14α-hydroxyhecogenin acetate (IVa): mp 232.5–235°, (lit.[1] mp 231–235°); λ_{max}^{KBr} 2.81, 5.77, 5.84, 8.02, 10.20, 10.90, 11.12, 11.49 μ.

Anal. Calcd for $C_{29}H_{44}O_6$: C, 71.28; H, 9.08. Found: C, 71.05; H, 9.13.

Treatment of Photohecogenin Acetate (IIIa) with Dilute Acetic Acid.—A mixture of 454 mg of IIIa,[1] 6 ml of glacial acetic acid, and 2 ml of water was stirred at room temperature for 0.5 hr during which time complete solution was effected. The reaction mixture was allowed to stand at room temperature for an additional 19.5 hr, after which it was poured into ice water. The colorless solid was collected, washed well with water, and dried, mp 207.5–217°. Thin layer chromatography indicated that the product was a mixture of at least two substances. Crystallization from methanol afforded 370 mg of 12α,14α-dihydroxytigogenin 3-acetate (VIIIa): mp 221–225° (lit.[1] mp 219–222.5°); λ_{max}^{KBr} 2.83, 2.88, 5.77, 8.00, 10.18, 10.91, 11.08, 11.52 μ.

Anal. Calcd for $C_{29}H_{46}O_6$: C, 70.98; H, 9.45. Found: C, 71.22; H, 9.41.

Thin layer chromatography indicated that VIIIa (mp 221–225°) was still contaminated with a small amount of a more polar substance. Separation of the contaminant by preparative thin layer chromatography on silica gel with 35% ethyl acetate in benzene as the solvent system gave a pure sample of VIIIa, mp 220–222°.

Treatment of Lumihecogenin Acetate (IIa) with Dilute Acetic Acid.—A mixture of 319 mg of IIa,[1] 6 ml of glacial acetic acid, and 2 ml of water was stirred at room temperature for 20 hr during which time complete solution was effected. The reaction mixture was poured into ice water. The resultant colorless solid was collected, washed with water, and dried, mp 213–219.5°. Thin layer chromatography indicated that the crude product was a mixture having the same composition as that obtained from photohecogenin acetate (IIIa). The infrared spectra of the two mixtures were indistinguishable. Crystallization from methanol gave 190 mg of 12α,14α-dihydroxytigogenin 3-acetate (VIIIa), mp 213–217.5°. Its infrared spectrum was identical with that of VIIIa, mp 221–225°, obtained from photohecogenin acetate (IIIa).

12α,14α-Dihydroxytigogenin 3,12-Diacetate (VIIIb).[1]—A solution of 86 mg of 12α,14α-dihydroxytigogenin 3-acetate (VIIIa), 0.2 ml of pyridine, and 0.2 ml of acetic anhydride was heated on the steam bath for 3 hr. The cooled reaction mixture was poured into ice water. The colorless solid was collected, washed well with water, and dried. Crystallization from methanol gave 45 mg of VIIIb, mp 227–229° (lit.[1] mp 223–225.5°). Admixed with the starting material, it melted at 194–196°.

Anal. Calcd for $C_{31}H_{48}O_7$: C, 69.89; H, 9.08. Found: C, 69.90; H, 9.18.

Registry No.—V, 10075-96-4; VII, 10102-97-3; IVa, 10102-98-4; VIIIa, 10102-99-5; VIIIb, 10075-97-5; IIa, 10075-98-6; IIIa, 10102-96-2.

Experiments Directed toward the Total Synthesis of Terpenes. XI. The Total Synthesis of (±)-Rimuene and (±)-13-*epi*-Rimuene[1a]

ROBERT E. IRELAND[1b] AND LEWIS N. MANDER

Contribution No. 3402 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, and the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan

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A stereoselective total synthesis of the diterpenoid hydrocarbon rimuene (1) is described. In order to ascertain the configuration about the 13 position of rimuene (1), 13-*epi*-rimuene (16) was synthesized as well and both compounds related to the pimaradiene series of known C-13 configuration.

The diterpenoid hydrocarbon rimuene (1) has in recent years been the subject of intensive structural study by several groups.[2] Initial structural postulates[2a,b] were shown to be untenable by synthetic work in these laboratories,[3] and it was not until the work of Overton[2e] and Corbett[2d] and their respective collaborators that the final answer to this structural problem was provided. The structure 1, on which both groups agree, represents a skeletal rearrangement of the more common tricyclic diterpenoid backbone as found in the pimaradenes 19 and 22*. As such rimuene (1) is structurally more closely related to the mould metabolite rosenenolactone,[4] and indeed may arise by a biogenetic pathway that is similar to the early stages of the proposed rosenonolactone scheme.[5]

Our historical connection[3] with the rimuene problem, as well as our continuing interest in developing synthetic methods for the construction of diterpenoid structural variants, prompted us to undertake a total synthesis of this new structure.

The framework of rimuene molecule 1 is sufficiently different from that of the pimaradienes to require a somewhat different synthetic approach. In particular, the nuclear double bond is far removed from the vinyl group at C-13[6] in rimuene (1). Therefore each of these functional groups will have to be developed independently in contrast to the approach used in the pimaradiene-type syntheses.[3]

Recognizing the lability of the C-13 vinyl group toward common reaction conditions, we chose to introduce the substituents at C-13 in the last stages of the synthesis. A logical functional group that could serve as the root for this branching was a ketone, and hence our consideration was shifted to the tricyclic ketone (2).

The principal remaining synthetic complexity in rimuene skeleton 1 is the arrangement of carbon atoms that make up ring A. Of particular note is *the lack of a C-10[6] angular methyl group*. The fact that the A/B ring fusion is unencumbered by a quaternary carbon at C-10 suggested to us that a suitably substituted

(1) (a) A portion of the work here recorded was reported in preliminary form: see R. E. Ireland and L. N. Mander, *Tetrahedron Letters*, 3453 (1964). Support for this work in the form of a research grant (GM-09067-03) from the Public Health Service is gratefully acknowledged. (b) Alfred P. Sloan Foundation Research Fellow, 1962–1966.

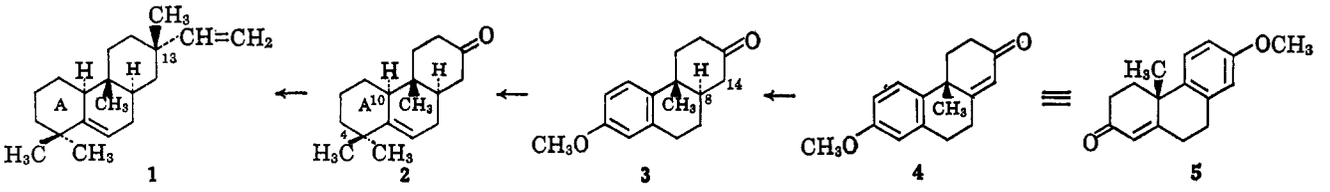
(2) (a) L. H. Briggs, B. F. Cain, and J. K. Wilmhurst, *Chem. Ind.* (London), 599 (1958); (b) L. H. Briggs, B. F. Cain, and R. C. Cambie, *Tetrahedron Letters*, 17 (1959); (c) R. M. Carman, *Australian J. Chem.*, **16**, 225 (1963); (d) R. E. Corbett and S. G. Wylie, *Tetrahedron Letters*, 1903 (1964); (e) J. D. Connolly, R. McCrindle, R. D. H. Murray, and K. H. Overton, *J. Chem. Soc.*, 273 (1966); (f) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).

(3) R. E. Ireland and P. W. Schiess, *ibid.*, **28**, 6 (1963); R. F. Church and R. E. Ireland, *ibid.*, **28**, 17 (1963).

