for 15 min. A white solid precipitated and was collected. The solid was shaken with water to remove the triethylamine hydrochloride and with cold ethyl ether to remove any occluded organic impurities [unreacted alcohol (0.8 g, 40%) was recovered from these ether washings] leaving 1.6 g (56%) of *trans*-4α-cyano-1α-decalyl methanesulfonate (**5b**): mp 141.5–142.5°; ir ($CHCl_3$) 2242, 970, 917 cm^{-1}; nmr ($CHCl_3$) δ 0.6–2.5 (m, 15), 3.00 (s, 3, CH_3SO_2), 4.70 (broad, 7 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 55.68; H, 7.28; N, 5.26; S, 12.36.

trans-4β-Cyano-1β-decalyl methanesulfonate (**6b**) was prepared similarly from 3.4 g of **6a** in 76% yield, mp 152–153°. Spectral characteristics of **6b** are ir ($CHCl_3$) 2232 (C≡N), 969, 934, 897 cm^{-1}; nmr ($CHCl_3$) δ 0.8–2.4 (m), 2.77 (7 cps width at half-height, 1, CHCN), 3.02 (s, 3, CH_3SO_2), 4.28 (broad, 16 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 56.28; H, 7.28; N, 5.42; S, 12.40.

trans-4β-Cyano-1α-decalyl Methanesulfonate (**7b**).—From 2.5 g of **7a** there was obtained 2.0 g (**7b**) of *trans*-4β-cyano-1α-decalyl methanesulfonate, mp 138–139°. Spectral properties of **7b** are ir ($CHCl_3$) 2237 (C≡N), 968, 924 cm^{-1}; nmr ($CHCl_3$) δ 1.0–2.3 (m), 2.83 (7 cps width at half-height, 1, CHCN), 3.02 (s, 3, CH_3SO_2) 4.73 (7 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 55.75; H, 7.26; N, 5.28; S, 12.33.

trans-1β-Decalol was prepared by sodium and alcohol reduction of *trans*-1-decalone[20] and crystallization of the crude product from hexane: mp 61.5–62.0° (lit.[20,21] mp 58–59.5°, 63°); nmr ($CHCl_3$) δ 0.6–2.4 (m), 3.13 (15 cps width at half-height, 1, CHO). From this alcohol, *trans*-1β-decalyl methanesulfonate was prepared and purified by crystallization from hexane: mp 44.5–45.0°; nmr ($CHCl_3$) δ 0.5–2.5 (m), 2.90 (s, 3, CH_3SO_2), 4.17 (16 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.85; H, 8.68; S, 13.80. Found: C, 56.98; H, 8.62; S, 13.66.

Kinetic Measurements.—The usual sealed ampoule technique was used. The concentration of the sulfonate ester was 0.012 *M* in anhydrous acetic acid containing sodium acetate (0.025 *M*) and acetic anhydride (0.022 *M*). At appropriate time intervals 5-ml samples were titrated with perchloric acid in acetic acid using a Metrohm Model 336 recording Potentiograph equipped with a 5-ml automatic delivery buret.

Rate constants were calculated using a nonlinear least-squares program.[22] Precision was generally better than ±1%, always better than ±3%.

Registry No.—**1**, 19556-82-2; **2**, 19556-83-3; **4a**, 19556-84-4; **4b**, 19556-85-5; **5a**, 19556-86-6; **5b**, 19556-87-7; **6a**, 19556-88-8; **6b**, 19556-89-9; **7a**, 19556-90-2; **7b**, 19556-91-3; *trans*-1β-decalol, 6549-76-4; 1-acetoxy-4α-cyano-$\Delta^{1,10}$-octalin, 19556-93-5; 1-acetoxy-4β-cyano-$\Delta^{1,10}$-octalin, 19556-94-6; *trans*-1β-decalyl methanesulfonate, 19556-95-7.

(20) W. Hückel, *Ann.*, **441**, 1 (1925).

(21) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Amer. Chem. Soc.*, **76**, 4420 (1954).

(22) LSKIN2, written by C. E. DeTar and D. F. DeTar, Florida State University, as modified by Dr. H. A. Hammond.

Resin Acids. XV. Oxidative Transformations of the Levopimaric Acid–Acetylenedicarboxylic Ester Adduct[1,2]

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Received September 30, 1968

The oxidation of certain Diels–Alder adducts of levopimaric acid was investigated with a view to preparing intermediates suitable for the synthesis of polycyclic molecules. Oxidation proceeded satisfactorily only in the presence of a 1a–4a double bond. Because of its accessibility the adduct of levopimaric acid and acetylenedicarboxylic ester was used as model for studying the oxidative transformations of such compounds and was found to undergo a number of unusual reactions.

Diels–Alder adducts of levopimaric acid such as **1**[4] are potential starting materials for the synthesis of naturally occurring polycyclic systems if a way can be found to degrade the five-carbon bridge across ring C. Unfortunately the *endo* configuration of the most useful adducts appears to render the double bond inaccessible to the common oxidizing agents,[5–11] ozonolysis and permanganate oxidation proceeding normally only in the case of those adducts where R_1 and R_2 are *trans*, as in **3**,[1,12,13] or where R_1 = H.[1,12] In the present paper we describe our work on the oxidative transformations of some derivatives of **1** and of **4**,[14] which was undertaken with a view toward overcoming this difficulty (Chart I).

Our first efforts were directed at **5**,[4] **6**,[4] and **7**.[4,15] None of these substances was attacked by ozone or by potassium permanganate under conditions which effected smooth oxidation of compounds of type **3**; more drastic conditions led to intractable mixtures. More-

(1) Previous paper: W. Herz, R. N. Mirrington, H. Young, and Y. Lin, *J. Org. Chem.*, **33**, 4210 (1968).

(2) Supported in part by a grant from the National Science Foundation (GP-6362).

(3) U. S. Public Health Service Fellow, 1962–1965; Ethyl Corp. Fellow, 1964–1965.

(4) W. Herz, R. C. Blackstone, and M. G. Nair, *J. Org. Chem.*, **32**, 2992 (1967). The numbering of **1** and its transformation products is discussed in ref 15 of this reference. Compounds of type **4** are numbered as shown according to the usual convention. The *Chemical Abstracts* name for **4** is 5a,8-dimethyl-12-isopropyl-1,2,8-tricarboxymethyl-4,4a,5,5a,6,7,8,8a,-9,10-decahydro-3,10a,-ethenophenanthrene.

(5) The only compounds of this type which have been studied are maleopimaric acid (**2**) and some of its derivatives.[6–11]

(6) L. Ruzicka and St. Kaufmann, *Helv. Chim. Acta*, **23**, 1346 (1940); **24**, 939 (1941).

(7) L. Ruzicka and W. A. Lalande, *ibid.*, **23**, 1357 (1940).

(8) L. H. Zalkow, R. A. Ford, and J. P. Kutney, *J. Org. Chem.*, **27**, 3535 (1962).

(9) L. H. Zalkow and N. Girotra, *ibid.*, **28**, 2033 (1963).

(10) Le-Van-Thoi and C. P. Ngoc-Son, *C.R. Acad. Sci., Paris*, **257**, 2495 (1963).

(11) L. H. Zalkow, M. V. Kulkarni, and N. Girotra, *J. Org. Chem.*, **30**, 1679 (1965).

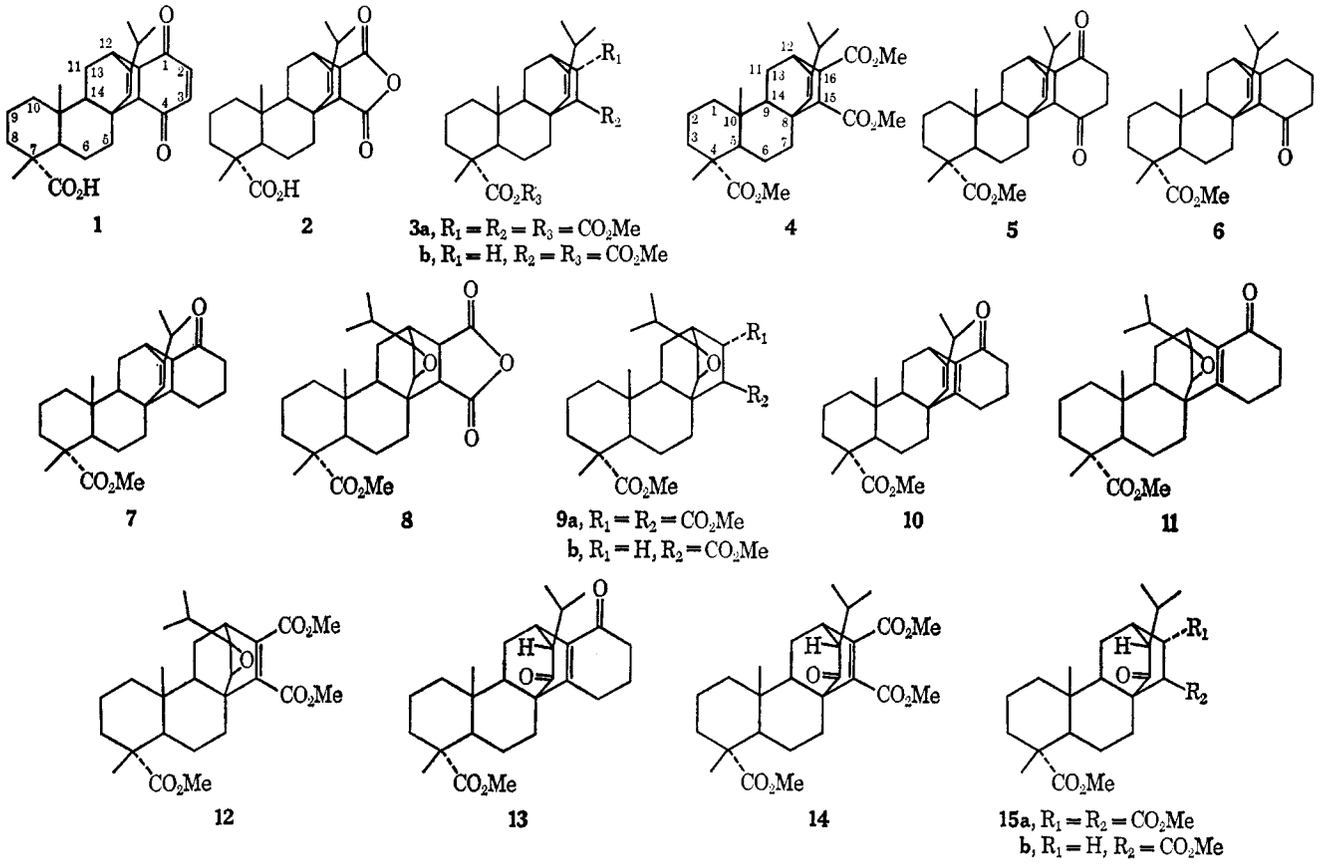
(12) N. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *ibid.*, **29**, 1017 (1964). This paper contains an unfortunate misprint. On p 1019, in column 1, lines 45 and 47, and in column 2, line 4, XV should be replaced by XVI. The numbering of adducts of type **3** and **4** is given in this reference.

