Resin Acids. XIX. Structure and Stereochemistry of Adducts of Levopimaric Acid with Cyclopentenone and 1-Cyclopentene-3,5-dione. Favorskii Reaction of an Enedione Epoxide[1,2]

WERNER HERZ AND M. G. NAIR

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

Received May 21, 1969

The diene reaction of levopimaric acid (**1**) with cyclopentenone proceeds in mediocre yield at elevated temperature and affords an *endo,cis* adduct as major product and an *exo,cis* adduct in small quantity. The reaction of **1** with 1-cyclopentene-3,5-dione affords a mixture of enolic *endo,cis* adducts. The structure and stereochemistry of these adducts have been determined by photolytic methods and by correlating them with the product of a novel Favorskii reaction on the epoxide of the known levopimaric acid–benzoquinone adduct.

As part of our program aimed at the utilization Diels–Alder adducts of levopimaric acid (**1**) for complex syntheses,[3-6] we investigated the reaction of **1** with cyclopentenone, which, it was hoped, would yield starting materials useful for further contemplated transfromations. Although the original motive was frustrated by low yields, our efforts to establish the structure and stereochemistry of the adducts led to interesting discoveries which will be detailed in this and future publications.

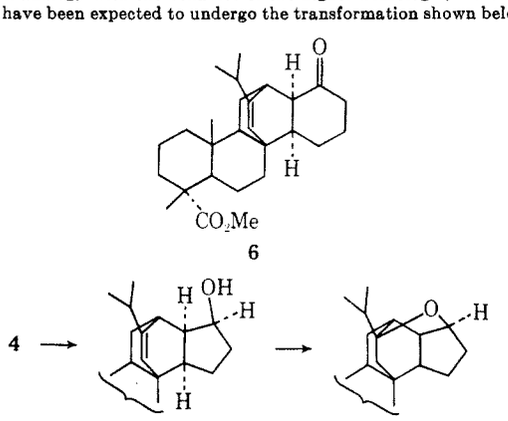
Condensation of **1** with cyclopentenone at 200° resulted in formation of two adducts which were isolated as methyl esters in 22 and 0.8% yield.[7] The predominating adduct, mp 136–138°, displayed a strong positive Cotton effect. Application of the octant rule showed that this was consonant with structure **2** or **3**, but, since the diene reaction of **1** generally results in predominant if not exclusive formation of the *endo,cis* adduct,[3-6,8-11] **2** seemed much more probable. The minor adduct, mp 120–121°, exhibited a negative Cotton effect of considerably smaller amplitude. This, and the *endo,cis* rule, suggested formula **4**, although it was not immediately obvious why the amplitude of **4** should be smaller than that of **2**. In view of the low yield, the possibility that the minor isomer was the *exo,cis* isomer **5**, for which a negative Cotton effect was predicted, could not be dismissed out of hand. This would have accounted for the observation that both adducts were reduced by sodium borohydride to monohydric alcohols, neither of which could be converted to an ether on treatment with acid.[12]

Condensation of levopimaric acid with 1-cyclopentene-3,5-dione, a better dienophile than cyclopentenone,[13] in ether solution at 0° afforded in 35% yield a mixture of two isomeric enols (nmr spectrum). Methylation with diazomethane yielded two enol ethers, **7** and **8** (3:4 ratio), readily separable by chromatography.[14] Both substances exhibited uv absorption characteristic of α,β-unsaturated ketones. In the nmr spectrum of the less polar material (**7**), mp 155°, the two vinyl protons resonated at the same field strength (5.16 ppm), while those of the more polar isomer **8**, mp 181–182°, resonated at 5.19 and 5.02 ppm.

Theoretically, it was possible to formulate a scheme by which one of the two isomeric enol ethers could be converted to **2**, provided that the configuration at C-13 and C-14[15] remained unchanged. Structure elucidation of **2** or of either **7** or **8** would then prove the structure of all three compounds.

To define the nature of the ring junction of **8** which, in accordance with previous knowledge, was expected to be *endo,cis*,[3-6,8-11] **8** was photolyzed (methanol, Pyrex filter). In addition to the expected[4b,16] cage structure **9** (20%), whose formation substantiated our expectation, there was formed an isomer **10** which resulted

(12) In analogy with the behavior of the higher homolog **6**,[4b] a substance **4** might have been expected to undergo the transformation shown below.



(1) Previous paper: W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 3473 (1969).

(2) Supported in part by grants from the National Science Foundation (GP-6362) and the Petroleum Research Fund, administered by the American Chemical Society.

(3) N. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *ibid.*, **29**, 1017 (1964).

(4) (a) W. Herz, R. C. Blackstone, and M. G. Nair, *ibid.*, **31**, 1800 (1966); (b) *ibid.*, **32**, 2992 (1967).

(5) W. Herz, R. N. Mirrington, H. Young, and Y. Y. Lin, *ibid.*, **33**, 4210 (1968).

(6) W. Herz and R. C. Blackstone, *ibid.*, **34**, 1257 (1969).

(7) Repeated attempts to effect condensation between **1** and 2-cyclohexen-1-one resulted in failure. This again illustrates that cyclopentenone is a better dienophile than cyclohexenone.

(8) W. D. Lloyd and G. W. Hedrick, *ibid.*, **26**, 2029 (1961).

(9) L. A. Zalkow, R. A. Ford, and J. P. Kutney, *ibid.*, **27**, 3535 (1962).

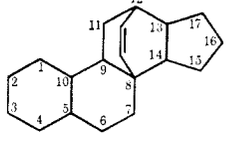
(10) W. L. Meyer and R. W. Huffman, *Tetrahedron Lett.*, 691 (1962).

(11) W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41**, 1113 (1963).

(13) C. H. Depuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **81**, 4920 (1959).

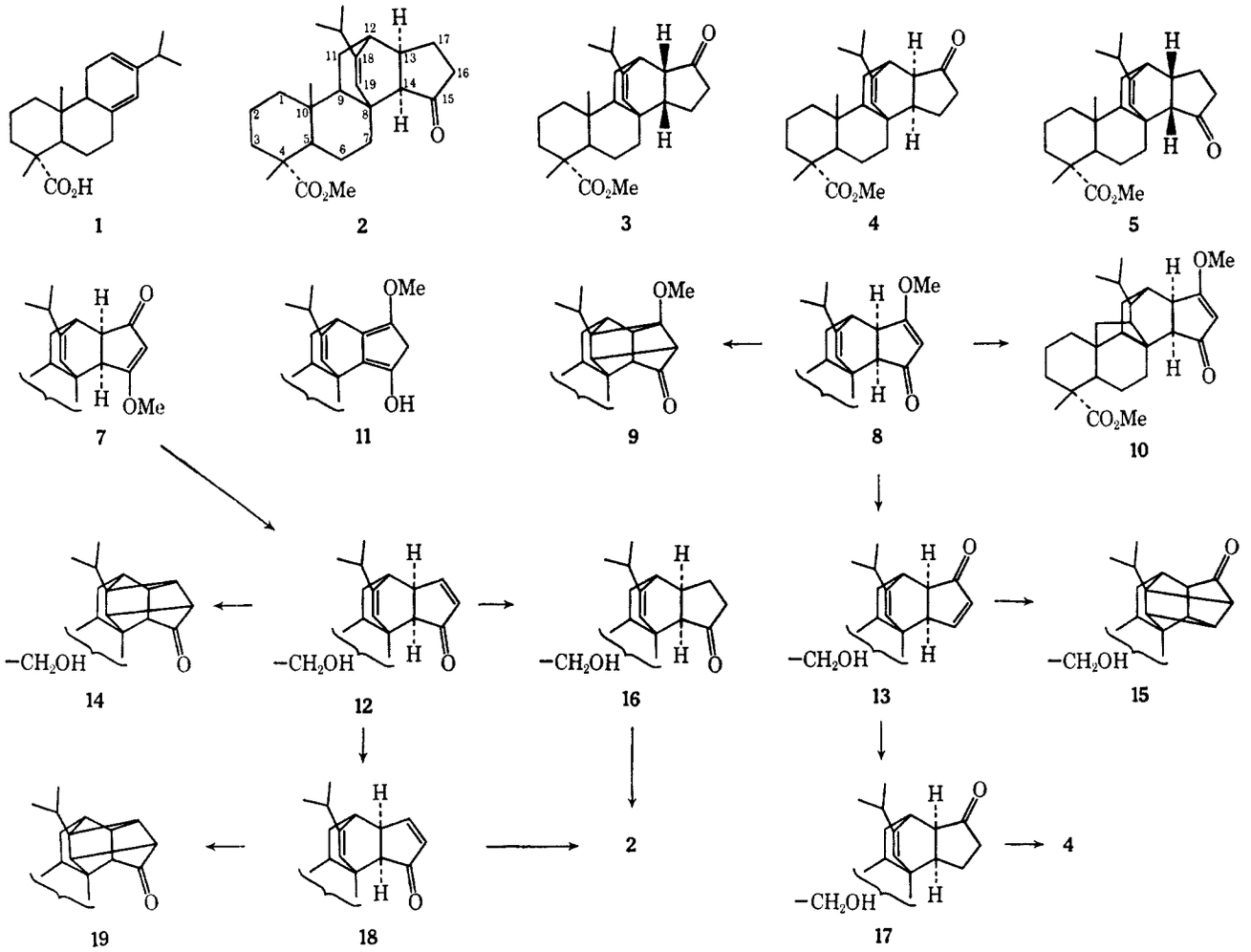
(14) To simplify the discussion, we identify these and other substances by numbers attached to formulas later shown to be correct. The 3:4 proportion represents the ratio at equilibrium (*vide infra*).

