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(31) The path leading to **54** involves initial formation of an oxonium ion followed by cleavage of a C–O bond. If one of the carbon atoms bonded to oxygen can be easily attacked by acetate in an SN2 displacement reaction, a diacetate is formed with inversion at the carbon atom attacked and retention at the other carbon. Ethers which are hindered toward attack by acetate cleave by the SN1 mechanism to yield epimeric acetates or olefins.[32]

In the case of **52**, SN2 displacement on C-1 and C-11 to which oxygen is bonded equatorially is impossible. Hence the ether linkage must open to give a carbonium ion and attack by the nucleophile at either of the two possible sites from the least hindered direction would furnish an equatorial diacetate. Hydrolysis of the C-1 acetate may have occurred during the work-up (see Experimental Section) due to assistance by the axial carbomethoxy group. On the other hand, it has been suggested by a reviewer that the C-1 oxygen being complexed to BF_3 might never have been acetylated and that the BF_3 complex was hydrolyzed during work-up.
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Resin Acids. XXV. Chromic Acid Oxidation of $\Delta^{8(9)}$-Pimaranes and Isopimaranes. Long Range Deshielding in 8,9-Epoxides[1]

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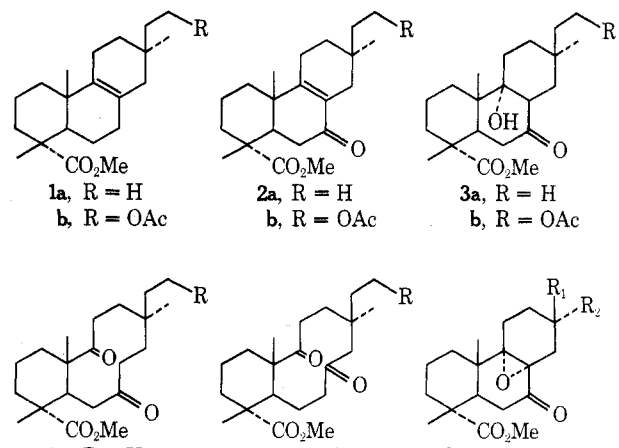
The substances formed by chromic acid oxidation of methyl pimar-8(9)-en-18-oates and isopimar-8(9)-en-18-oates have been identified as 8,9-epoxy 7-ketones. Long-range shielding effects in 8,9-epoxides of abietanes, pimaranes, and isopimaranes are discussed.

In the course of work on the synthesis of (−)-hibaene, it was noted[2] that chromium trioxide–glacial acetic acid oxidation of the pimaric acid derivatives **1a** and **1b** did not yield the hoped-for α,β-unsaturated ketones **2a** and **2b**, but gave products which contained an extra oxygen atom and did not exhibit unsaturation. These were tentatively formulated as the diketones **4**, possibly as the result of retroaldol reaction of **3** formed from **2**, or as **5**. We now report that these oxidation products actually possess the epoxy ketone structures **6a** and **6b**.

In connection with other studies, we undertook the chromic acid oxidation of methyl isopimar-8(9)-en-18-oate (**7a**). Three of the products were assigned structures **8**, **9**, and **10** on the basis of their spectroscopic properties (see Experimental Section) and corresponded to a similar set of ketones obtained by *tert*-butyl chromate oxidation of the abietane analog **7b**.[3] A fourth substance X seemed abnormal and bore a close resemblance to the "diketones" from **1a** and **1b**. However, further treatment of **10** and a still extant small sample of **2b** with acid under conditions approximating the reaction conditions under which the presumed diketones were formed resulted in recovery of starting material. Hence the theory of a retroaldol cleavage leading to **4** and **11** was abandoned. Since attempts to induce substance X and the "diketone" from **1a** to undergo an aldol condensation were also fruitless, formulas **5** and **12** seemed similarly doubtful.

To resolve the doubt, synthesis of authentic **5a**, **12a**, and the corresponding compound **12b** of the abietane series was undertaken. Osmylation of **1a**, **7a**, and **7b** afforded in each case only one ditertiary glycol **13** in high yield, presumably the result of preferred α-attack.[4] Subsequent cleavage of the diols with lead tetraacetate or periodic acid produced the three authentic diketones **5a**, **12a**, and **12b**, two of which, **5a** and **12a**, were markedly different from the substances obtained by chromic acid oxidation of **1a** and **7a**.



