred in a hydrogen atmosphere at room temperature and atmospheric pressure for 22 hr. After the catalyst was removed by filtration and the solvent was removed from the filtrate at reduced pressure, bulb-to-bulb distillation of the residue at 98° and 0.08 mm afforded 167 mg (96%) of a colorless liquid which consisted of two volatile components on GLC (200°) in a ratio of 92:8. A sample of the major component—the tricyclic ether **15**—was obtained by preparative GLC (200°) and analytical GLC (200°) showed a single volatile component in >99% yield: ir (CCl_4) 1610 and 1575 cm^{-1} (C=C, Ar); NMR (CCl_4) δ 0.71 (s, 3, C-8a CH_3), 3.70 (s, 3, OCH_3), 6.50 (d, 1, $J_{1,3}$ = 2 Hz, C-1 H), 6.55 (d of d, 1, $J_{1,3}$ = 2, $J_{3,4}$ = 9 Hz, C-3 H), and 6.98 (d, 1, $J_{3,4}$ = 9 Hz, C-4 H); $\Delta_{1,4}$ = 0.54 ppm (trans isomer).[23]

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.35; H, 9.52.

8aβ-Methyl-4,4aβ,4bα,5,6,7,8,8a,9,10-decahydro-2(3*H*)-phenanthrenone (16). A solution of 167 mg (0.73 mmol) of a 92:8 mxture of the trans/cis isomers of the tricyclic ether **15** and 20 ml of dry *tert*-butyl alcohol in 25 ml of dry tetrahydrofuran was

added over 10 min to a solution of 240 mg (34 mg-atoms) of lithium in 62 ml of dry ammonia under a nitrogen atmosphere. The blue mixture was stirred for 3.5 hr, and then 25 ml of methanol was added to discharge the blue color. After the ammonia was removed in a stream of nitrogen on the steam bath, the residue was diluted with water, and the product was isolated by benzene extraction.[32] The resulting crude product was dissolved in 130 ml of methanol; 55 ml of 5 *N* hydrochloric acid solution was added, and then the mixture was heated under reflux for 2 hr. After dilution of the mixture with 200 ml of saturated brine, the product was isolated by benzene extraction,[32] including a base wash. Crystallization of the residue from ether–hexane afforded 105 mg (74%) of the enone **16** in two crops of 91 mg (mp 125–128°) and 14 mg (mp 120–123°), both of which consisted of a single volatile component on GLC (200°). The analytical sample, obtained after one further crystallization of a portion of the first crop material from ether–hexane, melted at 126–128° (lit.[22] mp 125–127°): ir ($CHCl_3$) 1660 (C=O) and 1615 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.98 (s, 3, C-8a CH_3) and 5.86 (br s, 1, C-1 H); uv (CH_3OH) 243 nm (ϵ 14,400).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.58, H, 10.07.

8aβ,10aβ-Dimethyl-3,4,4aβ,4bα,5,6,7,8,8a,9,10,10a-dodecahydro-2-phenanthryl *N,N,N′N′*-Tetramethyldiamidophosphorodiamidate (17). A solution of 55 mg (0.25 mmol) of the enone **16** in 4 ml of dry ether was added dropwise over 15 min to a solution of lithium dimethylcuprate, prepared from 625 μl (1.25 mmol) of a 2 *M* ethereal methyllithium solution and 119 mg (0.625 mmol) of copper(I) iodide in 6 ml of dry ether. After the mixture was stirred under a nitrogen atmosphere for 2 hr at 0°, 0.2 ml of hexamethylphosphoramide was added, and then a solution[28] of 0.4 ml of *N,N,N′,N′*-tetramethyldiamidophosphorochloridate in 1 ml of dry ether was added dropwise over 5 min. After stirring for 2.5 hr at room temperature, the mixture was diluted with 50 ml of dilute aqueous ammonium hydroxide solution, and the product was isolated by ether extraction, including both an acid and base wash. Chromatography of the residue (87 mg) on 10 g of silica gel (ether, 100 ml, followed by 3:2 ether–ethyl acetate, 150 ml) afforded a colorless oil which on evaporative distillation at 117° and 0.06 mm gave 76 mg (86%) of the phosphoradiamidate **17** which consisted of >97% of a single volatile component on GLC (230°): ir ($CHCl_3$) 1675 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.81 (s, 3, C-8a CH_3), 1.06 (s, 3, C-10a CH_3), 2.68 (d, 12, J = 10 Hz, NCH_3), and 5.03 (br s, 1, C-1 H).

Anal. Calcd for $C_{20}H_{37}N_2O_2P$: C, 65.18; H, 10.12; N, 7.60; P, 8.40. Found: C, 65.05; H, 10.06; N, 7.52; P, 8.31.

8aβ,10aβ-Dimethyl-3,4,4aβ,4bα,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene. To a solution of 25 mg (3.6 g-atoms) of lithium in 40 ml of dry ethylamine was added a solution of 69 mg (0.19 mmol) of the phosphorodiamidate **17** and 0.1 ml of dry *tert*-butyl alcohol in 6 ml of dry tetrahydrofuran, and the reaction mixture was stirred under a nitrogen atmosphere for 2.5 hr. After the addition of 10 ml of ethanol, the ethylamine was removed in a stream of nitrogen, and the mixture was then diluted with 50 ml of water. After isolation of the product by petroleum ether extraction,[32] including an acid and base wash, and then filtration of the residue through 2 g of silica gel with petroleum ether, bulb-to-bulb distillation of the resulting oil at 74° and 0.55 mm afforded 35 mg (83%) of colorless liquid which consisted of a single volatile component on GLC (170°): ir ($CHCl_3$) 1645 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.83 (s, 3, C-8a CH_3), 1.05 (s, 3, C-10a CH_3), 5.26 (d, 1, $J_{1,2}$ = 7 Hz, C-1 H), and 5.63 (d of m, 1, $J_{1,2}$ = 7 Hz, C-2 H).

Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.96; H, 11.90.

8aβ,10aβ-Dimethyl-4aβ,4bα-perhydrophenanthrene (18). A. From the Tricyclic Dienes 10. A solution of 49 mg (0.23 mmol) of the dienes **10** in 5 ml of ethanol in which was suspended 10 mg of 10% palladium on carbon was stirred in an atmosphere of hydrogen at room temperature and atmospheric pressure for 1 hr. After removal of the catalyst and then evaporation of the ethanol at reduced pressure, the residue (48 mg) was chromatographed on 1.5 g of silica gel impregnated with 10% silver nitrate. Elution with 15 ml of petroleum ether and then bulb-to-bulb distillation (73–75° at 0.35 mm) of the residue remaining after solvent evaporation afforded 40 mg (80%) of the hydrocarbon **18** as a colorless oil: ir (neat) 2950, 1450 (CH), and 1375 cm^{-1} (CH_3); NMR ($CDCl_3$) δ 0.73 and 1.00 (2 s, 3 each, C-8a and C-10a CH_3).

Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.22; H, 13.00.

The properties [TLC, GLC (170°), ir, NMR] of this material were identical with those of the authentic sample prepared below.

B. From the Tricyclic Olefin. A solution of 30 mg (0.14 mmol) of the tricyclic olefin prepared above in 8 ml of hexane in which was suspended 10 mg of 10% plladium on carbon was stirred in an atmosphere of hydrogen as above in part A for 5 hr. After the same work-up there resulted 30 mg (100%) of the hydrocarbon **18** which showed idntical ir (neat), TLC (petroleum ether), and NMR ($CDCl_3$) with the material prepared in part A and on GLC (170°) the two samples were indistinguishable by peak enhancement.[35]

Cyclization of 4-Methyl-4-(3′,4′,7′-trimethyl-(*E*)3′,7′-octadienyl)-2-cyclohexenol. A solution of 198 mg (0.76 mmol) of the alcohol from the ketone **9** in 85 ml of dry dichloromethane was cooled to −78°, and then 150 μl of stannic chloride was added. After stirring at −78° for 1 hr, the mixture was warmed to −6° in an ice–salt bath, and stirring was continued for 0.5 hr. The mixture was then poured into 50 ml of water and 15 g of potassium carbonate, and after stirring for 0.5 hr, the layers were separated and the aqueous layer was extracted twice with 30-ml portions of dichloromethane. After the combined organic layers were washed with water and then dried ($MgSO_4$), evaporation of the solvent at reduced pressure afforded 199 mg of a colorless oil. On GLC (180°) this oil consisted of seven volatile components, one of which comprised ca. 75% of the material. On chromatography of this product on 55 g of silica gel, the first 50 ml of petroleum ether eluted 41 mg of material judged to contain >75% of the major component on GLC (180°), and then 35 mg (19%) of material that consisted of >98% of the single major volatile component on GLC (180°) was eluted with an additional 155 ml of the same eluent. Rechromatography on neutral alumina (activity I) (petroleum ether) or preparative[34b] GLC (200°, retention time 17.6 min) of the first 41-mg fraction afforded additional quantities of the major component in >99% homogeneity by GLC (180°). The total isolated yield of this major component, **2,4aα,8aβ,10aβ-tetramethyl-1,4,4a,4bβ,7,8,-8a,9,10,10a-decahydrophenanthrene (11),** by these procedures was 58 mg (32%).

The analytical sample, prepared by evaporative distillation of the material at 102° and 0.6 mm, solidified on storage at −20° and melted at 44–47°: ir ($CHCl_3$) 1670–1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.83 (s, 3) and 0.91 (s, 2 × 3) (C-4a, C-8a, and C-10a CH_3), 1.67 (br d, 3, J = 3 Hz, C-2 CH_3), 5.28 (m, 1, $W_{1/2}$ = 7.5 Hz, C-3 H), and 5.56–5.96 (m, 2, C-5 and C-6 H).

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.55; H, 11.42.

12-*m*-Methoxyphenyl-2,5,6,9-tetramethyl-(*E,E*)-5,9-dodecadienoic Acid. To a solution of lithium diisopropylamide [prepared from 1.44 ml (1.045 g, 10.35 mmol) of dry diisopropylamine and 4.31 ml (9.28 mmol) of a 2.13 *M* hexane solution of *n*-butyllithium] in 6 ml of dry tetrahydrofuran under an argon atmosphere was added at −5 to 2° 1.424 g (4.14 mmol) of **12-*m*-methoxyphenyl-5,6,9-trimethyl-(*E,E*)-5,9-dodecadienoic acid,** which was obtained in 88% overall yield by Collins[11] and then silver oxide oxidation of the alcohol **24,** and was an oil [evaporative distillation at 184° (0.0005 mm)]: ir ($CHCl_3$) 3400–2800 (CH and bonded OH) and 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.60 (masked d, 3, C-9 CH_3), 1.63 (s, 2 × 3, C-5 and C-6 CH_3), 3.80 (s, 3, OCH_3), 5.21 (br t, 1, J = 9 Hz, C-10 H), and 6.61–7.41 (m, 4, ArH). Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.79; H, 9.38. After 15 min 1.04 ml of hexamethylphosphoramide and then 0.37 ml (0.85 g, 6 mmol) of dry methyl iodide were added, and the resulting mixture was stirred at 23° for 1.5 hr. Isolation of the product by ether extraction,[32] including an acid wash, afforded 1.43 g (97%) of the methylated acid as an oil that was not further purified but used directly in the following experiment. An analytical sample was obtained by evaporative distillation of a portion of this material at 178° and 0.0005 mm: ir ($CHCl_3$) 3450–2620 (CH and bonded OH) and 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.21 (d, 3, J = 7 Hz, C-2 CH_3), 1.60 (masked d, 3, C-9 CH_3), 1.63 (s, 2 × 3, C-5 and C-6 CH_3), 3.80 (s, 3, OCH_3), 5.20 (br t, 1, J = 6.5 Hz, C-10 H), and 6.61–7.41 (m, 4, ArH).