(15) Compounds are numbered in accordance with the *Chemical Abstracts* system, the adducts being derivatives of 8,12-etheno-15H-cyclopenta[*a*]-phenanthrene.



(16) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind.* (London), 1003 (1959); R. C. Cookson, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3043 (1964); R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *ibid.*, 3062 (1964).

SCHEME I



from an unprecedented photochemical transformation. The latter will be dealt with in a subsequent paper.[17]

Photolysis of the isomeric enol ether **7** could not be accomplished satisfactorily, but that its configuration was also *endo,cis* was suggested by the following experiment. Treatment of either pure **7** or **8** with *p*-toluenesulfonic acid in methanol afforded the same ratio (*ca.* 3:4) of enol ethers, presumably by way of ether cleavage, equilibration, and remethylation. However, although this observation could be rationalized by assuming the same configuration for **7** and **8** at C-13 and C-14, the possibility that epimerization of **7** and **8** had taken place through an admittedly highly strained intermediate such as **11** could not be ruled out completely. Hence, independent evidence for the *endo,cis* configuration of **7** was sought.

Lithium aluminum hydride reduction of **7** afforded a ketol **12**, which had a somewhat atypical infrared (1670 and 1600 cm^{-1})[18] but a characteristic ultraviolet (λ_{max} 235 nm) and nmr spectrum [7.24 (dd, J = 6 and 3 Hz, H-17) and 5.98 ppm (dd, J = 6 and 2 Hz, H-16)] indicative of an α,β-unsaturated cyclopentenone. Similar treatment of **8** gave an isomeric α,β-unsaturated ketone **13** which had ir bands at 1675[18] and 1590 cm^{-1} and nmr signals at 7.33 (dd, J = 6 and 3 Hz, H-15) and 6.05 ppm (dd, J = 6 and 2 Hz, H-16). The Cotton effects of the $n-\pi^*$ transitions of **12** and **13** had opposite signs, that of **12** being positive and that of **13** being negative. Photolysis of **12** and **13** (methanol, Pyrex filter) gave the cage compounds **14** and **15**, whose spectral properties were fully in accord with the postulated structures. The formation of **14** and **15** proved that **12** and **13**, and by inference the precursors **7** and **8**, had the *endo,cis* configuration[19] and differed only in location of the ketone and methoxyl group on the five-membered ring.

Correlation of **7** with **2** was achieved as follows. Hydrogenation of **12** afforded the saturated ketol **16**. Oxidation of **16** with Jones reagent to the aldehyde, further oxidation with Tollensr eagent to the acid, and esterification with diazomethane yielded a substance identical in all respects with the major product **2** resulting from the Diels–Alder reaction between levopimaric acid and 2-cyclopentenone and subsequent methylation. Hence, the ketone carbon of **2** corresponded to the methoxylated carbon of **7**.

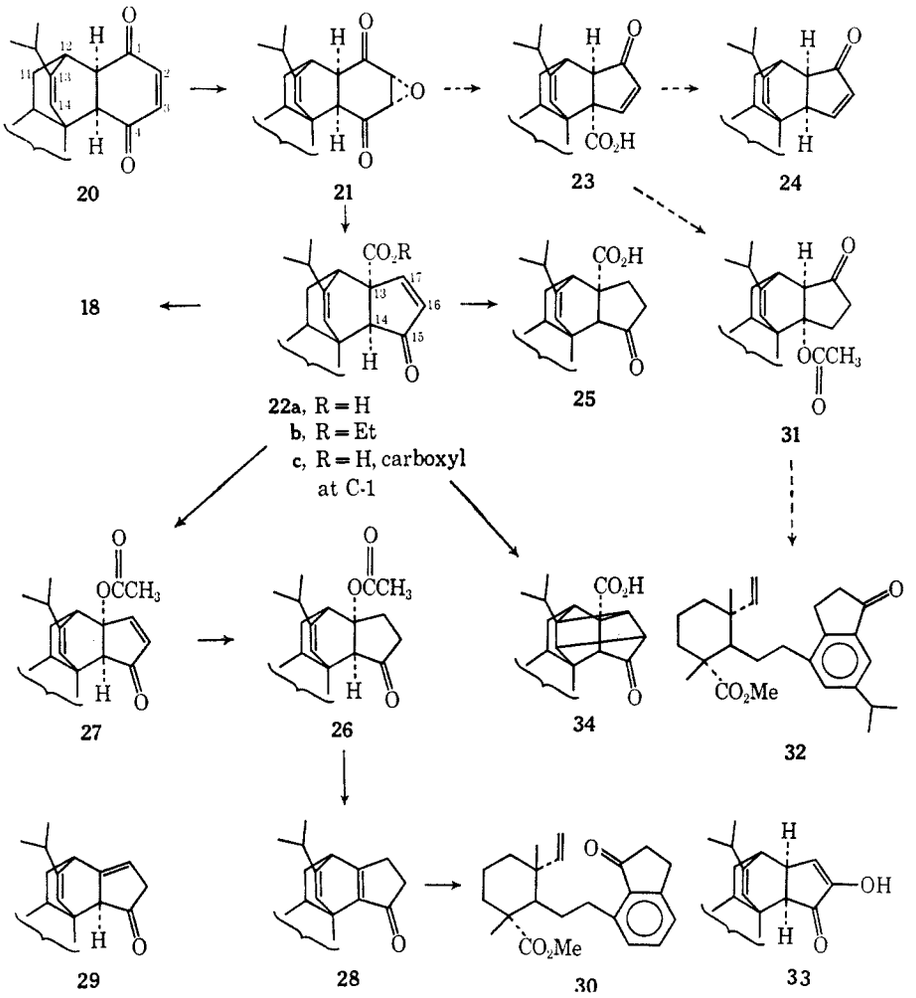
In a similar manner, **13** was transformed through **17** to the saturated keto ester **4**, which was *not* identical with the minor isomer obtained by direct condensation of 2-cyclopentenone with levopimaric acid. Since the carbon bearing the carbonyl function of **4** corresponds to the carbon carrying the methoxyl of **8**, this result im-

(17) W. Herz, M. G. Nair, and J. Saltiel, to be published. Part of this material has been published in preliminary form: W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967).