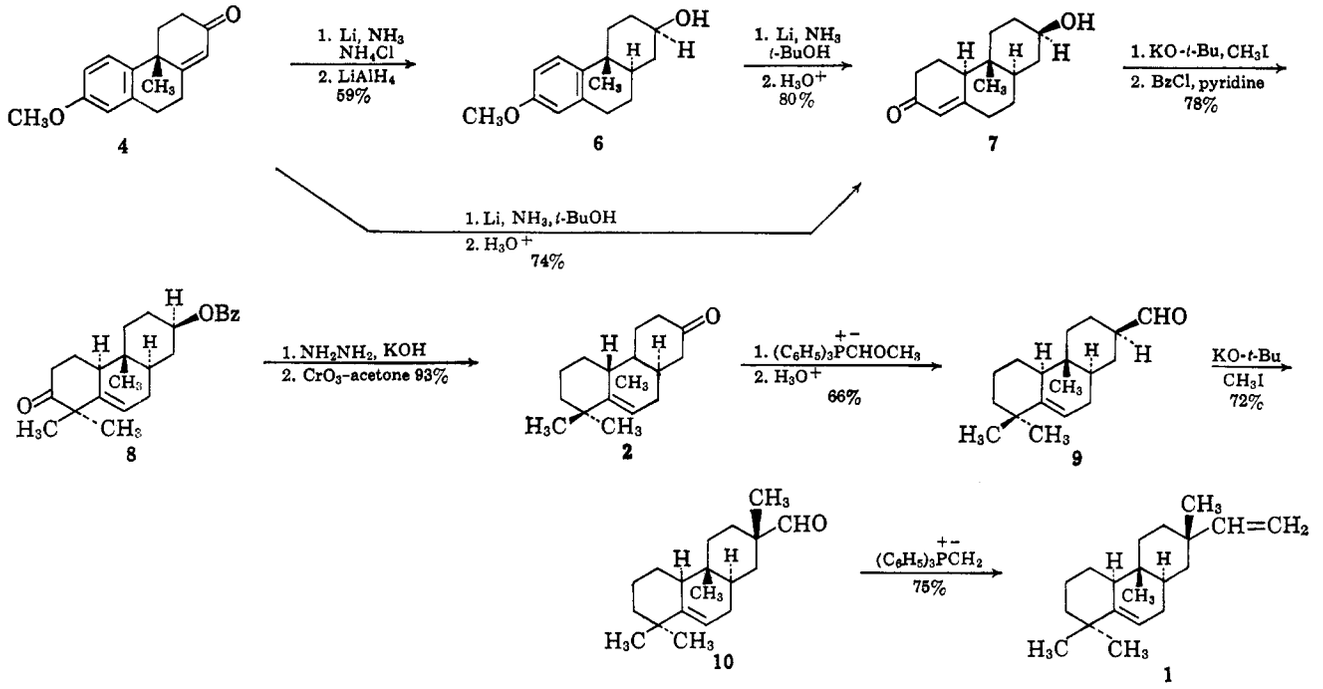
(4) G. A. Ellestad, B. Green, A. Harris, W. B. Whalley, and H. Smith, *J. Chem. Soc.*, 7246 (1965).

(5) A. J. Birch, R. W. Rickards, H. Smith, A. Harris, and W. B. Whalley, *Proc. Chem. Soc.*, 223 (1958); J. J. Britt and D. Arigoni, *ibid.*, 224 (1958).

(6) Unless specifically indicated by an asterisk following the formula number, all compounds referred to in this report are racemic modifications although only one enantiomer is depicted in the drawings.



SCHEME I
THE SYNTHESIS OF (±)-RIMUENE



aromatic A ring would suffice as the precursor of this ring in rimuene (1). Inclusion of the C-3 oxygen function at this stage foreshadowed its use to introduce the *gem*-dimethyl grouping at C-4. Thus the next step in the simplification of rimuene structure 1 is represented by aromatic ketone 3.

The remaining synthetic task is the establishment of a B/C *trans*-ring fusion in the aromatic ketone (3). It was a simple matter to provide for this eventuality through the inclusion of a double bond in conjugation with the carbonyl group of ketone 3. In this fashion we were able to reduce rimuene carbon framework 1 to the unsaturated aromatic ketone (4). The final task was the realization that aromatic ketone 4 was indeed identical[6] with the very familiar tricyclic ketone (5), for which there is a vast lore already recorded.[7] The synthetic sequence actually employed to realize this plan in practice is outlined in Scheme I. Several, though not all, steps in this scheme are worthy of further comment.

The keto alcohol (7) could be obtained by either a stepwise lithium–ammonia reduction *via* the aromatic alcohol (6) or directly when *t*-butyl alcohol was included in the initial reduction mixture. Such an overall reduction of starting unsaturated aromatic ketone 4 has been reported[7a] previously; however, the procedure here recorded affords a much more satisfactory yield. Methylation of unsaturated keto alcohol 7 produced $\Delta^{5(6)}$ derivative 8 (after benzoylation) only when unsaturated ketone 7 and the base were allowed to remain in contact for 10 min at 30° prior to the addition of methyl iodide. The signal owing to the C-6 vinyl hydrogen in the nmr spectrum of ketobenzoate 8 was a broad multiplet centered at 5.7 ppm. This signal, characteristic of the vinyl hydrogen on the nuclear double bond of rimuene as well integrated for one proton when the above methylation procedure was followed. After longer ketone–base contact periods, significant amounts of the $\Delta^{5(10)}$ derivative were obtained, as judged by the lower integration of the C-6 vinyl hydrogen signal in the nmr spectrum and the weakening of double-bond absorption in the infrared.

Two procedures were used for the conversion of ketone 2 into aldehyde 9 with similar results. There seemed to be little preference between the methoxymethylene triphenylphosphorane procedure[8] depicted (66% yield) and a sequence that employed the Corey–Chaykovsky oxirane synthesis[9] and the boron trifluoride catalyzed rearrangement[10] to the aldehyde 9 (70% yield).

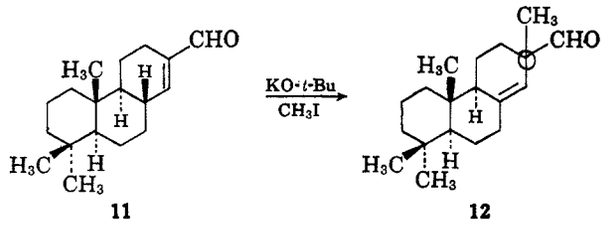
The most striking thing we observed during this set of reactions was the high stereoselectivity of the methylation of aldehyde 9. Contrary to our previous experience[3] with unsaturated aldehyde 11, which led to a mixture of methylated aldehydes (12), the saturated aldehyde (9) afforded a 72% yield of a single isomer of the methylated aldehyde (10). Careful chromatog-

(7) (a) F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 1248 (1958); (b) G. Stork, A. Meisels, and J. E. Davies, *J. Am. Chem. Soc.*, **85**, 3419 (1963).

(8) S. G. Levine, *ibid.*, **80**, 6150 (1958); G. Wittig, W. Böll, and K. Kruck, *Ber.*, **95**, 2514 (1962).

(9) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

(10) H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.*, 4596 (1956).