(13) L. H. Zalkow and D. R. Brannon, *ibid.*, **29**, 1296 (1964).

(14) W. Herz, R. C. Blackstone, and M. G. Nair, *ibid.*, **31**, 1800 (1966).

(15) The preparation of **7** from **1** is relatively tedious and proceeds in poor over-all yield.[4] Several attempts to prepare **6** and/or **7** more directly by inducing a diene condensation between methyl levopimarate and cyclohexenone failed. This provides another example of the sluggishness of cyclohexenone as a dienophile since the lower homolog cyclopentenone affords a mixture of adducts, albeit in only mediocre yield (W. Herz, R. C. Blackstone, and M. G. Nair, to be published).

CHART I



over, as has been reported previously,[4] treatment of **5** with excess *m*-chloroperbenzoic acid resulted only in Baeyer–Villiger oxidation of the less hindered carbonyl group and did not affect the double bond.[16,17] If the lack of reactivity of **5**, **6**, and **7** toward oxidizing agents were indeed due to steric hindrance around the double bond as indicated by Dreiding models, introduction of a 1a–4a double bond as shown in **10**[4] should restore normal accessibility. This proved to be the case. Epoxidation of **10** occurred rapidly and preferentially at the bridge double bond as shown by the spectral properties of product **11** which retained the α,β-unsaturated ketone chromophore of **10** but exhibited the expected upfield shift of H-14 from 5.45 to 3.08 ppm. Similarly, epoxidation of **4** with *m*-chloroperbenzoic acid proceeded smoothly to **12** which displayed its H-14 resonance at 2.97 instead of at 5.45 ppm for **4** and had the ultraviolet absorption characteristic of an α,β-unsaturated ester. Other indications for the location of the epoxide ring on the bridge were the downfield shift of the angular methyl group signal[18–20] and the pronounced nonequivalence of the signals of the methyls of the isopropyl group.[21]

The stereochemistry depicted for **11** and **12** (and that of the other epoxides **8**, **9a**, and **9b**) is based on the severe interference, apparent from models, with approach of oxidizing agent from the side of ring A and on the chemical shift of the angular methyl group which would be expected to exhibit a considerable degree of shielding in the alternative formula.

Attempts to convert epoxides **11** and **12** into glycols by exposure to acidic reagents for the purpose of eventual further degradation encountered the same difficulties as experienced earlier[1] in the case of **9b**. The only compounds formed and obtained in optimum yield by brief treatment with boron trifluoride etherate in benzene were ketones **13** and **14**. In the case of **14**, the ultraviolet spectrum [λ_{max} 233 and 306 nm (ϵ 6800 and 550)] showed the strongly enhanced n–π^* transition characteristic of β,γ-unsaturated ketones as well as the chromophore of the unsaturated ester. The ORD curve exhibited a strong negative Cotton effect which is in accordance with the octant rule if the double bond were in the lower right rear octant as is apparent from the model, but does not permit a decision between the two possible orientations of the isopropyl group. However, an assignment is possible on other grounds.

Undoubtedly the severe hindrance to displacement of the epoxide function, after its coordination with acidic reagents, is responsible for the preference of pinacol rearrangement over rearside attack by an ex-

(16) For this reason the action of stronger oxidizing agents on **6** and **7** was not investigated in the present work. Reaction of **2** with *m*-chloroperbenzoic acid was said to be ineffective[11] but use of pertrifluoroacetic acid[11] or *p*-nitroperbenzoic acid[17] resulted in formation of epoxide **8**. By contrast, epoxidation of **3a** and **3b** to **9a** (see Experimental Section) and **9b** proceeded smoothly with *m*-chloroperbenzoic acid.

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

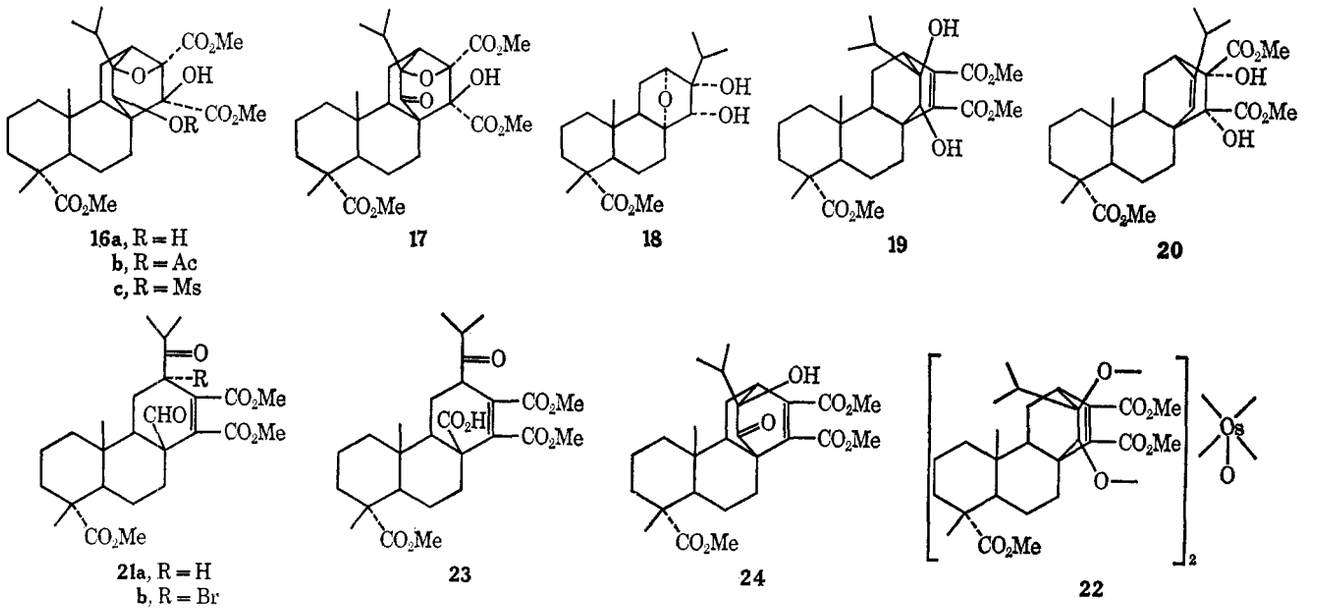
(18) Diels–Alder adducts of levopimaric acid and other compounds containing unsaturation in the bridge display this signal at 0.6–0.7 ppm because of strong shielding by the double bond.[12,19,20] In epoxides **8**,[11,17] **9a**, **9b**,[1] **11**, and **12** it is found 12–15 cycles farther downfield.

(19) W. L. Meyer and R. W. Hoffman, *Tetrahedron Lett.*, 691 (1962).

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

(21) In the nmr spectra of all Diels–Alder adducts and of compounds such as **10**, the isopropyl group is represented by a set of two superimposed or narrowly split methyl doublets near 1 ppm.[4,12,14,20] In epoxides **8**,[11,17] **9a**, **9b**,[1] **11**, and **12**, there are two widely separated doublets near 1.05 and 0.7 ppm, the latter representing the methyl being shielded more effectively by the epoxide ring.

CHART II



ternal nucleophile. Intramolecular rearside attack by hydride ion requires inversion at C-13 and formulation of the ketones as **13** and **14**, an arrangement which from inspection of the models should also be favored thermodynamically and seems to be reflected in the nmr spectra. Comparison of the signals of the isopropyl group in the nmr spectra of the ketones with the corresponding signals in the nmr spectra of precursors **11** and **12** shows that the methyl doublet at lower field (at 1.07 and 1.04 ppm) has not been affected significantly by the pinacol rearrangement, whereas the more shielded methyl doublet, formerly at 0.80 and 0.76 ppm, has experienced a further upfield shift to 0.67 and 0.63 ppm, respectively. This is consistent with that orientation, *i.e.*, **13** and **14**, in which one of the methyl groups experiences greater shielding by the conjugated double bond and perhaps the carbonyl and which, from inspection of the models, should interpose a very considerable amount of steric hindrance to the potential reactions of the carbonyl group.[22] This is actually the case and interferes with the projected utilization of these compounds. **14**, **15a**, and **15b** were not only unreactive toward the usual carbonyl reagents and toward sodium borohydride, but did not undergo the Baeyer–Villiger oxidation. Attempts to effect bromination of **14** or to prepare an enol acetate[23] with a view toward carrying out eventual cleavage reactions were unsuccessful as well.[24]

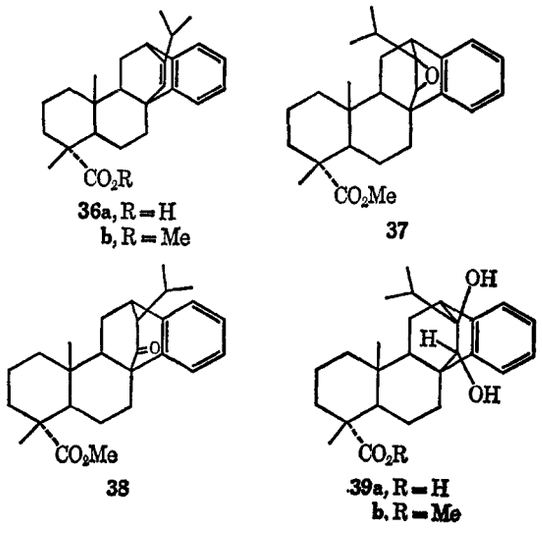
(22) Epoxide **9a** prepared in the course of this study for comparison purposes was noncrystalline and had spectroscopic properties which while clearly in harmony with the postulated structure (see Experimental Section) differed considerably from the properties of a substance of presumably the same structure, mp 179–181°, which was prepared[11] from trimethyl fumaropimarate with pertrifluoroacetic acid. Rearrangement of noncrystalline **9a** with boron trifluoride afforded ketone **15a** (weak positive Cotton effect as predicted superimposed on plain negative background curve), mp 183–185°, whose nmr spectrum exhibited the same signals as reported for the presumed epoxide. Comparison of **15a** with a slightly impure sample of the "epoxide" furnished by Professor Zalkow established identity. A possible reason for the misidentification[11] of the "epoxide" is an nmr peak at 3.13 ppm which was erroneously assigned to an epoxidic proton (H-14), but which is actually due to H-15 or H-16. This could be demonstrated by comparing the nmr spectrum of **30** which has an nmr signal at 3.30 ppm due to allylic H-12 with that of its dihydro derivative **31** which exhibits a two-proton signal at 3.10 due to H-15 and H-16 and a one-proton signal at 2.70 due to H-12.

