mixture. The amine hydrochloride was filtered from the reaction mixture; the ether was removed under vacuum; and the remaining residue was distilled. The mixed phosphites were formed in the amounts shown in Table I.

Ethyl dichlorophosphite (50 g, 0.34 mol), prepared by reaction of equimolar amounts of phosphorus trichloride and ethanol in dry diethyl ether,[13] was added to a mixture of N,N-dimethylaniline (82.4 g, 0.67 mol) and isopropyl alcohol (40.8 g, 0.68 mol) dissolved in 500 ml of dry Skelly F. During the addition of the ethyl dichlorophosphite, the reaction flask was cooled in an ice bath, and the mixture was stirred vigorously. After removal of the amine hydrochloride by filtration and the Skelly F by distillation at atmospheric pressure, the remaining residue was distilled under vacuum yielding ethyldiisopropyl phosphite (see Table I).

In all cases, the ir and nmr spectra of the mixed phosphite esters were consistent with their assigned structures.

Reactions of Mixed Phosphites with Acetic Acid.—The quantities of acetic acid and mixed phosphites shown in Tables II–V were sealed in Pyrex tubes and heated for approximately 12 hr in a constant temperature oil bath set at 125°. During this period of heating, the mixtures remained homogeneous. Upon cooling, the tubes were opened, and an accurately weighed amount of the reaction mixture was added to a known amount of an inert compound (chlorobenzene, toluene, tetralin or anisole) which served as an internal standard for the gas chromatographic analysis. The amounts of the ethyl acetate and other alkyl acetate produced in the reaction were determined from comparison of their gas chromatographic peak areas with that of the internal standard. Duplicate or triplicate runs were made for each mixed phosphite.

Separation of *exo*- and *endo*-norbornyl acetates could not be accomplished by gas chromatographic analysis. The compositions of these norbornyl acetates produced in these reactions (Table IV) were determined by ir analysis of the norbornyl acetates which were separated from the reaction mixtures by preparative gas chromatography using a 10 ft × 3/8 in. column packed with 30% phenyldiethanolamine on Chromosorb W. Acetolysis of 0.99 g (4.3 mmol) of diethyl-*exo*-norbornyl phosphite with 0.26 g (4.4 mmol) of acetic acid at 125° for 12 hr yielded on isolation 50.9 mg of *exo*-norbornyl acetate with an ir spectrum identical with that of an authentic sample. Acetolysis of diethyl-*endo*-norbornyl phosphite (1.00 g, 4.3 mmol) with acetic acid (0.26 g, 4.4 mmol) at 125° for 12 hr yielded on isolation 25.9 mg of norbornyl acetates. Ir analysis showed the characteristic absorption at 1072 cm^{-1} displayed by *exo*-norbornyl acetate as well as an absorption at 1039 cm^{-1} found in the spectrum of an authentic sample of *endo*-norbornyl acetate. The amounts of the *endo*- and *exo*-norbornyl acetates were determined from the relative intensities of the absorptions by comparing them with the intensities observed for synthetic mixtures of the two esters.

Acetolysis of Diethyl-(+)-2-octyl Phosphite.—Diethyl-(+)-2-octyl phosphite (2.01 g, 8.03 mmol) and acetic acid (0.481 g, 8.01 mmol) were heated for 12 hr at 125°. The 2-octyl acetate formed was separated from the reaction mixture by preparative gas chromatography on a 20 ft × 3/8 in. column packed with 30% Carbowax on Chromosorb P. The isolated 2-octyl acetate, which amounted to 0.142 g, had a specific rotation of $[\alpha]^{27}D$ −2.6 (*c* 11.2, ethanol). In a similar reaction employing 1.15 g (4.62 mmol) of diethyl-(+)-2-octyl phosphite and 0.28 g (4.7 mmol) of acetic acid, 0.125 g of 2-octyl acetate was isolated which had $[\alpha]^{27}D$ −2.7 (*c* 10.0, ethanol).

(13) R. W. Young, K. H. Wood, R. J. Joyce, and G. W. Anderson, *J. Amer. Chem. Soc.*, **78**, 2126 (1956).

Registry No.—I, 17448-38-3; II, 14540-27-3; III, 17448-39-4; IV, 17448-40-7; V, 17448-41-8; VI, 17448-42-9; VII, 17448-43-0; VIII, 17448-44-1; IX, 17448-45-2.

The Synthesis of Methyl 13,16-Cycloatisan-18-oate (Methyl *anti*-Trachylobanate)[1,2]

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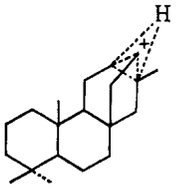
The synthesis of the pentacyclic diterpene methyl 13,16-cycloatisan-18-oate, the enantiomer of methyl trachylobanate, is described. The successful route involved as the initial step the condensation of methyl levopimarate with *n*-butyl crotonate. The major adduct whose structure and stereochemistry were elucidated was transformed by oxidation with potassium permanganate, ozonolysis, reduction with chromous chloride, and oxidative decarboxylation to 8-carboxymethyl-2,5a,8-trimethyl-1H-3,10a-Δ^1-decahydroethanophenanthren-12-one (**30a**). Cationically induced cyclization of the major alcohol obtained by hydride reduction of **30** gave the title compound. Other approaches to the trachylobane system are presented.

The trachylobanes or *ent*-13,16-cycloatisanes[3-5] (**1**) comprise a class of interesting pentacyclic diterpenes which were isolated[4] from the seed pods of *Trachylobium verrucosum* Oliv. Their importance stems from the circumstance that their occurrence in nature completes the array of diterpenoids theoretically derivable from the ion A which has been suggested[6] as the common intermediate leading to tetracyclic diterpenes and in fact helps to substantiate current notions concerning the biogenesis of diterpenes in general.



A

Our interest in the transformation of common resin acids into diterpenes with novel skeletons[7,8] prompted us to examine possible routes to the partial synthesis of this interesting pentacyclic skeleton. We have

(1) Resin Acids. XIV. A preliminary communication has appeared. W. Herz, R. N. Mirrington, and H. Young, *Tetrahedron Lett.*, 405 (1968).

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

(3) In deference to the discoverers[4] of this series of compounds, we shall refer to **1a** as trachylobane and **1b** as trachylobanic acid. However, in accordance with a proposal for systematic nomenclature subscribed to by most workers in this area,[5] the preferred systematic name for **1a** is enantiomeric 13,16-cycloatisane (**2a**) or *ent*-13,16-cycloatisane; **1b** would then be *ent*-13,16-cycloatisan-18-oic acid. The preferred[6] common names for **2a** and **2b** are *anti*-trachylobane and *anti*-trachylobanic acid.

(4) G. Hugel, L. Lods, J. M. Mellor, D. W. Theobald, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1974 (1963); 2282, 2888 (1965). G. Hugel, L. Lods, J. M. Mellor, and G. Ourisson, *ibid.*, 2894 (1965).

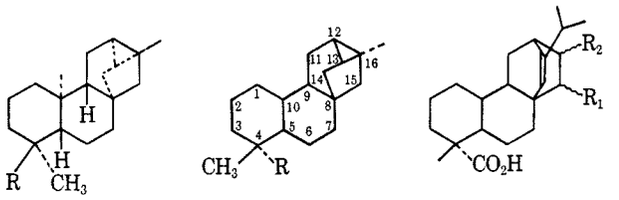
(5) J. W. Rowe, in preparation.

(6) E. Wenkert, *Chem. Ind.* (London), 282 (1955).

(7) W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 3195 (1965).

(8) W. Herz, A. R. Pinder, and R. N. Mirrington, *ibid.*, **31**, 2257 (1966).

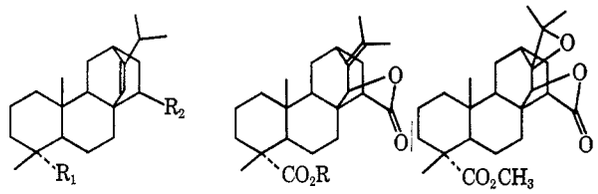
achieved our objective and now report the synthesis of methyl 13,16-cycloatisan-18-oate (**2c**), the enantiomer of methyl trachylobanate[9] (**1c**, methyl *anti*-trachylobanate),[5] which confirms the structure and stereochemistry assigned previously to the trachylobanes.



1a, R = CH_3
b, R = CO_2H
c, R = CO_2CH_3

2a, R = CH_3
b, R = CO_2H
c, R = CO_2CH_3

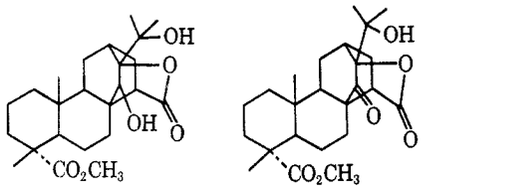
3



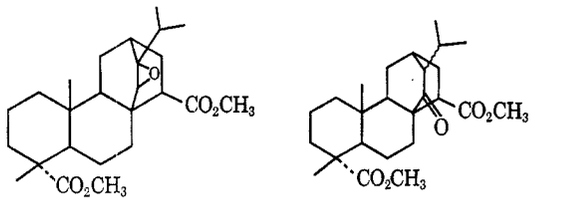
4a, $R_1 = R_2 = CO_2H$
b, $R_1 = R_2 = CO_2CH_3$
c, $R_1 = CO_2CH_3$; $R_2 = CO_2H$

5a, R = H
b, R = CH_3

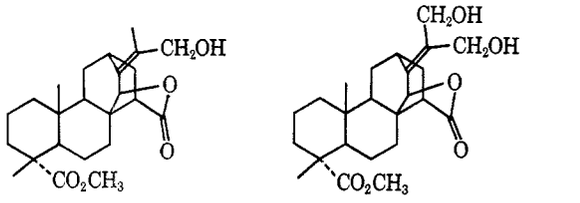
6



7 **8**



9 **10**



11 **12**

Levopimaric acid was chosen as starting material because of its availability and, more importantly, because the isopropyl group in the well-known 2,2,2-bicyclooctene system **3**,[10] easily prepared by diene synthesis of levopimaric acid with a variety of dienophiles,[11] can be readily removed[11,12] from adducts **3** (R_1 = *endo*-COOH) by permangante oxidation followed by ozonolysis.[13]