Anal. Calcd for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.16; M, 9.61.

12-*m*-Methoxyphenyl-2,5,6,9-tetramethyl-(*E,E*)-5,9-dodecadienal. The reduction and oxidation of the above methylated acid was accomplished in the same manner as that described above for the formation of the aldehyde **6.** Thus, reduction of 1.41 g (3.96 mmol) of the above carboxylic acid with 228 mg (6 mmol) of lithium aluminum hydride in 25 ml of dry ether afforded 1.27 g (94%) of the corresponding alcohol which consisted of >93% of a single volatile component on GLC (280°) after chromatography on 100 g of Florisil with 1.1 l. of 20% ether–petroleum ether. The analytical sample was obtained by bulb-to-bulb distillation of a portion of

this material at 160° and 0.0008 mm: ir ($CHCl_3$) 3620 (OH) and 1670 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.95 (d, 3, J = 6 Hz, C-2 CH_3), 1.38 (s, 1, OH), 1.60 (d, 3, J = 1.5 Hz, C-9 CH_3), 1.65 (s, 2 × 3, C-5 and C-6 CH_3), 3.52 (d, 2, J = 5 Hz, C-1 H_2), 3.83 (s, 3, OCH_3), 5.23 (t, 1, J = 6 Hz, C-10 H), and 6.61–7.41 (m, 4, ArH).

Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.05; H, 10.62.

Oxidation of 250 mg (0.73 mmol) of this alcohol with a solution of chromium trioxide–dipyridine complex[11] [prepared from 500 mg (5 mmol) of chromium trioxide and 796 μl (791 mg, 10 mmol) of pyridine] in 14.5 ml of dry dichloromethane afforded 227 mg (92%) of the methylated aldehyde as an oil which consisted of >97% of a single volatile component on GLC (280°) after evaporative distillation at 153° and 0.001 mm: ir ($CHCl_3$) 2720 (CHO), 1725 (C=O), and 1670 cm^{-1} (C=C); NMR ($CHCl_3$) δ 1.11 (d, 3, J = 6 Hz, C-2 CH_3), 1.60 (d, 3, J = 1.5 Hz, C-9 CH_3), 1.63 (s, 2 × 3, C-5 and C-6 CH_3), 3.80 (s, 3, OCH_3), 5.20 (t, 1, J = 5.5 Hz, C-10 H), 6.61–7.41 (m, 4, ArH), and 9.65 (d, 1, J = 2 Hz, C-1 H).

Anal. Calcd for $C_{23}H_{34}O_2$: C, 80.65; H, 10.01. Found: C, 80.67; H, 10.10.

4-Methyl-4-(10′-*m*-methoxyphenyl-3′,4′,7′-trimethyl-(*E,E*)-3′,7′-decadienyl)-2-cyclohexenone (25). By a similar procedure to that described above for the formation of the enone **8**, the enamine of the above aldehyde [prepared from 1.40 g (4.1 mmol) of the aldehyde and 453 μl (386 mg, 5.44 mmol) of dry pyrrolidine by heating for 2.5 hr in 50 ml of dry benzene under a Dean-Stark water separator] and 622 μl (538 mg, 7.68 mmol) of methyl vinyl ketone in 50 ml of dry benzene was heated under reflux for 17 hr, and then a solution of 0.25 g of sodium acetate and 0.5 ml of water in 0.5 ml of glacial acetic acid was added, whereupon heating was continued for an additional 4 hr. Chromatography of the crude product on 160 g of silica gel afforded 1.48 g (92%) of the enone **25** with 1 l. of 16% ether–petroleum ether after forefractions of 1 (100 ml), 2 (100 ml), 4 (100 ml), 8 (1800 ml), and 12 (750 ml) of ether–petroleum ether. This material consisted of >94% of a single volatile component on GLC (290°). The analytical sample was obtained by evaporative distillation at 194° and 0.0025 mm: ir ($CHCl_3$) 1675 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.16 (s, 3, C-4 CH_3), 1.60 (d, 3, J = 1.5 Hz, C-7′ CH_3), 1.63 (s, 2 × 3, C-3′ and C-4′ CH_3), 3.80 (s, 3, OCH_3), 5.21 (t, 1, J = 6 Hz, C-8′ H), 5.90 (d, 1, J = 10 Hz, C-2 H), 6.73 (d, 1, J = 10 Hz, C-3 H), and 6.63–7.50 (m, 4, ArH).

Anal. Calcd for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71. Found: C, 82.25; H, 9.69.