Because of the relative inaccessibility[4] of **10** further studies on the degradation of the bridge in the presence of a 1a–4a double bond were therefore carried out on **4** as a model. These will now be discussed.

Reaction of **4** with potassium permanganate in acetone proceeded in an unexpected manner and resulted in a noncrystalline diol $C_{27}H_{40}O_9$ (**16a**) (Chart II) which contained an extra oxygen atom and was characterized by conversion into a crystalline monoacetate (**16b**) and monomesylate (**16c**). That a secondary hydroxyl group had been esterified during these conversions and that a tertiary hydroxyl group was also present was shown by the nmr spectra. The ultraviolet spectrum of **16a** indicated the disappearance of the conjugated double bond; the extra oxygen was therefore presumably present in the form of an ether function.

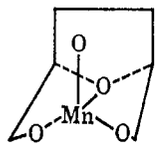
(23) This cannot be due to instability of the enol since a C-13–C-14 double bond is quite stable.

(24) The Experimental Section also contains a description of the conversion of **36a**[4] into **37** and **38** by a sequence analogous to the one applied to **4**, **9a**, **9b**, and **10**. The stereochemical assignments are particularly clear in the present instance since one of the methyl signals of the isopropyl group exhibits the expected large diamagnetic shift (0.35 ppm) in going from **37** to **38**. Osmylation of **36a** gave **39a**.

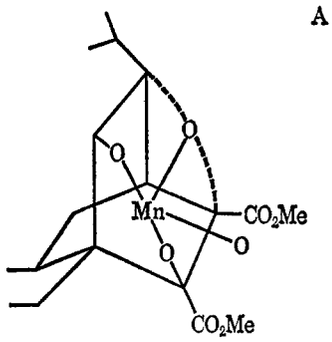


That the secondary hydroxyl group was attached to C-14 was shown by oxidation of **16a** to **17** which exhibited a new infrared frequency at 1755 cm^{-1} characteristic of a strained ketone. Attempts to dehydrate **16a** or its derivatives were unsuccessful; this excluded C-13 as the locus of the tertiary hydroxyl group. Treatment with strong acid did not affect **16b**, a result which made the presence of an epoxide linkage unlikely.

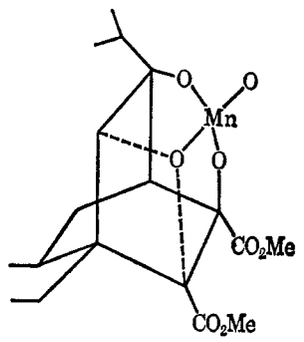
Now ether linkages are occasionally formed in the course of permanganate oxidations of dienes when the double bonds occupy certain spatial relationships. The formation of tetrahydrofurans from 1,5-dienes, more specifically the formation of *cis*-2,5-bishydroxymethyltetrahydrofuran from 1,5-pentadiene,[25] can be explained in terms of the intermediate permanganate ion complex A. Such a complex is also possible for



A

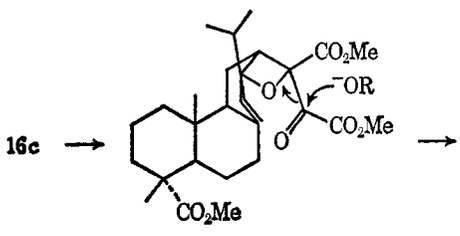


B

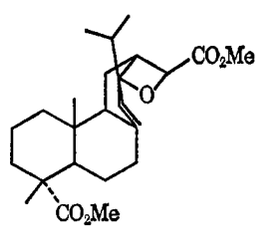


C

levopimaric acid which would lead to the diol of postulated formula **18**,[26] and for **4** which would lead to **16a** through an intermediate complex B.[27] Further evidence for the structure assigned to **16a** was the fragmentation of **16c** with potassium *t*-butoxide to a substance $C_{23}H_{34}O_5$ whose nmr spectrum exhibited signals characteristic of one vinyl proton and two methoxyl groups. This observation could be rationalized by the process **16c** → D → E.



D



E

(25) E. Klein and W. Rojahn, *Tetrahedron*, **21**, 2353 (1965).

(26) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, England, 1952, p 439.

(27) Inspection of models suggests that the isomeric complex C is equally probable, although only the product corresponding to B was isolated.

The conversion of **4** into **16a** did not augur well for the use of potassium permanganate on other potentially more useful substrates containing a 1a–4a double bond. Hence other oxidation methods were investigated. Treatment of **4** with osmium tetroxide in benzene proceeded somewhat sluggishly, but gave the hoped-for though difficultly crystallizable **19** (stereochemistry based on relative ease of approach of reagent and on the normal chemical shift of the C-10 methyl signal). Osmylation in pyridine which increases the reactivity of the reagent toward olefins resulted in a diminished yield of **19** and the formation of an isomeric diol **20** whose structure was apparent from the spectra (absence of conjugation in ir and uv spectra, presence of vinyl proton and characteristically shielded C-10 methyl resonances). The effect of ruthenium tetroxide and other oxidizing agents is described in the Experimental Section, as is the osmylation of **10** which could not be carried out selectively, but affected both double bonds and gave a tetrol.

Periodic acid cleavage of **19** to the noncrystalline ketoaldehyde **21a** proceeded very sluggishly, the structure of the product being evident from the uv (λ_{max} 235 nm), ir (aldehyde stretching frequency of 2700 cm^{-1}), and nmr spectra (aldehyde resonance at 9.3, H-12 resonance at 2.86 ppm). The ketoaldehyde was characterized by preparation of the crystalline bromo derivative **21b**.[28] Catalytic oxidation methods with the aim of effecting the conversion of **4** into **21a** in one step proved abortive. Attempted oxidation of **4b** with periodic acid or sodium metaperiodate in the presence of catalytic amounts of osmium tetroxide led to recovery of starting material. Use of larger amounts of osmium tetroxide resulted in the isolation of an osmate(VI) ester **22**[29] whose formation explains the failure of the various catalytic oxidation procedures. Finally it was discovered that **21a** could be prepared conveniently by ozonolysis of **4** in ethyl acetate at −70° in the presence of tetracyanoethylene.[30-32]

The successful cleavage of **4** to **21a**, with the incidental bonus of generating an aldehyde function of C-8 capable of eventual conversion into a methyl group, represented a partial realization of our goal. It was also hoped to effect the cleavage in such a way so as to generate a carboxyl group at C-8 which, being part of an β,γ-unsaturated acid function, might be subject to facile decarboxylation.

Attempts to accomplish this aim by oxidizing the aldehyde group of **21a** or **21b** to **23** were unsuccessful.[33] Consequently we returned to glycol **19**. Oxida-

(28) The assignment of bromine to C-12 is based on the absence of the usual H-12 resonance near 2.9 ppm.

(29) For a previous report on the formation of such an ester, see R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942).

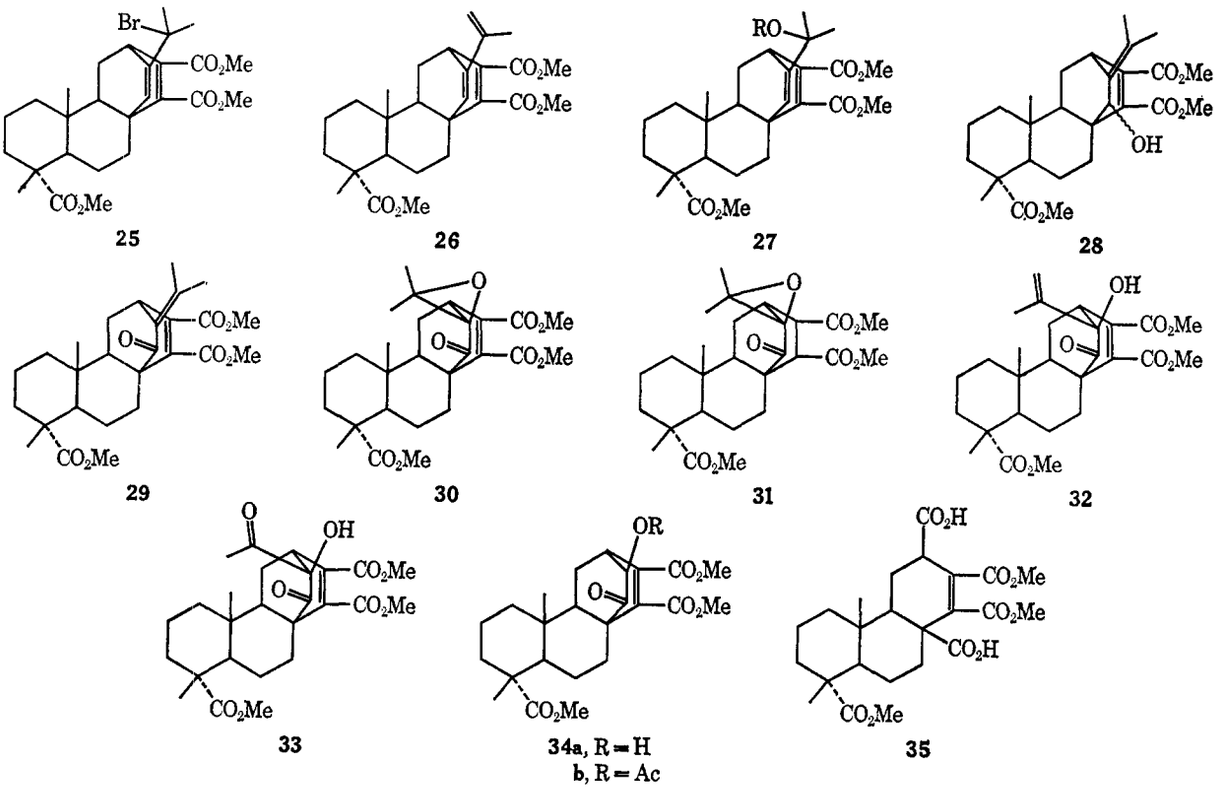
(30) These conditions were modelled on the experience of Munavalli and Ourisson,[31] who observed that addition of tetracyanoethylene altered the course of longifolene ozonolysis from production of an epoxide by abnormal attack of ozone to production of the norketone, after it had been found that ozonolysis of **4** in methanol gave a complex mixture containing epoxide **12** and that addition of pyridine[32] resulted in **12** and recovery of starting material.