(18) The reason for the displaced infrared frequency, normally found in the range of 1695–1710 cm^{-1}, is not immediately obvious.

(19) Since **12** and **13** were recovered unchanged from prolonged treatment with sodium methoxide, the possibility that $LiAlH_4$ reduction of **12** and **13** might have been accompanied by epimerization at C-13 or C-14 was excluded.

SCHEME II



mediately excluded an *endo,cis* configuration for the minor isomer. The choice among the two possible *exo,cis* structures **3** and **5** was clear. The octant rule predicts a strong positive Cotton effect for **3** and a negative Cotton effect for **5**. Since the minor isomer exhibited a negative Cotton effect (*vide supra*), it had to be **5**.

The conversion of **7**, for which an *endo,cis* fusion had been established earlier, to **2** had included treatment of intermediates with acid and with base. Conceivably this could have resulted in epimerization of a *cis*-D/E to a *trans*-D/E intermediate, either by protonation of the C-15 keto group or by formation of an anion at C-14, and did not necessarily establish a *cis*-D/E ring junction for **2**. It was therefore thought desirable to correlate **7** and **2** by an alternate procedure which would eliminate this ambiguity.

Jones oxidation of **7**, subsequent treatment with Tollens reagent, and methylation afforded the cyclopentenone **18** (uv, ir, and nmr spectrum). That epimerization had not taken place during this series of transformations and that **18** had retained the *endo,cis* configuration was shown by photolysis of **18** to the cage structure **19**. Hydrogenation of **18**, which cannot affect the configurations at C-13 and C-14, yielded **2** as the sole product. It was clear, therefore, that **2**, **4**, **7**, and **8** all possessed the *endo,cis* D/E ring junction, that the carbon bearing the carbonyl group of **2** corresponded to the carbon bearing the methoxyl group of **7**, and that the carbon bearing the carbonyl group of **4** corresponded to the carbon bearing the methoxyl group of **8**.

The problem of locating the keto group in ring E of any one of the four compounds remained. A solution to this problem was achieved as follows (Scheme II).

Treatment of the methyl levopimarate-*p*-benzoquinone adduct **20** of established structure and stereochemistry[4b] with hydrogen peroxide–sodium carbonate furnished the epoxide **21** (stereochemistry of epoxide ring predicted on ease of approach of reagent from the α side[20]). That epoxidation had affected the enedione system of **20** and not the bridge double bond was evident from the infrared spectrum, which showed the absence of the conjugated double bond and shifts of the carbonyl bands to higher frequencies, and from the nmr spectrum, which exhibited the usual broad singlet at 5.61 ppm due to H-14,[21] a broad two-proton singlet at 3.13 ppm due to H-2 and H-3, and the characteristically shielded signal of the angular C-10a methyl group.

Now it has been shown earlier[4b] that the C-4 carbonyl and H-4a of **20** or of its dihydro derivative are much more resistant to chemical attack than the C-1 carbonyl and H-1a. Hence we considered the possibility of inducing a Favorskii-type rearrangement on **21**. This, it was hoped, would result in preferential forma-

(20) Proof for this assumption will be provided in the subsequent discussion.

(21) Numbering by *Chemical Abstracts* system as described in ref 4b.

tion of **22a** (rather than **23**) due to proton removal from C-1a rather than from C-4a. The resulting vinylogous β-keto acid should be subject to facile decarboxylation to an unsaturated ketone which should be convertible to a ketone also accessible from that cyclopentenedione adduct whose carbonyl group was attached to C-17.[22]

Indeed, treatment of **21** with 10% ethanolic sodium hydroxide at room temperature and chromatographic purification gave an unsaturated keto acid in 40% yield and a second, neutral substance (10%). The acidic rearrangement product was assigned structure **22a**[24] and the neutral material formula **22b**[24] on the following grounds.

Both **22a** and **22b** had ultraviolet spectra of α,β-unsaturated cyclopentenones. The nmr spectrum of **22a** showed the typical AB pattern of H-17 and H-16 as two clean doublets at 7.35 and 6.05 ppm (J = 6 Hz). It retained the H-19 signal as a broad singlet at 5.3 ppm and the characteristically shielded C-10 methyl resonance at 0.61 ppm. A sharp singlet at 2.61 ppm was attributed to H-14. In the alternate structure **23**, the proton α to the keto group (H-14) is expected to display a doublet unless the dihedral angle between H-12 and H-13 in **23** is such that the coupling constant is zero, which did not appear plausible. The infrared spectrum of **22b** did not show the hydroxyl stretching band of the carboxyl group; the nmr spectrum displayed the characteristic signals corresponding to OCH_2-CH_3 but was otherwise superimposable on that of **22a**. Confirmation for the conclusion that **22b** was the ethyl ester of **22a** was provided by hydrolysis of **22a** and **22b** to the same dicarboxylic acid **22c**.

If the assignment of the 2.61-ppm singlet in the nmr spectra of **22a** and **22b** to H-14 were correct, decarboxylation of **22a** would result in the formation of a substance which, because of the presence of a proton on C-13, should display the resonance of H-14 as a doublet. On the other hand, decarboxylation of the alternate structure **23** would yield a substance **24** with a more complex signal for H-13 α to the carbonyl. In fact, decarboxylation of **22b** gave in excellent yield substance **18** previously obtained from **7**, as shown in Scheme I. Examination of the nmr spectrum of **18** revealed that the 2.61-ppm singlet of **22a** was replaced by a clean doublet (J = 5 Hz), as required by the formula, H-14 being spin coupled to H-13. Since **18** can be hydrogenated to **2**, the sequence **1** → **20** → **21** → **22** → **18** provides a simple method for preparing **2** in quantity.

As has been pointed out previously, the carbon bearing the methoxyl group of **7** corresponds to the carbon bearing the carbonyl group of **2**. Hence, these transformations required that the structure and stereochemistry of **2** and **7** be as depicted in the formulas. Moreover, it was proved earlier that **7** and **8** differed only in the position of the keto group and methoxyl substituent in ring E. From this it follows that the keto group of **8** is attached to C-15.

(22) The use of enedione epoxides for the ring contraction envisaged in this paragraph has not been described previously, although the Favorskii-type rearrangement of simple α-epoxy ketones to vinylogous β-keto acids was reported by Olofson and coworkers[23] after our work on **21** was completed. The reaction seems to be general; we are currently studying the synthesis and Favorskii rearrangement of other enedione epoxides for the purpose of developing a route to hydrindanones.

(23) G. R. Treves, H. Stauge, and R. A. Olofson, *J. Amer. Chem. Soc.*, **89**, 6257 (1967).

(24) The correct stereochemistry at C-13 anticipated in these formulas will be discussed subsequently.

The arguments of the previous three paragraphs depend on an examination of the molecular models of **18**, **22a**, **23**, and **24**, and comparison of anticipated with the observed vicinal coupling constants. Such arguments have occasionally proved deceptive. It was therefore desirable to adduce independent evidence for the location of the keto group of **2**.

The retro Diels–Alder reaction used in earlier papers of this series[4] seemed made to order for this but required the introduction of a double bond between C-13 and C-14 as a prerequisite. If the substance of highly probably structure **22a** could be transformed to an α,β-unsaturated cyclopentenone of structure **28**, a retro Diels–Alder reaction would furnish **30**. If, on the other hand, the unsaturated keto acid had the very unlikely structure **23**, the same series of transformations should lead to **31**, which should decompose to **32**. Now, as in the case of α-tetralones,[4b] the *peri* hydrogen on the aromatic ring in substituted 1-indanones is deshielded appreciably (35–50 Hz) compared with the other aromatic protons. By examining the chemical shifts of the aromatic protons (H-12 and H-19) of the thermolysis product, it should therefore be possible to locate the keto group in the precursor.