Our initial attempts to prepare a compound of type **3** (R_1 = *endo*- or *exo*-COOH, R_2 = *exo*- or *endo*-methyl) suitable for conversion into **2b** by condensation of levopimaric acid with crotonic acid or methyl or ethyl crotonate were not promising. We therefore explored the use of **4a**, prepared by hydrolysis of the adduct of levopimaric acid and methyl acrylate,[11a] which was oxidized with alkaline potassium permanganate in the described[11a] manner, the crude product being methylated with diazomethane. In spite of many trials the reported[11a] high yield of the acid corresponding to the ester lactone **5b** could not be repeated and never exceeded 40–50%. Instead the formation of by-products, which were the result of further oxidation and were very difficult to separate, except by tedious chromatography, interfered with the smoothness of the operation. Apparently the oxidizing agent attacked the initial product **5a** as rapidly as it attacked starting material. This led to the isolation of two new products, the epoxy lactone **6** (6%, configuration of the isopropyl group based on the most likely direction of attack by the oxidizing agent), whose structure was established by epoxidation of **5b** and comparison of samples, and the diol **7** (14%). The structural assignment of the latter derives from (1) presence of a δ-lactone frequency superimposed on the ester band in the ir spectrum; (2) presence in the nmr spectrum of a singlet proton at 4.35 ppm characteristic of hydrogen under hydroxyl flanked by fully substituted carbon atoms and two superimposed methyl singlets at 1.38 ppm indicative of the dimethyl carbinol grouping; (3) oxidation of **7** with chromic acid to the ketone alcohol **8**, whose physical properties were consonant with the proposed structure. Hydroxyketo lactone **8** was subjected to base treatment in the hope that it might undergo a retroaldol reaction, thus resulting in the desired loss of the isopropyl group, but no useful products could be isolated.

Several alternative routes to **5a** were investigated in efforts to improve the yield. Epoxidation of **4b** gave **9** which on treatment with acid invariably furnished **10**, instead of the hoped-for diol or **5a**. The exclusive operation of the pinacol rearrangement is understandable if the pronounced steric hindrance to displacement of the epoxide function, apparent from inspection of models, is taken into account, hydride migration being preferable to rear-side attack by an external nucleophile.

The action of bromine on **4a** or **4c** was also studied with a view to obtaining the bromo lactone which it was hoped could be converted into **5**, perhaps spontaneously. Partial realization of this objective was achieved under radical conditions (see Experimental Section) but offered no significant improvements. Worthy of note is the observation that addition of bromine in chloroform–methanol solution resulted after methylation and chromatography over alumina in the isolation of a bromo lactone (**13a** or **b**, 15%) and a hydroxy lactone (**11**, 25%). The latter substance must be the product of allylic bromination at one of the vinyl methyl groups in the presumed intermediate

(9) The French workers[4] reported the isolation of trachylobanic acid (**1b**). They did not report its physical properties but characterized it as the methyl ester **1c**.

(10) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. 3, Cambridge University Press, Cambridge, 1952, p 431.

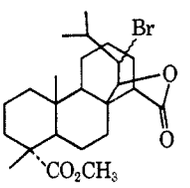
(11) For leading references, see (a) N. J. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *J. Org. Chem.*, **29**, 1017 (1964); (b) W. Herz, R. C. Blackstone, and M. G. Nair, *ibid.*, **31**, 1800 (1966); **32**, 2992 (1967).

(12) (a) L. H. Zalkow, R. A. Ford, and J. P. Kutney, *ibid.*, **27**, 3535 (1962), and references cited therein; (b) L. H. Zalkow and D. R. Brannon, *ibid.*, **29**, 1296 (1964).

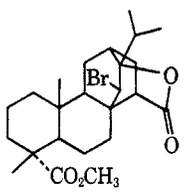
(13) Ozonolysis proceeds very slowly, if at all, when R_2 is also *endo* (except R_2 = H).[12a]

5a, the halogen being replaced by hydroxyl under the basic conditions of chromatography. When the bromination was conducted in chloroform, a dihydroxy lactone **12** was isolated as well. Structures of **11** and **12** were apparent from the nmr spectra which exhibited only one (for **11**) and no (for **12**) vinyl methyl singlets, as contrasted with **5b** which had two, and displayed signals corresponding to one (for **11**) and two (for **12**) hydroxymethyl groups. Ozonolysis of **11** and **12** to **15** (*vide infra*) confirmed the assignments.

The nature of the bromo lactone (**13a** or **b**) requires comment. Because it could not be dehydrohalogenated by treatment with base or acid, it probably did not represent the bromo lactone intermediate on the route from **4a** to **5**, **11**, or **12** which apparently undergoes spontaneous dehydrohalogenation. The alternative formula **14** was, however, ruled out on the basis of the ir spectrum which clearly identified it as a γ-lactone (carbonyl band at 1785 cm^{-1}).[14] It is therefore



13a, α-Br
b, β-Br



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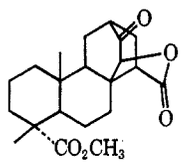

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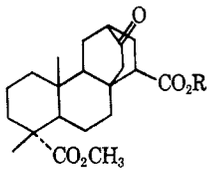
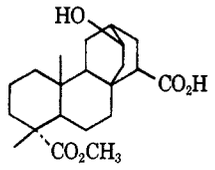


16a, R = H
b, R = CH_3



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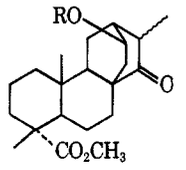

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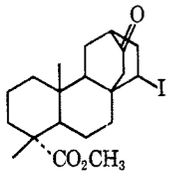

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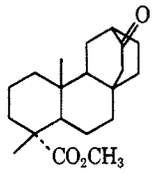

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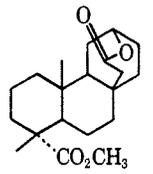

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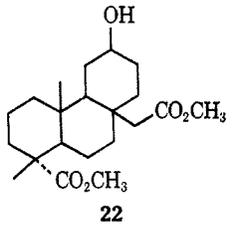

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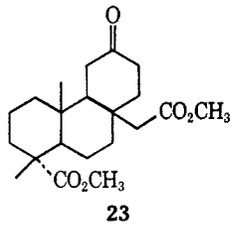

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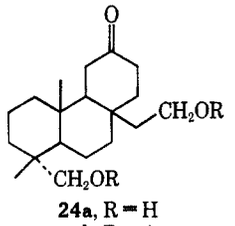


24a, R = H
b, R = Ac

possible that bromo lactonization of **4a** results in the formation of both C-13 epimeric bromo lactones **13a** and **13b** by *cis* as well as by the usual *trans* mode of addition to the bridge double bond, because, as has already been mentioned earlier, the peculiar geometry of levopimaric acid adducts interferes greatly with attack from the side of ring A.[15,16] Only one of the two epimers might then be favorably disposed conformationally or sterically for the elimination reaction which leads to **5**.[17]

Ozonolysis of **5b** proceeded smoothly to the keto lactone **15** which was reduced to **16a** in 90% yield with chromous chloride. Contrary to expectations, reduction of **16a** with various metal hydrides did not effect exclusive or even predominant formation of hydroxy acid **17** by reagent approach from the unhindered side. Instead, a difficultly separable mixture of epimers was produced from which a small amount of **17** was eventually isolated by preparative tlc.[18] This result interfered with the projected route to trachylobanic acid which required protection of the C-13 hydroxyl group of **17**, degradation of the carboxyl group at C-15 to a ketone, methylation to **18**, and intramolecular base-catalyzed alkylation at C-16 *via* the mesylate or tosylate.

In exploring an alternate path to **2b**, **17a** was converted into **19** (configuration at C-15 tentative) in 79% yield by the Barton modification[19] of the Hunsdiecker reaction. Reduction of **19** with tri-*n*-butyltin hydride[20] proceeded quantitatively and afforded the previously reported[21] ketone **20**. Treatment of this now readily available substance with *m*-chloroperbenzoic acid furnished the lactone **21** whose nmr spectrum (H-12 triplet at 4.56, AB system of H-14a and H-14b centered at 2.75 ppm) demonstrated that the Baeyer–Villiger oxidation had taken the expected course.

An attempt to reduce the lactone to the hydroxyaldehyde with diisoamylborane was not successful, so recourse was had to a more circuitous route. Hydrolysis of **21** and reesterification furnished **22**, which on dehydration gave a mixture of olefins, since ring C had reverted into the chair form on opening of the lactone bridge, thus making the hydroxyl group equatorial. Oxidation of **22** with Jones reagent yielded **23** which was converted into the ketodiol **24a**, characterized as the diacetate **24b**, *via* the ketal, lithium aluminum hydride reduction, and deketalization. An attempt to prepare **24a** more directly by hydride reduction of **21** and oxidation of the secondary hydroxyl group of the resulting triol with N-bromoacetamide was not satisfactory because of poor yields in the first step due to solubility problems and failure to achieve selective oxidation in the second.

The proposed route to the trachylobanes from **24a** required elaboration into a 8-formylmethyl-Δ^{12}-13-methyl derivative which in the form of its tosylhydra-

(14) The nmr signal of H-14 at 4.85 ppm is also more nearly in the range of hydrogen under lactone ether oxygen than of R_2CHBr.

(15) A similar instance of *cis* addition to the 13,14 bridge of maleopimaric anhydride has been claimed recently.[16]

(16) N. Langlois and B. Gastambide, *Bull. Soc. Chim. Fr.*, 2966 (1965).

(17) Because of the appearance of the C-10 methyl signal at the somewhat deshielded frequency of 1.08 ppm, we tentatively assign formula **13b**, the product of the usual *trans*-bromo lactonization reaction, to the unreactive bromo lactone.

(18) The assignment was based on a comparison of the C-10 methyl frequency at 1.10 ppm with the C-10 methyl frequencies of **31** and **32** (*vide infra*).

(19) D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965).

(20) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); see also H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965).