(31) S. Munavalli and G. Ourisson, *Bull. Soc. Chim. Fr.*, 729 (1964).

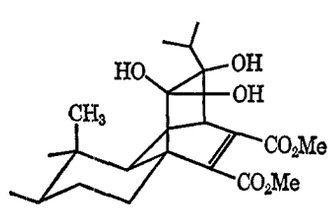
(32) G. Slomp, Jr., and J. L. Johnson, *J. Amer. Chem. Soc.*, **80**, 915 (1958).

(33) Use of silver and other oxidizing agents in basic solution resulted in a mixture of neutral substances, possibly the result of intramolecular aldol condensation as demonstrated in a related series by V. Baburao of this laboratory (unpublished results). Neutral or acidic oxidizing agents were without effect. For similar difficulties in oxidizing a tertiary aldehyde, see E. Caspi, W. Schmid, and B. T. Khan, *Tetrahedron*, **18**, 767 (1962).

CHART III



tion with Jones reagent[34] gave ketol **24**, whose spectral properties were similar to those of **14** and characteristic of a β,γ-unsaturated bicyclic ketone. Unfortunately **24** was not attacked by periodic acid, presumably because formation of *gem*-diol F, thought to be the necessary precursor for the formation of a cyclic iodate ester as a prelude to oxidation, would be inhibited by the C-10 methyl group.



F

As an alternative approach we studied the effect on **4** of various agents known to attack allylic positions because we hoped to obtain a product containing an oxygen function at C-13a. Such a function was expected to facilitate removal of the isopropyl group following ozonolysis. N-Bromosuccinimide afforded an unstable bromide **25** which underwent dehydrohalogenation with diazabicyclononene[35] to diene **26** (Chart III) whose nmr spectrum (see Experimental Section) was in conformity with the postulated structure. Attempted hydrolysis of **25** afforded mainly **26** which, though it appeared to be an ideal candidate for oxidative cleavage, could not be converted into a useful product by ozonolysis.

Oxidation of **4** with *t*-butyl chromate gave in 40% yield a substance containing two additional oxygen atoms. The ir spectrum showed the absence of hydroxyl groups, the uv spectrum the presence of a β,γ-unsaturated ketone, and the ORD curve a Cotton effect indistinguishable from that of **14**, thus locating a ketone group on C-14. The conjugated ester system was still present, but the nmr spectrum showed no signal characteristic of the isopropyl group. Instead, two additional methyl singlets at 1.53 and 1.47 ppm suggested that the second oxygen atom was attached to C-13a. Catalytic hydrogenation of **30** to **31** reduced the unsaturated ester system (uv spectrum) without affecting the oxygen functions.

That the second oxygen atom was that of an epoxide became evident on treatment of **30** with strong acid. This resulted in formation of an isomer which had a tertiary hydroxyl (ir, nmr spectrum), two new vinyl protons apparently part of a methylene group (nmr spectrum), and a vinyl methyl group resonating at 1.94 ppm. The methyl signals near 1.5 ppm had disappeared. These changes are consistent with the transformation of α-epoxy ketone **30** into **32**. The formation of **30** from **4** probably proceeds through the initial allylic oxidation product **27**, or its equivalent which could rearrange to **28** or its equivalent. Oxidation of the latter to **29** followed by epoxidation of the double bond would complete the necessary series of reactions. Epoxidations of double bonds in the course of chromate oxidations have been observed.[36,37]

Ozonolysis of **32** in the presence of tetracyanoethylene furnished additional proof for the assigned structures by yielding the methyl ketone **33** (nmr signal at 2.4 ppm). Treatment of the latter with base resulted

(34) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 142.

(35) E. Truscheit and K. Eiter, *Ann.*, **658**, 65 (1962).

(36) W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961).

(37) For steric reasons we assume that the configuration at C-13 is as depicted in **32** and hence the same in all compounds derived therefrom (**32-36**).

in cleavage of the β-diketone system and afforded gummy **34a** (loss of methyl ketone signal) which was characterized as the crystalline acetate **34b**. Although **33** did not react with periodic acid, it was cleaved slowly and in poor yield by lead tetraacetate in benzene[38] to **35** which underwent decarboxylation on heating. Treatment of **33** with excess peracetic acid effected conversion into **35** in somewhat improved yield, presumably through a series of Baeyer–Villiger reactions. This constituted realization of our original objective in relatively few steps (**4** → **30** → **32** → **33** → **35**) although the over-all yield was low.

Experimental Section[39]

Epoxidation of 10.—To a solution of 3 g of **10** in 15 ml of chloroform was added with stirring 1.5 g of *m*-chloroperbenzoic acid (85% assay). Stirring was continued for 1 hr during which time the solution warmed up noticeably. The reaction mixture was diluted with 50 ml of ether and extracted with 5% sodium bicarbonate solution, washed with water, and evaporated to give a colorless product (**11**) which was recrystallized from ethyl acetate and had mp 155–158°; yield 1.9 g; $[\alpha]D$ 100°; ir 1725 (ester), 1658 (conjugated ketone), and 1630 cm^{-1} (conjugated double bond); nmr 3.67 (methoxyl), 3.48 br (H-12), 3.08 (H-14 on epoxide), 1.20 (C-7 methyl), 1.07 d and 0.80 d (J = 7, isopropyl), and 0.93 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98; O, 15.00. Found: C, 75.91; H, 8.95; O, 15.27.

Preparation of 13.—To a solution of 3 g of **11** dissolved in 50 ml of benzene was added 0.5 ml of boron trifluoride etherate. The solution was allowed to stand for 10 min, extracted with sodium bicarbonate solution, washed with water, and evaporated to dryness. The residue was chromatographed on 100 g of alumina to yield 1.2 g of **13** which after recrystallization from methanol had mp 205–208°; $[\alpha]D$ −140°; ir 1725 (ester), 1710 (ketone), 1678 (conjugated ketone), and 1630 cm^{-1} (conjugated double bond); nmr 3.63 (methoxyl), 3.55 br (H-12), 1.17 (C-7 methyl), 1.02 d and 0.67 d (J = 7, isopropyl), and 0.80 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98; O, 15.00. Found: C, 76.10; H, 9.05; O, 14.82.

Attempts to hydrolyze **11** to a glycol using aqueous perchloric acid in acetone were not successful; compound **13** was the major product.

Epoxidation of 4.—To a solution of 30 g of **4** in 125 ml of chloroform was added with stirring 13.8 g of *m*-chloroperbenzoic acid. Stirring was continued overnight, after which *m*-chlorobenzoic acid was removed by filtration, the filtrate was evaporated to dryness in a rotary evaporator, and the residue was dissolved in ether. The ether solution was extracted twice with 5% sodium bicarbonate solution, washed with water, dried with anhydrous sodium sulfate, and evaporated to dryness to give a colorless syrup (**12**) which began to crystallize after standing for 2 weeks. Using seed crystals, the epoxide was recrystallized several times from chloroform–hexane. The yield was 21 g; the product had mp 135–137°, $[\alpha]D$ 65°; ir 1730 (ester), 1715 (conjugated esters), 1601 cm^{-1} (weak, conjugated double bond); nmr 3.67, 3.63, and 3.69 (methoxyls), 3.28 (allylic H-12), 2.96 H-14 on epoxide), 1.10 (C-4 methyl), 1.04 d and 0.76 d (J = 7, isopropyl), and 0.86 (C-10 methyl); λ_{max} 237 nm (ε 4610).

Anal. Calcd for $C_{27}H_{38}O_7 \cdot H_2O$: C, 65.83; H, 8.19. Found: C, 65.86; H, 7.90.

Preparation of 14.—Rearrangement of 10 g of **12** in 50 ml of dry benzene with 1 ml of boron trifluoride etherate was carried out in the usual fashion. The product was crystallized from ethanol to yield 6 g of **14** which had mp 190–191°; ir 1730–1705 (carbonyls not resolved) and 1630 cm^{-1} (double bond); nmr 3.77 (double intensity) and 3.66 (methoxyls), 3.50 (allylic H-12), 1.15 (C-4 methyl), 1.05 d and 0.63 d (J = 7, isopropyl), and 0.78 ppm (C-10 methyl); λ_{max} 312 (ε 520, enhanced n–π* absorption), and 239 nm (5200, conjugated esters); ORD curve $[\alpha]_{400}$ −1270°, $[\alpha]_{350}$ −4180°, $[\alpha]_{325}$ −10,300°, $[\alpha]_{308}$ 0°, $[\alpha]_{285}$ 10,100°, $[\alpha]_{284}$ 0°.

Anal. Calcd for $C_{27}H_{38}O_7$: C, 68.33: H, 8.07; O, 23.60. Found: C, 68.55; H, 7.98; O, 23.68.

The same substance was produced in 35% yield by heating a sample of **12** to 250° in a nitrogen atmosphere for 10 min, dissolving the glassy residue in methanol, and chilling.

Attempted Baeyer–Villiger oxidation of **14** with *m*-chloroperbenzoic acid in chloroform for 1 month resulted in recovery of starting material. Oxidation with pertrifluoroacetic acid yielded a complex mixture in which the uv absorptions of 312 and 239 nm were considerably reduced. Attempted reduction with sodium borohydride gave a quantitative recovery of starting material as did attempts to carry out brominations with bromine–acetic acid, N-bromosuccinimide, and pyridinium bromide perbromide. Treatment with isopropenyl acetate–*p*-toluenesulfonic acid or acetic anhydride resulted in recovery of starting material as did exposure to aqueous perchloric acid–acetone.