Hydrogenation of **22a** gave a saturated keto acid **25** whose infrared and nmr spectrum indicated retention of the bridge double bond. An attempt to carry out an oxidative decarboxylation on **25** with lead tetraacetate–cupric acetate[25] for the purpose of preparing **26** was unsuccessful because of the formation of a complex mixture. This result prompted the investigation of the decarboxylation reaction directly on **22a** because the resulting radical at C-13 should be stabilized by the conjugated chromophore. Indeed, examination of the product obtained in 65% yield showed that it was the desired allylic acetate **27**, since the nmr spectrum displayed the AB system of H-16 and H-17 as two clean doublets (7.61 and 6.05 ppm, J = 6 Hz), the broad singlet of H-19 at 5.26, the shielded C-10 methyl group at 0.63, and, in addition, a new acetate resonance at 2.03 ppm.

Hydrogenation of **27** afforded **26**, but hydrolysis of the latter, remethylation with diazomethane, and treatment with phosphorus oxychloride or thionyl chloride failed to effect dehydration. This difficulty suggested that the orientation of the acetate function of **26** and **27** was quassequatorial, bimolecular elimination proceeding by preference from a *trans* diaxial conformation. If this were so, it was anticipated that **26** under the conditions of *cis* elimination should yield **30** *via* the intermediates **28** or **29** or both.

In fact, pyrolysis of **26** at 325° yielded the indanone **30**, the structure of which was apparent from its nmr spectrum. The two aromatic protons H-12 and H-19 displayed their resonances at 7.01 and 6.83 ppm as two broad singlets (*meta* coupling). H-9 appeared as a quartet centered at 5.69 ppm and the multiplet of H-11a and H-11b appeared in the region 4.6–5 ppm. As there was no downfield signal near 7.8 ppm as expected for **32**, the results clearly demonstrated the correctness of formula **30** for the pyrolysis product, hence the structures of the precursors **28**, **26**, and **22a**, and, because of the correla-

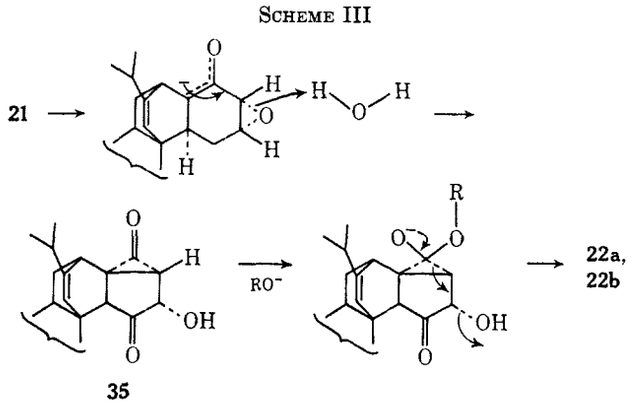
(25) J. K. Kochi, *J. Amer. Chem. Soc.*, **87**, 1811 (1965); J. D. Bacha and J. K. Kochi, *Tetrahedron*, **24**, 2215 (1968).

tion with **18**, the structures and stereochemistry of the adducts **2**, **7**, and **8**.[26]

That the carboxyl group of **22** and **25** was α oriented as shown in the formulas was deduced from the following evidence. All attempts to convert **22a** to a lactone under mild conditions met with failure and gave complete recovery of starting material. More vigorous conditions resulted in decarboxylation. Attempted lactonization of **25** under vigorous conditions was unsuccessful. The *endo,cis* attachment of the five-membered ring deduced from these negative results was demonstrated in a positive manner by photolysis of **22a**, which furnished in excellent yield the cage product **34**.

The α configuration of the carboxyl group of **22a**, which has been established by this transformation, can be attributed to the collapse of a "Loftfield" intermediate[27,28] **35** containing an α-oriented cyclopropanone ring (see Scheme III). The formation of this intermediate[29] requires the displacement of the oxirane of **21** by the enolate at C-1a from the β face of the molecule and consequent inversion of C-2. Attack on **35** in the usual manner by hydroxide or alkoxide ion is followed by collapse of the cyclopropane ring and ejection of the hydroxyl group from C-3 in the manner also postulated for the base-catalyzed rearrangement of α-epoxy ketones.[22]

SCHEME III



The Loftfield mechanism predicts β orientation of the carboxyl group of product if the oxirane ring of starting material has the β configuration. Conversely, occurrence of the Favorskii rearrangement in an α-oriented epoxide requires inversion at C-1a prior to displacement of the oxygen function at C-2 and should result in **22a** with the carboxyl group α. Since the *endo,cis* stereochemistry of **20** is without question[4] and the bonds involved in the displacements of Scheme III have to be antiparallel, the configuration of the oxirane ring of **21** should be α. This result is in harmony with the conclusion derived from an examination of Dreiding models, which indicates that the α side of **20** is less hindered.

(26) In the Experimental Section we record an attempt to introduce a C-13–C-14 double bond into **2** directly by subjecting it to the Barton reaction. This goal was not realized. The reaction furnished instead in excellent yield substance **33** (Scheme II).

(27) R. B. Loftfield, *J. Amer. Chem. Soc.*, **72**, 632 (1950); **73**, 4707 (1951); **76**, 35 (1954).

(28) A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(29) For recent work supporting the intermediacy of cyclopropanones in stereospecific Favorskii-type rearrangements and references to earlier studies, see N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **87**, 3258 (1965).

Experimental Section[30]

Condensation of Levopimaric Acid with Cyclopentenone.[31]—A mixture of 7 g of 2-cyclopenten-1-one and 20 g of **1**[32] was heated with a trace of hydroquinone under nitrogen to 200°. The course of the reaction was monitored by tlc (appearance of a spot more polar than levopimaric acid) and nmr (appearance of the shielded C-10 methyl resonance). The amount of adduct reached a maximum after heating for 2 hr; further heating caused little change. The reaction mixture was chromatographed over 400 g of silicic acid. The column was eluted with benzene to remove all unreacted resin acids. When resin acids were no longer detected in the eluate, the column was eluted with benzene–chloroform and then with chloroform to remove the product (mixture of adducts as shown by nmr spectroscopy), which was eluted as a visible light tan band, total crude yield 9 g.

The combined fractions containing the adducts were methylated with excess diazomethane in ether. The resulting solution was slowly evaporated to dryness and allowed to stand for several days, during which time seed crystals formed. The mixture was then triturated with cold methanol and filtered. The solid (**2**, 6 g) was crystallized twice from methanol to give 4 g of pure **2**: mp 136–138°; $[\alpha]_D$ +81°; ir 1740 (ketone) and 1722 cm^{-1} (ester); nmr 5.30 (br, H-19), 3.60 (methoxyl), 1.12 (C-4 methyl), 1.04 (d, J = 7 Hz, isopropyl), and 0.57 ppm (C-10 methyl); ORD $[\alpha]_{350}$ +500°, $[\alpha]_{314}$ +1970°, $[\alpha]_{303}$ 0°, $[\alpha]_{278}$ −2540°.

Anal. Calcd for $C_{26}H_{38}O_3$: C, 78.35; H, 9.61; O, 12.04. Found: C, 78.58; H, 9.43; O, 12.43.

The mother liquor appeared homogeneous on tlc, but nmr spectroscopy showed it to be a mixture of two adducts. The mixture was carefully chromatographed on 125 g of Florisil. Elution with benzene yielded several noncrystalline fractions followed by two fractions totaling 200 mg which the nmr spectrum showed to be nearly pure. Recrystallization from petroleum ether yielded 120 mg of **5**: mp 120–122°; $[\alpha]_D$ −24°; ir 1737 (ketone) and 1722 cm^{-1} (ester); nmr 5.33 (br, H-19), 3.63 (methoxyl), 1.12 (C-4 methyl), 1.03 (d, J = 7 Hz, isopropyl), and 0.62 ppm (C-10 methyl); ORD $[\alpha]_{400}$ −107°, $[\alpha]_{350}$ −310°, $[\alpha]_{325}$ −745°, $[\alpha]_{309}$ 0°, $[\alpha]_{284}$ +870°.