11 12

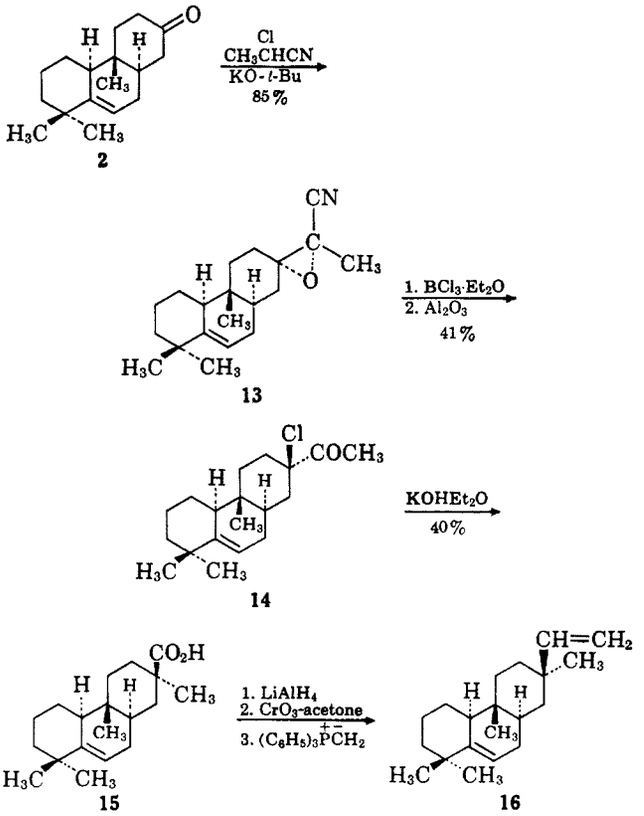
raphy of the reaction product and analysis of the intermediate fractions by vapor phase chromatography failed to reveal any components other than methylated aldehyde **10** and starting material **9**. This rather surprising result has been verified[11] with other similarly substituted cyclohexanecarboxaldehydes. As became apparent later (*vide infra*), the new methyl group in aldehyde **10** had the equatorial (β) orientation, a fact that might be construed as a reflection of the sterically more favorable approach of the methyl iodide from the equatorial side of the exocyclic aldehyde enolate. The similarity between this result and the protonation of exocyclic enolates as discussed most recently by Johnson[12] is satisfying. In each case the attacking reagent appears to approach the less hindered side of a conformationally fixed system. A corollary of this conclusion pertains to the methylation of the α,β-unsaturated aldehyde **11**. Here the extended conjugation of the enolate flattens the C ring more and removes one 1,3-diaxial hydrogen interaction (C-8β-H) from the β face of the molecule. The result is to lessen the steric preference for attack by the methyl iodide on the equatorial α face, and a mixture of methylated aldehydes (**12**) is produced.

Methylenetriphenylphosphorane[13] served to convert aldehyde **10** to (±)-rimuene (**1**), mp 85–88°. Comparison of the infrared and nmr spectra of this synthetic sample and those of natural (+)-rimuene,[14] mp 55–55.5°, revealed the identity of the two substances. Unfortunately, the absence of the C-13 epimeric aldehyde in the methylation mixture left our synthesis dependent upon the degradative work[2e] for proof of the orientation of the methyl and vinyl groups at C-13 in our (±)-rimuene (**1**). Thus while we had devised a highly stereoselective and high yield (20% over-all from the ketone **4**) total synthesis of (±)-rimuene (**1**), the importance of the C-13 epimeric material to the synthetic conclusions drawn could not be overlooked. In order to remedy this situation we undertook the synthesis of (±)-13-*epi*-rimuene (**16**).

The system we employed for this synthesis is shown in Scheme II. Inasmuch as the only variation we sought in the present synthesis occurred at the 13 position of the tricyclic system, the same ketone **2** could serve this effort as well. For the present work we needed a pathway that led to a C-13 α-oriented methyl group, and to accomplish this we chose to employ the Favorskii rearrangement[15] to introduce the required methyl and carboxyl groups. Our choice was predicated on the availability of a highly stereoselective route to the requisite α-chloro ketone (**14**) *via* the glycidonitrile (**13**). The stereoselectivity of both the glycidonitrile method

(11) L. N. Mander, unpublished results in these laboratories.
(12) S. K. Malhotra and F. Johnson, *J. Am. Chem. Soc.*, **87**, 5493 (1965).
(13) A. Wittig and V. Schollkopf, *Ber.*, **87**, 1318 (1954).
(14) We are indebted to Professor L. H. Briggs for providing us with this comparison sample.
(15) J. A. Barltrop and A. C. Day, *Tetrahedron*, **14**, 310 (1961).

SCHEME II
THE SYNTHESIS OF (±)-13-*epi*-RIMUENE



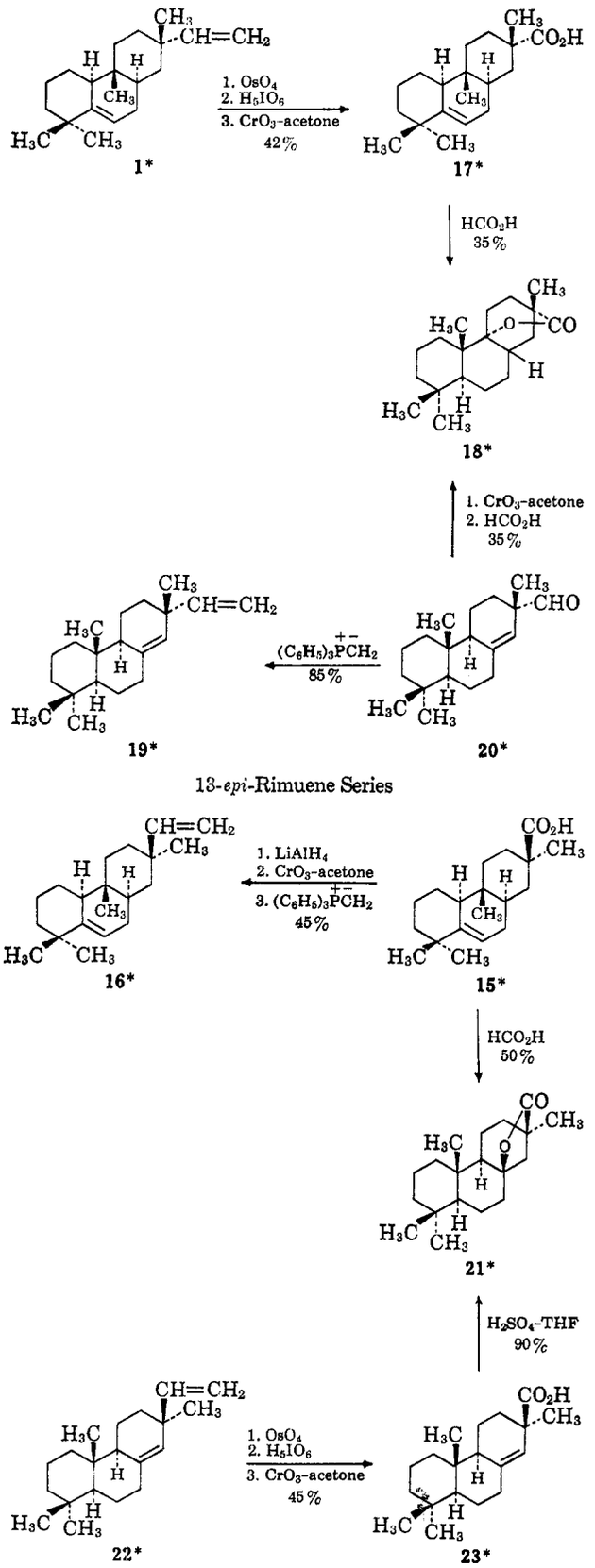
for the formation of α-chloro ketones and the subsequent Favorskii rearrangement has been demonstrated by Stork and co-workers,[16] and these results made the sequence admirably suited to our needs. Based on our experience with the methylation of the aldehyde **9**, we expected the initial glycidonitrile formation to take place so as to form a β-oriented carbon–carbon bond. We reasoned that attack of the C-13 carbonyl group should proceed in a fashion similar to attack of the C-13 enolate of the aldehyde **9**. The latter case resulted in exclusive β-oriented methylation, and hence it appeared reasonable to expect glycidonitrile formation to result in a β-oriented carbon–carbon bond. This point was, of course, crucial to the stereochemical outcome of the sequence, as the two inversions that occur during the subsequent transformations make the configuration of final acid **15** dependent on that of initial glycidonitrile **13**.

When the Stork–Favorskii sequence[16] was in fact applied to ketone **2**, the only complication that arose was on cleavage of glycidonitrile **13** with hydrogen chloride in ether. Under these conditions a significant portion of the product was material in which the $\Delta^{5(6)}$ double bond had rearranged to the $\Delta^{5(10)}$ position. This obstacle was overcome by brief exposure of glycidonitrile **13** to boron trichloride in ether at low temperatures. These conditions were sufficient to open the oxide ring but were not vigorous enough to cause double-bond migration.

The remainder of the synthesis was satisfactory and provided a stereoselective route to (±)-13-*epi*-rimuene (**16**) *via* acid **15**. The material so prepared was an oil in contrast to (±)-rimuene (**1**), and the infrared and

(16) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960); G. Stork, W. S. Worrall, and J. J. Pappas, *ibid.*, **82**, 4315 (1960).