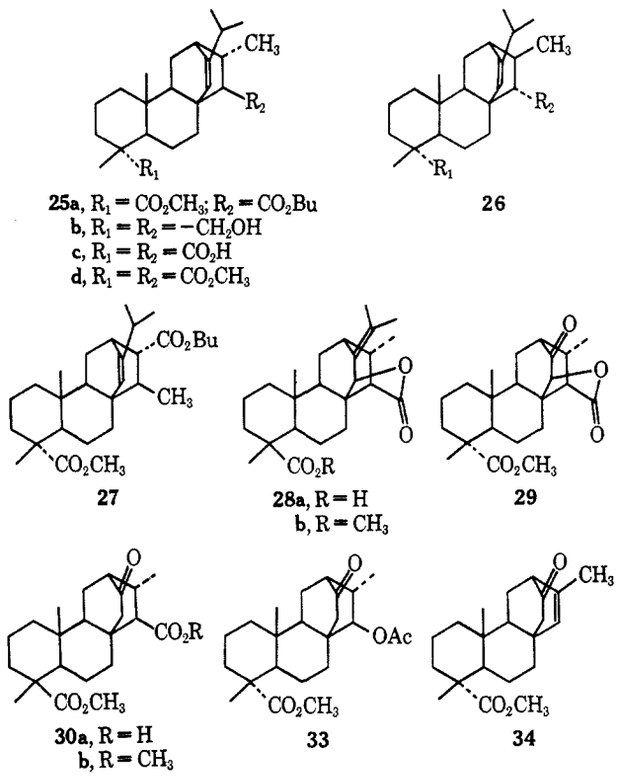
(21) L. H. Zalkow and N. N. Girotra, *ibid.*, **28**, 2037 (1963).

zone was expected to undergo intramolecular cyclization to **2b** in an aprotic medium.[22] However, the number of steps envisaged in this and the preceding scheme prompted us to reexamine the more direct approach requiring a Diels–Alder reaction between levopimaric acid and a crotonic derivative which, it will be recalled, had been studied earlier without success. After considerable experimentation it was finally discovered that the reflux temperature of a mixture of methyl levopimarate and *n*-butyl crotonate provided optimum conditions for the formation of two adducts in approximately 60% total yield. Isomerization to abietic acid and disproportionation to dehydroabietic acid accounted for the remainder of starting material. The yield of the two adducts (52 and 7%) was based on glpc analysis since they could not be separated satisfactorily by column chromatography. In practice the mixture was hydrolyzed directly, most of the diacid corresponding to the major adduct, crystallizing on acidification. The mother liquors were converted into the methyl esters which were separated by column chromatography.

Lithium aluminum hydride reduction of the two adducts separately yielded the same diols obtained by reduction of the methyl esters. Hence hydrolysis of the adducts was not accompanied by epimerization, and the acids or methyl esters could be used to assign structures to the adducts. The reactions to be discussed subsequently clearly demonstrate that the carbobutoxy group of the major adduct is attached to C-15 of the basic carbon skeleton and that its orientation is *endo* to the unsaturated bridge or β. If the configuration of the dienophile were maintained during the diene synthesis, the orientation of the C-16 methyl group of the major adduct should be *trans* to the carbobutoxy group or α, as in **25a**. Evidence for the correctness of this formulation will be presented in the sequel together with a discussion of the probable configuration of the minor adduct.

Oxidation of the dibasic acid **25c** obtained from the major adduct whose nmr spectrum was comparable to that of **4b**[11a] but had an extra signal attributable to the secondary methyl group presented the same difficulties encountered during the oxidation of **4c**, due to facile further oxidation of the primary product. In practice it proved simplest to carry out the oxidation with a limited amount of oxidizing agent at low temperature for a short time period. This resulted in the formation of the desired lactone **28a** in about 35% yield, mixed with a considerable amount of starting material and some over-oxidation products. Separation was effected by partitioning with carbon tetrachloride in which **27a** was insoluble and converting the acid into the methyl ester **28b**. That **28b** was a γ-lactone was revealed by the ir spectrum which had carbonyl bands at 1783 (γ-lactone) and 1730 cm^{-1} (ester). That the lactone ring was closed to C-14 was shown by the nmr spectrum which, just like that of **5b**, displayed a singlet at 4.83 and two vinyl methyl signals at 1.77 and 1.71 ppm. The lactone carbonyl of **28b**, and hence the carbobutoxy group of **25a**, was therefore attached to C-15 and had the β orientation.

(22) For analogies, see G. Büchi and J. D. White, *J. Amer. Chem. Soc.*, **86**, 2884 (1964); G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *ibid.*, **87**, 935 (1965); M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).



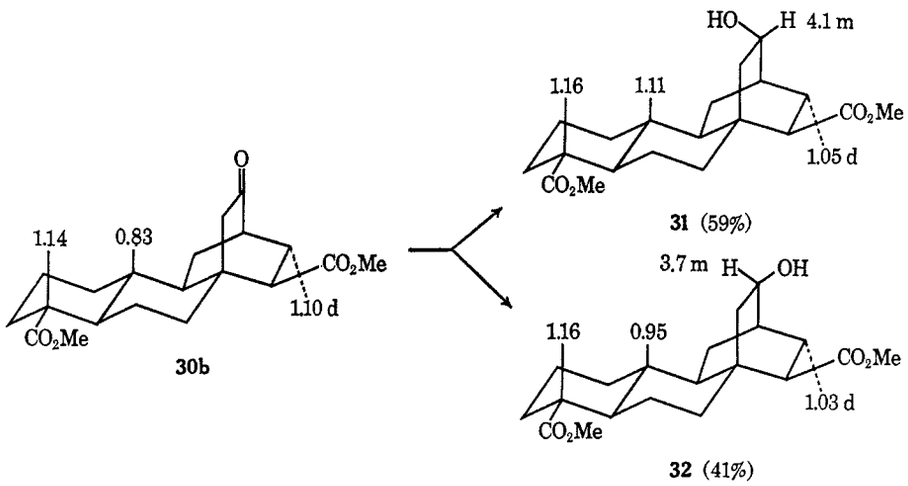
Our experience with the lower homolog **5b** now saved us the trouble of further experimentation and resulted in uniformly high yields. Ozonolysis of **28b** proceeded quantitatively. The resulting keto lactone **29** which possessed the required spectral properties — carbonyl bands at 1797, 1745 (γ-keto lactone), and 1723 cm^{-1} (ester) — was converted with chromous chloride in quantitative yield into **30a** which was further characterized as the methyl ester **30b**. Sodium borohydride reduction of the latter gave two epimeric alcohols **31** and **32** (Scheme I) in 59 and 41% yield,[23] respectively, the examination of whose nmr spectra permitted assignment of configuration to the C-16 methyl group, although this was not relevant to the contemplated synthesis.

The premise that the predominating direction of attack by hydride ion should lead to epimer **31** was supported by the nmr spectrum of the major product which displayed chemical shifts for C-10 methyl and H-13 significantly lower than those found for the corresponding signals in the nmr spectrum of the minor product. In a compound of formula **31**, C-10 methyl would be deshielded by C-13 hydroxyl, and H-13 would be deshielded by C-15 carbomethoxy, compared with the effects to be expected in a substance of formula **32**. Hence, the major epimer was indeed **31**. Since the chemical shift of the methyl doublet (C-16 methyl) was the same in both **31** and **32**, the secondary methyl group of **32** is not subject to the deshielding influence of a hydroxyl group and must be α in **32**, **31**, and all of their precursors. This settled the structure of the major Diels–Alder adduct as **25a**.

With this matter clearly established, some comments on the structure of the minor Diels–Alder adduct for

(23) In view of the obstruction generally interposed to attacks from the side of ring A, this relatively even proportion of products was somewhat surprising, but may to a certain extent be due to interference by the carbomethoxy group.

SCHEME I



which we adopt the tentative formula **26a** are in order. Failure to obtain a saturated lactone by acid treatment of **26c** or a hydroxylated or unsaturated lactone by permanganate oxidation indicated that the carbobutoxy group of the minor adduct should be *exo* to the bridge double bond. Furthermore in the nmr spectra of **26b–d**, the signal of C-16 methyl group appeared at considerably higher field (*ca.* 0.8 ppm) than in the nmr spectra of **25b–d** (*ca.* 1.05 ppm).[24,25] This observation could be accounted for by assuming that the secondary methyl group of the minor adduct and its derivatives was *endo* to, hence shielded by, the bridge double bond and required that its structure be formulated as **26a** or **27**.

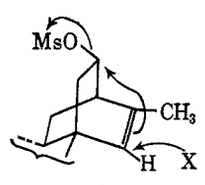
An attempt to distinguish between these two possibilities encountered unexpected complications with which we shall deal in a subsequent report. For reasons too involved to discuss here we have, however, tentatively adopted **26a** as the structure of the minor adduct.

We now return to the sequence of reactions which led to the synthesis of methyl *anti*-trachylobanate. Oxidative decarboxylation of **30a** with lead tetraacetate in the conventional manner resulted in a 45% yield of **33** (*endo* configuration of acetate suggested by the coupling constant of H-15). When the reaction was carried out in the presence of cupric acetate as recommended by Kochi,[26] the main product, formed in 79% yield, was the olefin **34**. This was evident from the nmr spectrum which exhibited not a methyl doublet like the precursor **30a** or **33**, but a narrowly split signal at 1.75 ppm characteristic of vinyl methyl which was spin coupled to the signal of a vinyl proton at 5.8 ppm. Small amounts of **29** and **33** were also formed.

Reduction of **34** with lithium tri-*t*-butoxyaluminum hydride furnished two epimeric alcohols in 82 and 16% yield. The major isomer was assigned formula **35** on steric grounds and because of the nmr spectra (Scheme II). In the major isomer the signal of C-10 methyl is found farther downfield, due to deshielding by the hydroxyl group, and the signal of H-13 is much farther upfield, due to shielding by the π-electron system of the double bond, as would be expected if the hydroxyl group were oriented toward ring A. Because the minor isomer **36** could be reoxidized to **34**, the over-all yield of the desired isomer **35** was better than 90%.

When an attempt was made to protect the hydroxyl group of **35** through the mesylate prior to hydroboration of the double bond, spontaneous cyclization of **35** to a compound possessing the trachylobane skeleton took place unexpectedly. The structure of **37**, which was isolated in 60% yield, was manifested in the nmr spectrum (Scheme II) which, instead of the vinyl methyl and vinyl proton signals of precursor **35**, displayed a methyl singlet at 1.21 and a singlet at 3.30 ppm characteristic of hydrogen under hydroxyl. Further proof for the pentacyclic nature of the new alcohol was provided by its oxidation in 85% yield to **38** which was clearly a cyclopropyl ketone as revealed by the uv spectrum [λ_{max} 211 and 285 nm (ϵ_{max} 2620 and 72)].