Epoxidation of 3a.—A solution of 2.5 g of fumaropimaric acid in ether was mixed with excess ethereal diazomethane. Removal of ether yielded 2.7 g of the noncrystalline trimethyl ester **3a**. It was dissolved in 10 ml of chloroform and 1.2 g of *m*-chloroperbenzoic acid was added with stirring. The reaction mixture was stored in the dark for 4 days. The solvent was removed and the residue dissolved in ether, washed with sodium carbonate, dried, and evaporated to yield 3 g of noncrystalline **9a**: ir 1740 and 1722 cm^{-1} (esters); nmr at 3.56, 3.50, 3.44 (methoxyls), 2.99 (H-14 on epoxide), 1.11 (C-4 methyl), 1.04 d and 0.60 d (J = 7, isopropyl), and 0.75 ppm (C-10-methyl). Since **9a** could not be purified satisfactorily for analysis it was used directly for the next experiment.

Preparation of 15a.—Rearrangement of 3 g of **9a** in 30 ml of benzene with 0.5 ml of boron trifluoride etherate was carried out as described for the preparation of **13**. The crude product crystallized after standing for 1 week to give 2.1 g of **15a**. The analytical sample was prepared by recrystallization from methanol and had mp 183–185°; $[\alpha]D$ +46°; ir 1742, 1722 (esters), and 1710 cm^{-1} (sh, ketone); nmr 3.72, 3.62, 3.58 (methoxyls), 1.28 d and 0.97 d (J = 7, isopropyl), 1.11 (C-4 methyl), and 0.70 ppm (C-10 methyl); ORD curve $[\alpha]_{400}$ −68°, $[\alpha]_{338}$ −110°, $[\alpha]_{324}$ −46°, $[\alpha]_{284}$ −290°, $[\alpha]_{274}$ −280°, $[\alpha]_{245}$ −390°. This material was identical (tlc, ir, and nmr spectrum) with a somewhat impure sample of Zalkow's[22] "epoxide IV".

Anal. Calcd for $C_{27}H_{40}O_7$: C, 68.04; H, 8.46; O, 23.50. Found: C, 67.90; H, 8.69; O, 23.53.

Attempts to oxidize this compound with *m*-chloroperbenzoic acid were unsuccessful as were attempts to hydrolyze it to a glycol.

Epoxidation of 36b (by M. G. Nair).—Methylation of 0.5 g of **36a**[4] with ethereal diazomethane gave a gum which was homogeneous by nmr and tlc criteria and was oxidized with 1.5 g of *m*-chloroperbenzoic acid in 25 ml of chloroform. After 18 hr at room temperature the mixture was heated on the steam bath for 1 min, allowed to cool, and mixed with 2 g of potassium iodide in 15 ml of water. The iodine was destroyed with a saturated solution of sodium thiosulfate, and the chloroform layer washed with water, dried, and evaporated. The residual gum was chromatographed over 3 g of silicic acid. Benzene eluted 0.4 g of **37** which was recrystallized from petroleum ether and had mp 155–157°; ir 1745 (ester); nmr 7.35 (four aromatic protons), 3.70 (methoxyl), 3.25 (H-14), 1.25 (7-methyl), 0.95 d and 0.85 d (J = 7, isopropyl), and 0.90 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88; O, 11.75. Found: C, 79.15; H, 81.73; O, 12.16.

(38) The reaction was considerably more rapid in pyridine but very little acidic material could be isolated, probably because of oxidative decarboxylation of **35** in pyridine solution.

(39) Melting points are uncorrected. Analyses were carried out by Dr. F. Pascher, Bonn, Germany. Nmr spectra were run on a Varian A-60 instrument with deuteriochloroform as solvent and tetramethylsilane as the internal standard unless otherwise noted. Values for all line positions are expressed in parts per million (ppm) from tetramethylsilane. Signals are characterized in the usual way: d, doublet; t, triplet; br, broad singlet or unresolved multiplet; c, complex band whose center is given. Coupling constants are expressed in cycles per second. Infrared spectra were determined on a Perkin-Elmer Model 257 spectrophotometer or a Perkin-Elmer Infracord instrument in chloroform solution unless otherwise noted. Infrared wavelengths are reported in cm^{-1}. Ultraviolet spectra were determined on a Carey 14 recording spectrophotometer in 95% ethanol solution unless otherwise noted. Optical rotatory dispersion curves were run on a Jasco Model ORD-5 instrument in 95% ethanol. All petroleum ether used was low boiling (30–60°). All alumina used in chromatography was Alcoa F-20, all silicic acid used was Mallinckrodt 100 mesh, all silica gel used was Baker 3405, and all Florisil used was Floridin Co. 100/200 mesh product activated at 1200°F.

Preparation of 38 (by M. G. Nair).—Rearrangement of 0.1 g of **37** in 20 ml of anhydrous ether with 0.5 ml of boron trifluoride etherate was carried out as described for the preparation of **13**. The product was recrystallized from methanol: yield 0.085 g; mp 152°; $[\alpha]^{25}D$ −25° ($CHCl_3$, *c* 0.03); λ_{max} 307 nm [enhanced n,π* transition of β,γ-unsaturated ketone; *cf.* λ_{max} of 5-norbornenone 305 nm (ϵ 290[40])]; ir 1750 and 1745 cm^{-1} (esters); nmr 7.25 (four aromatic protons), 3.70 (methoxyl), 1.20 (C-7 methyl), 0.95 d and 0.40 d (*J* = 6, isopropyl), and 0.90 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88; O, 11.75. Found: C, 78.94; H, 8.98; O, 12.09.

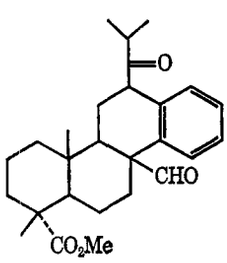
Preparation of 39a (by M. G. Nair).—Solutions of 0.5 g of **36a** in 5 ml of pyridine and 0.6 g of osmium tetroxide in 21 ml of benzene were mixed and kept for 3 days. The solution was saturated with hydrogen sulfide and filtered. The precipitate was washed with hot chloroform and the combined filtrate and washings were combined, dried, and evaporated. The residue was recrystallized from benzene: yield 0.3 g; mp 176–177°; ir 3550–3500 (hydroxyls) and 1720 cm^{-1} (carboxyl). Analysis and nmr spectrum indicated that this material was a benzene solvate. The solvent was removed by heating at 180° under high vacuum, but the melting point remained unchanged.

Anal. Calcd for $C_{26}H_{36}O_4$: C, 75.69; H, 8.80; O, 15.51. Found: C, 75.56; H, 8.71; O, 15.92.

Methyl ester **39b** melted at 191° and had $[\alpha]^{25}D$ 41.7° ($CHCl_3$, C 0.012); ir 3450 (two hydroxyls) and 1725 cm^{-1} (ester); nmr 7.35 (four aromatic protons), 4.0 (H-14), 3.70 (methoxyl), 3.20 dd (H-12), 1.25 (C-7 methyl), 1.15 (C-10a methyl), 1.05 d and 0.95 d (*J* = 6, isopropyl). The chemical shift of the isopropyl group indicated that it is not shielded by the aromatic ring and that the stereochemistry is that depicted by formula **39**.

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98. Found: C, 75.63; H, 9.01.

Oxidation of **39b** with periodic acid gave the expected but unstable product **40**. Rapid work-up permitted isolation of the substance in relatively low yield. In a typical experiment 0.1 g of **39b** in 75 ml of methanol was mixed with 0.5 g of periodic acid in 15 ml of water. After 8 hr at room temperature with stirring, the solution was concentrated *in vacuo*, diluted with water, and extracted with ether. The washed and dried ether extracts were chromatographed over silicic acid. Benzene eluted 10 mg of a yellow gum. The more polar fraction constituted 25 mg of **40** which showed a single spot in tlc. Recrystallization from petroleum ether afforded material which melted at 70–71° and decomposed on standing: ir 2800 (1745, 1720, and 1715 cm^{-1}); nmr 10.1 (aldehyde), 7.4 (four aromatic protons), 3.70 (methoxyl), 1.30 d and 1.10 d (*J* = 6, isopropyl), 1.20 (C-7 methyl), and 0.96 ppm (C-10a methyl).



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Oxidation of 4 with Potassium Permanganate.—To a solution of 20 g of **4** in 300 ml of acetone was added with stirring 5 g of potassium permanganate. The permanganate was rapidly consumed and the solution assumed a clear brown color. Upon addition of 100 ml of water, a heavy precipitate of manganese dioxide formed which was removed by suction filtration. The solution was evaporated to dryness. Thin layer chromatography showed the presence of only two substances, one of which was starting material. Chromatography on Florisil yielded 11 g of a colorless gum (**16a**) which was homogeneous according to spectral and tlc criteria, but could not be crystallized. The compound displayed ir 3540 br (bonded OH), 1740, and 1722 cm^{-1} (esters), but no double-bond absorption; nmr 3.92 (H-14), 3.76, 3.73, and 3.55 (methoxyls), 1.03 (C-4 methyl), 0.92 d and 0.85 d (*J* = 7, isopropyl), and 0.96 ppm (C-10 methyl); nmr (benzene) 4.16 (H-14), 3.74 (H-12), 3.37 (all methoxyls), 1.16 (C-4 methyl), 1.08 d and 0.95 d (*J* = 7, isopropyl), and 0.75 ppm (C-10 methyl); uv end absorption only.

Monoacetate **16b** was prepared by heating 1 g of **16a** with acetic anhydride for 4 hr. Excess acetic anhydride was removed under vacuum, and the residue was crystallized from methanol. It had mp 171–172°; $[\alpha]D$ −36.2°; ir 3540 (hydroxyl), 1745 and 1725 cm^{-1} (esters), no double-bond absorption; nmr 5.72 (H-14), 3.77, 3.71, and 3.62 (methoxyls), 3.60 (OH), 2.12 (acetate), 1.15 (C-4 methyl), 1.12 (C-10 methyl), 1.02 d and 0.87 d ppm (*J* = 7, isopropyl); nmr (benzene) at 5.92 (H-14), 3.85 (OH), 3.42 and 3.38 (methoxyls), 1.66 (acetate), 1.19 (C-4 methyl), 1.04 (C-10 methyl), 1.03 d and 0.87 d ppm (*J* = 7, isopropyl).

Anal. Calcd for $C_{29}H_{42}O_{10}$: C, 63.25; H, 7.69; O, 29.06. Found: C, 63.24; H, 7.58; O, 29.19.