4-Methyl-4-(10′-*m*-methoxyphenyl-3′,4′,7′-trimethyl-(*E,E*)-3′,7′-decadienyl)-2-cyclohexenol. Reduction of 2.10 g (5.3 mmol) of the enone **25** with 103 mg 2.7 mmol) of lithium aluminum hydride in 45 ml of dry ether at 0° afforded 2.09 g (99%) of the corresponding allylic alcohol as an oil that decomposed on GLC, but showed one spot on TLC (50% ether–petroleum ether). The analytic sample was prepared by evaporative distillation of a porton of this material at 205° and 0.001 mm: ir ($CHCl_3$) 3590 (OH), 1670, and 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.96 (s, 0.4 × 3, C-4 CH_3 in αC-1 OH), 1.01 (s, 0.6 × 3, C-4 CH_3 in βC-1 OH), 1.60 (d, 3, J = 1.5 Hz, C-7′ CH_3), 1.63 (s, 2 × 3, C-3′ and C-4′ CH_3), 3.80 (s, 3, OCH_3), 4.16 (m, 1, C-1 H), 5.20 (t, 1, J = 5 Hz, C-8′ H), 5.60 (m, 2, C-2 and C-3 H), and 6.61–7.40 (m, 4, ArH).

Anal. Calcd for$C_{22}H_{40}O_2$: C, 81.77; H, 10.17. Found: C, 81.68; H, 10.16.

3-Methoxy-6bβ,8aβ,12bα,14aβ-tetramethyl-5,6,6aα,6b,7,8,-8a,9,10,12aβ,12b,13,14,14a-tetradecahydropicene (26). To a solution of 240 mg (0.61 mmol) of the above allylic alcohol in 24 ml of dry dichloromethane cooled to −63.5° (cryostatic chloroform bath) was added 13.5 ml of a 0.1 M dichloromethane solution of stannic chloride precooled to −63.5°, followed 30 sec later by 40 μl of dimethyl carbonate. After stirring for 15 min, the mixture was poured into 75 ml of 20% aqueous potassium hydroxide solution, and then the product was isolated by ether extraction.[32] Chromatography of the crude product (240 mg) on 20 g of silica gel afforded 112 mg of a mixture [GLC (300°) showed four major volatile components in a ratio of 2:1:2:6] with 150 ml of 10% ether–petroleum ether. Rechromatography (25% benzene–petroleum ether, 40 ml) of this material on 14 g of silica gel impregnated with 10% silver nitrate gave 38 mg in which the last major volatile component represented 85% of the mixture on GLC (300°). Trituration of this mixture in ether at −20° gave 28 mg (12%) of the pentacyclic olefin **26**, mp 185–188°, which consisted of >98% of a single volatile component on GLC (300°). The analytical sample, obtained after crystallization of this material from ether–dichloromethane and then ether–hexane, melted at 186–190°: ir ($CHCl_3$) 1655 (w, C=C), 1602, and 1575 cm^{-1} (Ar); NMR ($CDCl_3$) δ 0.90. 0.93, 1.05, 1.21 (4 s, 3 each, C-6b, C-8a, C-12b, and C-14a CH_3), 2.66–3.13 (m, 2, C-5 H_2), 3.75 (s, 3, OCH_3), 5.60–5.80 (m, 2, C-11 and C-12 H), and 6.50–7.30 (m, 3, ArH).

Anal. Calcd for $C_{27}H_{38}O$: C, 85.66; H, 10.12. Found: C, 85.66; H, 10.25.

3-Methoxy-6bβ,8aβ,12bα,14aβ-tetramethyl-5,6,6aα,6b,7,8,-8a,9,10,11,12,12aβ,12b,13,14,14a-hexadecahydro-11β-picenol. To a solution of 59 mg (0.16 mmol) of the pentacyclic olefin **26** in 1.5 ml of dry tetrahydrofuran cooled to 0° under an argon atmosphere was added 1.5 ml of an 0.85 M tetrahydrofuran solution of diborane, and the mixture was stirred for 9 hr. After decomposition of the excess diborane with 0.75 ml of water, the mixture was treated with 3 ml of 20% aqueous sodium hydroxide solution and 3 ml of 30% hydrogen peroxide, and the resulting solution was allowed to stir at room temperature for 4 hr. After isolation of the product by ether extraction,[32] the residue (75 mg) was separated into two components by preparative TLC (40% ether–petroleum ether): band A (R_f 0.3, 18 mg, 22%) and band B (R_f 0.2, 48 mg, 77%).

Crystallization of the material from band B from acetone afforded 40 mg (64%) of the 11β-alcohol: mp 190–192.5°; ir ($CHCl_3$) 3600 (OH), 1602, and 1575 cm^{-1} (Ar); NMR ($CDCl_3$) δ 0.96, 1.00, 1.11, 1.20 (4 s, 3 each, C-6b, C-8a, C-12b, and C-14a CH_3), 2.66–3.16 (m, 2, C-5 H_2), 3.75 (s, 3, OCH_3), 3.93 (m, 1, $W_{1/2}$ = 22 Hz, C-11 H), and 6.46–7.30 (m, 3, ArH).

Anal. Calcd for $C_{27}H_{40}O_2$: C, 81.77; H, 10.17. Found: C, 81.78; H, 9.97.

The material in band A was not further purified but was judged to be the corresponding 12β (axial) alcohol from the regeneration of the olefin **26** by treatment with phosphorus oxychloride in pyridine and the spectra: ir ($CHCl_3$) 3600 (OH), 1602, and 1575 cm^{-1} (Ar); NMR ($CDCl_3$) δ 0.98, 1.00, 1.20, 1.25 (4 s, 3 each, C-6b, C-8a, C-12b, and C-14a CH_3), 2.66–3.16 (m, 2, C-5 H_2), 3.76 (s, 3, OCH_3), 4.23 (m, 1, $W_{1/2}$ = 7 Hz, C-12 H), and 6.46–7.44 (m, 3, ArH).