The cyclization of the bicyclo[2.2.2]octenol **35** is formally analogous to the acetolysis of bicyclo[2.2.2]-oct-5-en-2-ol tosylate[27] which leads to the predominant formation of tricyclo[2.2.2.$0^{2,6}$]octan-3-ol owing to participation by the 2,3 double bond. Hence, the formation of **37** might be represented by process B (X = H_2O). Since evidence for the formation of a mesylate could not be procured, it is also possible that mesyl chloride acts as a Lewis acid which, assisted by the double bond of **35**, produces a stabilized cationic inter-



B

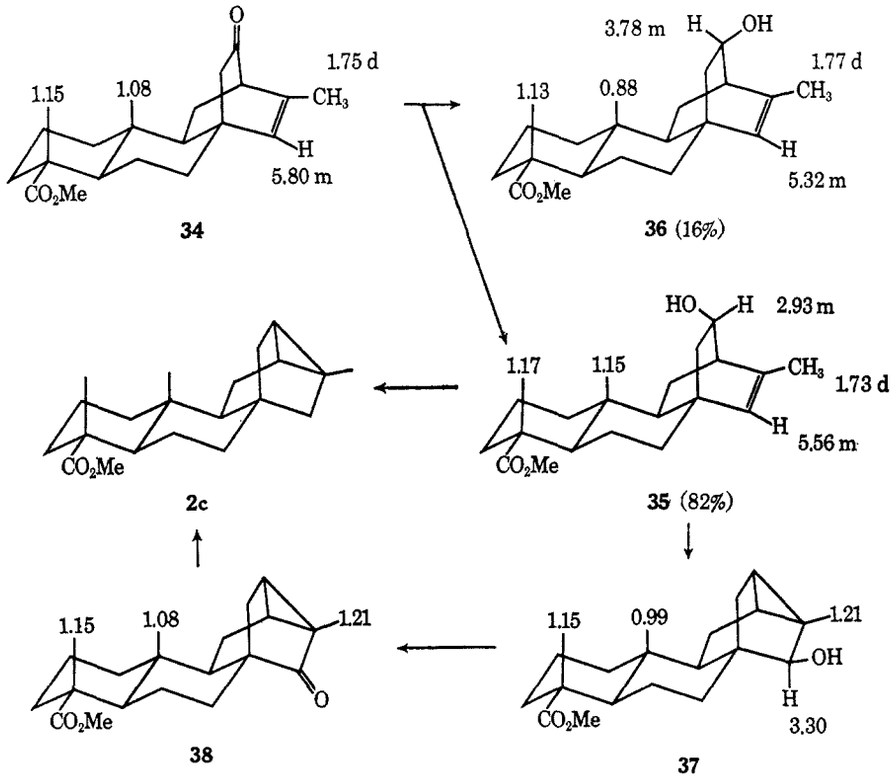
(24) Although this signal is generally a doublet, it is a singlet in **25b, c,** and **d** and some esters of **25c** not reported in this paper, presumably because *endo* H-16 in these compounds is shielded by the bridge double bond, thus reducing $\Delta\delta$ 16-methyl, H-16 to a value smaller than $J_{16\text{-Me, H-16}}$. Other reports of this phenomenon have appeared.[25]

(25) G. Slomp, Jr., and B. R. McGarvey, *J. Amer. Chem. Soc.*, **81**, 2200 (1959); F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961); J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960).

(26) J. K. Kochi, *J. Amer. Chem. Soc.*, **87**, 1811 (1965); J. D. Bacha and J. K. Kochi, *Tetrahedron*, **24**, 2215 (1968). According to these authors, the formation of olefin is due to the circumstance that cupric ion is a far better oxidizing agent for the intermediate radical than tri- or tetravalent lead and that the oxidation with cupric ion proceeds directly to alkene, if a β hydrogen is present, rather than through a carbonium ion which can rearrange or collapse to acetate.

(27) N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, **85**, 3193 (1963).

SCHEME II



mediate which then reacts with added nucleophile to form **37**.

The facile cyclization of **35** to **37** suggested that addition of hydride ion to a solution of the mesylate or cationic intermediate might, by the process adumbrated in B (X = H^-), lead directly to methyl 13,16-cycloatisanoate (**2c**).[28] In fact the reaction proceeded as hoped for though only in about 17% yield and gave material identical in all respects (ir, nmr, glpc, tlc) with methyl trachylobanate (**1c**). The analogous cyclization of the *anti*-tosylate of bicyclo[2.2.2]oct-5-en-ol under the influence of lithium aluminum hydride has been described recently.[29]

Although substitution of boron trifluoride for methanesulfonyl chloride effected a yield improvement to 40%, **2c** from this as well as from the preceding cyclization experiment could not be freed satisfactorily from small amounts of contaminants, possibly rearrangement products,[29] which lowered the melting point of the synthetic material to 105–110° as compared with the reported mp 110–112°. A somewhat purer sample of **2c** was therefore prepared in 60% yield from **38** *via* the ethylene thio ketal. This material, mp 109–111°, was indistinguishable from authentic methyl trachylobanate (**1c**)[30] in all respects, but had the opposite rotation.

Experimental Section[31]

Oxidation of 4a with Alkaline Permanganate.—The high yield of lactone **5a** reported previously could not be realized. The experiment which follows illustrates the separation of the minor products. The benzene solvate of diacid **4a**,[11a] 3.78 g (8.2 mmol), was dissolved in 25 ml of water containing 0.8 g (20 mmol) of sodium hydroxide. The solution was cooled to 10°, and to it was added an ice-cold solution of 1.58 g (10 mmol, 3.8 equiv) of potassium permanganate in 75 ml of water. The mixture was kept in the refrigerator for 6 hr. The manganese dioxide was removed by filtration with the aid of Celite, and the colorless filtrate was acidified with 5 *N* aqueous hydrochloric acid. The precipitate was extracted with ether, and the washed and dried extract was concentrated to about 5 ml. Carbon tetrachloride was added, and the insoluble material was collected, taken up in methanol, and methylated with excess ethereal diazomethane. Removal of the solvents gave diol **7** as a colorless solid which crystallized from chloroform–methanol as needles: yield, 0.49 g (14%); mp 226–227°; ν_{max} 3550 (OH) and 1735–1725 cm^{-1} (double intensity, δ-lactone and ester); $\nu_{max}^{CHCl_3}$ 3550 (OH), 1755 (δ-lactone), and 1725 cm^{-1} (ester); nmr 4.39 (H-14), 3.69 (methoxyl), 3.48 (methanol of crystallization), 1.38 (6 H, isopropyl), 1.20 (C-4 methyl), and 1.12 ppm (C-10 methyl). This compound clung tenaciously to methanol which could not be removed completely, even after drying at 100° (1 mm) for 18 hr. The analytical sample was dried at 78° (1 mm) for 16 hr.

Anal. Calcd for $C_{24}H_{36}O_6 \cdot 0.5CH_3OH$: C, 67.44; H, 8.77. Found: C, 67.25; H, 8.72.

The carbon tetrachloride filtrate remaining after separation of **7** was evaporated, and the residue was methylated with diazomethane to give 1.2 g of solid, mp 170–190°, which was taken up in benzene and chromatographed on 100 g of alumina. Elution benzene gave 0.05 g (1.5%) of diester **4b** which crystallized from aqueous methanol as colorless needles: mp and mmp 68–69°; ir spectrum identical with that of authentic material.

Continued elution with benzene furnished 1.05 g (33%) of lactone **5b** which crystallized from ethanol as colorless needles: mp 196–197°; $[\alpha]D$ −90° (*c* 0.575); ν_{max} 1780 (γ-lactone), 1725 (ester), and 1675 cm^{-1} (w) (olefin); $\nu_{max}^{CCl_4}$ 1785 (γ-lactone), 1730 (ester), and 1670 cm^{-1} (olefin); nmr 5.03 (H-14), 3.66

(28) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **84**, 4876 (1962); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewis, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(29) R. A. Appleton, J. C. Fairlie, and R. McCrindle, *Chem. Commun.*, 690 (1967).

(30) We wish to thank Professor G. Ourisson and Dr. G. Hugel for a generous sample of **1c**.

(31) Melting points were taken in capillaries and are uncorrected. Unless otherwise specified, rotations were run in chloroform, uv spectra in 95% ethanol, ir spectra as Nujol mulls and nmr spectra in deuteriochloroform with tetramethylsilane as the internal standard. R_f values apply to thin layer chromatograms on silica gel G plates using benzene–ethyl acetate (5:1) as the solvent system unless otherwise stated. Analyses were made by Dr. F. Pascher, Bonn, Germany.

(methoxyl), 1.78, 1.73 (vinyl methyl singlets), 1.18 (C-4 methyl), and 0.73 ppm (C-10 methyl); R_f 0.70.

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.91; H, 8.56.

Elution with benzene–ether (7:3) afforded 0.20 g (6%) of epoxy lactone **6** which crystallized from benzene–hexane as colorless prisms: mp 261–262°; ν_{max} 1785 (γ-lactone) and 1725 cm^{-1} (ester); $\nu_{max}^{CCl_4}$ 1795 (γ-lactone) and 1735 cm^{-1} (ester); nmr 4.35 (H-14), 3.69 (methoxyl), 1.40 (6 H, isopropyl methyl singlets), 1.20 (C-4 methyl), and 0.83 ppm (C-10 methyl); R_f 0.3.

Anal. Calcd for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 71.26; H, 8.53.

In subsequent work use of stoichiometric amounts of potassium permanganate at pH 8.5–10 (measured on a pH meter) gave 40–50% **5a**, 40–50% starting material **4a**, and some by-products (nmr and glpc analysis). Since starting material was easily precipitated with carbon tetrachloride, in which **5a** is soluble, reasonably pure **5a** was obtained relatively readily by this procedure. Use of excess potassium permanganate resulted in a lower yield of **5a** and lower yields of starting material. Use of a large excess of potassium permanganate and destruction of excess oxidant, after 26 sec by pouring the mixture into hydroxylamine hydrochloride solution, gave a 60–70% yield of lactone **5a** when carried out on less than 1-g quantities; but on a larger scale the volume of liquid involved made this method impractical.