Monomesylate **16c** was prepared by treating 1 g of **16a** in pyridine with excess methanesulfonyl chloride at 0° for 2 hr. The solution was poured into ice water and all organic material was extracted into ether. The ether layer was washed with water, acid, water, and dried. Evaporation yielded 0.9 g of **16c** which had mp 167–169°; $[\alpha]D$ −42.0°; ir 3540 (hydroxyl), 1740–1720 cm^{-1} (esters); nmr 5.41 (H-14), 3.73, 3.66 and 3.58 (methoxyls), 3.04 (mesylate), 1.14 (C-4 methyl), 1.03 (C-10 methyl), 1.09 d and 0.96 d ppm (*J* = 7, isopropyl).

Anal. Calcd for $C_{28}H_{42}O_{11}S$: C, 57.32; H, 7.22; O, 30.00; S, 5.46. Found: C, 57.30; H, 7.55; O, 30.13; S, 5.06.

Fragmentation of 16c.—To a solution of potassium *t*-butoxide prepared from 1 g of potassium and 50 ml of anhydrous *t*-butyl alcohol was added with stirring 2 g of **16c**. The mixture was allowed to stand at room temperature for 4 days. At the end of this period tlc analysis indicated that starting material had disappeared and that only one product, much less polar than **16c**, was present. The solution was carefully neutralized with dilute hydrochloric acid and evaporated at reduced pressure. The residue was taken up in ether, washed thoroughly, dried, and evaporated. The residue (E, 1.1 g), could not be induced to crystallize. It had ir bands at 1747, 1722 (ester), and 1640 cm^{-1} (double bond), and no hydroxyl absorption; nmr signals at 5.55 (vinyl proton), 3.79 br (hydrogen under epoxide) 3.66 (two methoxyls), 1.16 (C-4 methyl), 0.96 d (*J* = 7, six protons, isopropyl), and 0.90 ppm (C-10 methyl).

Anal. Calcd for $C_{28}H_{36}O_5$: C, 70.74; H, 8.78; O, 20.49. Found: C, 70.99; H, 8.60; O, 20.40.

Preparation of 17.—To a solution of 3 g of **16a** in 40 ml of acetone was added dropwise with stirring Jones reagent[34] until an excess of the reagent was present. The solution was allowed to stand for 1 hr, then diluted with 200 ml of water and extracted with ether. The ether layer was washed with dilute sodium bicarbonate solution, and water, dried, and evaporated. The residue was recrystallized several times from acetone–hexane to give 3.1 g of the ketol which had mp 129–131°; ir 3540 (bonded hydroxyl), 1755 (strained-ring ketone), 1740, and 1728 cm^{-1} (esters), no double-bond absorption; nmr (benzene) at 4.12 br t (H-12), 3.72 (D_2O exchangeable, hydroxyl), 3.46 (six protons) and 3.43 (methoxyls), 1.23 (C-4 methyl), 1.17 d and 1.04 d (*J* = 7, isopropyl), and 0.68 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{38}O_9$: C, 64.01; H, 7.56; O, 28.43. Found: C, 64.12; H, 7.59; O, 28.46.

Osmium Tetroxide Oxidation of 4.—To a solution of 2 g of **4** in 75 ml of benzene was added with stirring 500 mg of osmium tetroxide. The solution began to darken slowly. After standing 70 hr, the solution was saturated with hydrogen sulfide, allowed to stand overnight, and the precipitate was removed by filtration. Thin layer chromatography of the filtrate revealed two main components, one of which was starting material. The filtrate was evaporated to dryness, and the residue was chromatographed on 40 g of Florisil. Elution with benzene–chloroform (1:1) removed all starting material from the column. Elution with chloroform and chloroform–ether (1:1) yielded 700 mg of a gum which was homogeneous by nmr spectral and tlc criteria. Seed crystals were obtained only after the gum was allowed to stand for 4 months. Using the seed crystals, the remainder was crystallized twice from methanol. The yield of **19** was 510 mg. It had mp 162–165°; $[\alpha]D$ +85.5°; ir 3540 br (–OH), 1740–1720 (carbonyls not resolved), 1601 (conjugated double bond), 1435 and 1387 cm^{-1} (isopropyl doublet); nmr 3.84, 3.80, and 3.7 (methoxyls), 3.42 t (H-12 allylic to double bond), 2.73 d and 2.57 (D_2O exchangeable, hydroxyl protons), 1.20 (C-4 methyl), 1.07 (C-10 methyl), 0.96 d and 1.04 d ppm (isopropyl, *J* = 7).

(40) H. Labhart and B. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

Anal. Calcd for $C_{27}H_{40}O_8$: C, 65.83; H, 8.19; O, 25.99. Found: C, 65.67; H, 8.19; O, 25.98.

The nmr spectrum run in benzene revealed the presence of H-14 (under the secondary hydroxyl) at 3.83 d (J = 8) which collapsed to a singlet upon addition of D_2O.

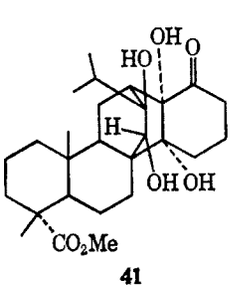
Oxidation of 4 with Osmium Tetroxide–Pyridine.—To a solution of 2 g of 4 in 75 ml of benzene–pyridine (1:1) was added with stirring 500 mg of osmium tetroxide. The solution darkened rapidly, and after 48 hr, the reaction mixture was worked up with hydrogen sulfide as described in the preceding section. Preparative tlc afforded after crystallization 300 mg of 19 and 180 mg of 20 which had mp 135–136°; $[\alpha]D$ 20°; nmr 5.30 t (J = 1.5, H-14), 4.17, and 4.03 (D_2O exchangeable, protons on OH), 3.82, 3.68, and 3.66 (methoxyls), 1.14 (C-4 methyl), 1.10 d and 1.07 d (J = 7, isopropyl), and 0.64 ppm (C-10 methyl); ir 3500 (OH), 1740–1720 (ester carbonyls not resolved), and 1640 cm^{-1} (isolated double bond); uv end absorption only.

Anal. Calcd for $C_{27}H_{40}O_8$: C, 65.83; H, 8.19; O, 25.99. Found: C, 66.05; H, 8.07; O, 25.74.

Oxidation of 4 with ruthenium tetroxide gave a 10% yield of 19 and a complex mixture of other products, presumably due to further cleavage of the two isomeric diols. Reaction of 4 with perosmic acid in *t*-butyl alcohol resulted in recovery of 85% of starting material after 6 months; similar results were obtained with pervanadic and perchromic acid.

Osmium Tetroxide Oxidation of 10 (by M. G. Nair).—To a solution of 0.78 g of 10 in 20 ml of benzene was added dropwise a solution of 0.5 g of osmium tetroxide in 30 ml of benzene and 5 ml of pyridine. After 3 days, the solution was saturated with hydrogen sulfide and filtered. Evaporation of the filtrate and recrystallization from methanol afforded 0.34 g of tetrol 41 which had mp 249–250° ir; 3500–3300 (hydroxyls), 1740 (ester), and 1718 cm^{-1} (ketone); nmr 4.12 (H-14), 3.61 (methoxyl), 0.98 d and 0.96 d (J = 6, isopropyl), 1.20 (C-7 methyl), and 1.01 ppm (C-10a methyl).

Anal. Calcd for $C_{27}H_{44}O_7$: C, 67.47; H, 9.23; O, 23.30. Found: C, 67.64; H, 8.91; O, 23.27.



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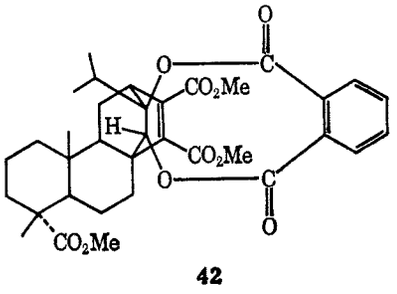

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Reaction of 4 with Phthaloyl Peroxide.—A solution of 1.00 g of monomeric phthaloyl peroxide (peroxide content 95%)[41] and 2.25 g of 4 in 200 ml of carbon tetrachloride was refluxed for 16 hr and evaporated to dryness *in vacuo*. The residue was taken up in ether, washed with dilute base, water dried, and evaporated. Tlc showed three components the least polar of which appeared to be starting material. Preparative tlc on 120 g of silica gel PF gave 4 as the least polar fraction. The most polar fraction appeared to be a mixture arising from oxidation of both double bonds and was not studied further. The remaining fraction, *ca.* 1 g, was homogeneous. Two recrystallizations from methanol–water yielded 610 mg of fluffy needles which had mp 185–186°; $[\alpha]D$ −132°; ir 1737 (sh), 1725, 1710 (sh, phthalate ester), 1648 (aryl double bond), 1604 (double bond), 1436, and 1390 cm^{-1} (isopropyl doublet); nmr 7.54 (four aromatic protons), 5.30 (H-14 under ester), 3.80, 3.67, 3.60 (methoxyls) 1.25 (C-4 methyl), 1.12 (C-10 methyl), 1.09 d (J = 7, isopropyl methyl), 0.98 d ppm (J = 7, isopropyl methyl). The analysis and spectral properties identified this compound as phthalate 42. The reaction could be scaled up easily by substituting column chromatography for tlc.

Anal. Calcd for $C_{35}H_{42}O_{10}$: C, 67.51; H, 6.80; O, 25.69; Found: C, 67.28; H, 7.02; O, 25.30.

Hydrolysis of 0.6 g of 42 with methanolic sodium hydroxide followed by neutralization with phosphoric acid, reesterification of the hydrolysate with ethereal diazomethane, and recrystallization from methanol gave 0.39 g (80%) of 19, identical in all respects with the material from the osmylation reaction.

Reaction of 4 with Osmium Tetroxide–Potassium Metaperiodate.—A solution of 3 g of 4, 2 g of potassium metaperiodate, and 15 mg of osmium tetroxide in 200 ml of 30% aqueous dioxane was stirred for 3 weeks. At the end of this period, tlc showed that no reaction had taken place. After addition of 100 mg of osmium tetroxide, the mixture gradually turned green. Tlc showed that a small amount of green product had formed, but that most of the starting material was still present. After 2 months, the solution was evaporated *in vacuo* and the residue dissolved in benzene and chromatographed over Florisil. Chloroform eluted 4 and ether eluted 0.38 g of osmate 22 which had mp 310–312°; ir 1730 and 1722 (esters), 1645 (double bond), 1440 and 1395 cm^{-1} (isopropyl doublet); nmr 5.02 (H-14), 4.82, 4.80, and 4.76 (methoxyls), 1.23 (C-4 methyl), 1.10 (C-10 methyl), 1.16 and 0.46 br d (J = 7, isopropyl).