1a, R = H; **b**, R = OAc
2a, R = H; **b**, R = OAc
3a, R = H; **b**, R = OAc
4a, R = H; **b**, R = OAc
5a, R = H; **b**, R = OAc
6a, R_1 = Et; R_2 = Me
b, R_1 = CH_2CH_2OAc; R_2 = Me
c, R_1 = Me; R_2 = Et
d, R_1 = *i*-Pr; R_2 = H

Experimental Section[8]

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(8) For details concerning methods, see footnote 32 of Ref. 3.

Dihydropimaric acid was isolated from Staybelite resin kindly supplied by Mr. T. F. Sanderson, Hercules Powder Co., and converted to 1 a by the method of Edwards and Howe[8] followed by methylation with diazomethane. Isopimaric acid was isolated fr WW gum rosin, kindly supplied by Mr. R. V. Lawrence and Dr. Glen W. Hedrick, Naval Stores Laboratory, Olustee, Florida, by the procedure of Baldwin, Loeblich and Lawrence[10] and converted to

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(10) O. E. Baldwin, V. M. Loeblich and R. V. Lawrence, J. Org. Chem. 23, 25 (1958).

7 a by the method of Edwards and Howe[9].

Oxidation of 7 a. --To a solution of 10.44g of 7 a in 150 ml of acetic acid was added with stirring a solution of 11g of CrO_3 in 100 ml of acetic acid and 15 ml of H_2O. Stirring was continued for 2.5 hr, 100 ml of ether was added and the acid partially neutralized with 50% KOH solution. Complete neutralization was accomplished by adding solid $NaHCO_3$, small quantities of ether being added to reduce foaming. The two phase system was separated and the aqueous layer thoroughly extracted with ether. The combined washed and dried ether extracts were evaporated; the residue was taken up in methanol and yielded 1.24g of crystalline 6 c. The material from the mother liquor was quickly chromatographed over Florisil (seven fractions). The first fraction was nearly pure 8. The remaining fractions were further separated by preparative tlc (20 x 40 cm plates, ca. 0.8g per plate). The following substances were isolated:

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1) Methyl 11-oxo-8(9)-isopimaren-18-oate 8 (0.92g from the initial chromatography, the remainder from tlc). Recrystallization from methanol-water raised the mp to 107-108°; ir bands 1718, 1686 and 1650 cm^{-1}; nmr signals at 0.95 (C-13 methyl), 1.15 and 1.19 (C-4 and C-10 methyls) and 3.63 (methoxyl).

Anal. Calcd. for $C_{21}H_{32}O_3$: mol. wt. 332.2351. Found: mol. wt. (MS) 332.2344.

2) Methyl 7, 11-dioxo-8(9)-isopimaren-18-oate 9 (1.6g), recrystallized from methanol-water, mp 93.5-94.5°, $[\alpha]_D$ +18°(c 2.40, $CHCl_3$), ir bands 1722 and 1672 cm^{-1}; nmr signals at 0.87 (C-13 methyl), 1.29 and 1.36 (C-4 and C-10 methyls), and 3.70 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{30}O_4$: C,72.80; H, 8.73; O, 18.47. Found: C, 72.84; H, 8.57; O, 18.63.

3) Methyl 7-Oxo- 8a, 9a-oxidoisopimaran-18-oate 6 c (2.44 g), recrystallized from methanol-water, mp 91-92.5°, $[\alpha]_D$-67° (c 1.95, $CHCl_3$); ir bands at 1720 and 1698 cm^{-1}; nmr signals in Table I.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26; O, 18.36. Found: C, 72.57; H, 9.25; O, 18.48.

This substance was also prepared from 10 in low yield as follows. A mixture of 0.28 g of 10, 0.5 ml of H_2O_2, 0.04 g of NaOH and 40 ml of methanol was stirred for 8 hr, diluted with H_2O and extracted with ether. The aqueous layer was acidified and again extracted with ether. The acid extracts were washed, dried and evaporated, remethylated with diazomethane since hydrolysis of the ester function had taken place and combined with the product from the basic extraction. Preparative tlc (ether-hexane 4:6) separated the mixture into two compounds,

JOC-33-3

0.09 g of starting material and 0.035 g of 6 c.

4) Methyl 7-oxo-8(9)-isopimaren-18-oate 10 (1.2 g), gum which could not be purified satisfactorily for analysis, ir bands 1724, 1661 and 1612 cm^{-1}; nmr signals at 0.82 (C-13 methyl), 1.12 (C-10 methyl), 1.26 (C-4 methyl and 3.61 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{32}O_3$: mol. wt. 332.2351. Found: (MS): 332.2344.