SCHEME III
RIMUENE. PIMARADIENE INTERRELATIONSHIPS[a]



[a] See ref 6.

nmr spectra of (±)-13-*epi*-rimuene (**16**) were distinct from those of (±)-rimuene (**1**). However, in spite of the internal consistency of the two syntheses with regard to the orientation of the C-13 substituents, there was no positive proof that the assigned stereochemistry was correct. Now that members of both stereochemical series were in hand, we had an opportunity to settle this question beyond any doubt. To do this we chose to interrelate derivatives of the rimuene skeleton with those of the pimaric acid skeleton where the orientation of the substituents at C-13 is known[3] with certainty. The necessary pimaric acid derivatives—aldehyde **20** (the precursor[3] of sandaracopimaradiene **19**) and pimaradiene **22***—were available from our earlier work[3] and were converted to their corresponding C-13 carboxylic acids by the oxidative procedures outlined in Scheme III. Treatment of the acid derived from aldehyde **20** with formic acid caused lactonization to δ-lactone **18**, while sulfuric acid treatment of acid **23*** resulted in formation of γ-lactone **21***. These two lactones were distinct by the usual spectral as well as physical criteria, and there is no reason to believe that the stereochemical integrity of the substituents at C-13 in either case has been altered. Therefore lactones **18** and **21*** must possess both the structural and stereochemical features depicted.

Similar degradative treatment of (+)-rimuene (**1***) led through C-13 carboxylic acid **17*** to δ-lactone **18***. In this case rearrangement of the rimuene skeleton has occurred, but again there is no reason to believe that the orientation of the substituents at C-13 in acid **17*** has changed during the lactonization process. Thus δ-lactone **18*** provides the link between sandaracopimaradiene system **19** of known stereochemistry and rimuene series **1***. Hence the orientation of the methyl and vinyl groups at C-13 in rimuene must be as shown in structure **1**.

As a check on this rationalization, the lactonization of acid **15**—the precursor of (±)-13-*epi*-rimuene (**16**)—was investigated. Formic acid treatment of this acid led to γ-lactone **21** which was previously obtained pimaradiene (**22***) *via* acid **23***. This interrelation assures the β orientation of the C-13 vinyl group in (±)-13-*epi*-rimuene (**16**) inasmuch as such is known[3] to be the configuration at this center in pimaradiene (**22***). Therefore not only are the syntheses of (±)-rimuene (**1**) and (±)-13-*epi*-rimuene (**16**) stereorational and internally consistent, but these final correlations with the pimaric acid series also verify the assignments made.[17]

Experimental Section[18]

I. (±)-Rimuene (1). 7-Methoxy-4aβ-methyl-1,2,3,4,4a,9,-10,10aα-octahydro-2-oxophenanthrene.—A solution of 633 mg (0.0027 mole) of the ketone **4** in 80 ml of dry tetrahydrofuran was added dropwise, in an atmosphere of nitrogen, to a stirred solution of 46 mg (0.0066 g-atom) of clean lithium metal in 100 ml of liquid ammonia (distilled from sodium). The reaction mixture was stirred for a further 30 min and then quenched with excess ammonium chloride. After evaporation of the ammonia, the residue was treated with 200 ml of ether and 50 ml

(17) The correlation of the rimuene skeleton with isopimaric acid through the partial synthesis of (−)-rimuane has also been achieved by W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 3195 (1965).

(18) Unless otherwise specified, the term petroleum ether refers to reagent grade material boiling in the range 30–60°. Melting points were determined on a Kofler hot stage and are corrected for stem exposure. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on a Perkin-Elmer Model 237 spectrometer, and nmr spectra were measured on a Varian Associates Model A-60. Florisil refers to the product of the Floridin Co., Tallahassee, Fla., 60–100 mesh. The oxidant Jones reagent is 8 *N* chromic acid prepared according to the procedure of C. Djerassi, R. R. Engle, and A. Bowers, *ibid.*, **21**, 1547 (1956).

of water. The ether layer was washed with brine, dried (Na_2SO_4), and concentrated to a pale yellow oil. This product was adsorbed onto 16 g of alumina, and the desired ketone was eluted with benzene. Recrystallization from hexane gave colorless needles (370 mg, 59%), mp 89–92°. Two further recrystallizations afforded needles: mp 100–102°; infrared ν_{max}^{Nujol} 1695 (s, C=O); 1600, 1575 cm^{-1} (m, aryl). Further elution with benzene–ether (10:1) gave corresponding alcohol **6** (95 mg, 15%).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.26.

2β-Hydroxy-7-methoxy-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (6).—A solution of the above ketone (278 mg, 1.14 mmoles) in 30 ml of anhydrous ether was treated with 50 mg (1.43 mmoles) of lithium aluminum hydride, and the mixture was stirred at room temperature for 12 hr. Excess moist ether was then added slowly, and the ethereal solution was washed with ammonium chloride solution. After drying (Na_2SO_4) and removal of solvent, the desired carbinol **6** was obtained as a colorless oil (280 mg, "quantitative," homogeneous by tlc): infrared ν_{max}^{film} 3350 (s, OH), 1605, 1570 cm^{-1} (m, aryl). The derived benzoate, obtained by treatment with benzoyl chloride in pyridine solution, was recrystallized twice from ether–hexane to give colorless rods, mp 120–121°.

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.68; H, 7.42.

1,2,3,4,4a,4bα,5,6,7,9,10,10aα-Dodecahydro-2β-hydroxy-4aβ-methyl-7-oxophenanthrene (7). A. From Alcohol 6.—A solution of 340 mg of alcohol **6** (0.0014 mole) in 30 ml of dry tetrahydrofuran was added slowly to a stirred solution of 310 mg of lithium metal (0.044 g-atom) in 100 ml of liquid ammonia. After 15 min, 30 ml of *t*-butyl alcohol was added and stirring was continued for 2 hr. Methanol (20 ml) was then added and the ammonia was removed under a stream of nitrogen. The residue was fractionated between 200 ml of ether and 50 ml of water, and the ether layer was washed thoroughly with brine and dried (Na_2SO_4). Removal of the solvent and crystallization of the residue from ether–hexane gave colorless prisms (294 mg, 86%) of the dihydroanisole, mp 132–133°. Two further crystallizations from acetone yielded glistening needles: mp 134–136°; infrared ν_{max}^{Nujol} 3220 (s, OH), 1692, 1656 cm^{-1} (m, enol ether).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.38; H, 9.71.

A solution of the above dihydroanisole (200 mg) in 30 ml of methanol at 60° was treated with 10 ml of 5 *N* hydrochloric acid and the temperature was maintained for 30 min. The cooled solution was extracted with ether–benzene (5:1, three 50-ml portions), and the combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent afforded a deep red gum (190 mg) which crystallized on standing overnight. Four recrystallizations from ether and then acetone–hexane produced colorless prisms of unsaturated keto alcohol **7**: mp 119–121°; infrared ν_{max}^{Nujol} 3400 (s, OH), 1656 (s), 1609 cm^{-1} (m, C=CC=O).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.82; H, 9.53.

B. From Ketone 4.—A solution of 5.5 g (0.023 mole) of ketone **4** in dry tetrahydrofuran (120 ml) was added in a nitrogen atmosphere to a solution of 4.2 g of clean lithium metal (0.60 g-atom) in liquid ammonia (300 ml) over a 10-min period. After a further 15 min, 80 ml of *t*-butyl alcohol was slowly added, and the mixture was stirred until the deep blue color had dissipated (4 hr). Methanol (40 ml) was added, and the ammonia was removed under a stream of nitrogen. The residue was worked up as above, and the crude product was chromatographed on 120 g of alumina. Elution with benzene–ether (10:1) yielded the desired dihydroanisole (3.75 g, 68%), mp 130–132°.