Oxidation of 7.—A stirred solution of 0.2 g of **7** in 20 ml of acetic acid was treated dropwise at room temperature with Jones reagent until a brown color persisted. The mixture was diluted with water and saturated with salt, and the precipitate was collected. Crystallization from aqueous methanol gave 0.16 g of **8** as colorless needles: mp 198–199°; ν_{max} 3550 (OH), 1755 (γ-keto δ-lactone), 1740 (ester), and 1705 cm^{-1} (ketone); nmr 3.68 (methoxyl), 1.47, 1.36 (isopropyl methyl singlets), 1.20 (C-4 methyl), and 0.85 ppm (C-10 methyl).

Anal. Calcd for $C_{24}H_{34}O_6$: C, 68.87; H, 8.19. Found: C, 68.53; H, 8.12.

Epoxidation of 5a.—A mixture of 0.27 g of **5a** and 0.30 g of *m*-chloroperbenzoic acid in 30 ml of chloroform was kept at room temperature for 18 hr then shaken successively with aqueous potassium iodide and aqueous sodium thiosulfate. The layers were separated; the aqueous layer was extracted with chloroform; and the extract was combined with the original chloroform phase and washed thoroughly with 1 *N* aqueous sodium hydroxide to remove *m*-chlorobenzoic acid. Evaporation of the washed and dried organic phase gave 0.23 g (82%) of **6** which crystallized from benzene–hexane: mp and mmp 261–262°; ir spectra identical with that of **6** above. Compound **6** was unaffected by treatment with perchloric or formic acids.

Epoxidation of 4b.—A mixture of 1.77 g of **4b** and 3.4 g of *m*-chloroperbenzoic acid in 100 ml of chloroform was kept at room temperature for 16 hr. Work-up as usual gave 1.75 g (95%) of oily **9**: R_f 0.61; $\nu_{max}^{CCl_4}$ 1725 cm^{-1} (esters) and no olefinic absorption; nmr 3.63 and 3.61 (2 methoxyls), 3.13 (H-14), 1.17 (C-4 methyl), 1.03 (d), 0.74 (d, isopropyl methyls, both J = 7 cps), and 0.83 ppm (C-10 methyl). The same epoxide was also prepared by epoxidation of diacid **4a**, methylation of the crude product, and chromatography on alumina. Elution with benzene gave oily **9** (55%); ir and nmr spectra were superimposable.

Acid Treatment of 9.—Two drops of 70% perchloric acid was added to a solution of 1.04 g of **9** in 30 ml of acetone, and the mixture was kept for 8 hr at room temperature. Water was added until incipient crystallization, and the crystalline product was collected. Crystallization from methanol gave 0.4 g of **10** as colorless needles: mp 180–181°; ν_{max} 1740–1710 (broad, esters and ketone) and no hydroxyl; nmr 3.65 and 3.61 (2 methoxyls), 1.27 (d, 6 H, isopropyl methyl), 1.12 (C-4 methyl), 0.93 (d, 6.5 H, isopropyl methyl), and 0.73 ppm (C-10 methyl); R_f 0.70.

Anal. Calcd for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found: C, 71.61; H, 9.20.

Treatment of **9** for 1 hr at 25° with 90% formic acid and dilution with water gave the same ketone **10** (mixture melting point, nmr) in 60% yield.

Bromination of 4a. A. In Methanol–Carbon Tetrachloride.—A solution of 2 g of **4a** in 50 ml of methanol was treated with excess bromine in carbon tetrachloride for 40 min at 25°, then diluted with water, and extracted with ether. The extract was washed with water, aqueous sodium thiosulfate, and water, dried, and evaporated. The residue was methylated with diazomethane to give an oil which was chromatographed on a column of 80 g of alumina prepared in benzene. Elution with benzene–ether (4:1) gave 0.3 g of bromo lactone **13** which crystallized from methanol as needles: mp 260–262° dec; $\nu_{max}^{CHCl_3}$ 1780 (γ-lactone) and 1725 cm^{-1} (ester); nmr 4.85 (H-14), 3.68 (methoxyl), 1.20 (s, C-4 methyl), 1.08 (C-10 methyl), 1.02 (d), and 0.99 (d, each 6.5 H, isopropyl methyls).

Anal. Calcd for $C_{24}H_{35}O_4Br$: C, 61.66; H, 7.54; Br, 17.09. Found: C, 61.36; H, 7.64; Br, 17.30.

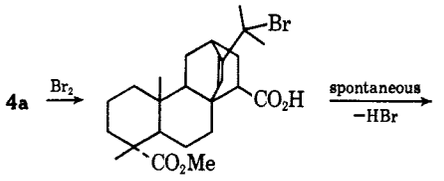
Elution with benzene–ether (7:3, 1:1) gave 0.5 g of **11** which crystallized from acetone–hexane as needles: mp 241–243°; ν_{max} 3500 (OH), 1760 (γ-lactone), and 1715 cm^{-1} (ester); nmr 5.01 (H-14), 4.18 (2 H, C≡C—CH_2OH), 3.68 (s, methoxyl), 1.87 (vinyl methyl), 1.19 (C-4 methyl), and 0.73 ppm (C-10 methyl).

Anal. Calcd for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 71.11; H, 8.55.

B. In Chloroform.—A solution of diacid **4a** in chloroform was treated with bromine in chloroform for 10 hr at 25°. Copious fumes of HBr were evolved shortly after addition. The mixture was worked up and methylated as above, and the product was chromatographed on alumina. Benzene–ether (9:1) eluted 1.6 g of **13**; benzene–ether (4:1, 1:1) gave 6.4 g of **11**. Finally, ether–methanol (4:1) gave 2.8 g of dihydroxy lactone **12** which crystallized from acetone–hexane as colorless needles: mp 218–219°; ν_{max} 3400 (OH), 1780 (γ-lactone), 1750 (possibly γ-lactone intermolecularly hydrogen bonded), and 1720 cm^{-1} (ester); nmr 5.15 (H-14), 4.41, 4.35 (2 H each, C≡C—CH_2OH), 3.67 (s, methoxyl), 1.20 (C-4 methyl), and 0.80 ppm (C-10 methyl).

Anal. Calcd for $C_{24}H_{34}O_6$: C, 68.87; H, 8.19. Found: C, 69.56; H, 8.11.

C. Direct Bromination.—A mixture of 1 g of monomethyl ester **4c** and 2.1 g of sodium acetate in 10 ml of carbon tetrachloride was irradiated with a 250-W light bulb while 10 ml of 0.92 *m* solution of bromine in carbon tetrachloride was being added dropwise with stirring; the temperature was kept at −30 to −20°. Stirring was continued for 2.5 hr. Excess bromine was destroyed with sodium sulfite. The solvent was removed *in vacuo*, and the residue was taken up in ether, washed, dried, concentrated, and purified by preparative tlc. There was obtained 0.64 g of **5a** contaminated by a trace of an unknown impurity. Scaling up of this procedure reduced the yield. When the bromination was carried out at 0° or higher, the formation of side product complicated the reaction mixture. Indications (nmr analysis) were that the reaction proceeded *via* the path shown.



i

5b $\xrightarrow{Br_2}$ further bromination products

The presence of intermediate i was suggested by the nmr spectrum which revealed a component containing a vinyl proton at C-14 and four tertiary methyl groups, two of them attached to carbon containing halogen.

Iodo Lactonization of 4a.—A solution of 7.25 g of **4a** in 250 ml of water containing 25 g of sodium bicarbonate was mixed with a solution of 10 g of iodine and 19.24 g of potassium iodide in 60 ml of water, stirred for 7 days at room temperature (a longer reflux period did not increase the per cent conversion), acidified with 10% sulfuric acid solution, and extracted thoroughly with ether. The ether extracts were washed with water, thiosulfate, and water, dried, and evaporated. The residue was refluxed with 200 ml of N,N-dimethylformamide for 2 hr; the solvent was removed at reduced pressure; and the residue was methylated with ethereal diazomethane. The crude product, 5.85 g, was chromatographed over 210 g of Alcoa alumina F-20. Elution with benzene (1400 ml) and ether–benzene (1:19, 400 ml) furnished 3.0 g of **4b**. Further elution with ether–benzene (1:9, 1,4,2,3) gave 1.9 g of **5b**.

Ozonolysis of 5b.—A slow stream of ozone was passed through a solution of 2.5 g of **5b** in 50 ml of chloroform until a potassium

iodide trap became discolored, and passage of ozone was continued for 1 hr (total time about 3 hr). The solution was shaken successively with aqueous potassium iodide, aqueous sodium thiosulfate, and water, dried, and evaporated. The solid residue (**15**) crystallized from either ethanol or acetone as colorless plates: mp 263–264°; yield, 1.2 g; ν_{max} 1805 (γ-lactone), 1735 (ester), and 1720 cm^{-1} (ketone); nmr 4.31 (H-14), 3.70 (methoxyl), 1.18 (C-4 methyl), and 0.77 (C-10 methyl).

Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 70.31; H, 8.13.

The same substance was obtained by ozonolysis of **11** and **12**.

Chromous Chloride Reduction of 15.—A solution of 0.2 g of **15** in 100 ml of methanol was deaerated by cautious addition of Dry Ice. Excess 2 *M* chromous chloride in 2 *N* hydrochloric acid was added, and after 0.5 hr the mixture was diluted with water, saturated with salt, and extracted thoroughly with ether. The extracts were washed with water and then extracted well with 2 *N* aqueous sodium hydroxide solution. The ether layer was washed again with water, dried, and evaporated to give a trace of starting material. The alkaline washings were cooled in ice and acidified with excess 5 *N* hydrochloric acid. The white precipitate of **16a** was collected, washed well with water, and dried by suction. Crystallization from methanol gave 0.18 g of colorless prisms: mp 271–272°; ν_{max} 1725 (ester and ketone) and 1690 cm^{-1} (acid); nmr 8.66 (broad, COO**H**, removed by shaking with D_2O), 3.68 (methoxyl), 1.15 (C-4 methyl), and 0.82 (C-10 methyl).

Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.58; H, 8.34. Found: C, 69.14; H, 8.37.