Methyl 7-Oxo-8a, 9a-oxidopimaran-18-oate (6 a).--Oxidation of 2.5 g of methyl pimar-8(9)-en-18-oate (1 a) with CrO_3-acetic acid-water in the manner described in the previous section and trituration of the crude product with methanol afforded 1.6 g of 6 a which was recrystallized from methanol-water and had mp 130-130.5°, ir bands at 1721 cm^{-1}, nmr signals in Table I.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26; O, 18.36. Found: C, 72.61; H, 9.21; O, 18.40.

Methyl 8a, 9a-Dihydroxypimaran-18-oate (13 a).--To a solution of 1.4 g of 1 a in 25 ml of dry ether was added 1. g of OsO_4 in 25 ml of dry ether. The flask was stoppered and stirred for 2 weeks. The mixture was diluted with 75 ml of CH_3OH and H_2S gas was passed through for 2 hr. The mixture was stirred overnight, again treated with H_2S for 1 hr, filtered through Celite and evaporated. Chromatography of the residue (wt. 1.3g) over 70g of alumina yielded initially 0.25g of starting material in the ether-hexane (1:9) fractions. Ether-hexane (7:13) eluted 0.81g of solid 13 a which was recrystallized from methanol-water and melted at 114-114.5°, ir band, 3455 (sharp evidence of intramolecular bonding) and 1704 cm^{-1}, nmr signals at 1.13 and 1.14 (C-10 and C-13 methyls), 1.22 (C-4 methyl) and 3.66 ppm (methyl).

Anal. Calcd. for $C_{21}H_{36}O_4$: C, 71.55; H, 10.30; O,18.15. Found: C, 71.61; H, 10.09; O, 18.21.

JOC-33-4

Methyl 8a, 9a-Dihydroxyisopimaran-18-oate (13 b).--Osmylation of 0.95 g of 7 a with 0.7g OsO_4 in the manner described in the previous paragraph and chromatography of the crude product over alumina gave 0.10 g of starting material and 0.81g of diol 13 b. Recrystallization from methanol afforded crystals, mp 139.5-141°; $[\alpha]_D$ +12° (c 1.36, $CHCl_3$); ir 3476 (sharp, evidence of intramolecular hydrogen bonding) and 1700 cm^{-1}; nmr signal at 0.83 (C-13 methyl), 1.20 (C-10 methyl), 1.23 (C-4 methyl) and 3.65 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{36}O_4$: C, 71.55; H, 10.30; O, 18.15. Found: C, 71.62; H, 10.11; O, 18.56.

Methyl 8a, 9a-Dihydroxyabietan-18-oate (13 c).--Osmylation of 1.36g of 7 b with 1g of OsO_4 in the usual manner and chromatography of the crude product over Florisil gave 0.551g of a mixture of starting material, methyl dehydroabietate and methyl tetrahydroabietate (by disproportionation of dehydration product?). Subsequent fractions (hexane-ether 4:1) yielded 0.78g of slightly impure diol. Rechromatography over silica gel furnished 0.693g of non-crystalline 13 c, ir bands at 3510, 1735 and 1720 cm^{-1} (bonded and non-bonded carbonyls), nmr signals at 0.85 d (J = $6H_2$, isopropyl), 1.12 (C-10 methyl), 1.17 (C-4 methyl) and 3.63 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{36}O_4$: mol. wt. 352.2613. Found (MS): 352.2623.

Cleavage of the Diols.--A)--To a solution of 0.50g of 13 a in 7 ml of dry benzene was added 0.70g of $Pb(OAc)_4$ slurried in 11 ml of dry benzene with stirring. Stirring was continued overnight. The mixture was washed with a saturated solution of $NaHCO_3$, and water. The dried benzene solution was evaporated; the residue

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(wt. 0.56g) solidified on trituration with methanol. Recrystallization from methanol furnished 12 a, mp 124-125°, $[\alpha]_D$ (c 2.88, $CHCl_3$) ; ir bands at 1724 and 1700 cm^{-1}; nmr signals at 1.00 (C-13 methyl), 1.22 and 1.23 (C-4 and C-10 methyls) and 3.80 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78; O, 18.78. Found: C, 72.21; H, 9.82; O, 18.52.