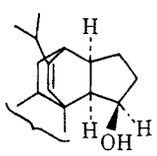
Anal. Calcd for $C_{26}H_{38}O_3$: C, 78.35; H, 9.61; O, 12.04. Found: C, 78.13; H, 9.77; O, 12.26.

Further elution gave several fractions which were mixtures followed by several large fractions containing a total of 1.2 g of **2**.

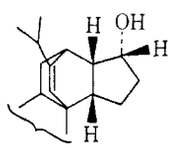
Reduction of 2 and 5 with Borohydride.[31]—To a solution of 1 g of **2** in 25 ml of ethanol was added 0.5 g of sodium borohydride. The solution was allowed to stand at room temperature for 7 days, after which excess sodium borohydride was decomposed by addition of acetone. Solvent was removed at reduced pressure, and the residue was taken up in ether, washed with water, and evaporated to yield 900 mg of crude **35**. Recrystallization from methanol furnished the analytical sample: mp 147–148°; $[\alpha]_D$ +41°; ir 3610 (hydroxyl) and 1722 cm^{-1} (ester); nmr 5.64 (br, H-19), 4.1 (c, proton on carbon bearing OH), 3.63 (methoxyl), 2.5 (exchanges with D_2O, hydroxyl proton), 1.16 (C-4 methyl), 1.05 (d, J = 7 Hz, isopropyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.07; O, 11.98. Found: C, 78.07; H, 10.14; O, 11.85.

In the same manner, **5** was reduced to noncrystalline **36**: $[\alpha]_D$ −17°; ir 3540 (hydroxyl) and 1722 cm^{-1} (ester); nmr 5.32



35



36

(30) For details concerning methods, etc., see footnote 52 of Resin Acids. XVII: W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 3464 (1969). Infrared spectra were run as Nujol mulls unless otherwise noted. Silicic acid was Mallinckrodt 100 mesh. Glpc analyses were done on an F & M 5750 research chromatograph using the flame detector and a 6 ft × 1/8 in. stainless steel Uc-W98-80-1005 column maintained at 500°F. Flame detector and injection port were maintained at 600°F; carrier flow was kept at 2.1 (meter reading), oxygen at 22 psig, and hydrogen at 5 psig.

(31) This reaction was carried out by Dr. R. C. Blackstone.

(32) We are grateful to Dr. G. W. Hedrick for generous supplies of longleaf yellow pine oleoresin for the preparation of starting material.

(br, H-19), 4.25 (c, proton on carbon bearing OH), 3.62 (methoxyl), 3.16 (exchanges with D_2O, hydroxyl proton), 1.13 (C-4 methyl), 0.99 (d, J = 7 Hz, isopropyl), and 0.60 ppm (C-10 methyl). The analytical sample was prepared by preparative tlc.

Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.07; O, 11.98. Found: C, 77.86; H, 10.02; O, 11.87.

Condensation of Levopimaric Acid with 1-Cyclopentene-3,5-dione.[33]—To a solution of 32 g of **1** in 70 ml of chloroform was added 14 g of 1-cyclopentene-3,5-dione. The reaction mixture was stored in the refrigerator for 18 hr and then for 24 hr at room temperature. Evaporation of solvent and addition of petroleum ether furnished a white solid (35% yield) which decomposed above 340°. The nmr spectrum indicated that it was a mixture of enols.

Methylation of the crude adduct with ethereal diazomethane and evaporation of the solvent yielded a gum which showed two major spots on tlc. The mixture of methyl ethers was chromatographed over 1500 g of alumina. Elution with chloroform removed the less polar isomer (**7**) from the column. It was recrystallized from methanol: mp 151–152°, raised to 155° by recrystallization from cyclohexane; yield 10.8 g; $[\alpha]D$ +13.6°; ir 1722 (ester) and 1707 cm^{-1} (conjugated double bond); nmr 5.16 (br, 2 vinyl protons), 3.66 and 3.63 (methoxyls), 1.15 (C-4 methyl), 0.94 (d, J = 7 Hz, isopropyl), and 0.62 ppm (C-10 methyl); uv λ_{max} 242 nm (ϵ 9700).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 75.69; H, 8.80; O, 15.51. Found: C, 75.47; H, 8.83; O, 15.60.

Elution with ether yielded the more polar isomer **8**, which was recrystallized from ether: yield 14 g; mp 181–183°; $[\alpha]D$ +27.0°; ir 1722 (ester), 1706 (ketone), and 1617 cm^{-1} (conjugated double bond); nmr 5.37 and 5.22 (vinyl protons), 3.77, and 3.70 (methoxyls), 1.20 (C-4 methyl), 0.95 (d, J = 7 Hz, isopropyl), and 0.62 ppm (C-10 methyl); uv λ_{max} 237.5 nm (ϵ 11,200) and 295 (ϵ 11)2.

Anal. Calcd for $C_{27}H_{38}O_4$: C, 75.69; H, 8.80; O, 15.51. Found: C, 75.72; H, 8.90; O, 15.24.

Attempts to reduce either **7** or **8** with sodium borohydride resulted in recovery of starting material.

Equilibration of 7 and 8.—A solution of 100 mg of **8** in 50 ml of methanol and a trace of *p*-toluenesulfonic acid was stirred under reflux for 8 hr, the solvent was removed under reduced pressure, and the gum was dissolved in 25 ml of absolute ether. After addition of 500 mg of finely powdered sodium carbonate with vigorous stirring, the mixture was washed several times with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The resulting gum was dried at 100° (0.01 mm) for 3 hr. The nmr spectrum showed that it was a mixture of **8** and **7**. Quantitative analysis by gas chromatography showed that the composition of **8** and **7** was 4:3. The same result was obtained by repeating the reaction starting with pure **7**.

Photolysis of 8. Preparation of 9 and 10.—A 100-ml solution of 0.01 *M* **8** in methanol was irradiated for 48 hr in a quartz immersion well with a Pyrex filter, using a Hanovia 679-A-36 lamp. The solvent was evaporated *in vacuo* and the residue was chromatographed over 7 g of silicic acid. Benzene eluted 85 mg of pure **9** which was recrystallized from cyclohexane: mp 145°; ir 1770 (strained ketone) and 1750 cm^{-1} (ester); nmr 3.6 and 3.13 (methoxyls), 2.8–3.2 (c, cyclobutane protons and protons α to carbonyl), 1.05 and 1.02 (both d, J = 6 Hz, isopropyl), 1.12 (C-4 methyl), and 0.77 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98; O, 15.00. Found: C, 76.50; H, 8.91; O, 14.87.

Chloroform eluted 15% of starting material. The most polar fraction contained 275 mg of **10** which was recrystallized from cyclohexane: mp 209°; ir 1750 (ester), 1675 (cyclopentenone), and 1600 cm^{-1} (conjugated double bond); uv λ_{max} 247 nm (ϵ 12,500) and 290 (ϵ 170); nmr 5.27 (H-16), 3.73 and 3.6 (methoxyls, (C-4 methyl), 0.82 and 0.70 (both d, J = 7 Hz, isopropyl), and 3.6 and 3.73 (methoxyls).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98; O, 15.00. Found: C, 75.91; H, 8.99; O, 15.22.