Treatment with methanolic hydrochloric acid as above afforded a deep red oil which was dissolved in pyridine (20 ml) and treated dropwise with 2.5 g of benzoyl chloride. After standing for 5 hr at room temperature, excess reagent was destroyed with aqueous acetone, and the crude product was extracted into ether. The residue, obtained by removal of the solvent, was adsorbed onto 120 g of alumina and elution with benzene yielded the benzoate of ketone **7** (5.57 g, 74% over-all from the ketone **4**). Two crystallizations from acetone gave colorless needles, mp 177–180°.

Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.13; H, 7.84.

(±)-2β-Benzoyloxy-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-dodecahydro-7-oxo-4aβ,8,8-trimethylphenanthrene (8).—A solution of 5 g of ketone **7** (0.022 mole) in 200 ml of dry benzene was added to a solution of 7 g of potassium *t*-butoxide (0.063 mole) in 50 ml of *t*-butyl alcohol, and the mixture was sitrred in an atmosphere of nitrogen for 5 min at 30°. Methyl iodide (12 ml, 0.19 mole) was then added in one portion, and the mixture was stirred for 1 additional hr at 25°. The reaction mixture was diluted with an equal volume of ether, washed with water (four 100-ml portions), and concentrated under reduced pressure. The residue was dried by azeotropic distillation with benzene–ethanol and then dissolved in a mixture of 30 ml of pyridine and 30 ml of benzene, and treated dropwise with 5 ml (0.036 mole) of benzoyl chloride. The reaction mixture was stirred at room temperature for 12 hr, the benzene was removed under reduced pressure, and the excess reagent was decomposed with aqueous acetone. The product was extracted into ether–benzene (200 ml, 5:1) and this extract was washed successively with 1 *N* hydrochloric acid, 1% sodium hydroxide, and water. The dried (Na_2SO_4) solution was evaporated to dryness, and the residue was chromatographed on 200 g of alumina.

Elution with petroleum ether–benzene (1:1) afforded ketone **8** (6.3 g, 78%). Recrystallization from ether–hexane and then methanol gave colorless needles: mp 179–181°; infrared ν_{max}^{Nujol} 1705 (s, benzoate), 1698 cm^{-1} (s, ketone); nmr δ = 5.7 ppm (vinyl H).

Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. Found: C, 78.58; H, 8.38.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β-hydroxy-4aβ,8,8-trimethylphenanthrene. A. From Wolff–Kishner Reduction of Ketone 8.—Ketobenzoate **8** (2.8 g, 0.0077 mole) was dissolved in a mixture of 100 ml of diethylene glycol and 10 ml of anhydrous hydrazine at 110°. After 30 min, 10 g of solid NaOH was cautiously added, and the solution was stirred for 1 additional hr at 116° in an atmosphere of nitrogen. The temperature was then raised to 216° for 3.5 hr. The cooled reaction mixture was diluted with 100 ml of water and extracted with ether–benzene (10:1, two 200-ml portions). This extract was washed with water (three 100-ml portions), dried (Na_2SO_4), and evaporated to dryness. Recrystallization of the residue from hexane gave colorless needles (1.82 g, 97%), mp 112–115°. Two recrystallizations from methanol gave colorless needles of the desired alcohol: mp 116–118°; infrared ν_{max}^{Nujol} 3280 (s, OH), 3045 cm^{-1} (w, C=CH).

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.01; H, 11.33.

B. From Raney Nickel Desulfurization of the Dithioketal Derived from Ketone 8.—A solution of ketone **8** (1.30 g, 0.0041 mole) in 40 ml of glacial acetic acid (containing 3 ml of ethanedithiol, 0.032 mole) was cooled to 15° and treated dropwise with 3 ml of boron trifluoride etherate (0.024 mole). The thioketal began to crystallize after 2 min. The reaction mixture was stirred for 30 min and cooled to 0°, and the colorless, crystalline precipitate (1.50 g, 96%) was collected and washed with 40 ml of cold 90% methanol. Recrystallization from acetone gave feathery needles, mp 183.5–185°, of the analytically pure thioketal.

Anal. Calcd for $C_{26}H_{34}O_2S$: C, 70.54; H, 7.74. Found: C, 70.22; H, 7.72.

A solution of the above thioketal (440 mg, 0.001 mole) in 20 ml of absolute ethanol in which was suspended approximately 2 g of W2 Raney nickel was heated under reflux for 30 min. After removal of the catalyst by filtration, the filtrate was evaporated to dryness, and the residue was crystallized from methanol. In this manner there were obtained colorless needles (288 mg, 82%), mp 119–123°, of the corresponding benzoate.

Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.74; H, 9.17.

A solution of the above benzoate (280 mg, 0.8 mmole) in 25 ml of 5% methanolic sodium hydroxide was heated under reflux for 2 hr. The cooled solution was diluted with water and extracted with ether–benzene (two 100-ml portions, 5:1). The combined extracts were washed with water (two 30-ml portions), dried (Na_2SO_4), and evaporated to dryness at reduced pressure on the steam bath. A colorless, crystalline residue amounting to 198 mg (100%) resulted. Recrystallization from methanol gave fine needles, mp 116–118°, of the desired alcohol, which was identical with the Wolff–Kishner product (infrared spectral comparison and mixture melting point).

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2-oxo-4aβ,8,8-trimethylphenanthrene (2).—A solution of 700 mg of the above olefin alcohol (2.84 mmoles) in 60 ml of acetone was treated dropwise with Jones reagent until the color of the reagent persisted (0.75 ml, 3.00 mmoles). After 5 min, excess reagent was

destroyed with isopropyl alcohol; the deep green solution was then diluted with excess water and extracted with ether–benzene (1:1, two 100-ml portions). The combined extracts were washed with water (three 30-ml portions), dried (Na_2SO_4), and evaporated to dryness. Crystallization of the residue from pentane afforded colorless flakes (670 mg, 96%), mp 107–110°, of the ketone **9**. Further recrystallization of this material from methanol yielded flaky crystals: mp 108–111°; infrared $\tilde{\nu}_{max}^{Nujol}$ 3045 (w, C=CH), 1705 cm^{-1} (s, >C=O).

Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.73; H, 10.51.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-4aβ,8,8-trimethyl-2β-phenanthrenecarboxaldehyde (9). A. From the Oxirane Derivative of Ketone 2.—After the procedure of Corey and Chaykovsky,[9] sodium hydride (347 mg of oil-dispersed material, 7.2 mmoles) was added to a stirred solution of trimethyl sulfoxonium iodide (1.58 g, 7.2 mmoles) in 10 ml of dimethyl sulfoxide in an atmosphere of nitrogen. After the evolution of hydrogen was complete (30 min), a solution of 1.60 g of the ketone **2** (6.5 mmoles) in 70 ml of dimethyl sulfoxide was added, and the mixture was stirred for 15 min at 28°, and then at 60–65° for 1.5 hr. The cooled reaction mixture was diluted with 100 ml of water and extracted with petroleum ether–ether (two 200-ml portions, 4:1). The combined extracts were washed with water (three 50-ml portions), dried (Na_2SO_4), and evaporated to dryness. Rapid filtration of this material in cyclohexane solution through 20 g of neutral alumina afforded the crystalline oxide (1.59 g, 95%). Recrystallization of this material from pentane and then methanol yielded needles: mp 71–72°; infrared $\tilde{\nu}_{max}^{film}$ 920, 792 cm^{-1} (s, epoxide).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.89; H, 10.74.

According to the procedure of Henbest,[10] a stirred solution of 1.35 g of the above oxide (5.2 mmoles) in 100 ml of benzene was cooled to 7° and treated with a solution of 1.0 ml of boron trifluoride etherate (7.9 mmoles) in 10 ml of benzene. After 5 min at 6°, excess sodium bicarbonate solution was added, and the mixture was extracted with ether (two 100-ml portions). The ethereal extract was washed with further sodium bicarbonate solution (two 50-ml portions), dried (Na_2SO_4), and evaporated to dryness, and the residue (1.4 g) was chromatographed on 87 g of Florisil. Elution with heptane–benzene (4:1) gave successively 177 mg of a 1:1 mixture of aldehydes (δ_{CHO}^{TMS} = 574 and 580 cps) and then 817 mg of pure equatorial aldehyde **10** (δ_{CHO}^{TMS} = 575 cps, doublet; J = 1.5 cps, total yield 74%). Two recrystallizations at −70° of a sample of the latter fraction from pentane afforded clusters of needles of aldehyde **9**: mp 58–61°; infrared $\tilde{\nu}_{max}^{film}$ 3050 (w, C=CH), 2720 (w), 1720, cm^{-1} (s, CH=O).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.76; H, 10.88.