B) To 0.220g of diol 13 b in ether was added 15.5 ml of a satd. solution of periodic acid (0.248g). The mixture was stirred for 2 hr, and 2 drops of glycerol was added to decompose excess reagents. The solution was washed, dried and evaporated; the residue, wt. 0.15g, was taken up in methanol and recrystallized to give 6 a, mp 83.5-84.5°; ir bands at 1724 and 1697 cm^{-1}; nmr signals at 0.82 and 1.00 (C-10 and C-13 methyls), 1.20 (C-4 methyl) and 3.72 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78, O, 18.26. Found: C, 72.30; H, 9.84; O, 18.12.

C) 0.63g of 13 c was treated with 0.85g of $Pb(OAc)_4$ in the manner described for 13 a. Evaporation of the solvent furnished 0.58g of solid 12 b which was recrystallized from methanol and had mp 97.5-98.5°, $[\alpha]_D$ +17° (c 2.66, $CHCl_3$), ir bands at 1727, 1698, 1690, cm^{-1}; nmr signals at 0.88d (J = $6H_2$ isopropyl), 1.15 (C-10 methyl), 1.23 (C-4 methyl) and 370 ppm (methoxyl).

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.99; H, 9.78; O, 18.26. Found: C, 71.77; H, 9.94; O, 18.30.

Treatment of 12 b with methanolic KOH gave a gum whose infrared spectrum indicated the presence of α, β-unsaturated ketones, presumably 21 and isomers.[11] The formation of such

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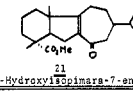
(11) A. Tahara and T. Ohsawa, Tetrahedron Letters, 2469 (1969); Chem. Pharm. Bull., 21 483 (1973).

products accounts for the failure of runs designed to produce 5 a, 12 a and 12 b by one-step reactions (OsO_4-HIO_4, RuO_4-HIO_4, RuO_4) from 1 a, 7 a and 7 b and an occasional failure with the periodic reagent, since the infrared spectra of the mixtures obtained from such runs indicated that aldol reactions had taken place.



21

Methyl 9a-Hydroxyisopimara-7-en-18-oate (16a).--To 1.5g of 6 c in 30 ml of methanol was added a solution of 3 ml of 85% hydrazine hydrate in 12 ml of methanol followed by 1 ml of acetic acid in 9 ml methanol. The mixture was heated at reflux for 0.5 hr (nitrogen atmosphere) until nitrogen evolution had ceased, evaporated and diluted with ether. The washed and dried ether layer was evaporated and the residue chromatographed over 140g of Florisil. The allylic alcohol 16a could not be induced to crystallize, yield 0.786g, ir bands at 3460, 1724 and 1682 cm^{-1}, nmr signals at 0.71, 1.00, 1.28 (C-13, C-10 and C-4 methyls), 3.58 (methoxyl) and 5.3 c (H-7).

Anal. Calcd. for $C_{21}H_{34}O_3$: mol. wt., 334.2508. Found: (MS): 334.2516.

Methyl Isopimara-7, 9 (11)-dien-18-oate (17 b).--A) A solution of 0.15g of 16a in 15 ml of acetic acid was subjected to solvent evaporation in a rotary evaporator at about 60°. The process was repeated with another 15 ml portion of acetic acid; the residue, essentially pure 17 b, was purified by preparative tlc. It could not be induced to crystallize, ir bands at 1729

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cm^{-1}; nmr signals at 0.78, 0.97, 1.22 (C-13, C-10 and C-4 methyls), 3.57 (methoxyl) and 5.25 c (2H, H-7 and H-11); uv λ_{max} 241 nm (ε 8200). An attempt to prepare 17 b by heating 16 with acetic acid and the steam bath gave a complex mixture.

B) A mixture of 0.19g of 18 a, 15 ml of freshly distilled collidine and 1.5g of LiI was refluxed for 18 hr (nitrogen atmosphere), cooled, diluted with ether and thoroughly extracted with 6 HCl. After the usual work-up[6], the product 17 a which could not be induced to crystallize was converted to the 2-amino-2-methyl-1-propanol salt. Recrystallization of the precipitate from ethanol gave the salt, mp 182-184.5° (dec.), $[\alpha]$-57° (c 2.18, CH_3OH), ir bands at 3400, (-OH) 2610 and 2117 (NH_3^+), 1679 (carboxylate) and 1512 (NH_3^+).

Anal. Calcd. for $C_{24}H_{41}NO_3$: C, 73.61; H, 10.55; N, 3.58; O, 12.26. Found: C, 73.30; H, 10.68; N, 3.59; O, 12.33.