The methyl ester **16b** was prepared by treating **16a** with ethereal diazomethane and was crystallized from aqueous methanol as colorless needles: mp 132–133°; R_f 0.63; ν_{max} 1730–1720 cm^{-1} (broad, two esters and ketone); nmr 3.68 (two methoxyls), 1.16 (C-4 methyl), and 0.83 (C-10 methyl).

Anal. Calcd for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57. Found: C, 70.21; H, 8.51.

$NaBH_4$ Reduction of 16a.—A solution of 0.2 g of **16a** in 40 ml of methanol was mixed with 2 ml of aqueous 2 *N* sodium hydroxide solution containing 42 mg of $NaBH_4$. Tlc indicated little reduction after 4 hr at room temperature, so a large excess of $NaBH_4$ was added, and the mixture was left overnight, diluted with water, acidified, and worked up in the usual way. Tlc of the crude product (0.2 g) indicated the presence of two main products. Preparative tlc (4% methanol–chloroform developed twice, then 10% isopropyl alcohol–chloroform developed twice) resulted in the isolation of crystalline **17** which was recrystallized from carbon tetrachloride and then had mp 260–262°; nmr 4.1 (c, H-13), 3.74 (methoxyl), 1.18 (C-4 methyl), and 1.10 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85; O, 21.95. Found: C, 69.02; H, 9.11; O, 21.98.

Repetition of the reduction and acetylation of the crude product with acetic anhydride resulted in a 1:1 mixture (nmr spectrum) of epimeric acetates which could not be separated by tlc. Reduction followed by reflux with acetic anhydride resulted in a gummy neutral fraction (lactone bands at 1760 and 1730 cm^{-1}) and a small yield of acid, mainly **17a**. Reduction with sodium borohydride or lithium tri-*t*-butoxyaluminum hydride also gave mixtures of epimers.

8-Carboxymethyl-5a,8-dimethyl-1-iodo-1H-3,10a-dodecahydroethanophenanthren-12-one (19).—A mixture of 0.3 g (0.83 mmol) of **17a** and 0.50 g (1.15 mmol) of lead tetraacetate in 15 ml of carbon tetrachloride was refluxed under nitrogen for 10 min and then irradiated with a 250-W lamp while a solution of iodine in carbon tetrachloride was added dropwise. When the iodine color persisted (after about 4 hr), the mixture was cooled and filtered, and the precipitate of lead acetate was washed well with chloroform. The filtrate and washings were washed successively with aqueous sodium thiosulfate, water, 2 *N* aqueous sodium hydroxide, and water, dried, and evaporated under reduced pressure at 40° to prevent decomposition. The residual colorless oil crystallized from methanol at 0° to give 0.29 g (79%) of iodide **19** as colorless needles: mp 163–164°; R_f 0.82; ν_{max} 1725 cm^{-1} (ester and ketone); nmr 4.33 (t, broad, 7.5 H, H-16), 3.66 (methoxyl), 1.14 (C-4 methyl), and 0.81 ppm (C-10 methyl).

Anal. Calcd for $C_{20}H_{29}IO_3$: C, 54.05; H, 6.58; I, 28.56. Found: C, 54.40; H, 6.40; I, 28.71.

Reduction of 19 with Tri-*n*-butyltin Hydride.—A solution of crude **19** (from 6 g of acid **17a**) in 50 ml of benzene was stirred at room temperature for 18 hr with a excess (about 10 ml) of tri-*n*-butyltin hydride.[20] The reaction mixture was shaken with dilute hydrochloric acid to convert excess reagent into the chloride, and the dried organic phase was concentrated and poured onto a column of alumina prepared in hexane. Elution with hexane gave tri-*n*-butyltin chloride and iodide, while elution with benzene–ether (9:1) gave 4.1 g of **20** (78% from **17a**) which crystallized from hexane and had mp 129–130° (lit.[21] mp 129–130°); R_f 0.62.

Baeyer–Villiger Oxidation of 20.—A mixture of 4.8 g of **20** and 9.0 g of *m*-chloroperbenzoic acid in 400 ml of chloroform was refluxed for 18 hr. The cooled solution was washed with 1 *N* aqueous sodium hydroxide and water, dried, and evaporated to furnish a solid which was purified by chromatography on alumina in hexane. Elution with benzene–ether (4:1) gave 3.0 g of **21** which crystallized from methanol as colorless needles: mp 187–188°; ν_{max} 1735–1720 cm^{-1} (broad, ester and lactone); nmr 4.56 (t, H-12, $J \cong 3$ cps), 3.65 (methoxyl), 3.00 (*ca.* d), 2.53 (broad, 1 H each, C-14 methylene, $J_{doublet} = 1.5$ cps), 1.17 (C-4 methyl), and 0.98 ppm (C-10 methyl).

Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.50; H, 8.56.

Preparation of 23.—A mixture of 3.6 g of **20** and 3.5 g of sodium hydroxide in 150 ml of 10% aqueous ethanol was refluxed for 2 hr, then poured into water, and extracted once with ether to remove traces of neutral material. The aqueous layer was acidified with 5 *N* hydrochloric acid, saturated with salt, and extracted with ether thrice. The extracts were washed with brine, dried, concentrated, and treated with excess ethereal diazomethane. Removal of the solvent afforded 3.0 g of **22** as an oil: $\nu_{max}^{CHCl_3}$ 3500 (OH) and 1730 cm^{-1} (esters); nmr 3.68, 3.66 (methoxyls sitting on H-12 multiplet), 2.57 (two protons, CH_2–CO_2Me), 1.17 (C-4 methyl), and 0.86 ppm (C-10 methyl).

The crude alcohol **22** was oxidized with Jones reagent in acetone until a brown color persisted. The product was isolated with ether. Evaporation of the washed and dried extract gave **23** as an oil which slowly crystallized from aqueous 2-propanol: mp 118–120°; nmr 3.68 (two methoxyls), 2.70 (2 H, CH_2CO_2Me), 1.20 (C-4 methyl), and 0.90 ppm (C-10 methyl). The yellow dinitrophenylhydrazone was crystallized from methanol and had mp 212–213°.

The ketone also formed a crystalline ketal which crystallized from aqueous methanol as colorless needles: mp 87–88°; ν_{max} 1725 cm^{-1} (esters) and no hydroxyl absorption; nmr 3.94 (4 H, ketal), 3.65, 3.62 (methoxyls), 2.54 (2 H, CH_2CO_2Me), 1.16 (C-4 methyl), and 0.83 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{36}O_6$: C, 67.62; H, 8.88. Found: C, 67.57; H, 8.62.

Preparation of 24b.—A solution of 0.4 g of the preceding ketal in anhydrous ether was added to a suspension of lithium aluminum hydride in anhydrous ether, and the mixture was refluxed for 1.5 hr. Excess reagent was decomposed with wet ether, methanol, and 1 *N* HCl. The washed and dried ether layer was evaporated, and the residue was treated with aqueous hydrochloric acid in acetone at 25° for 1 hr. The mixture was diluted and saturated with salt, and the product was isolated with ether to give **24a**, contaminated with some ethylene glycol.

The crude diol was acetylated to the keto diacetate **24b**, which was purified by chromatography on a column of silica gel prepared in hexane. Elution with benzene–ether (4:1) gave pure **24b** as an oil: $\nu_{max}^{CCl_4}$ 1740 (two acetates) and 1705 cm^{-1} (ketone); nmr 4.16 (t, 2 H, $-CH_2-CH_2-OAc$, $J = 7.5$ cps), 3.94, 3.65 (AB quartet, 2 H, CH_2OAc a tC-4, $J_{AB} = 11$ cps), 2.06 (two acetates), 0.94 (C-4 methyl), and 0.87 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{36}O_5$: C, 70.38; H, 9.24. Found: C, 70.19; H, 9.16.

Diels–Alder Reaction of Methyl Levopimarate and *n*-Butyl Crotonate.—Crystalline methyl levopimarate, prepared from 30 g of levopimaric acid and diazomethane in ether, was dissolved in 30 ml of freshly distilled *n*-butyl crotonate and refluxed in a nitrogen atmosphere (liquid temperature 190–200°) for 18 hr. An additional 30 ml of *n*-butyl crotonate was added slowly to maintain the temperature at 190–200°. Distillation at 50–80° (0.05 mm) resulted in removal of excess crotonate; the residue on glpc (glass column packed with 5% SE-30 on Anakrom S. D.) exhibited two low retention time peaks corresponding to two adducts in a 7.5:1 ratio. Chromatography over 550 g of alumina (acid washed and activated at 250°) and elution with hexane–ether (99:1, 24:1, 19:1) gave 6 g of a mixture containing methyl abietate, butyl crotonate, and unidentified substances

Elution with hexane–ether (19:1, 93:7, 9:1, 17:3, 4:1, 3:1, 10:3) gave 23 g of a mixture of **25a** and **26a**. Elution with hexane–ether (5:2, 2:1, 1:3) and ether gave 3.8 g of pure **25a** as an oil: glpc single peak on 5% SE-30 column at 264°; $\nu_{max}^{CCl_4}$ 1730; nmr 5.53 (H-14), 3.97 (t, $-CO_2CH_2CH_2CH_2CH_3$), 3.65 (methoxyl), 1.13 (C-4 methyl), 1.06 (d, isopropyl and C-16 methyl), 1.03 (t, $-CH_2CH_3$), and 0.63 ppm (C-10 methyl); total yield of **25a** and **26a**, 59%.

Anal. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11; O, 13.95. Found: C, 75.74; H, 10.08; O, 14.18.

Rechromatography of the mixture did not provide pure **26a**, although glpc indicated the presence of **25a**, **26a**, and a third component in small amount. This substance had a retention time on an SE-30 column very close to that of **25a**, and its peak was masked in the presence of a large amount of the latter.

A small sample of pure **26a** was obtained in one run which utilized methyl levopimarate from 10 g of levopimaric acid. The initial chromatogram over 300 g of Alcoa F-20 alumina resulted in separation of 2.2 g of forerun, 2.8 g of mixture, and 2.1 g of **25a**. The mixture was rechromatographed over 300 g of alumina. Hexane and benzene–hexane (1:19, 1:9, 1:6, 1:4, 2:3, 3:2) eluted nothing. Benzene–hexane (4:1) eluted 0.4 g of **26a**: nmr 5.40 (broad H-14), 4.07 (t, 6 H, $-OCH_2CH_2CH_2CH_3$), 3.58 (methoxyl), 1.12 (C-4 methyl), 1.00 (d, 6.5 H, isopropyl), 0.80 (d, 7 H, C-16 methyl), 0.60 ppm (C-10 methyl). The triplet of $-CH_2CH_3$ was masked.