Anal. Calcd for $C_{54}H_{76}O_{17}Os$: C, 54.62; H, 6.46; O, 22.91. Found: C, 54.61; H, 6.35; O, 22.29.

Periodic Acid Cleavage of 19.—To a solution of 500 mg of 19 in 25 ml of methanol was added 500 mg of periodic acid with stirring. The progress of the reaction was followed by tlc. After 12 days nearly all of the glycol had reacted. The solution was evaporated to dryness and the residue taken up in ether. The ether solution was washed with water, very dilute sodium bisulfite to remove traces of iodine, and again with water. Evaporation yielded about 500 mg of ketoaldehyde 21a as a colorless gum which could not be induced to crystallize. The compound exhibited ir absorption at 2710 (aldehyde CH), 1725 (carbonyls not resolved), and 1601 cm^{-1} (conjugated double bond); nmr 8.84 (aldehyde proton), 3.60 (six protons) and 3.56 (methoxyls), 2.73 q (J = 7, H-12 allylic and α to ketone), 1.03 d and 0.95 d (J = 7, isopropyl), 0.97 (C-4 methyl), and 0.68 ppm (C-10 methyl). The analytical sample was prepared by preparative thin layer chromatography.

Anal. Calcd for $C_{27}H_{38}O_8$: C, 66.10; H, 7.81; O, 26.09. Found: C, 66.28; H, 7.70; O, 26.41.

Ozonolysis of 4.—A solution of 5.0 g of 4 and 1.4 g of freshly recrystallized tetracyanoethylene in 100 ml of ethyl acetate was ozonized at −70° until the blue color of excess ozone was present. The solution was then purged with pure oxygen at −70° to remove all excess ozone. (If the solution is warmed to room temperature while it still contains excess ozone, extensive decomposition takes place.) The solution was allowed to warm to room temperature and the ethyl acetate was removed in a rotary evaporator. Tlc of the residue revealed only two spots, one whose R_f was identical with that of an authentic sample of ketoaldehyde 21a, the other near the origin being due to tetracyanoethylene oxide. The residue was taken up in chloroform and chromatographed on a silica gel column. The tetracyanoethylene oxide decomposed on the column to a brown polymer which could not be eluted; elution with chloroform gave an almost quantitative yield of ketoaldehyde 21a. The reaction was easily scaled up to quantities as large as 20 g.

Ozonolysis in methanol at −70° and oxidative work-up with sodium hypochlorite in the manner described for the ozonolysis of fumaropimaric acid[12] gave no acidic material. The neutral fraction consisted of at least seven components (tlc), one of which was epoxide 12. Ozonolysis of 3 g of 4 in 100 ml ether and 2 ml of pyridine at −70° until the blue color of excess ozone was present, removal of pyridine by washing with dilute acid, evaporation, and chromatography gave 2.1 g of starting material and 0.78 g of 12.

Bromination of 21a.—To a solution of 10 g of 21a and 3 g of sodium acetate in 500 ml of 60% aqueous acetic acid was added 4 g of bromine. The solution was allowed to stand at room temperature. Within 24 hr, crystals began to appear and after 4 days the bromine color had largely faded. The solid material was recrystallized from methanol to yield 4 g of 21b which gave a positive Beilstein test, and had mp 175–176°; $[\alpha]D$ −71°; ir 2730 (aldehyde CH stretch), 1735, 730–1705 (carbonyls only partly resolved), 1640 (medium, conjugated double bond), 1437 and 1391 cm^{-1} (isopropyl doublet); nmr 8.80 (aldehyde proton), 3.70, 3.68, and 3.66 (methoxyls), 1.26 d and 1.18 d (J = 7, isopropyl), 1.15 (C-4 methyl), and 0.76 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{37}O_8Br$: C, 56.94; H, 6.55; Br, 14.03. Found: C, 57.33; H, 6.57; Br, 14.14.

Oxidation of 21a or 21b with silver oxide gave no acidic fraction. The ir spectrum of the neutral fraction indicated the

(41) K. E. Russell, *J. Amer. Chem. Soc.*, **77**, 4814 (1955).

presence of hydroxyl groups. At least three components were present which were not separable by preparative tlc. Similar results were obtained with Tollens reagent and Fehlings solution. Jones reagent did not attack **21a** and chromic acid in acetic acid led to extensive decomposition.

Preparation of 24.—To a solution of 200 mg of **19** in 20 ml of acetone, Jones reagent was added dropwise until an excess was present. After standing for 0.5 hr, the reaction mixture was poured into 100 ml of ether and washed with water. The ether layer was separated, dried, and evaporated, and the residue was subjected to preparative tlc. There was isolated 110 mg of **24** which had mp 174–176°; $[\alpha]_D$ −132°; ir 3500 br (OH), 1725 br (carbonyls not resolved), and 1601 cm^{-1} (conjugated double bond); nmr 3.78, 3.75, and 3.66 (methoxyls), 3.57 b (allylic H-12), 1.17 (C-4 methyl), 1.09 d and 1.02 d (J = 7, isopropyl), and 0.82 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{38}O_8$: C, 66.10; H, 7.81. Found: C, 66.23; H, 7.95.

This compound was not attacked by periodic acid.

Bromination of 4 with N-Bromosuccinimide.—To a solution of 20 g of **4** in 400 ml of carbon tetrachloride was added 7.7 g of freshly recrystallized N-bromosuccinimide. The suspension was refluxed with illumination. After a brief induction period, the initial light orange faded, and a rapid reaction ensued. When all N-bromosuccinimide had reacted, the solution was cooled and filtered. The filtrate was evaporated to dryness, and the residue (crude **25**) was dissolved in either benzene or ether and treated with 5 g of diazabicyclononene. After 0.5 hr the solution was extracted with dilute hydrochloric acid and washed with water. Evaporation of the solvent yielded 19 g of crude **26**. Recrystallization from benzene–hexane yielded 14 g of pure **26** which had mp 104–106°; $[\alpha]_D$ +91°; ir 1730, 1722 (esters), 1645, 1620, and 1602 cm^{-1} (double bonds); nmr 5.90, 5.70, 4.90 (vinyl protons), 4.42 (doubly allylic H-12), 3.77, 3.70, 3.65 (methoxyls), 1.85 (vinyl methyl), 1.15 (C-4 methyl), and 0.68 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{36}O_6$: C, 71.02; H, 7.95; O, 21.03. Found: C, 70.99; H, 8.07; O, 21.01.

Treatment of the intermediate allylic bromide **25** with sodium acetate in acetic acid or sodium carbonate in aqueous acetone also resulted in almost quantitative conversion into **26**. Chromatography of 10 g of freshly prepared **25** over silicic acid containing 10% by weight of water and elution with benzene resulted in isolation of 7.5 g of **26**. Elution with more polar solvents yielded 700 mg of a mixture of polar products. Tlc showed the presence of two main components which were separated by preparative tlc. These substances were identified as the epimeric allylic alcohols **28** on the basis of their nmr spectra, but could not be purified sufficiently to give good analyses. One epimer had nmr signals at 4.10 (H-14), 3.80, 3.74, 3.67 (methoxyls), 3.60, (H-12), 2.20, 1.50 (vinyl methyls), 1.19 (C-4 methyl), and 0.73 ppm (C-10 methyl); the other had signals at 4.46 (H-14), 4.14 (H-12), 3.84, 3.76, 3.70 (methoxyls), 2.16, 1.98 (vinyl methyls), 1.21 (C-4 methyl), and 0.87 ppm (C-10 methyl). The ir spectra of both compounds showed bands at 3540 (hydroxyl), 1730–1720 (esters), 1640, and 1601 cm^{-1} (double bonds).

Oxidation of 4 with *t*-Butyl Chromate. Preparation of 30.—A solution of 25 g of **4** dissolved in 400 ml of carbon tetrachloride was added to 700 ml of *t*-butyl chromate solution (prepared from 68 g of chromium trioxide, 600 ml of carbon tetrachloride, 200 ml of *t*-butyl alchol, 100 ml of acetic acid, and 30 ml of acetic anhydride). The mixture was refluxed for 28 hr, a heavy green precipitate forming during this time. Cold water was added and the layers were separated with the help of added chloroform. The aqueous layer was extracted once with chloroform, and the combined solvent layers were filtered, washed with water, base, and again with water, dried, and concentrated. The residual brown mixture (tlc) was chromatographed over 1 kg of Florisil using chloroform as the eluent. An initial impure fraction was followed by approximately 15 g of nearly pure **30** which was crystallized several times from acetone–*n*-hexane to give 12 g of **30** which had mp 165–166°; $[\alpha]_D$ −136°; ir 1735, 1722 (esters) 1710 cm^{-1} (ketone); nmr 3.78, 3.74, 3.67 (methoxyls), 3.30 (H-12), 1.53, 1.47 (methyls on epoxide), 1.13 (C-4 methyl), and 0.70 ppm (C-10 methyl); uv λ_{max} 316 nm (ϵ 565) and 234 (4650); ORD curve $[\alpha]_{400}$ −2970°, $[\alpha]_{339}$ −9900°, $[\alpha]_{315}$ 0°, $[\alpha]_{291}$ +6100°.

Anal. Calcd for $C_{27}H_{36}O_8$: C, 66.37; H, 7.43; O, 26.20. Found: C, 66.52; H, 7.34; O, 26.39.

Hydrogenation of 30.—A solution of 3 g of **30** in 100 ml of acetic acid was shaken overnight with 100 mg of platinum oxide at 40-lb hydrogen pressure. The catalyst was removed by filtration and the solvent was removed *in vacuo*. The residue was dissolved in ether, washed, and dried. Evaporation yielded a colorless oil which was chilled and scratched to induce crystallization of **31** in almost quantitative yield. The analytical sample was recrystallized from methanol and had mp 176–178°; $[\alpha]_D$ +23°; ir 1740, 1722, (esters), 1714 cm^{-1} sh (ketone); nmr 3.62, 3.57, 3.54 (methoxyls), 2.70 (H-12), 1.52 (six protons, methyls on epoxide), 1.12 (C-4 methyl), 0.64 ppm (C-10 methyl); uv spectrum λ_{max} 308 nm (ϵ 80) and end absorption; ORD curve $[\alpha]_{356}$ 0°, $[\alpha]_{330}$ −408°, $[\alpha]_{314}$ 0°, $[\alpha]_{288}$ 735°, $[\alpha]_{252}$ 0°, $[\alpha]_{230}$ −980°.