Lithium Aluminum Hydride Reduction of 7. Preparation of 12.—A solution of 4 g of **7** in 200 ml of dry ether was reduced with 450 mg of lithium aluminum hydride in the usual amnner. The excess lithium aluminum hydride was decomposed with ethyl acetate, and 150 ml of 20% H_2SO_4 was added with vigorous stirring. The ether layer was washed, dried, and evaporated. The residue was mixed with 20 ml of methanol and the solid which separated was filtered and recrystallized from cyclohexane: yield 2.8 g; mp 161–162°; ir 3475 (OH), 1670 (cyclopentenone), and 1600 cm^{-1} (conjugated double bond); uv λ_{max} (cyclohexane) 235 (ϵ 7340) nm and 310 (ϵ 100); nmr 7.24 (dd, H-17, $J_{H\text{-}17,16}$ = 6 Hz, $J_{H\text{-}17,13}$ = 2.5 Hz), 5.98 (dd, H-16, $J_{H\text{-}16,13}$ = 2 Hz), 5.28 (br, H-19), 3.48, 3.31, 3.15, and 2.96 (q, RCH_2OH), 0.96 (C-4 methyl), 0.6 (C-10 methyl), and 0.78 ppm (d, J = 7 Hz, isopropyl); ORD $[\alpha]_{400}$ +1500°, $[\alpha]_{320}$ +400°, $[\alpha]_{285}$ 0°, $[\alpha]_{254}$ −5000°.

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85; O, 8.68. Found: C, 81.52; H, 9.36; O, 9.12.

Lithium Aluminum Hydride Reduction of 8. Preparation of 13.—Reduction of **8** in the manner described in the previous paragraph gave crude material which could not be induced to crystallize. Thin layer chromatography indicated the presence of a complex mixture. Repeated chromatography over silicic acid yielded **13** in *ca.* 15% yield in the $CHCl_3$ eluate. Variations such as adding excess lithium aluminum hydride, prolonging the reflux period, etc., did not result in an increase in yield. The product was recrystallized from cyclohexane: mp 167–168°; ir 3420 (hydroxyl), 1675 (cyclopentenone), and 1590 cm^{-1} (conjugated double bond); nmr 7.33 (dd, H-15, $J_{H\text{-}15,16}$ = 6 Hz, $J_{H\text{-}15,14}$ = 3 Hz), 6.05 (dd, H-16, $J_{H\text{-}16,15}$ = 6 Hz, $J_{H\text{-}16,14}$ = 2 Hz), 5.05 (br, H-19), 3.5, 3.33, 3.16, and 3.0 (q, RCH_2OH), 0.9 (d), 0.91 (d, J = 6 Hz, isopropyl), and 7.33 and 6.16 ppm (C-10 and C-4 methyls); ORD $[\alpha]_{400}$ −1890°, $[\alpha]_{345}$ −5400°, $[\alpha]_{320}$ 0°, $[\alpha]_{305}$ +2430°.

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85; O, 8.68. Found: C, 81.34; H, 9.72; O, 9.19.

Photolysis of 12. Ppreparation of 14.—A solution of 1 g of **12** in 100 ml of methanol was photolyzed for 22 hr in a photochemical reactor using a Pyrex filter. The solution was evaporated at reduced pressure and the resulting gummy material was chromatographed over 10 g of silicic acid. The product was eluted with chloroform and recrystallized from petroleum ether: yield 800 mg; mp 225°; ir 3470 (hydroxyl), 1765 (strained ketone), and 850–1000 cm^{-1} (cyclobutane); nmr no vinyl protons, 2.09–2.93 (c, 4 protons, 2 α to carbonyl and 2 cyclobutane protons), 0.98 (d), 0.88 (d, J = 7 Hz, isopropyl), 0.79 and 0.75 ppm (C-4 and C-10 methyls); uv (EtOH) λ_{max} 298 nm (ϵ 65).

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85; O, 8.68. Found: C, 81.33; H, 10.07; O, 9.13.

Photolysis of 13. Preparation of 15.—A solution of 45 mg of **13** in 50 ml of methanol was irradiated for 22 hr in a quartz immersion reactor using a Pyrex filter. Removal of solvent at reduced pressure and chromatography over neutral alumina yielded, after recrystallization from methanol, 40 mg of **15**: mp 195–196°; ir 3450 (hydroxyl), 1765 (strained ketone), and 850–1000 cm^{-1} (cyclobutane ring vibrations); nmr no vinyl protons, 3.46, 3.3, 3.13, and 2.96 (q, RCH_2OH), 0.96 and 0.73 (both d, J = 6 Hz, isopropyl), 0.78 and 0.73 (C-10 and C-4 methyls), and 2.1–2.9 ppm (c, 4 protons).

Anal. Calcd for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85; O, 8.68. Found: C, 81.80; H, 9.95; O, 9.31.

Hydrogenation of 12.—A solution of 1 g of **12** in 50 ml of absolute ethanol was hydrogenated with 100 mg of 10% palladium on carbon for 24 hr at 30 psig of hydrogen. Removal of the solvent after filtration yielded a solid which was recrystallized from methanol to yield 950 mg of **16**: mp 131°; ir 3450 (OH) and 1720 cm^{-1} (cyclopentanone); nmr 5.33 (br, H-19), 1.03 (d, J = 6 Hz, isopropyl), 0.71 and 0.56 ppm (C-4 and C-10 methyls).

Anal. Calcd for $C_{25}H_{38}O_2$: C, 81.03; H, 10.34; O, 8.64. Found: C, 80.58; H, 10.44; O, 9.03.

Hydrogenation of 13.—A solution of 600 mg of **13** in 50 ml of absolute ethanol was hydrogenated with 50 mg of 10% palladium on carbon at 35 psig of hydrogen for 24 hr. Filtration and concentration of the solvent led to the isolation of **17** as a solid which was recrystallized from methanol in quantitative yield: mp 153–155°; ir 3500 (OH) and 1725 cm^{-1} (cyclopentanone); nmr 5.33 (br, H-19), 3.5, 3.33, 3.16, and 3.0 (q, RCH_2OH), 1.02 (d), 0.93 (d, J = 6, isopropyl), 0.75 (C-4 methyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{25}H_{38}O_2$: C, 81.03; H, 10.34; O, 8.64. Found: C, 81.02; H, 10.63; O, 8.35.

Conversion of 16 to 2.—To a solution of 500 mg of **16** in 20 ml of spectrograde acetone, 2 ml of Jones reagent was added dropwise with stirring for 0.5 hr until the color of the reagent persisted. Stirring was continued for an additional 3.5 hr at room tempera-

(33) This reaction was first carried out by Dr. R. C. Blackstone.

ture. The mixture was diluted with water, and the organic material was extracted with ether. The ether layer was washed, dried, and concentrated on a steam bath. The resulting gum, 480 mg, was stirred with 30 ml of 10% sodium hydroxide and 3 g of freshly prepared Ag_2O for 18 hr. The mixture was filtered, acidified with concentrated HCl, and extracted with ether. The ether layer was washed, dried, and evaporated on the steam bath, and the microcrystalline residue was esterified with ethereal diazomethane. Removal of solvent and addition of 2 ml of methanol yielded 350 mg of crystalline **2**: mp 135–136°; identical in all respects (nmr, ir, tlc, melting point) with the major adduct obtained by condensation of levopimaric acid with 2-cyclopentenone and subsequent methylation.

Conversion of 17 to 4.—The experimental procedure was the same as described for the oxidation of **16**. Starting with 500 mg of **17**, 300 mg of **4** was isolated after chromatography of the final product over neutral alumina and recrystallization from methanol: mp 111–112°; ir 1730 (ester) and 1720 cm^{-1} (cyclopentanone); nmr 5.32 (br, H-19), 3.67 (methyl ester), 1.18 (C-4 methyl), 1.03 (d, J = 7 Hz, isopropyl), and 0.58 ppm (C-10 methyl). This material was not identical with the minor isomer resulting from the condensation of levopimaric acid with 2-cyclopentenone and subsequent methylation.