Anal. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11; O, 13.95. Found: C, 75.69; H, 10.01; O, 14.08.

In subsequent runs the crude reaction mixture from 50 g of levopimaric acid was hydrolyzed with sodium hydroxide, and the free acids were crystallized from acetonitrile–carbon tetrachloride. This furnished 25 g of pure **25c** (*vide infra*). The mother liquors were concentrated, and the residue was methylated with diazomethane. Elution from 1 kg of Merck acid-washed alumina with hexane–ether (19:1, 9:1) yielded 10.5 g of high R_f material. Elution with hexane–ether gave 3.5 g of **26d**: nmr 5.42 (broad H-14), 3.66 and 3.62 (methoxyls), 1.12 (C-4 methyl, shifted to 1.27 ppm in benzene), 1.03 (d, 6.5 H, isopropyl, resolved into two doublets at 1.0 and 0.98 ppm in benzene), 0.75 (d, 7 H, C-16 methyl), and 0.60 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{40}O_4$: C, 74.96; H, 9.68; O, 15.36. Found: C, 74.78; H, 9.78; O, 15.11.

Elution with hexane–ether (17:3) gave 6 g of a mixture of **25d** and **26d**. Continued elution with hexane–ether (17:3, 2:3, 1:4) and ether gave 6.5 g of **25d**: ν_{max}^{film} 1730 and 1648 (weak) cm^{-1}; nmr 5.27 (broad H-14), 3.60 and 3.57 (methoxyls), 1.13 (C-4 methyl), 1.07 (C-16 methyl), 1.03 (d, 6.5 H, isopropyl), and 0.63 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{40}O_4$: C, 74.96; H, 9.68; O, 15.36. Found: C, 74.72; H, 9.92; O, 15.05.

Hydrolysis of 5.6 g of **25a** with 100 ml of ethanol and 10 ml of water containing 10 g of sodium hydroxide for 18 hr, dilution with water, ether extraction, and acidification gave after the usual work-up and crystallization of the solid residue from acetonitrile–carbon tetrachloride 4.7 g of **25c**: mp 217–220° dec; $\nu_{max}^{CCl_4}$ 1690 cm^{-1}; nmr 5.33 (broad, H-14), 1.12 (C-4 methyl), 1.02 (d, 6.5, H isopropyl), 1.07 (C-16 methyl), and 0.62 ppm (C-10 methyl). The analysis was unsatisfactory owing to solvent retention.

Hydrolysis of **26a** in the same manner gave **26c**: mp 286–289°; nmr 5.51 (broad, H-14), 1.12 (C-4 methyl), 1.03 (6.5 H, isopropyl), 0.81 (d, 6.5 H, C-16 methyl), and 0.61 ppm (C-10 methyl).

Anal. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.35; O, 16.47. Found: C, 73.97; H, 9.27; O, 16.65.

Lithium Aluminum Hydride Reductions of 25a, 25d, 26a, and 26d.—A mixture of 0.2 g of **25a** and 0.1 g of lithium aluminum hydride in anhydrous ether was refluxed for 2.5 hr. The product **25b**, isolated in the usual way, crystallized from methanol as colorless prisms or from acetone as colorless needles: mp 187–188°; ν_{max} 3300, 1060, 1020 (–OH), and 840 cm^{-1} (olefin); nmr (acetone-d_5) 5.20 (broad, H-14), 1.05 (C-16 methyl), 1.00 (d, 6.5 H, isopropyl), 0.67 (C-14 methyl), and 0.62 (C-10 methyl); (pyridine-d_5) 5.29, 3.29 (2 H, AB quartet, J = 11 cps, C-4 CH_2OH), 3.2–4.0 (m, 2 H, C-15, CH_2OH), 1.27 1.04 (d), 0.87, and 0.69 ppm. The same substance was obtained by reduction of **25c** and **25d**.

Anal. Calcd for $C_{24}H_{40}O_2$: C, 79.94; H, 11.18. Found: C, 79.39; H, 11.12.

Lithium aluminum hydride reduction of **26a** gave an essentially quantitative yield of **26b** which was recrystallized from ethyl acetate and then melted at 162–163°: nmr (acetone-d_6–DMSO-d_6) 5.43 (broad, H-14), 4.0 (m, C-4 $-CH_2OH$), 3.8–2.9 (m, C-15 $-CH_2OH$), 1.03 (d, 6.5 H, isopropyl), 0.80 (d, 6.5 H, C-16 methyl), 0.67 (C-14 methyl), and 0.63 ppm (C-10 methyl). The same substance was obtained by reduction of **26d**.

Anal. Calcd for $C_{24}H_{40}O_2$: C, 79.94; H, 11.18; O, 8.88. Found: C, 80.00; H, 11.12; O, 9.23.

Oxidative Lactonization of 25c.—A solution of 2.92 g of $KMnO_4$ in 50 ml of water was added as rapidly as possible to a vigorously stirred solution of 13.0 g of **25c** in 1000 ml of aqueous sodium hydroxide. Dilute sulfuric acid was also added dropwise such that the pH was maintained as close to 9 as possible. When the pH remained constant (after about 30 min), excess hydroxylamine hydrochloride was added to decompose the precipitated manganese dioxide. Acidification and work-up in the usual manner gave 14 g of a glass which was stirred with carbon tetrachloride. This resulted in separation of 5 g of the acid lactone **28a** as a solid. The soluble material was essentially pure **25c** (tlc and ir spectrum). Recrystallization of **28a** from ethanol furnished crystalline material: mp 280–285° dec; ν_{max} 1730 cm^{-1} (broad).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87; O, 16.56. Found: C, 74.71; H, 8.91; O, 16.55.

The acid lactone was suspended in ether and converted into the methyl ester **28b** by treatment with an ethereal solution of diazomethane. After two crystallizations from ethanol, the product had mp 190–191°; $\nu_{max}^{CCl_4}$ 1783, 1730, and 1670 cm^{-1}; nmr 4.95 (broad, H-14), 3.65 (methoxyl), 1.77, 1.71 (two vinyl methyls), 1.13 (C-4 methyl), 1.10 (d, 6.5 H, C-16 methyl), and 0.71 ppm (C-10 methyl).

Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06; O, 15.98. Found: C, 75.07; H, 9.11; O, 15.90.

Ozonolysis of 28b.—A solution of 0.27 g of **28b** in 20 ml of chloroform was ozonized at 0–5° for 13 min. Potassium iodide solution was added, and the mixture was stirred overnight. The chloroform layer was separated, washed with saturated sodium chloride solution, dried, and evaporated. The residue of **29**, 0.26 g, was recrystallized twice from ethanol: mp 225–226°; $[\alpha]D$ +33.6° (c 0.654, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1797, 1745, and 1723 cm^{-1}; nmr 4.27 (H-14, 3.67 (methoxyl), 1.26 (d, 7 H, C-16 methyl), 1.17 (C-4 methyl), and 0.77 ppm (C-10 methyl).

Anal. Calcd for $C_{22}H_{30}O_5$: C, 70.56; H, 8.08; O, 21.36. Found: C, 70.88; H, 8.18; O, 21.20.

1-Carboxy-8-carboxymethyl-2,5a,8-trimethyl-1H-3,10a-dodecahydroethanophenanthren-12-one (30a).—A solution of 1.46 g of the preceding compound in 20 ml of tetrahydrofuran was deaerated with argon, and excess 1 M chromous chloride in aqueous 1 N HCl was added dropwise. The solution was stirred for 12 hr, and the organic solvent was removed at room temperature *in vacuo*. The residue was partitioned between water and ether, and the aqueous layer was again thoroughly extracted with ether. The combined ether layers were washed with water and extracted twice with 2 N sodium hydroxide solution. The combined basic extracts were acidified and worked up in the usual manner to give 1.4 g of **30a**. Two recrystallizations from ethanol gave crystals: mp 275–285° dec; ν_{max} 3160 (broad), 1725, 1695 cm^{-1}; nmr 3.67 (methoxyl), 1.14 (C-4 methyl), 1.11 (d, 6.5, H, C-16 methyl), and 0.83 ppm (C-10 methyl).

Anal. Calcd for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57; O, 21.25. Found: C, 69.60; H, 8.57; O, 21.54.

Methylation of 0.6 g of **30a** with ethereal diazomethane furnished 0.53 g of the diethyl ester **30b** which was recrystallized from methanol: mp 183–184°; $\nu_{max}^{CCl_4}$ 1730 cm^{-1}; nmr 3.70 (two methoxyls), 1.14 (C-4 methyl), 1.10 (d, 6.5 H, C-16 methyl), and 0.83 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78; O, 20.49. Found: C, 70.33; H, 8.85; O, 20.68.

Reduction of 30b.—To a solution of 0.43 g of the preceding ester in 20 ml of anhydrous ether was added, with stirring, 0.48 g of sodium borohydride. After stirring at room temperature for a period of 4 hr, the mixture was poured into ice–water, and the precipitated salts were dissolved by adding 1 N hydrochloric acid. The solution was extracted with ether. The ether was washed, dried, and evaporated, and the solid residue, 0.45 g, was separated by preparative tlc (ether–hexane, 7:10) into 0.18 g of a more polar component and 0.25 g of a less polar component. Both were recrystallized from ethyl acetate–hexane. The more polar material was **32**: mp 225–226°; $\nu_{max}^{CCl_4}$ 3500 and 1730 cm^{-1};

nmr 3.7 (m, H-13), 3.68 (two methoxyls), 1.16 (C-4 methyl), 1.03 (d, 6.5 H, C-16 methyl), and 0.95 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{36}O_5$: C, 70.37; H, 9.24; O, 20.38. Found: C, 70.15; H, 9.24; O, 20.37.

The less polar compound (**31**) had mp 172–173°; $\nu_{max}^{CCl_4}$ 3500 and 1730 cm^{-1}; nmr 4.1 (m, H-13), 3.68 and 3.66 (two methoxyls), 1.16 (C-4 methyl), 1.11 (C-10 methyl), and 1.05 (d, 6.5 H, C-16 methyl).