10-Methoxy-4aβ,6bα,12bβ,14aα-tetramethyl-3,4,4a,5,6,6a,-6bα,7,8,12b,13,14,14a,14bβ-tetradecahydro-2(1*H*)-picenone (27). A solution of 75 mg (0.19 mmol) of the 11β-alcohol above in 8 ml of dry acetone cooled to 0° was treated with excess 8 N aqueous chromic acid solution[24] (persistent brown-yellow coloration) and then stirred for 15 min. After decomposition of the excess oxidant with isopropyl alcohol, the product was isolated by ether extraction.[32] On crystallization of the residue from acetone there resulted 68 mg (92%) of the ketone **27**, mp 200.5–204.5°, which showed one spot on TLC (20% ether–petroleum ether, R_f 0.2). The analytical sample, obtained after one further crystallization from acetone, also melted over the same range: ir ($CHCl_3$) 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.83, 1.00, 1.20, 1.26 (4 s, 3 each, C-4a, C-6a, C-12b, and C-14a CH_3), 2.20–2.56 (m, 4, C-1 and C-3 H_2), 2.66–3.20 (m, 2, C-8 H_2), 3.73 (s, 3, OCH_3), and 6.46–7.26 (m, 3, ArH).

Anal. Calcd for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71. Found: C, 82.03; H, 9.68.

X-Ray Structure of 3,4,4a,5,6,6a,6bβ,7,8,12b,13,14,14a,-14bα Tetradecahydro-10-methoxy-4bα,6aα,12bα,14aβ-tetramethyl-2(1*H*)-picenone (1). Unit cell dimensions were obtained from least-squares refinement of the 2θ angles of 36 reflections measured on a Datex automated General Electric diffractometer. Unit cell parameters are a = 50.1255 ± 0.0016 Å; b = 7.5886 ± 0.0003 Å; c = 11.4010 ± 0.0004 Å; β = 90.504 ± 0.002°.

The absence of hkl reflections for $h + k$ odd and hl for h odd indicated that the space group is $C2/C$/ The crystal density was found to be 1.23 ± 0.02 g cm^{-3}. The calculated density is 1.21 g cm^{-3} for eight molecules of molecular weight 394.603 per unit cell.

Intensity data were collected by the θ–2θ scan method with iron-filtered Co Kα radiation (λ 1.79021 Å). Reflections were collected to a maximum value of 2θ = 135° with a scan rate in 2θ of 2° min^{-1}. Three reflections monitored at regular intervals during the data collection showed no significant variation in intensity.

The intensities of 2505 reflections were measured. The intensities of 186 of thee were found to be less than one standard deviation above background and were assigned a value of zero with zero weight throughout the refinement. The data were corrected for Lorentz–polarization effects but not for absorption (μ = 8.8 cm^{-1}). The data were placed on an absolute scale by Wilson's method.[36] A Howells, Phillips, and Rogers' plot[37] confirmed that the crystal is centrosymmetric.

The phases of 253 reflections with an E value greater than 1.50 were assigned by the CRYM[38] symbolic addition[39] program. The phase assignment with the smallest conflict ratio gave an E map in

which 27 of the heavier atoms were located. Least-squares refinement of the coordinates and isotropic temperature factors converged at an R index of 0.168%. In the last cycle of refinement the average shift of a refined parameter, except for atom C(2), was 0.56 of the estimated standard deviation of that parameter. The weighted R index was 12.4%, and the goodness-of-fit was 7.2. The average standard deviation in atomic position is 0.008 Å, the average standard deviation in bond length is 0.011 Å, and the average standard deviation in bond angle is 0.7°.[40]