The acid was regenerated by adding 10% HCl to a suspension of the salt in a water-ether mixture. Pure 17 a had nmr signals at 0.80, 0.98, 1.25 (C-13, C-10 and C-4 methyls), 5.37 c (2H, H-7 and H-11) and 10.33 ppm (carboxyl -OH). Methylation with diazomethane furnished material identical with 17 b prepared by dehydration of 16a.

Methyl 8a, 9a and 8β, 9β-Oxidoisopimaran-18-oate. (18 a and 19 a).--A mixture of 3.1 g of 7 a, 50 ml of $CHCl_3$ and 2.0 g of m-chloroperbenzoic acid was stirred for 1.5 hr, shaken with a solution of KI to destroy excess reagent and then with sodium thiosulfate to remove I_2, extracted with 1 N NaOH solution, washed and dried. Evaporation of solvent furnished 3.5 g of residue which was chromatographed over Florisil. The less polar component 19 a did not crystallize, yield 1.02 g, ir band at 1726 cm^{-1}, nmr signals in Table I.

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Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25; O, 14.35. Found: C, 75.58; H, 10.28; O, 14.28.

The more polar component 18 a was recrystallized from methanol, yield 1.83 g, mp 86-87°; $[\alpha]_D$ 0° (c 2.04, $CHCl_3$), ir bands at 1717 cm^{-1}, nmr signals in Table I.

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25; O, 14.35. Found: C, 75.23; H, 10.16; O, 14.20.

19-Acetoxy-8a, 9a- oxido- and 19-Acetoxy-8β, 9β-oxidoisopimarane (18 c and 19 c).--To a slurry of 2 g of $LiAlH_4$ in 450 ml of dry THF was added dropwise with stirring a solution of 11 g of 7 a in 50 ml of THF. After 48 hr, the mixture was decomposed with 20 ml of 1 N NaOH, filtered and the precipitate extracted twice with hot THF. The combined filtrate and washings were evaporated, yield of crude 19-hydroxy-isopimar-8(9)-ene (20 a) ca 10.5 g. A small fraction was chromatographed over Florisil but the product could not be induced to crystallize. It had ir bands at 3335 and 1660 cm^{-1}, nmr signals at 0.81 (6H, C-10 and C-13 methyls), 1.00 (c-4 methyl) and 3.51 ppm (2H, center of AB quartet of H-19).

Anal. Calcd. for $C_{20}H_{34}O$: mol. wt. 290.2610. Found: (MS): 290.2617.

Acetylation of 10 g of the preceding alcohol with acetic anhydride-pyridine in the usual fashion gave gummy 19-acetoxy-isopimar-8(9)-ene (20 b) which could not be induced to crystallize even after chromatography over alumina, ir bands at 1742 cm^{-1}, nmr signals at 0.82, 0.88 and 1.01 (C-13, C-10 and C-4 methyls), 2.06 (acetate) and 3.82 ppm (2H, center of AB quartet, H-19).

Anal. Calcd. for $C_{22}H_{36}O_2$: Mol. wt., 332.2715. Found: (MS): 332.2711.

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Epoxidation of 8.0 g of the foregoing ester with 5.5 g of m-chloroperbenzoic acid for 40 min and work-up in the manner described for 18 a and 19 a gave a gum which was chromatographed over Florisil. Elution with hexane gave 0.32 g of 19 c which did not crystallize, ir bands at 1740 cm^{-1}, nmr signals in Table I.

Anal. Calcd. for $C_{22}H_{36}O_3$: Mol. wt. 348.2664. Found: (MS): 348.2667.

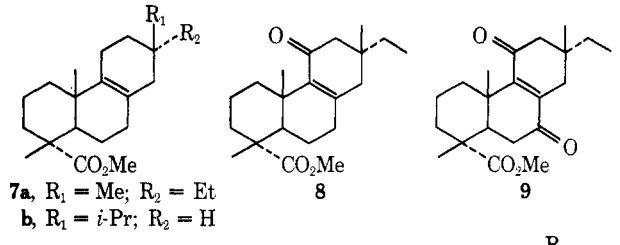
Elution with ether-hexane (1:9) gave 6.25 g of 18 c which did not crystallize, ir band at 1742 cm^{-1}; nmr signals in Table I.

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.82; H, 10.41; O, 13.77. Found: C, 75.99; H, 10.46; O, 13.88.