Anal. Calcd for $C_{27}H_{38}O_8$: C, 66.10; H, 7.81; O, 26.09. Found: C, 66.38; H, 7.87; O, 25.98.

Preparation of 32.—To a solution of 3 g of **30** in 25 ml of 90% formic acid was added 1 ml of concentrated sulfuric acid. After standing at room temperature for 72 hr the solution was poured into 200 ml of ice water. The precipitate was extracted with ether, washed, dried, and evaporated to dryness. The residue was crystallized from methanol to give 1.7 g of **32** which had mp 180–181°; $[\alpha]_D$ −143°; ir (Nujol) 3460 br (hydroxyl), 1740, 1723 (esters), and 1643 cm^{-1} (double bond); nmr 5.23, 5.17 (vinyl protons), 3.80, 3.76, 3.67 (methoxyls), 1.94 (vinyl methyl), 1.13 (C-4 methyl), and 0.68 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{36}O_8$: C, 66.37; H, 7.43; O, 26.20. Found: C, 66.65; H, 7.38; O, 26.36.

Preparation of 33.—A solution of 1 g of **32** in methanol was ozonized at −70° until the blue color of excess ozone was present. The solution was purged with nitrogen at −70° until all excess ozone was removed and then allowed to come to room temperature. The solvent was removed *in vacuo* and the residue crystallized from acetone–hexane to give 600 mg of **33** which had mp 183°; $[\alpha]_D$ −131°; ir 3440 (hydroxyl), 1730–1705 cm^{-1} (carbonyls not resolved); nmr 3.78, 3.74, 3.64 (methoxyls), 2.35 (acetyl), 1.14 (C-4 methyl), and 0.67 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{34}O_9$: C, 63.66; H, 6.99; O, 29.36. Found: C, 63.78; H, 6.96; O, 29.49.

Preparation of 34b.—A solution of 200 mg of **33** in 20 ml of ethanol containing 500 mg of sodium hydroxide was refluxed for 5 hr and then neutralized with dilute hydrochloric acid. The solvent was removed by evaporation and the residue was extracted with ether. The organic product **34a** could not be crystallized. It was therefore converted with acetic anhydride into acetate **34b** which had mp 201°; ir 1730–1710 cm^{-1} (carbonyls not resolved); nmr 4.93 d (J = 3.5, H-13) 3.81, 3.79, 3.67 (methoxyls), 2.14 (acetate), 1.16 (C-1 methyl), and 0.84 ppm (C-10 methyl); λ_{max} 236 nm (ϵ 4620).

Anal. Calcd for $C_{26}H_{34}O_9$: C, 63.66; H, 6.99; O, 29.36. Found: C, 63.50; H, 6.82; O, 28.96.

Preparation of 35. A.—A solution of 100 mg of **33** and 200 mg of lead tetraacetate in 25 ml of benzene was allowed to stand for 4 weeks. Ethylene glycol was added to destroy excess lead tetraacetate. The solution was filtered and extracted several times with 5% sodium carbonate solution. The combined extracts were carefully neutralized with dilute hydrochloric acid. This resulted in a precipitate of 11 mg of **35** which was recrystallized from methanol and had mp 210–214° dec; ir 3200–2500 acid hydroxyl, 1730–1700 cm^{-1} (carbonyls not resolved); nmr 3.80, 3.76, 3.65 (methoxyls), 1.17 (C-4 methyl), and 0.87 ppm (C-10 methyl); λ_{max} 238 nm (ϵ 4730).

Anal. Calcd for $C_{24}H_{32}O_{10}$: C, 59.99; H, 6.71; O, 33.30. Found: C, 60.15; H, 6.39; O, 33.59.

B.—A solution of 0.7 g of **33** and 0.1 g of sodium acetate in 5 ml of 90% peracetic acid was allowed to stand, progress of the oxidation being monitored by tlc. After 2 weeks, excess peracetic acid was destroyed by adding acetone and the mixture was evaporated *in vacuo*. The residue was taken up in ether and the acid fraction was isolated by extraction of the ether layer with sodium carbonate solution and subsequent acidification. This gave 0.17 g of crude and after recrystallization 0.11 g of pure **35**.

The substance underwent decarboxylation on being heated above the melting point.

Registry No.—**11**, 19543-00-1; **12**, 19543-01-2; **13**, 19581-56-7; **14**, 19543-02-3; **15a**, 19543-03-4; **16a**,

19543-04-5; **16b**, 19613-62-8; **16c**, 19543-05-6; residue E, 19543-06-7; **17**, 19543-07-8; **19**, 19543-08-9; **20**, 19543-09-0; **21a**, 19543-10-3; **21b**, 19543-11-4; **22**, 19624-50-1; **24**, 19543-12-5; **26**, 19543-13-6; **28**, 19543-14-7; **30**, 19614-21-2; **31**, 19614-22-3; **32**, 19581-57-8; **33**, 19553-07-2; **34b**, 19581-58-9; **35**, 19614-23-4; **37**, 19581-59-0; **38**, 19553-08-3; **39a**, 19553-09-4; **39b**, 19553-10-7; **40**, 19553-11-8; **41**, 19553-12-9.

Studies on the Mechanism of Decomposition of Alkyl Diphenylphosphinates[1]

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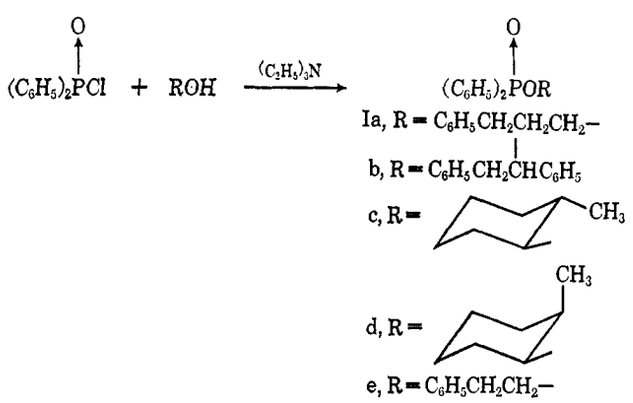
Received October 9, 1968

The following esters of diphenylphosphinic acid have been prepared and pyrolyzed: 3-phenylpropyl (Ia), 1,2-diphenylethyl (Ib), *trans*-2-methylcyclohexyl (Ic), *cis*-2-methylcyclohexyl (Id), 2-phenylethyl (Ie), menthyl (If), and bornyl (Ig). Pyrolysis was conducted in a static system under N_2 at atmospheric pressure or in a boiling solvent [dimethyl sulfoxide (DMSO) or diphenyl ether]. Although a concerted mechanism is used to explain most of the thermal pyrolyses, decomposition of Ia, If, and particularly Ig gives pyrolysates containing several alkenes which suggests an ionic process perhaps involving ion pairs. In boiling DMSO, Ic and Id appear to decompose by an E2 mechanism.

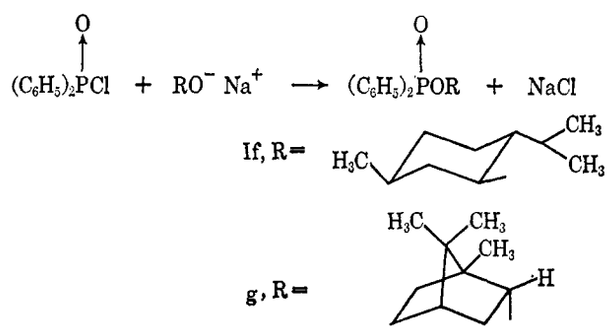
A recent report indicated the usefulness of the pyrolytic decomposition of alkyl diphenylphosphinates I in the preparation of olefins.[5] A mechanism was postulated to involve a cyclic transition state. Several new esters (see Table I) have been prepared and pyrolyzed with the intent of further elucidating this reaction mechanism. From the new results herein, it is apparent that a concerted cyclic mechanism cannot account for the product distribution.

The selected esters used in this study were prepared by the reaction of the appropriate alcohol with diphenylphosphinic chloride in the presence of triethylamine[6] (method I), or by the reaction of diphenylphosphinic chloride with the sodium salt of the alcohol in toluene (method II). Pyrolysis was effected in a static system under a nitrogen atmosphere at atmospheric pressure or in the presence of a boiling solvent [dimethyl sulfoxide (DMSO) or diphenyl ether]. Once the pyrolysis temperatures (Table II) were reached, the reactions were, in all cases, apparently complete within 15 min.

Method I

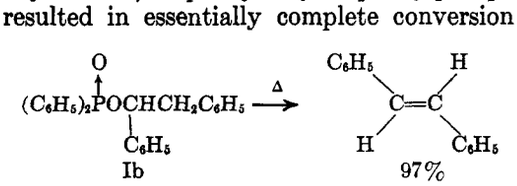


Method II



When 3-phenylpropyl diphenylphosphinate (Ia) was pyrolyzed (Table II) at 185°, a mixture containing 78% allylbenzene and 22% 1-phenyl-1-propene was obtained. When the terminal alkene was heated to 200° (15° above the pyrolysis temperature) for 45 min in a sealed tube, both neat and in the presence of diphenylphosphinic acid, no detectable isomerization occurred. It appears then that the isomeric alkenes must arise directly as a consequence of the mechanism of the decomposition. However, one might anticipate formation of a greater amount of the more conjugated 1-phenyl-1-propene in the event of a carbonium ion involvement. Allylbenzene has been prepared in 76% yield by the pyrolysis of 3-phenyl-1-propyl acetate.[7]

Pyrolysis of 1,2-diphenylethyl diphenylphosphinate (Ib) resulted in essentially complete conversion into



trans-stilbene. In both a static pyrolysis (220–240°) and in DMSO (190°) the *trans* isomer was obtained in high yield. Examination of Newman projection formulas of the transition states leading to the two stilbenes

(1) We gratefully acknowledge partial support of this research by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-132-67. Partial support by the Research Foundation, Oklahoma State University, is also acknowledged.

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