Anal. Calcd for $C_{23}H_{36}O_5$: C, 70.37; H, 9.24; O, 20.38. Found: C, 70.25; H, 9.30; O, 20.34.

Oxidative Decarboxylation of 30a. A.—A stirred solution of 0.1 g of **30a** and 0.13 g of lead tetraacetate in 10 ml of dry benzene was refluxed in a slow stream of nitrogen. The exit gas was bubbled through calcium hydroxide solution. When carbon dioxide evolution had ceased (*ca.* 4 hr), the mixture was refluxed for an additional 30 min, cooled, and filtered, and the precipitate was washed with benzene. The combined filtrate and washings were washed with 1 *N* sodium hydroxide solution, water, and brine, dried over magnesium sulfate, and concentrated. The residue, 80 mg, was subjected to preparative tlc (ether–hexane, 1:1). The fastest moving zone contained 17 mg of **34** (*vide infra*), the next 46 mg of **33**, the slowest 18 mg of unidentified material. The sodium hydroxide washings yielded 17 mg of starting material. The main product, **33**, was recrystallized from ethanol: mp 160°; nmr 4.33 (d broad, 4 H, H-15), 3.62 (methoxyl), 2.01 (acetate), 1.20 (d, 6 H, C-16 methyl), 1.15 (C-4 methyl), and 0.83 ppm (C-10 methyl).

Anal. Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78; O, 20.48. Found: C, 70.58; H, 8.85; O, 20.35.

B.—A suspension of 0.1 g of anhydrous cupric acetate in 90 ml of dry benzene (distilled from calcium hydride and then from lead tetraacetate) was stirred overnight at room temperature in 1 atm of dry nitrogen. Lead tetraacetate, 1.3 g, and 1 g of **30a** was added, and the mixture was stirred and heated to 80° while a slow stream of dry nitrogen was passed through the flask to sweep carbon dioxide into a solution of calcium hydroxide. When carbon dioxide evolution ceased after *ca.* 14 hr, the mixture was cooled to room temperature. Stirring was continued overnight, the precipitated lead acetate was filtered, and the filtrate was washed with water, 1 *N* sodium hydroxide solution, water, and brine. After being dried over magnesium sulfate, the benzene solution was evaporated. Preparative tlc of the residue, 0.81 g, using ether–hexane (3:2) gave, in order of increasing R_f, 0.007 g of a mixture of **29** and an unidentified substance, 0.028 g of **29**, 0.022 g of **33**, and 0.64 g of **34** (79%). Acidification of the sodium hydroxide washings resulted in recovery of 0.080 g of starting material. Recrystallization of **34** from methanol gave material which had mp 97–98°; ν_{max} 3010 and 1725 cm^{-1}; nmr 5.80 (t, broad, 1.8 H, H-15), 3.67 (methoxyl), 1.75 (d, 1.8 H, C-16 methyl), 1.15 (C-4 methyl), and 1.08 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15; O, 14.53. Found: C, 76.41; H, 9.23; O, 14.58.

Reduction of 34.—To a solution of 0.680 g of **34** in 15 ml of anhydrous ether was added with stirring 0.765 g of lithium tri-*t*-butoxyaluminum hydride. The mixture was stirred for 6 hr and poured into ice–water. Ether (20 ml) was added, and then dilute hydrochloric acid was added to dissolve the inorganic precipitate. The ether layer was separated, washed, dried, and concentrated. Purification of the residue, 0.705 g, by preparative tlc gave 0.4 g of pure **35** and 0.3 g of a mixture of **35** and **36**. Rechromatography of the latter gave an additional 0.17 g of **35** and 0.12 g (17%) of **36**; total weight of **35** was 0.57 g (83%). The major product was recrystallized from methanol and had mp 172–173°; ν_{max} 3612, 3515 (broad), 3010, and 1730 cm^{-1}; nmr 5.56 (t, broad, H-15), 3.93 (m, H-13), 3.63 (methoxyl), 1.73 (d, 1.6 H, C-16 methyl), 1.17 (C-4 methyl, and 1.15 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.92; H, 9.70; O, 14.62.

The minor product **36** was recrystallized from methanol and had mp 140–141°; ν_{max} 3260 and 1722 cm^{-1}; nmr 5.82 (broad, H-15), 3.78 (m, H-13), 3.62 (methoxyl), 1.77 (d, 1.2 H, C-16 methyl), 1.13 (C-4 methyl), and 0.88 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.63; H, 9.63; O, 14.92.

Methyl 15β-Hydroxy-13,16-cycloatisan-18-oate (Methyl *anti*-15α-Hydroxytrachylobanate, 37).—Methanesulfonyl chloride, 0.3 ml, was added to a solution of 0.2 g of **35** in 3 ml of dry pyridine. The solution was kept at −10° for 56 hr and then poured into ice–water. The hydrolyzed mixture was extracted with ether, and the ether was washed thoroughly with water, dilute sulfuric acid, and water and dried. Removal of ether gave 0.17 g of gum which was purified by preparative tlc (ether–hexane, 1:1) to give 0.02 g of starting material and 0.12 g of **37**. The latter after recrystallization from methanol–water, had mp 104–105°; $\nu_{max}^{CCl_4}$ 3610 and 1730 cm^{-1}; nmr 3.63 (methoxyl), 3.30 (m, singlet on D_2O exchange, H-15), 1.21 (C-16 methyl), 1.15 (C-4 methyl), and 0.99 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.66; H, 9.75; O, 14.64.

Methyl 15-Keto-13,16-cycloatisan-18-oate (Methyl *anti*-15-Ketotrachylobanate, 38).—To a solution of 70 mg of **37** in 10 ml of anhydrous ether was added 10 ml of Jones reagent at room temperature. The solution was stirred for 1 hr and diluted with 50 ml of ether. The ether layer was separated, washed with water, bicarbonate solution, and water, and evaporated. The residue of **38**, 60 mg, was recrystallized from aqueous methanol and had mp 146–147°; $\nu_{max}^{CCl_4}$ 1728 cm^{-1}; λ_{max} 211 and 285 nm (ε 2620 and 72); nmr 3.59 (methoxyl), 1.21 (C-16 methyl), 1.15 (C-4 methyl), and 1.08 ppm (C-10 methyl).

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.17; H, 9.32; O, 14.41. Found: C, 76.32; H, 9.15; O, 14.53.

Methyl 13,16-Cycloatisan-18-oate (Methyl *anti*-Trachylobanate, 2c). A.—A solution of 35 mg of **38** in 1 ml of 1,2-ethanedithiol and 0.3 ml of BF_3–etherate was stirred at room temperature for 3 hr, poured into water, and extracted with ether. The ether layer was washed, dried, and evaporated to yield gummy thioketal: 30 mg; $\nu_{max}^{CCl_4}$ 1725 cm^{-1}; nmr (CCl_4) 3.20 (4 H, S–CH_2–CH_2–S), 1.19 (C-16 methyl), 1.15 (C-4 methyl), and 1.02 ppm (C-10 methyl). The product was dissolved in 20 ml of ethanol and refluxed with 200 mg of Raney nickel for 12 hr, filtered, and concentrated *in vacuo*. The residue, 20 mg, was recrystallized from methanol to give needles: mp 109–111° (lit.[4] mp 110–112°); $[\alpha]^{25}D$ +46° (*c* 0.29, $CHCl_3$) (lit.[4] $[\alpha]D$ −41°); $\nu_{max}^{CCl_4}$ 1727 and 1242 cm^{-1}; nmr 3.59 (methoxyl), 1.13, 1.08, and 0.97 ppm (three methyl singlets). Ir and nmr spectra were identical with those of authentic methyl trachylobanate as were the glpc retention times on several columns.

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.71; H, 10.00; O, 10.17. Found: C, 79.70; H, 10.19; O, 10.11.

B.—A solution of 100 mg of **35** in 2 ml of anhydrous pyridine was purged with dry nitrogen and cooled to −10°. Methanesulfonyl chloride (29.5 μl) was slowly added. The mixture was kept in the refrigerator for 24 hr and filtered in a nitrogen atmosphere. An excess of sodium borohydride was added to the filtrate with vigorous stirring. After 30 min at room temperature, 0.5 ml of water was added; stirring was continued for 30 min, and dilute hydrochloric acid was added to decompose the excess hydride. Work-up in the usual way and separation by preparative tlc gave 7 mg of methyl *anti*-trachylobanate, mp 105–110°, after sublimation, 60 mg of starting material, and 10 mg of unidentified substances.

C.—To a solution of 11.4 mg of sodium borohydride in 2 ml of diglyme was added dropwise 100 mg of **35** in 1.26 g of BF_3 etherate at 0° under nitrogen. The solution was stirred at room temperature for 12 hr, poured into ice–water, and extracted with ether. The ether extract was worked up in the usual way, and the crude product, 90 mg, was purified by preparative tlc (ether–hexane, 4:6). The top fraction, 40 mg, was slightly impure methyl *anti*-trachylobanate.

Registry No.—**2c**, 17458-33-2; **5b**, 17458-34-3; **6**, 17458-35-4; **7**, 17458-36-5; **8**, 17458-37-6; **9**, 17458-38-7; **10**, 17458-39-8; **11**, 17458-40-1; **12**, 17458-41-2; **13**, 17458-42-3; **15**, 17458-43-4; **16a**, 17458-44-5; **16b**, 17458-45-6; **17**, 17458-46-7; **19**, 17481-30-0; **21**, 17458-47-8; **22**, 17447-76-6; **23**, 17447-77-7; **23** (2,4-dinitrophenylhydrazine derivative), 17447-78-8; **23** (ethylene ketal), 17447-56-2; **24b**, 17447-79-9; **25a**, 17447-80-2; **25b**, 17447-81-3; **25c**, 17458-48-9; **25d**, 17458-49-0; **26a**, 17458-50-3; **26b**, 17458-51-4; **26c**, 17458-20-7; **26d**, 17458-21-8; **28a**, 17458-22-9; **28b**, 17458-23-0; **29**, 17458-24-1; **30a**, 17481-31-1; **30b**, 17481-32-2; **31**, 17458-25-2; **32**, 17458-26-3; **33**, 17458-27-4; **34**, 17458-28-5; **35**, 17458-29-6; **36**, 17458-30-9; **37**, 17458-31-0; **38**, 17458-32-1.