Ring C Functionalized Diterpenoids. Part IV.[1] Minor Products from the Cleavage of the Cyclopropane Ring in Methyl *ent*-Trachyloban-19-oate with Thallic Acetate

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Received June 25, 1974

HELEN MARGARET CAMPBELL, PATRICK ALISTAIR GUNN, ALAN JAMES MCALEES, and ROBERT MCCRINDLE. Can. J. Chem. **53**, 20 (1975).

Structures are assigned to seven minor products (**6***b*, **9**, **11***b*, **12***b*, **13***b*, **16**, and **25***b*) obtained from treatment of methyl *ent*-trachyloban-19-oate (**1**) with thallic oxide in acetic acid. The mechanism of the oxidative cleavage is discussed. Formation of the major products, described earlier, and all but one (**25***b*) of the minor products may be rationalized in terms of initial scission of the C_{13}—C_{16} bond.

HELEN MARGARET CAMPBELL, PATRICK ALISTAIR GUNN, ALAN JAMES MCALEES et ROBERT MCCRINDLE. Can. J. Chem. **53**, 20 (1975).

Des structures sont assignées à sept produits mineurs (**6***b*, **9**, **11***b*, **12***b*, **13***b*, **16** et **25***b*) obtenus par la réaction du trachyloban-*ent*-oate-19 de méthyle (**1**) avec l'oxyde thallique dans l'acide acétique. Le mécanisme du clivage oxidant est discuté. La formation des produits majeurs, décrite précédemment, et des produits mineur à l'exception de (**25***b*) peut être rationnalisée en termes d'une scission initiale de la liaison C_{13}—C_{16}. [Traduit par le journal]

In an earlier paper (2) we have assigned structures to the major components (**2**–**5**) of the very complex mixture obtained by oxidative cleavage of the cyclopropane ring in methyl *ent*-trachyloban-19-oate (**1**). The formation of these compounds involves scission of the C_{13}—C_{16} bond in **1**. The present paper is devoted to the minor products of this reaction and a more detailed consideration of the mechanism of the reaction.

Results

Seven new compounds have been isolated, six from the monoacetate fraction (2) and one from the diacetate fraction. Structures have been assigned to the first six on evidence which is outlined below. The structure suggested for the diacetate is tentative and based mainly on mechanistic considerations.

The monoacetate fraction was separated (2) into two parts, the more polar of which consisted largely of the major components **2** and **5**,[3] while the less polar contained a very complex mixture of products. The least polar of these, **6***b*, was isolated only with considerable difficulty. Since the material thus obtained contained residual impurities it was converted into the corresponding alcohol (**6***a*), m.p. 148–150°, which gave n.m.r. resonances attributable to a carbinyl proton (τ 6.43, d), an olefinic proton (τ 4.60, br s), and a methyl group on a double bond (τ 8.31, d). The principal evidence for the structures of **6***a* and *b* is the observation that the former is formed on aqueous treatment of the *p*-toluenesulfonate **7**. The multiplicities of the resonances due to the carbinyl and olefinic protons in **6***a* allowed us to discount the alternative structure **8**. The assignment of the α-orientation to the hydroxy group in **6***a*, which is predicted on both mechanistic (see below) and steric grounds, is supported by the observation that the carbinyl proton shows no appreciable 'W' coupling to αH-11 (3).

The next compound, **9**, m.p. 101–104°, proved to be a ketone, the n.m.r. spectrum of which shows sharp singlets at τ 9.34 (3 H-20), 8.85 (3 H-18), 7.97 (3 H-17), and 7.67 (2 H-15), and a broad singlet at 4.92 (H-12 + H-13). The ready reduction of **9** with sodium borohydride to **10** (probably a mixture of diastereoisomers), m.p. 79°, showed that the signal at

[1]For part III see ref. 1.

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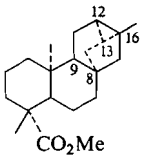
[3]Substituents designated α or β on the α-bridge of rings C–D refer to orientations *syn* and *anti* to C-20, respectively.



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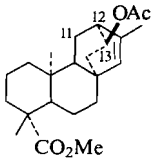

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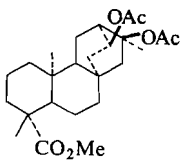

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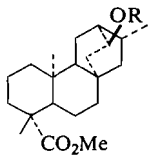

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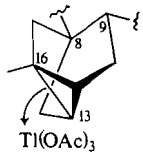

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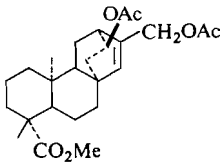

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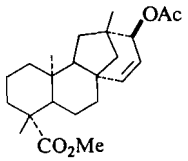

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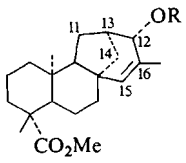

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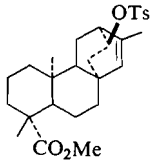

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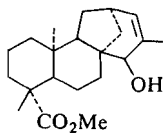

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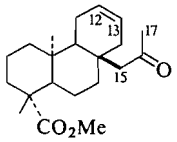

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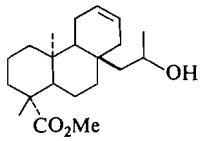

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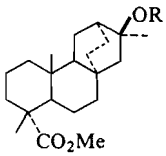