Anal. Calcd for $C_{26}H_{38}O_3$: C, 78.35; H, 9.61; O, 12.04. Found: C, 78.07; H, 10.02; O, 12.09.

Preparation of 18.—To a solution of 1 g of **12** in 25 ml of spectrograde acetone was added 5 ml of Jones reagent dropwise with vigorous stirring (3.5 hr) until the color of the reagent persisted. The mixture was diluted with 100 ml of water and the organic material was extracted with ether. The ether layer was washed, dried, and evaporated. The nmr spectrum of the gummy residue, 800 mg, indicated that it was a mixture of an aldehyde and an acid. The material was stirred with 3.5 g of freshly prepared silver oxide in 25 ml of 10% sodium hydroxide solution for 18 hr and filtered, and the filtrate was acidified with concentrated HCl. The precipitate was extracted with ether and the extract was washed, dried, concentrated, and allowed to stand with a saturated solution of diazomethane in ether until the yellow color of diazomethane persisted. Evaporation of solvent and chromatography over neutral alumina furnished 750 mg of **18**: mp 139°; $[\alpha]^{25}D$ −33.3° (c 5.64, $CHCl_3$); uv λ_{max} 237 nm (ϵ 9180) and 340 (ϵ 83); ir 1730 (ester), 1690 (cyclopentenone), and 1595 cm^{-1} (double bond); nmr 7.35 (dd, H-17, J = 6 and 2.5 Hz), 6.06 (dd, H-16, J = 6 and 2 Hz), 5.31 (br, H-19), 3.7 (methyl ester), 1.16 (C-4 methyl), 0.93 (d, J = 6 Hz, isopropyl), 0.63 (C-10 methyl), and 2.6 ppm (clean d, H-14).

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15; O, 12.10. Found: C, 78.83; H, 9.09; O, 12.19.

Photolysis of 18.—A solution of 600 mg of **18** in 150 ml of methanol was irradiated in a photochemical reactor for 22 hr using a Pyrex filter while being swept with a slow stream of nitrogen. Evaporation of solvent at reduced pressure yielded a solid which was chromatographed over neutral alumina to yield 580 mg of **19** which was recrystallized from methanol: mp 176–177°; ir 1760 (strained cyclopentanone), 1730 (ester), and 850–1000 cm^{-1} (cyclobutane ring vibrations); nmr 3.63 (methoxyl), 2.33–2.83 (4 cyclobutane protons and 2 protons α to the ketone), 1.13 (C-4 methyl), 0.96 (d), 0.86 (d, J = 6 Hz, isopropyl), and 0.8 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.75; H, 9.15; O, 12.10. Found: C, 78.35; H, 9.09; O, 12.54.

Epoxidation of 20.—To a solution of 10.5 g of **20**[4b] in 500 ml of acetone cooled in an ice bath to 5° was added 10 ml of a 10% solution of sodium carbonate and immediately thereafter 20 ml of 30% hydrogen peroxide in small portions during a period of 30 min. All the operations were carried out under vigorous stirring. The solution was allowed to warm to room temperature, diluted with 1 l. of water, and extracted with ether. The ether layer was washed, dried, and evaporated. The resulting gum crystallized on addition of methanol. Recrystallization from methanol gave colorless crystals of **21**: homogeneous on tlc; mp 204–205°; yield 7.7 g; ir 1735 (ester) and 1710 and 1715 cm^{-1} (ketones); nmr 5.61 (br, H-14), 3.66 (methoxyl), 3.13 (br, H-2 and H-3), 1.16 (C-7 methyl), 0.97 (d), 0.90 (d, J = 7 Hz, isopropyl), and 0.60 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{36}O_5$: C, 73.60; H, 8.24; O, 18.16. Found: C, 73.02; H, 8.13; O, 18.08.

Favorskii Rearrangement of 21. Formation of 22a and 22b.—To a solution of 4 g of **21** in 250 ml of 95% ethanol was added with stirring 60 ml of a 10% sodium hydroxide solution. The colorless solution became yellow after 2 min, brown after 5 min, and colorless again after 15 min. After 20 min, the solution slowly acquired a deep purple color in the course of 1 hr. The solvent was evaporated at reduced temperature (bath temperature 50°). The purple residue was dissolved in 100 ml of water and extracted thoroughly with ether. The ether layer was washed, dried, and chromatographed over silicic acid, which furnished *ca.* 400 mg of glassy material **22b**. The aqueous layer was acidified with 1 N hydrochloric acid, and the acidic material was extracted with ether and chromatographed over silicic acid. Chloroform eluted *ca.* 1.85 g of **22a**: mp 209–210° after recrystallization from cyclohexane; ir 3350 (acid), 1750 and 1720 cm^{-1} (ester and acid carbonyls), 1670 (cyclopentanone), and 1595 cm^{-1} (conjugated double bond); nmr 7.35 (d, H-17), 6.05 (d, H-16, J = 6 Hz), 5.3 (br, H-19), 3.65 (methoxyl), 2.61 (H-14), 1.15 (C-4 methyl), 0.95 (d, J = 6 Hz, isopropyl), and 0.61 (C-10 methyl); $[\alpha]^{25}D$ −17.8° (c 5.64, $CHCl_3$).

Anal. Calcd for $C_{27}H_{36}O_5$: C, 73.60; H, 8.24; O, 18.16. Found: C, 73.58; H, 8.27; O, 18.19.

The neutral material showed infrared bands at 1750 and 1745 cm^{-1} (esters). Its nmr spectrum was superimposable on that of **22a**, but exhibited an additional quartet at 4.25 (J = 7 Hz) and a triplet at 1.3 ppm (J = 7 Hz, ethoxyl). This material was not analyzed but was characterized as the crystalline diacid.

Hydrolysis of 22a and 22b to 22c.—A mixture of 200 mg of **22b** in 20% methanolic sodium hydroxide solution was heated on a steam bath for 24 hr until the solution became clear, acidified with concentrated hydrochloric acid, and extracted with ether. The ether layer was washed, dried, and evaporated. This furnished solid **22c**, which was recrystallized from methanol: yield 100 mg; mp 248°.

The same procedure was adopted for the hydrolysis of **22a**: yield 125 mg; mp 248°. The nmr and infrared spectra of the two products were identical: ir 3260 (br, acid), 1710 and 1730 (acids), 1685 (cyclopentenone), and 1610 cm^{-1} (conjugated double bond); nmr 7.5 (d), 6.01 (d, H-17 and H-16, J = 6 Hz), 5.3 (br, H-19), 2.93 (H-14), 1.31 (C-4 methyl), 0.95 (d, J = 6 Hz, isopropyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03; O, 18.75. Found: C, 72.85; H, 8.02; O, 18.94.

Thermal Decarboxylation of 22a and Conversion to 2.—A two-necked round-bottomed flask containing 500 mg of **22a** was swept with a steam of nitrogen, heated slowly, by means of an electrically heated oil bath, to 230°, and maintained at this temperature for 15 min. Decarboxylation of **22a** proceeded smoothly at the melting point. After the flask had cooled, 5 ml of methanol was added to crystallize the product: yield 430 mg of a single product (tlc) which was identical in all respects with **18** obtained previously by transformation of **12**.

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15; O, 12.10. Found: C, 78.67; H, 9.17; O, 12.34.

The decarboxylation was carried out somewhat more conveniently with acid.

A solution of 500 mg of **22a** in 25 ml of 95% ethanol and 6 drops of concentrated sulfuric acid was refluxed for 8 hr, concentrated *in vacuo*, and diluted with water. The precipitate was extracted with ether, and the ether layer was washed, dried, and evaporated. Tlc of the crystalline solid thus obtained showed a single spot. Recrystallization from methanol furnished pure **22a** in quantitative yield.