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Registry No.—**1**, 50676-11-4; **2**, 53359-96-9; **3**, 6044-73-1; **4**, 54062-32-7; **5**, 54062-33-8; **5** mono-OH analog, 54062-34-9; **6**, 54062-35-0; **6** 2,4-DNP, 54062-36-1; **7**, 54062-37-2; **7** 2,4-DNP, 54062-38-3; **8**, 54062-39-4; **8** *cis*-OH analog, 54062-40-7; **8** *trans*-OH analog, 54141-80-9; **9**, 54062-41-8; **9** semicarbazone, 54062-42-9; **9** *cis*-OH analog, 54062-43-0; **9** *trans*-OH analog, 54141-81-0; **10** Δ^2 isomer, 54062-44-1; **10** Δ^1 isomer, 54062-45-2; **11**, 54062-46-3; **12**, 54062-47-4; **12** OH analog, 54062-48-5; **13**, 54062-49-6; **13** OH analog, 54062-50-9; **14**, 54062-51-0; *trans*-**15**, 54062-52-1; *cis*-**15**, 54062-53-2; **16**, 54141-82-1; **17**, 54062-54-3; **18**, 54062-55-4; **19**, 54062-56-5; **20** α epimer, 54062-57-6; **20** β epimer, 54141-83-2; **21**, 54062-58-7; **22** ortho isomer, 54062-59-8; **22** para isomer, 54062-60-1; **24**, 54062-61-2; **25**, 54062-62-3; **25** OH analog, 54062-63-4; **26**, 54062-64-5; **27**, 54062-65-6; 4-methyl-(*E*)-4,8-nonadienol 54062-66-7; 1-chloro-4-methyl-(*E*)-4,8-nonadiene, 54062-67-8; 2,5-dimethyl-(*E*)-5,9-decadienoic acid, 54062-68-9; *cis*-4-(2′-methoxyphenyl)-1-methyl-1-(3′-methyloctyl)cyclohexane, 54062-69-0; *trans*-4-(2′-methoxyphenyl)-1-methyl-1-(3′-methyloctyl)cyclohexane, 54062-70-3; *cis*-4-(4′-methoxyphenyl)-1-methyl-1-(3′-methyloctyl)cyclohexane, 54062-71-4; *trans*-4-(4′-methoxyphenyl)-1-methyl-1-(3′-methyloctyl)cyclohexane, 54062-72-5; 2-methoxy-8a-methyl-6,7,8,8a,9,10-hexahydrophenanthrene, 54062-73-6; *N,N,N′,N′*-tetramethyldiamidophosphorochloridate, 1605-65-8; 8aβ,10aβ-dimethyl-3,4,4aβ,4bα,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene, 54062-74-7; 12-*m*-methoxyphenyl-2,5,6,9-tetramethyl-(*E,E*)-5,9-dodecadienoic acid, 54119-84-5; 12-*m*-methoxyphenyl-5,6,9-trimethyl-(*E,E*)-5,9-dodecadienoic acid, 54062-75-8; 12-*m*-methoxyphenyl-2,5,6,9-tetramethyl-(*E,E*)-5,9-dodecadienol, 54083-29-3; 12-*m*-methoxyphenyl-2,5,6,9-tetramethyl-(*E,E*)-5,9-dodecadienal, 54083-30-6; 3-methoxy-6bβ,8aβ,12bα,14aβ-tetramethyl-5,6,6aα,6b,7,8,8a,9,10,11,12,12aβ,12b,13,14,14a-hexadecahydro-11β-picenol, 54062-76-9; 3-methoxy-6bβ,8aβ,12bα,14aβ-tetramethyl-5,6,6aα,6b,7,8,8a,9,10,11,12,12aβ,12b,13,14,14a-hexadecahydro-12β-picenol, 54062-77-0; 2,5-dimethyl-(*E*)-5,9-decadienol, 54062-78-1.

Supplementary Material Available. Tables III–VII containing the observed and calculated structure factors, the heavier atom parameters, the hydrogen atom coordinates, the bond distances and angles, and the least-squares plane of the aromatic ring, respectively, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1007.

References and Notes

(1) The structural formulas containing one or more asymmetric carbon atoms depict one enantiomer, but refer to racemic compounds unless otherwise designated. In the text the (±) prefix will be omitted, and intermediates are assumed to be racemic. The tricyclic compounds will be described by the phenanthrene nomenclature, and each racemate is arbitrarily represented by that enantiomer that has the C-4b methyl group in the α configuration. The pentacyclic compounds will be described by the picene nomenclature, and each racemate is arbitrarily represented by that enantiomer that has the C-14a methyl group, respectively, in the α configuration. In discussions, where naturally occurring triterpenes are involved, the nomenclature and numbering suggested by S. Allred and G. Ourisson [*Tetrahedron*, **1**, 277 (1957)] will be used as necessary.

(2) Postdoctoral Fellow of the National Institute of General Medical Sciences (GM 50467) of the National Institutes of Health, 1972–1974.

(3) Predoctoral Trainee of the National Institute of General Medical Sciences of the National Institutes of Health, 1969–1973.

(4) R. E. Ireland, P. Bey, K.-F. Cheng, R. J. Czarny, J.-F. Moser, and R. I. Trust, *J. Org. Chem.*, **40**, 1000 (1975).

(5) W. S. Johnson, *Acc. Chem. Res.*, **1**, 1 (1968).

(6) R. E. Ireland, M. I. Dawson, S. C. Welch, A. Hagenbach, J. Bordner, and B. Trus, *J. Am. Chem. Soc.*, **95**, 7829 (1973).

(7) R. E. Ireland, M. I. Dawson, C. J. Kowalski, C. A. Lipinski, D. R. Marshall, J. W. Tilley, J. Bordner, and B. L. Trus, *J. Org. Chem.*, **40**, 973 (1975).

(8) (a) K. E. Harding, E. J. Leopold, A. M. Hudrlik, and W. S. Johnson, *J. Am. Chem. Soc.*, **96**, 2540 (1974); (b) R. L. Carney and W. S. Johnson, ibid., **96**, 2549 (1974); (c) W. S. Johnson and P. A. Bartlett, ibid., **95**, 750 (1973).

(9) G. Stork, A. Birzzolara, H. Landesmann, J. Szmuszkovicz, and R. Terrel, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(10) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963).

(11) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968); R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

(12) R. E. Ireland, M. I. Dawson, and C. A. Lipinski, *Tetrahedron Lett.*, 2247 (1970).

(13) O. J. Sweeting and J. R. Johnson, *J. Am. Chem. Soc.*, **68**, 1057 (1946).

(14) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. Li, D. J. Faulkner and M. R. Petersen, *J. Am. Chem. Soc.*, **92**, 741 (1970); R. I. Trust and R. E. Ireland, *Org. Syn.*, **53**, 116 (1973).

(15) W. S. Johnson, M. B. Gravestock, and B. E. McCarry, *J. Am. Chem. Soc.*, **93**, 4332 (1971).

(16) W. S. Trahanovsky and M. P. Doyle, *J. Am. Chem. Soc.*, **89**, 4867 (1967).