B. By the Wittig Procedure with Triphenylmethoxymethylenephosphorane.[8]—Methoxymethyl triphenyl phosphonium chloride (1.25 g, 4 mmoles) was added to a stirred solution of 0.45 0g of potassium *t*-butoxide in 100 ml of dry tetrahydrofuran at −16° in an atmosphere of nitrogen. After 15 min a solution of 200 mg of ketone **2** (0.88 mmole) in 50 ml of dry ether was added, and the reaction mixture was stirred for 3 hr. During this period the temperature of the reaction rose to 25°. The reaction mixture was evaporated to dryness under reduced pressure and the residue was fractionated between 200 ml of hexane and 30 ml of 75% methanol. The methanol layer was separated and extracted with a furhter 100 ml of hexane, and the combined hydrocarbon layers were washed with 75% methanol (two 30-ml portions) and water (30 ml), and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was chromatographed on 15 g of alumina. Elution with hexane gave 165 mg (80%) of the desired enol ether, which on recrystallization from pentane at −70° afforded needles: mp 62–65°; infrared $\tilde{\nu}_{max}^{Nujol}$ 3045 (w, C=CH), 1680 cm^{-1} (s, enol ether).

Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.25; H, 10.95.

The above enol ether (70 mg) was dissolved in 20 ml of ether previously saturated with 70% perchloric acid. The solution was kept at room temperature for 8 min, and then poured into excess sodium bicarbonate solution. Extraction with ether and chromatography on 6 g of Florisil as described above afforded 58 mg (83%) of aldehyde **9** which was identified by spectral (infrared and nmr) comparison with the above sample obtained from rearrangement of the oxirane.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β,4aβ,8,8-tetramethyl-2α-phenanthrenecarboxaldehyde (10).—A stirred solution of 2.35 g of potassium *t*-butoxide (21 mmoles) in 100 ml of dry dimethoxyethane at 8° in an atmosphere of nitrogen was treated dropwise with a solution of 817 mg of aldehyde **9** (3.16 mmoles) in a mixture of 50 ml of dimethoxyethane and 10 ml of methyl iodide (164 mmoles) over a 10-min period. After 1 additional hr at 25°, 100 ml of water was added and the mixture was extracted with ether–benzene (two 100-ml portions, 5:1). The combined extracts were washed with water (two 50-ml portions) and dried (Na_2SO_4), and the residue, after removal of the solvents, was chromatographed on 36 g of Florisil. Elution with hexane successively yielded (±)-rimuene aldehyde (**11**, 615 mg, 72%), an oily mixture of aldehydes (150 mg), and starting aldehyde **10** (25 mg).

Crystallization of (±)-rimuene aldehyde (**10**) from pentane at −70° afforded needles, mp 46–48°, the infrared spectrum of which was identical with that of (+)-rimuene aldehyde, mp 86–88°, obtained from degradation of (+)-rimuene:[14] infrared $\tilde{\nu}_{max}^{film}$ 3045 (w, C=CH), 2680 (m), 1725 cm^{-1} (s, CH=O).

Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.24; H, 10.94.

Vapor phase chromatography of the above intermediate aldehyde fraction revealed only two major components corresponding to (±)-rimuene aldehyde **10** and starting unmethylated aldehyde **9**.

(±)-Rimuene (1).—A suspension of methyltriphenylphosphonium bromide (380 mg, 1.06 mmoles) in 10 ml of dry ether was treated with 0.65 ml of a 1.48 *M* solution of butyllithium (0.96 mmole) in pentane, and the mixture was stirred in an atmosphere of nitrogen for 30 min. A solution of 40 mg of aldehyde **10** (0.07 mmole) in 10 ml of ether was then added, and stirring was continued for a further 1.5 hr. After this period the solvent was removed under reduced pressure, and the residue was fractionated between 50 ml of hexane and 50 ml of 75% methanol. The methanol layer was extracted with a further 50 ml of hexane, and the combined hexane layers were washed with 75% methanol (two 10-ml portions) and water (two 10-ml portions) and dried (Na_2SO_4). Filtration of the hexane solution through 12 g of alumina, and evaporation of the eluent to dryness afforded (±)-rimuene (**1**, 30 mg, 75%) as a colorless oil which was purified by evaporative distillation at 120° (0.01 mm). The distillate solidified after a few minutes and trituration with a few drops of carbon tetrachloride afforded needles, mp 85–88°. The infrared and nmr spectra of this material were identical with those of natural (+)-rimuene:[14] infrared $\tilde{\nu}_{max}^{film}$ 3080, 3045 (w, C=CH), 1820 (w), 1638 (m), 995, 913 cm^{-1} (both s, CH=CH_2).

Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.19; H, 11.62.

II. (±)-13-*epi* Rimuene (16). The Glycidonitrile (13).—A solution of 560 mg of potassium *t*-butoxide (5.00 mmoles) in 4.25 ml of dry *t*-butyl alcohol was added dropwise to a stirred solution of 570 mg (2.32 mmoles) of ketone **2** and 450 mg (5.00 mmoles) of α-chloropropionitrile in 30 ml of dry tetrahydrofuran in an atmosphere of nitrogen, at 2°. The reaction mixture was allowed to warm to 25° over a 2-hr period and to stir for 18 hr. longer The reaction was quenched with 30 ml of ice water, and the mixture was extracted with ether–benzene (two 125-ml portions, 10:1). The ethereal layer was washed with 50 ml of 0.1% hydrochloric acid and 50 ml of water, dried (Na_2SO_4), and evaporated to dryness. The residue (0.7 g) was chromatographed on 25 g of alumina and elution with petroleum ether and petroleum ether–benzene (10:1) afforded the glycidonitrile **13** (590 mg 85%). Recrystallization from hexane gave colorless prisms: mp 140–155° (constant); infrared $\tilde{\nu}_{max}^{Nujol}$ 3045 (w, C=CH), 2240 (w, CN), 890 cm^{-1} (s, epoxide).

Anal. Calcd for $C_{20}H_{29}NO$: C, 80.22; H, 9.76. Found: C, 80.27; H, 9.85.

(±)-2α-Acetyl-2β-chloro-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-dodecahydro-4aβ,8,8-trimethylphenanthrene (14).—A solution of boron trichloride (10 ml of 1 *M*) was added dropwise to stirred solution of 470 mg of glycidonitrile **13** (1.57 mmoles) in 100 ml of dry ether at 2° and in an atmosphere of nitrogen. The reaction mixture warmed to 25° over a 2-hr period, and the stirring was continued for a further 16 hr. The solution was then slowly poured into 200 ml of ice water, 200 ml of petroleum ether was added, and the organic layer was separated. The ethereal solution was washed with water (three 100-ml portions) and dried (Na_2SO_4). After removal of the solvents at reduced

pressure, trituration of the residual brown oil (0.5 g) with petroleum ether afforded the crystalline chlorhydrin (240 mg). Two further crystallizations from hexane (charcoal) gave colorless needles (215 mg, 41%): mp 180–182°; infrared ν_{max}^{Nujol} 3370 (s, OH), 3045 (w, C=CH), 2240 cm^{-1} (w, CN).

Anal. Calcd for $C_{20}H_{30}ClNO$: C, 71.49; H, 9.00. Found: C, 71.57; H, 8.88.

A solution of 120 mg of the above chlorhydrin in 20 ml of petroleum ether was filtered through 20 g of alumina. Elution was continued with 200 ml of petroleum ether–ether (10:1). Concentration of the combined eluates afforded 108 mg (100%) of a colorless, crystalline solid. Recrystallization from pentane at −70° afforded chloro ketone **14** as clumps of needles: mp 90–92°; infrared ν_{max}^{film} 3045 (w, C=CH), 1720 cm^{-1} (s, C=O).