A solution of 1 g of **18** in 50 ml of absolute ethanol was hydrogenated with 500 mg of 10% palladium on carbon for 24 hr at 35-psi hydrogen pressure. The solution was filtered, the filtrate was concentrated, and the residue was recrystallized. The product, which had mp 135–136°, was identical in all respects (nmr, ir, melting point, tlc, and glpc) with the major adduct **2** obtained by condensation of levopimaric acid with cyclopentenone and subsequent methylation.

Lead Tetraacetate Decarboxylation of 22a.—To 200 ml of spectrograde benzene distilled from lead tetraacetate was added 700 mg of lead tetraacetate. The solution was stirred for 5 min, 200 mg of freshly dried copper acetate was added with vigorous stirring, and 120 mg of **22a** was dissolved in 25 ml of benzene. The mixture was gradually heated to reflux and refluxing with stirring was continued for 12 hr. All operations were carried out with rigorous exclusion of moisture and air by passing a steady stream of dry nitrogen through the apparatus. The solution was allowed to cool, stirred for an additional 8 hr at room temperature in a nitrogen atmosphere, and filtered. The filtrate was washed with 1 N sodium hydroxide solution and water, dried, and

evaporated. The residual gum was chromatographed over 3.5 g of silicic acid. Chloroform eluted a glassy fraction which was contaminated with a minor impurity (tlc). On rechromatography over neutral alumina, benzene eluted 80 mg of pure **27**. This compound was not crystalline at room temperature but could be recrystallized from methanol below 0°: ir 1742 and 1735 (esters), 1685 (cyclopentenone), and 1600 cm^{-1} (conjugated double bond); nmr 7.61 (d), 6.05 (d, H-17 and H-16, J = 6 Hz), 5.26 (br, H-19), 3.63 (methoxyl), 2.03 (acetate), 1.16 (C-4 methyl), 1.12 (d, J = 7 Hz, isopropyl), and 0.63 ppm (C-10 methyl).

Anal. Calcd for $C_{28}H_{38}O_5$: C, 73.98; H, 8.43; O, 17.60. Found: C, 73.84; H, 8.54; O, 18.01.

Hydrogenation of 22a.—A solution of 1 g of **22a** in 75 ml of absolute ethanol was hydrogenated at 35 psi of hydrogen for 24 hr using 100 mg of 10% palladium on carbon as catalyst. The solution was filtered and concentrated, and the residue was recrystallized from methanol: yield 800 mg of **25**; ir 3450 (br, acid), 1740, 1735, and 1710 cm^{-1} (ester, acid, cyclopentanone); nmr 5.36 (br, H-19), 3.6 (methyl ester), 1.28 (C-4 methyl), 1.23 (d, J = 6 Hz, isopropyl), 2–3 (4 protons, H-12, H-14, H-16a, and H-16b), and 0.56 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{38}O_5$: C, 73.27; O, 18.08. Found: C, 73.38; H, 8.60; O, 18.01.

Attempted oxidative decarboxylation of **25** in the manner described for **22a** gave a complex mixture.

Hydrogenation of 27.—A solution of 300 mg of **27** in 100 ml of absolute ethanol was hydrogenated at 35 psi of hydrogen for 24 hr using 150 mg of 10% palladium on carbon as catalyst. Filtration and concentration of the filtrate furnished a gum which was chromatographed over neutral alumina. Benzene eluted 280 mg of **26** which could not be induced to crystallize: ir 1740, 1735, and 1732 cm^{-1} (esters, cyclopentanone); nmr 5.38 (br, H-19), 3.61 (methoxyl), 2.01 (acetate), 1.16 (C-4 methyl), 1.10 (d, J = 7 Hz, isopropyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{28}H_{40}O_5$: C, 73.65; H, 8.83; O, 17.52. Found: C, 73.62; H, 8.81; O, 17.52.

Thermolysis of 26. Formation of 30.—A four-bulb bulb-to-bulb distillation apparatus with a nitrogen inlet attached between the first and second bulb and containing 100 mg of **26** in the lowest bulb was swept with nitrogen. The lowest bulb was gradually heated to 325° and kept for 15 min at this temperature, while the acetic acid formed during the thermolysis was driven off by a continuous stream of nitrogen. The temperature was lowered to 250° and the nitrogen inlet was sealed off. The nitrogen outlet was connected to a vacuum (0.01 mm) and the material was distilled into the second bulb. Redistillation into the third bulb by lowering the second bulb into the furnace furnished pure **30**: yield 45 mg; ir 1735 (ester), 1695 (indanone), and 1600 cm^{-1} (aromatics); nmr 7.01 and 6.83 (both br, H-12 and H-19), 5.91, 5.76, 5.61, and 5.46 (q, 1 proton, H-9), 5.0, 4.9, 4.8, and 4.63 (all d, H-12a and H-12b), 3.63 (methoxyl), 1.23 (C-4 methyl), 1.2 (d, J = 6 Hz, isopropyl), and 1.0 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{30}O_3$: C, 78.74; H, 9.15; O, 12.10. Found: C, 79.12; H, 8.92; O, 11.96.

Preparation of 33.—A solution of 500 mg of **2** in 10 ml of *t*-butyl alcohol was added to potassium *t*-butoxide freshly prepared from 20 ml of *t*-butyl alcohol and 300 mg of potassium. Oxygen was bubbled through the mixture for 3–5 hr. The solution became brown during this period. The solvent was removed at reduced pressure, and the residue was diluted with 40 ml of water and acidified with concentrated hydrochloric acid. The precipitated **33** was filtered, dried, and recrystallized from methanol: yield 475 mg; mp 226°; ir 3350 (hydrogen-bonded hydroxyl), 1730, 1690, and 1645 cm^{-1} (ester, cyclopentenone, enolic double bond); nmr 6.13 (d, H-17, J = 3 Hz), 5.2 (br, H-19), 3.63 (methoxyl), 1.13 (C-4 methyl), 0.93 (d, J = 6 Hz, isopropyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{36}O_4$: C, 75.69; H, 8.80; O, 15.51. Found: C, 75.77; H, 8.90; O, 15.68.

Photolysis of 22.—A solution of 500 mg of **22a** in 175 ml of methanol was photolyzed in the usual manner for 22 hr using a Pyrex filter. Methanol was removed under reduced pressure after irradiation and the resulting gum was chromatographed over silicic acid. Elution with chloroform afforded **34**, which was recrystallized from petroleum ether: yield *ca.* 400 mg; mp 186–187°; ir 3250 (acid), 1770 (strained ketone), 1725 and 1710 cm^{-1} (ester, acid), and 850–1000 cm^{-1} (cyclobutane vibrations); nmr 3.61 (methoxyl), 2.41–2.8 (c, 4 protons, H-14, H-16, H-17, and H-19), 1.15 and 0.68 (C-4 and C-10 methyls), and 1.0 and 0.96 ppm (both d, J = 6 Hz, isopropyl).

Anal. Calcd for $C_{27}H_{36}O_5$: C, 73.60; H, 8.24; O, 18.16. Found: C, 73.42; H, 8.42; O, 18.47.

Registry No.—2-Cyclopenten-1-one. 930-30-3; 1-cyclopentene-3,5-dione, 930-60-9; **2**, 21727-49-1; **4**, 21727-50-4; **5**, 21727-51-5; **7**, 21727-52-6; **8**, 21727-53-7; **9**, 21766-44-9; **10**, 19086-60-3; **12**, 21727-54-8; **13**, 21727-55-9; **14**, 21728-90-5; **15**, 21728-91-6; **16**, 21727-56-0; **17**, 21727-57-1; **18**, 21727-58-2; **19**, 21728-92-7; **21**, 21727-59-3; **22a**, 21727-60-6; **22c**, 21766-45-0; **25**, 21713-20-2; **26**, 21766-46-1; **27**, 21713-21-3; **30**, 21713-22-4; **33**, 21713-23-5; **34**, 21728-89-2; **35**, 21766-47-2; **36**, 21713-24-6.