Deuteration of 6 c.--A solution of 0.30 g of 6 c in 2.5 ml of CH_3OD and 10 drops of a NaOD solution, prepared from 4 g of Na and 10 ml of D_2O, was refluxed overnight at which time 0.6 ml of a 38% solution of DCl in D_2O was added. The mixture was extracted with ether; the dried ether extract was mixed with excess diazomethane (a "dry" run with undeuterated reagent indicated that partial hydrolysis of the carboxyl functions had taken place) and allowed to stand. The solvent was removed and the residue was triturated to give crystalline 6 c - d_2, identical with starting material. The nmr spectrum given in Table I integrated for two less protons than 6 c.

Table I
Nmr Spectra of 8,9-Epoxides

Compd	H-5 (*J*, Hz)	C-4 Me	C-10 Me	OMe	C-13 Me	Isopropyl (*J*)
6a	2.90 (10.9, 8.1)	1.20	0.99	3.66	0.83	
6b	2.83 (11.3, 3.6)	1.21	1.01	3.67	0.93	
6c	2.84 (10.3, 7.5)	1.18	0.99	3.57	0.73	
6c-d_2	2.82	1.18	1.00	3.57	0.73	
15	2.84 (10.5, 8.0)	1.18	0.92	3.67		0.88 (6.1)
18a	2.48 (12.2, 3.6)	1.17	1.12	3.62	0.78	
18b	2.42 (12.2, 3.2)	1.28	1.17	3.66		0.96 (5)
18c	Not observed	0.84	1.13		0.79	
19a	Not observed	1.14	1.05	3.65	0.74	
19b	Not observed	1.14	1.05	3.67		0.81 (6.9)
19c	Not observed	0.80	1.06		0.74	



7a, R_1 = Me; R_2 = Et
b, R_1 = *i*-Pr; R_2 = H

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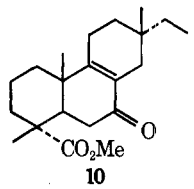

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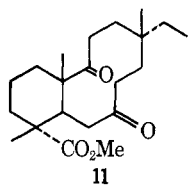

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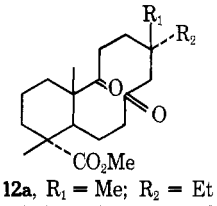
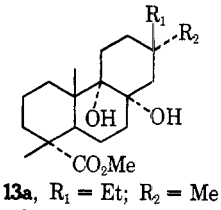
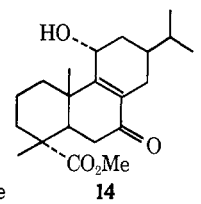


12a, R_1 = Me; R_2 = Et
b, R_1 = *i*-Pr; R_2 = H



13a, R_1 = Et; R_2 = Me
b, R_1 = Me; R_2 = Et
c, R_1 = *i*-Pr; R_2 = H



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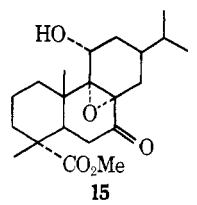

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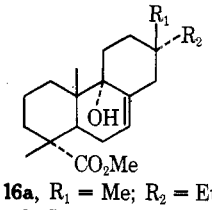
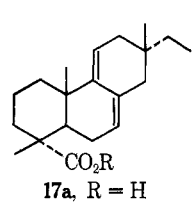
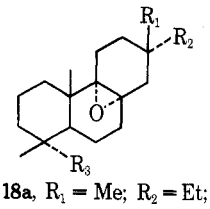


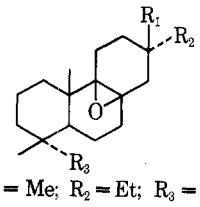
16a, R_1 = Me; R_2 = Et
b, R_1 = *i*-Pr; R_2 = H



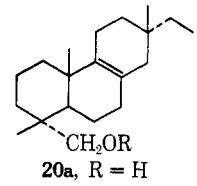
17a, R = H
b, R = Me



18a, R_1 = Me; R_2 = Et; R_3 = CO_2Me
b, R_1 = *i*-Pr; R_2 = H; R_3 = CO_2Me
c, R_1 = Me; R_2 = Et; R_3 = CH_2OAc



19a, R_1 = Me; R_2 = Et; R_3 = CO_2Me
b, R_1 = *i*-Pr; R_2 = Et; R_3 = CO_2Me
c, R_1 = Me; R_2 = Et; R_3 = CH_2OAc



20a, R = H
b, R = Ac

Although *tert*-butyl chromate oxidation[3] of **7b** had not furnished a substance comparable to the unknowns from **1a**, **1b**, and **7a**, two minor products were 14 and **15**, the latter an oxidation product of the former. This finding eventually suggested that the unknowns were actually the epoxy ketones **6a**, **6b**, and **6c**. Indeed, alkaline hydrogen peroxide oxidation of **10** furnished a small amount of substance X, although, since **10** was noncrystalline and often admixed with small amounts of X owing to the difficulty of chromatographic separation, this result was not considered as providing incontrovertible evidence for the identity of X with **6c**.