Anal. Calcd for $C_{19}H_{29}ClO$: C, 73.87; H, 9.46. Found: C, 73.91; H, 9.46.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2α,4aβ,8,8-tetramethyl-2β-phenanthrenecarboxylic Acid (15).—A solution of 120 mg (0.398 mmole) of chloro ketone **14** in 15 ml of dry ether was added to a slurry of 2 g of ground sodium hydroxide pellets in 15 ml of dry ether, and the mixture was stirred in an atmosphere of nitrogen at 25° for 16 hr. Ice water (50 ml) was then added, followed by 10 ml of methanol. The aqueous layer was separated, acidified to congo red, and extracted with two 50-ml portions of benzene–ether (1:5). The organic extract was washed with water (two 10-ml portions), dried (Na_2SO_4), and evaporated to dryness. Two recrystallizations (charcoal) of the residue from hexane afforded colorless, glistening flakes (45 mg, 40%) of the acid **15**: mp 190–192°; infrared ν_{max}^{Nujol} 3300–3000, 2750–2400 (w), 1695 (s), 945 cm^{-1} (s, COOH).

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.58; H, 10.21.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β-hydroxymethyl-2α,4aβ,8,8-tetramethylphenanthrene.—A solution of 40 mg (0.136 mmole) of acid **15** in dry tetrahydrofuran was treated with 50 mg of lithium aluminum hydride (1.43 mmoles), and the reaction mixture was stirred for 12 hr at 25° in an atmosphere of nitrogen. Excess reagent was decomposed by the addition of 50 ml of moist ether; then 10 ml of benzene was added, and the mixture was washed with 10 ml of 1 *N* hydrochloric acid, water (two 10-ml portions) and dried (Na_2SO_4). After removal of solvent, the carbinol was obtained as a colorless resin (40 mg, "quantitative"). The sample for analysis was purified by evaporative distillation at 120° (0.01 mm): infrared ν_{max}^{film} 3250 (s, OH), 3045 cm^{-1} (w, C=CH).

Anal. Calcd for $C_{19}H_{32}O$: C, 82.45; H, 11.66. Found: C, 82.44; H, 11.62.

(±)-1,2,3,4,4a,4bα,5,6,7,8,10,01aα-Dodecahydro-2α,4aβ,8,8-tetramethyl-2β-phenanthrenecarboxaldehyde.—A stirred solution of 32 mg (0.17 mmole) of the above carbinol in 15 ml of acetone at 0° was treated with 0.07 ml (0.28 mmole) of Jones reagent. After 2 min, 2–3 drops of isopropyl alcohol was added, followed by 30 ml of water and 100 ml of ether–benzene (5:1). The organic layer was separated and washed with two 20-ml portions of 1% sodium hydroxide in water–methanol (10:1) and 10 ml of water and dried (Na_2SO_4). From ether extraction of the acidified alkaline extract in the usual manner, 12 mg of acid **15** was recovered. Evaporation of solvent from the "neutral" fraction and chromatography of the residue (20 mg) of 12 g of Florisil afforded 15 mg (49%) of the oily aldehyde (hexane eluate) and 3 mg of starting carbinol. The analytical sample was purified by evaporative distillation at 120° (0.01 mm): infrared ν_{max}^{film} 3045 (w, C=CH), 2695 (w), 1725 cm^{-1} (s, CHO).

Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.21; H, 11.14.

(±)-13-*epi*-Rimuene (16).—Methyltriphenylphosphonium bromide (100 mg, 0.28 mmole) was added to a solution of 30 mg (0.27 mmole) of potassium *t*-butoxide in 1 ml of *t*-butyl alcohol and 5 ml of ether, and the mixture was stirred for 30 min in an atmosphere of nitrogen at 25°. A solution of 10 mg of the above aldehyde in 5 ml of dry ether was then added, and the mixture was stirred for an additional 3 hr. The residue, after removal of solvent, was fractionated between 30 ml of 80% methanol and 30 ml of hexane. The methanol layer was extracted with two further 30-ml portions of hexane, and the combined hexane fractions were washed with 30 ml of 80% methanol and 30 ml of water and dried (Na_2SO_4). After filtration of this solution through 30 g of neutral alumina and removal of solvent, there was obtained 9 mg (90%) of (±)-13-*epi*-rimuene (**16**) as a colorless oil. The analytical sample was prepared by evaporative distillation at 120° (0.01 mm): infrared ν_{max}^{film} 3084, 3048 (w, C=CH), 1818 (w), 1638 (m), 999, 914 cm^{-1} (s, C=CH_2).

Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.14; H, 11.81.

III. Correlation of the Rimuene Series with the Pimaradiene Series. 1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β,4aβ,8,8-tetramethyl-2α-phenanthrenecarboxaldehyde.—To a solution of 795 mg (2.92 mmoles) of (+)-rimuene (**1***) in 30 ml of dry dioxane was added 740 mg (2.92 mmoles) of osmium tetroxide. After the reaction mixture had stood at room temperature for 8 hr, the black solution was saturated with gaseous hydrogen sulfide and allowed to stand for 1 additional hr. The black precipitate was removed by filtration and washed with methylene chloride. The combined filtrates were then evaporated to dryness at reduced pressure on the steam bath, and the viscous, oily residue was dissolved in 50 ml of dry ether. To this ethereal solution was added a solution of 666 mg (3.77 mmoles) of paraperiodic acid in 40 ml of dry ether, and the reaction mixture was stirred at room temperature for 1 hr. The ethereal solution was decanted from the precipitated iodic acid, washed successively with 2% aqueous sodium hydroxide, water, and saturated salt solution, and dried (Na_2SO_4). After filtration of the drying agent and removal of the solvent at reduced pressure on the steam bath, the crystalline residue amounted to 630 mg. This material was chromatographed on 40 g of Florisil. Elution with 800 ml of 5% benzene in petroleum ether afforded 513 mg (64%) of the desired aldehyde, mp 85–86°. The analytical sample, obtained after one crystallization from methanol and sublimation at 70° (0.02 mm), melted at 85.5–86.5°.

Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.42; H, 11.17.

1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β,4aβ,8,8-tetramethyl-2α-phenanthrenecarboxylic Acid (17*).—Jones reagent (0.20 ml, 0.8 mmole) was added dropwise to a swirled solution of 100 mg of the above aldehyde (0.36 mole) in 30 ml of acetone. After 10 min at 25°, 2–3 drops of isopropyl alcohol was added, followed by excess water. This mixture was extracted with two 50-ml portions of ether–benzene (4:1), and the combined organic layers were then extracted with 1% sodium hydroxide in water–methanol (4:1, four 20-ml portions). The sodium hydroxide extract was washed with ether (20 ml), acidified to congo red, and extracted with ether–benzene (4:1, three 50-ml portions). The combined extracts were washed with water (two 20-ml portions) and dried (Na_2SO_4), and the solvents were removed at reduced pressure. In this manner there was obtained a pale yellow, crystalline residue (70 mg, 66%). Two recrystallizations from ether–hexane gave colorless needles of acid **17***: mp 208–209°; infrared ν_{max}^{Nujol} 3300–3200, 2750–2400 (w), 1690 (s), 940 cm^{-1} (s, COOH).

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.43; 10.29.

2,3,4,4aα,4b,5,6,7,8,8aα,9,10-Dodecahydro-2β,4bβ,8,8-tetramethyl-2α-phenanthrenecarboxylic Acid.—A solution of 72 mg (0.26 mmoles) of the aldehyde **20**[3] in 10 ml of acetone was treated with 0.8 ml of Jones reagent, and the whole was stirred for 30 min at room temperature. Excess oxidant was destroyed with isopropyl alcohol; 30 ml of water was added; and the mixture was extracted twice with 50-ml portions of ether–benzene (1:1). The organic extracts were combined, washed three times with 30 ml of water, and dried (Na_2SO_4). After filtration to remove the drying agent and removal of the solvents at reduced pressure on the steam bath, the solid residue was crystallized from petroleum ether at 0°. In this manner there was obtained 58 mg (76%) of desired acid, mp 182–184°. This material was not purified further for analysis.