(17) P. A. Bartlett, J. I. Brauman, W. S. Johnson, and R. A. Volkmann, *J. Am. Chem. Soc.*, **95**, 7502 (1973).

(18) R. Baltzly, E. Lorz, P. B. Russel, and F. M. Smith, *J. Am. Chem. Soc.*, **77**, 624 (1955).

(19) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5324 (1963).

(20) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(21) G. Stork, S. Vyes, T. Wakamatsu, P. Grieco, and J. Labovitz, *J. Am. Chem. Soc.*, **93**, 4945 (1971).

(22) Hydrogenation and Birch reduction: G. Stork, H. J. K. Lowenthal, and P. C. Mukharji, *J. Am. Chem. Soc.*, **78**, 501 (1956). Lithium dimethylcuprate addition: H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); G. H. Posner, *Org. React.*, **19**, 1 (1972). For another approach to the synthesis of the enone **16**, see G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).

(23) Based on spectral analysis according to W. Nagata, T. Terasawa, and K. Tori, *J. Am. Chem. Soc.*, **86**, 3746 (1964).

(24) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); see also C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

(25) M. Meisters and T. Mole, *J. Chem. Soc., Chem. Commun.*, 595 (1972).

(26) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(27) J. R. Shanklin, C. R. Johnson, J. Ollinger, and R. M. Coates, *J. Am. Chem. Soc.*, **95**, 3429 (1973).

(28) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).

(29) R. E. Ireland and L. H. Mander, *J. Org. Chem.*, **32**, 689 (1967).

(30) H. Dutler, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **38**, 1268 (1955); G. Brownlie, F. S. Spring, R. Stevenson, and W. S. Strachan, *Chem. Ind. (London)*, 656 (1955); E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **77**, 3667 (1955); R. M. Coates, *Tetrahedron Lett.*, 4143 (1967).

(31) Melting points labeled (vacuum) were taken in evacuated capillaries on a Hoover capillary melting point apparatus, while all others were determined on a Kofler micro hot stage melting point apparatus. All melting points and boiling points are uncorrected. Infrared (ir) spectra were determined on a Perkin-Elmer 237B grating infrared spectrometer, and nuclear magnetic resonance (NMR) spectra were recorded using either a Varian H-60A or T-60 spectrometer. Chemical shifts are reported as δ values in parts per million relative to TMS (δ_{TMS} 0.0 ppm) as an internal standard.

Gas–liquid phase chromatographic (GLC) analyses were determined on either a Hewlett-Packard 5750 or F & M 810 research chromatograph using helium carrier gas at a flow rate of 60 ml/min. Unless otherwise noted, all analytical GLC was conducted on a 6 ft × 0.125 in. column packed with 4% SE-30 on 60–80 mesh Chromosorb W AW-DMCS.

Preparative thin layer chromatography (preparative TLC) was carried out on 20 × 20 × 0.2 cm glass plates coated with silica gel $PF_{254+266}$ (Brinkman Instruments Co.). Analytical thin layer chromatography (TLC) was conducted on 1 × 3 in. microscope slides coated with a 0.5 mm layer of silica gel G or $PF_{254+266}$.

Alumina used for column chromatography refers to the grade I, neutral variety manufactured by M. Woelm, Eschwege, Germany, and made up to grade II or III as indicated by the addition of 3 or 6% water prior to use. Silica gel columns used the 0.05–0.2-mm silica gel manufactured "for column chromatography" by E. Merck & Co., Darmstadt, Germany. Preparative medium-pressure column chromatography was performed using 0.5 × 20 in. or 2 × 20 in. glass columns with fittings supplied by Chromatronix, Inc., Berkeley, Calif., and an instrument minipump supplied by Milton Roy Co., St. Petersburg, Fla. (instrumentation designed by R. H. Mueller, these laboratories, and copies are available on request). The columns were packed with silica gel H "for TLC acc. to Stahl" (10–40 μ) manufactured by E. Merck & Co., Darmstadt, Germany. Solvents were degassed under water aspirator vacuum prior to use.

"Dry" solvents were dried immediately prior to use. Ether, benzene, tetrahydrofuran, dioxane, and dimethoxyethane were distilled frm lithium

aluminum hydride; *tert*-butyl alcohol, dimethyl sulfoxide, pyridine, and hexamethylphosphoramide (HMPA) were distilled from calcium hydride; dichloromethane, carbon tetrachloride, diodomethane, and methyl iodide were distilled from phosphorus pentoxide; ammonia was distilled from the tank and then from a blue lithium or sodium solution; acetone was analytical reagent grade distilled from potassium permanganate; formic acid was distilled from boric anhydride. "Petroleum ether" refers to the "Analyzed Reagent" grade hydrocarbon fraction, bp 30–60°, which is supplied by J. T. Baker Co., Phillipsburg, N.J., and was not further purified.

Reactions described as run under nitrogen or argon employed a mercury bubbler arranged so that the system could be alternately evacuated and filled with the inert gas and left under a positive pressure.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(32) In cases where products were isolated 'by solvent extraction", the procedure generally followed was to extract the aqueous layer with several portions of the indicated solvent; then the organic layers were combined and washed with water, followed by saturated brine. The organic layer was dried over anhydrous sodium or magnesium sulfate, then filtered, and the solvent was evaporated from the filtrate under reduced pressure (water aspirator) using a rotary evaporator. The use of the terms "base wash" or "acid wash" indicate washing the combined organic layers with saturated aqueous sodium bicarbonate solution or with dilute aqueous hydrochloric acid, respectively, prior to the aforementioned washing with water.