However, further transformations of X conclusively established this fact. Treatment of X with 85% hydrazine[5] produced the allylic alcohol **16a** which had properties similar to those of the abietane analog **16b**[6] and could be transformed to the trans diene **17b** by treatment with acetic acid at 60°. This substance was prepared independently as follows.

Epoxidation of **7a** afforded a 90% yield of two epoxides in a 9:5 ratio. In accordance with the principle of preferential attack from the α side, the major product, mp 86–87°, was assigned formula **18a**, the minor noncrystalline isomer structure **19a**. This was supported by the presence in the nmr spectra of the major product of a doublet of doublets at 2.48 ppm (*vide infra*) and the similarities to α[6] and β epoxides[3] of the abietane series. Finally, treatment of **18a** with the LiI–collidine[6] reagent resulted in the hoped-for conversion to **17a**, which was methylated to **17b**. This established unequivocally the structure of X as **6c** and, by inference, the structures of the presumed "diketones" from **1a** and **1b** as **6a** and **6b**.

Long Range Deshielding in 8,9-Epoxides. The nmr spectrum of **15** contains a doublet of doublets whose origin was previously ascribed[3,7] to conformational changes which cause deshielding of 14β H by the carbonyl group at C-7. Examination of the compounds described in this report showed that **6a**, **6b**, and **6c** also display the same characteristic signal (Table I). However, it is also found in the spectra of the nonketonic substances **18a** and **18b** at somewhat higher field. If the doublet of doublets owes its origin to the same proton in all six compounds, as seemed more than likely, a new explanation was needed.

Examination of Dreiding models of the compounds in question revealed that in all six cases H-5 was above the plane of the epoxide ring and near the oxygen atom. Previous studies have shown that shielding above and below the plane of an epoxide ring can be expected except when the proton is close to the oxygen atom, in which case deshielding results. Hence the signal in question could arise from H-5. Partial proof for the validity of this assignment was found in the spectra of **19a** and **19b**, which revealed no trace of the doublet of doublets. Definite confirmation was obtained by examining the nmr spectrum of **6c-6,6-d_2** (Table I). Collapse of the doublet of doublets to a slightly broadened singlet of one-proton intensity necessitates that it be identified with the resonance of H-5.

Analysis of the line shape shows two basic shapes for the H-5 signal. In the presence of a C-7 ketone group $J_{5,6\alpha}$

and $J_{5,6\beta}$ are approximately 10.5 and 8 Hz, respectively. In the absence of the ketone group, the J values are 12.2 and 3.4 Hz. Thus, the presence of a 7-ketone group is manifest in two ways: (1) it deshields H-5 by about 0.4 ppm by a field effect or by potentiating the local field already produced by the epoxide function; (2) the introduction of an sp^2-hybridized carbon atom into ring B alters the conformation such that changes in vicinal coupling constants are induced.

To determine whether the paramagnetic shift of H-5 was entirely due to the α-epoxide ring, compounds **18c** and **19c** were synthesized and examined. Table I demonstrates that neither substance exhibited the doublet of doublets; hence the downfield shift of the H-5 resonance is the result of cooperative deshielding effects on H-5 by the α-epoxide ring and the equatorial carbomethoxy group. Although the magnitude of the two components of the shift is difficult to estimate with any degree of precision, comparison of **18a** and **18c** indicates that the carboxyl group contributes at least 0.5 ppm, since the most deshielded line in the H-5 signal moved from above 2.1 (in **18c**) to 2.6 ppm (in **18a**).

Registry No. **1a**, 3582-25-0; **5a**, 7643-40-5; **6a**, 42855-23-2; **6c**, 42855-24-3; **7a**, 33952-78-2; **7b**, 33892-15-8; **8**, 42855-28-7; **9**, 42855-29-8; **10**, 42855-30-1; **12a**, 42855-31-2; **12b**, 42855-27-6; **13a**, 42855-32-3; **13b**, 42855-33-4; **13c**, 42855-34-5; **16a**, 42855-35-6; **17a** 2-amino-2-methyl-1-propanol salt, 42855-36-7; **17b**, 42855-37-8; **18a**, 42855-38-9; **18c**, 42855-39-0; **19a**, 42855-40-3; **19c**, 42855-41-4; **20a**, 42855-42-5; **20b**, 42855-43-6.