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.38; H, 10.59.

The δ-Lactone of 4aα-Hydroxy-2β,4bβ,8,8-tetramethyl-2α-*trans,anti,trans*-perhydrophenanthrenecarboxylic Acid (18*). A. From 1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2β,4aβ,8,8-tetramethyl-2α-phenanthrenecarboxylic Acid (17*).—A solution of 100 mg (0.345 mmole) of acid **17*** in 30 ml of 90% formic acid was heated under reflux for 16 hr, and then cooled and diluted with 60 ml of water. This mixture was extracted twice with 100-ml portions of petroleum ether–ether (1:1), and the combined extracts were washed successively with water (three 30-ml portions), 1% aqueous sodium hydroxide (two 20-ml portions), and water 30 ml) and dried (Na_2SO_4). After removal of the drying agent and evaporation of the solvents, there was obtained

45 mg of a deep yellow oil which was chromatographed on 5 g of alumina. Elution of the column with petroleum ether–ether (20:1) afforded δ-lactone **18*** as a colorless, crystalline solid. Recrystallization of this material from petroleum ether at 0° gave colorless needles (35 mg, 35%): mp 180–182°; infrared ν_{max}^{Nujol} 1735 cm^{-1} (δ lactone>CO).

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.36; H, 10.49.

B. From 2,3,4,4aα,5,6,7,8,8aα,9,10-Dodecahydro-2β,4bβ,8,8-tetramethyl-2α-phenanthrenecarboxylic Acid.—A solution of 20 mg (0.07 mmole) of the olefinic acid in 10 ml of chloroform was treated with a steady stream of dry hydrogen chloride at 0° for 2 hr. The reaction mixture was then poured into water (20 ml) and extracted twice with 50-ml portions of ether–benzene (10:1). The organic layer was washed with water (two 10-ml portions), dried (Na_2SO_4), and evaporated to dryness. The resulting residue (presumed to represent principally the $\Delta^{8(9)}$-olefinic acid) was dissolved in 10 ml of 90% formic acid, and the solution was heated under reflux for 16 hr. The reaction mixture was then cooled, diluted with 50 ml of water, and extracted with two 50-ml portions of petroleum ether–ether (1:1). The combined extracts were washed with water (three 20-ml portions), dried (Na_2SO_4), and evaporated to dryness. The residue so obtained was chromatographed on 5 g of alumina. Elution with 200 ml of petroleum ether afforded 7 mg of a hydrocarbon (presumed to result from decarboxylation of the olefinic acid, but not further characterized). Continued elution with 300 ml of 10% ether–petroleum ether afforded 7 mg (35%) of δ-lactone **18**, the infrared spectrum of which was identical with that of optically active δ-lactone **18*** obtained above. Recrystallization of this material from petroleum ether afforded the analytical sample which melted at 141–143°.

Anal. Calcd for $C_{19}H_{30}O_2$: C, 7857; H, 10.41. Found: C, 78.44; H, 10.34.

2,3,4,4aα,4b,5,6,7,8,8aα,9,10-Dodecahydro-2α,4bβ,8,8-tetramethyl-2β-phenanthrenecarboxylic Acid (23*).—In the same manner as that described above for the degradation of (+)-rimuene (**1***), 180 mg (0.66 mmole) of (+)-pimaradiene (**22***)[3] was oxidized to the corresponding diol with 190 mg (0.75 mmole) of osmium tetroxide. From this procedure there was obtained 200 mg of crude, crystalline diol, a portion of which, recrystallized two times from petroleum ether, afforded the analytical sample, mp 121–126°.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.12; H, 11.29.

The remainder of the crude diol above (180 mg) was treated with 140 mg (0.6 mmole) of paraperiodic acid in 40 ml of dry ether, as described above for the cleavage of the corresponding rimuene diol. The oily aldehyde [infrared ν_{max}^{film} 2680, 1725 (CHO), 1653 cm^{-1} (>C=C<)] that resulted was not further purified but dissolved in 15 ml of acetone and oxidized with excess (1.5 ml) of Jones reagent. After the same work-up as described above for the oxidation of the corresponding rimuene aldehyde, there was obtained 78 mg (45%) of acid **23***, mp 149–151°, after one crystallization from pentane at 0°.

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.59; H, 10.38.

The γ-Lactone of 10aβ-Hydroxy-2α,4bβ,8,8-tetramethyl-2β-*trans*,*anti*,*trans*-perhydrophenanthrenecarboxylic Acid (21*). A. From 1,2,3,4,4a,4bα,5,6,7,8,10,10aα-Dodecahydro-2α,4aβ,8,8-tetramethyl-2β-phenanthrenecarboylic Acid (15).—A solution of 30 mg (0.10 mmole) of acid **15** in 20 ml of 90% formic acid was heated under reflux for 3 hr, and then the reaction mixture was cooled and diluted with 75 ml of water. The aqueous mixture was extracted with 200 ml of petroleum ether–ether (1:1), and the organic layer was washed successively with water (three 30-ml portions), 1% aqueous sodium hydroxide (two 20-ml portions), and water (30 ml) and dried (Na_2SO_4). After removal of the drying agent and evaporation of the solvents, there remained 15 mg (50%) of colorless, crystalline γ-lactone **21**, infrared ν_{max}^{Nujol} 1770 cm^{-1} (γ-lactone>C=O). On chromatography of this material on 10 g of alumina, there was eluted 14 mg (47%) of γ-lactone **21*** with 5% ether–petroleum ether (five 80-ml portions). The analytical sample, obtained after one crystallization of this material from petroleum ether, melted at 152–153°, infrared $\nu_{max}^{CS_2}$ 1775 cm^{-1} (γ-lactone >C=O).

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.50; H, 10.31.

B. From 2,3,4,4aα,4b,5,6,7,8,8aα,9,10-Dodecahydro-2α,4bβ,-8,8-tetramethyl-2β-phenanthrenecarboxylic Acid (23*).—To a solution of 20 mg (0.69 mmole) of acid **23*** in 5 ml of tetrahydrofuran maintained at −5° was added dropwise 10 ml of concentrated sulfuric acid. After the reaction mixture had stirred at 0° for 1 hr, the whole was poured onto crushed ice and extracted with 100 ml of ether–benzene (10:1). The organic extract was washed successively with water (10 ml), 1% aqueous sodium hydroxide (10 ml), and water (10 ml) and dried (Na_2SO_4). After removal of the drying agent and evaporation of the solvents, there was obtained 18 mg (90%) of γ-lactone **21** as a pale yellow, crystalline solid. The analytical solid, obtained after one crystallization from petroleum ether, melted at 142–145° and showed an infrared spectrum in carbon disulfide solution that was identical with that of γ-lactone **21** prepared above.

Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.50; H, 10.45.

Registry No.—**1**, 3895-07-6; **16**, 10036-89-2; 7-methoxy-4αβ-methyl-1,2,3,4,4a,9,10,10α-octahydro-2-oxophenanthrene, 1910-03-8; benzoate of **6**, 1910-05-0; **7**, 10036-92-7; benzoate of **7**, 1910-06-1; **8**, 1910-07-2; (±)-1,2,3,4,4a,4bα,5,6,7,8,10,10aα-dodecahydro-2β-hydroxy-4aβ,8,8-trimethylphenanthrene, 10036-95-0; thioketal of **8**, 10036-96-1; benzoate of **8**, 1910-10-7; **2**, 4062-07-1; **9**, 10036-99-4; **10**, 1910-13-0; oxirane deriv of ketone **2**, 10037-01-1; enol ether of **2**, 10037-02-2; **14**, 10037-03-3; chlorhydrin of **13**, 10037-04-4; **15**, 10037-05-5; carbinol of **15**, 10037-06-6; aldehyde of **15**, 10037-07-7; **13**, 10037-08-8; **17***, 10037-09-9; acid of **20***, 10037-10-2; **18***, 10037-11-3; **23***, 10037-12-4; **21***, 10037-13-5; aldehyde of **1***, 1970-13-0.