(33) F. Uhlig and H. R. Snyder, *Adv. Org. Chem.*, **1**, 35 (1960).

(34) Preparative GLC under the same conditions described above[31] except that the following columns were used: (a) 5% SE-30 on Chromosorb W AW-DMCS (6 ft × 0.125 in); (b) 10% Carbowax 20M on Chromosorb W AW-DMCS (10 ft × 0.25 in).

(35) For spectra, see R. I. Trust, Ph.D. Thesis, California Institute of Technology, 1974.

(36) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

(37) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).

(38) D. J. Duchamp, Program and Abstracts, ACA Meeting, Bozeman, Mont., 1964, Paper B-14, p 29.

(39) J. Karle and H. Hauptmann, *Acta Crystallogr.*, **3**, 181 (1950).

(40) See paragraph at end of paper regarding supplementary material.

Rearrangements in the Photolevopimaric Acid Series. A Paradigm of Bicyclo[2.2.0]- and Bicyclo[2.1.1]hexane Chemistry[1,2]

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Unexpected rearrangements of photolevopimaric acid derivatives are described. Hydroboration–oxidation of methyl levopimarate (**3c**) gave the previously reported *exo*-bicyclo[2.2.0]hexanol **7a** and a new tertiary alcohol **12a** which was prepared independently from the epoxide **5**. Treatment of **5** with Lewis acids resulted in rearrangement to **6**. Mercuric acetate oxidation of **3c** resulted in conversion to **13**. Contrary to an earlier report, Jones oxidation of **7a** proceeded with rearrangement to the bicyclo[2.1.1]hexanone **20**, whose structure was established by degradation to the cyclopentanone **30**, acid cleavage to **35**, base-catalyzed cleavage to **36**, and degradation of the latter to the drimane derivative **38**. Treatment of the *endo*-bicyclo[2.1.1]hexyl tosylate **23a** with tosyl chloride resulted in rearrangement to a bicyclo[3.1.0]hexane derivative, the new resin acid isomer methyl isophotolevopimarate (**39**). An unusual oxidation of the *exo*-bicyclo[2.2.0]hexanol **7a** to the lactone **14a** and **14b** with Fétizon's reagent was observed. Solvolytic reactions of the *exo*-bicyclo[2.2.0]hexyl tosylate **7c** resulted in rearrangement to the bicyclo[2.1.1]hexane derivatives **44** and **45**.

The observations which are described in the present report are the result of work originally aimed at the synthesis of 14-deuteriolevopimaric acid (**1b**). This substance was desired to help clarify the nature of the intramolecular hydrogen transfer which occurs on irradiation of the levopimaric acid–cyclopentenedione adduct **2**,[3,4] a problem which was eventually solved by X-ray analysis of one of the photolysis products.[5]

The simplest path to **1b** appeared to be introduction of deuterium in some fashion at C-14 of the photolevopimaric acid skeleton **3a**, since thermal reversion of the valence isomerization **1a** → **3a**[6,7] has been described.[7] The rearrangements which negated this approach and will be described in this report constitute not only an instructive paradigm of bicyclo[2.2.0]- and bicyclo[2.1.1]hexane chemistry, but illustrate several other unusual reactions which presumably occur because these strained systems are part of a relatively rigid diterpene skeleton. See Scheme I.

Attempts to Prepare Bicyclo[2.2.0]hexanone 8. Our failure to effect direct introduction of deuterium into **3c**[8a] forced us to investigate more circuitous routes to **3d** by way of **8**, which are outlined in Scheme II. The preparation of **8** from **7a** has been reported previously[7]; although Dauben and Coates did not discuss the stereochemistry of **7a** and **8**, it seemed likely that these substances possessed the configurations indicated in Scheme II, thus necessitating further reduction of **8** to **9**, which has the correct stereochemistry for bimolecular elimination to **3d**. However, as the reported[7] overall yield of **8** was rather low, we first explored its preparation from the epoxide **5**.

This substance, isolated in 81% yield, was assigned the exo configuration depicted in Scheme II because of the appearance of H-14 as a narrowly split doublet (J = 2.5 Hz) at 3.82 ppm. The W arrangement for such long-range coupling of H-14 to H-12 is achieved only if H-14 is α; this is also consonant with the deduction, from models, that the least hindered side of **3c** is the β face.

Treatment of **5** with acidic reagents generally produced complex mixtures which resisted attempts at separation, but contained no fraction corresponding to **8**. On the other hand, use of boron trifluoride etherate under carefully defined conditions resulted in rearrangement (64% yield) to an unsaturated aldehyde (sharp singlet at 9.3 ppm, broadened vinylic singlet, $W_{1/2}$ = 6.6 Hz, at 5.83 ppm). This substance was assigned structure **6**, formally derivable by the shifts depicted in Scheme III, rather than **10** for the following reason.

By sweeping the methylene region of the ^{1}H NMR spectrum, the center of the H-15 signal was found at 2.07 ppm. Irradiation at this frequency collapsed the isopropyl methyl doublets at 0.90 and 1.06 ppm to singlets and sharpened the vinyl proton signal ($W_{1/2}$ = 2.5 Hz). The existence of allylic coupling between the vinyl proton and H-15 was thus established, an observation which excludes structure **10**. The α configuration of the aldehyde is deduced on mechanistic grounds; an upfield shift of the C-10 methyl resonance to 0.86 ppm may be attributed to the shielding effect of the 12,13 double bond.

As a result of this rearrangement we returned to Dauben and Coates' method of preparing **8**. Slight modifications in