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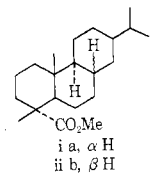
References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582). Previous paper: W. Herz and D. H. White, *J. Org. Chem.*, **39**, 1 (1974).
(2) W. Herz, A. R. Pinder, and R. N. Mirrington, *J. Org. Chem.*, **31**, 2257 (1966).
(3) W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 3464 (1969).
(4) Peracid oxidation is not nearly as selective (*vide infra*), presumably because of the higher steric requirements of the osmate ester.
(5) P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).
(6) W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30**, 1881 (1965).
(7) Our argument for assuming a conformational change in **15** was based on a comparison of the observed $\delta_{C\text{-}10Me}$ (0.92 ppm) with that calculated on the assumption that $\Delta\delta_{C\text{-}10Me}$ (18a − i) = 1.17 − 0.85 ppm or 0.32 ppm was the incremental value for an 8α,9α-epoxide. A more nearly correct standard for calculating the effect of an α-8,9-epoxide is ii ($\delta_{C\text{-}10Me}$ 1.08), thus $\Delta\delta_{C\text{-}10Me}$ (18a − ii) =



i a, α H
ii b, β H

1.17 − 1.08 = 0.09 ppm; *i.e.*, an 8α,9α-epoxide produces an apparent shift of less than 0.1 ppm in the methyl signal. Even on this basis, however, $\delta_{C\text{-}10Me}$ of **15** seems anomalously small compared with that of the epoxy ketones **6a**, **6b**, and **6c** (Table I).

Resin Acids. XXVI. Biogenetic-Type Rearrangements of the Homoallylic Cation from Methyl 15(*R*)-Hydroxypimar-8(14)-en-18-oate[1]

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A modification of the solvomercuration–demercuration reaction is described which prevents the formation of cyclic ethers from dienes. Application of the procedure to methyl pimarate permitted the stereospecific synthesis of the title compound (**5a**) and a study of the homoallylic cation derived from it. Treatment of **5a** with toluenesulfonyl chloride–pyridine resulted in rearrangement to a new cyclopropane resin acid derivative **10** and a strobane derivative **11**. Similar treatment of methyl 15(*R*)- and 15(*S*)-hydroxy-$\Delta^{8(14)}$isopimarate (**18a** and **19b**) did not result in rearrangement. The results are ascribed to differences in the geometries of the homoallylic cations produced from **5a**, **18a**, and **19a**. Generation of the homoallylic cation from **5a** and the amine analog **6a** under different conditions resulted in conversion to methyl dehydroabietate. The rearrangements can be viewed as *in vitro* analogs of biological processes.

Methyl migration in cation A derived from a pimaradiene (**1a**, Scheme I, stereochemistry at C-13 as pictured) or isopimaradiene (stereochemistry at C-13 inverted) has been postulated as the crucial step (path a, Scheme I) in the biogenesis of the abietane (**2**) skeleton.[2] Our interest in the *in vitro* genesis of cation A under mild conditions was whetted by the recent discovery[4] of yet another resin acid type, exemplified by strobic acid (**3a**)[5] and its congeners, which is formally derivable from A by an alternate cationic rearrangement (path b, Scheme I). The realization of both rearrangement paths from suitable progenitors of cation A is reported herewith.[8]

Our approach was based on the introduction of a functional group at C-15 of the pimarane skeleton which could be subjected to methods customarily employed for generating transitory carbonium ions. Unfortunately, application of the original solvomercuration–demercuration procedure to methyl primarate (**1b**) had, in the hands of previous workers,[10] furnished ether **4**[11] rather than the hoped-for alcohol **5a** owing to participation by the 8(14) double bond; our use of modified procedures[9,12] applicable to dienes did not alter this result. Consequently, our initial efforts were directed toward the synthesis of the amine **6a**.

Solvomercuration–demercuration of **1b** in the presence of acetonitrile[13] afforded in nearly quantitative yield an amide **6b**.[14] Conversion of **6b** to the imino ether **7** by treatment with triethyloxonium fluoroborate[15] followed by hydrolysis with dilute acetic acid furnished **6a** in high yield.

The mechanism[13] by which **6b** is produced involves an intermediate such as E where, in contrast to the situation