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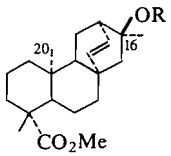

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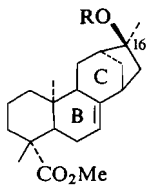

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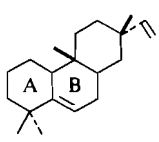
b R = Ac



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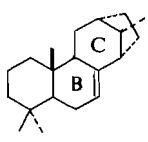

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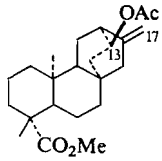


16

τ 7.97 in **9**, which is replaced by a doublet at τ 8.87, $J = 6$ Hz, in **10**, is due to a methyl ketone rather than an acetate. In addition, integration of the allylic proton region of the n.m.r. spectrum of **10** shows the presence of four allylic protons, thus establishing the position of the double bond in **10** and hence also in **9**.

As further components of the less polar monoacetate fraction could not be separated directly, the remaining mixture was subjected to mild base hydrolysis, which gave the corresponding alcohols without affecting the axial C-19 ester function. Preparative t.l.c. of the alcohols gave three significant fractions. In contrast to our findings for all the other products obtained, the n.m.r. spectrum of the least polar alcohol, **11***a*, m.p. 142–145°, isolated from this mixture showed no resonances attributable to olefinic or carbinyl protons. It did however reveal the presence of three methyl groups, two attached to quaternary carbon atoms and one on a carbon atom which carried a hydroxyl group. This led us to consider that **11***a* was simply the product of acid-promoted opening of the cyclopropane ring in **1**, and indeed, comparison of the physical constants of **11***a* with those published (4) for methyl 16β-hydroxy-*ent*-atisan-19-oate ratified the identity of these two. As anticipated, when **1** was treated with acetic acid alone at 75° for 5 days, it suffered partial conversion into the acetate **11***b*, m.p. 143–144°.

The second alcohol isolated, **12***a*, is also tertiary and has a particularly characteristic n.m.r. spectrum. This reveals the presence of a *cis*-disubstituted double bond, one olefinic proton of which is further coupled to an adjacent methine proton. In addition, the orientation of this double bond is such as to cause a marked shielding of the C-20 methyl group which resonates at τ 9.62. The absence of absorption attributable to OH—π bonding in the i.r.

spectrum of **12***a* allows assignment of the configuration at C-16 as shown.

The next component is also an olefinic tertiary alcohol, **13***a*, m.p. 120–121°, as evidenced by peaks in the n.m.r. spectrum at τ 4.82 (m, 1 H-7), 8.70 (s, 3 H-17), 8.83 (s, 3 H-18), and 9.36 (s, 3 H-20). The assignment of structure **13***a* to this compound rests largely on the observation of a particularly intense peak in its mass spectrum of *m/e* 146, attributable to a fragment derived by the retro-Diels–Alder fission and dehydration depicted in Fig. 1. The relatively high field position of the C-10 methyl resonance is similar to that observed (5) for rimuene, **14** (τ 9.38) but contrasts with that observed (6, 7) for **15** (τ 9.23, 9.25) although the latter, at first sight, might be expected to provide a closer analogy. However, examination of molecular models suggests that the 16β-substituent in **13***a* interacts sufficiently with H-9 to cause a slight flattening of rings B and C. As a result of this, the C-10 methyl group rotates towards the shielding cone of the C-7 double bond. Flattening of rings A and B in rimuene, **14**, which reduces various nonbonded interactions, could account for the upfield shift of the C-9 methyl resonance. In contrast, flattening of rings B and C in **15** does not lead to a comparable reduction in nonbonded strain.

A further product, **16**, m.p. 128–131°, has been isolated from the more polar monoacetate fraction (2) by preparative t.l.c. over silver nitrate – silica gel. The n.m.r. of **16** shows only two quaternary methyl groups at τ 8.82 (3 H-18) and 9.23 (3 H-20). A broad singlet at τ 5.20, which integrates for three protons, is ascribed to 2 H-17 + H-13. In addition, the hydrogenation of **16** gave a single product **17***b*, which was identical (t.l.c., g.l.c., and n.m.r.) with the single product obtained by hydrogenation of the isomer **2**. Since **17***b* was obtained as an oil which could not be induced to crystallize, final confirmation of its structure was achieved by converting it into the corresponding alcohol, **17***a*, m.p. 134–135°, which had been obtained previously (2).

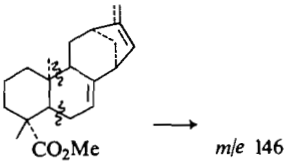


Fig. 1. Mass spectral fragmentation pattern.

Discussion

All but one (discussed below) of the products isolated from the cleavage of **1** with thallic acetate can be most readily envisaged as deriving from initial attack[4] at the C_{13}—C_{16} bond (**18** arrows) with development of considerable carbonium ion character at C-16 (**19**). Preferential cleavage of the C_{13}—C_{16} bond is anticipated on the basis of earlier reports on the cleavage of trachylobanes with acids (8–10).[5] Indeed, it is consistent with the results of cleavage of simple bicyclo[*n*.1.0.] alkanes by thallic acetate (12), where it is found that the relative ease of internal (O bridge) bond cleavage increases with decreasing *n*. The structures of the products isolated suggest that at least three competing processes determine the eventual fate of carbonium ion **19** (Scheme 1).

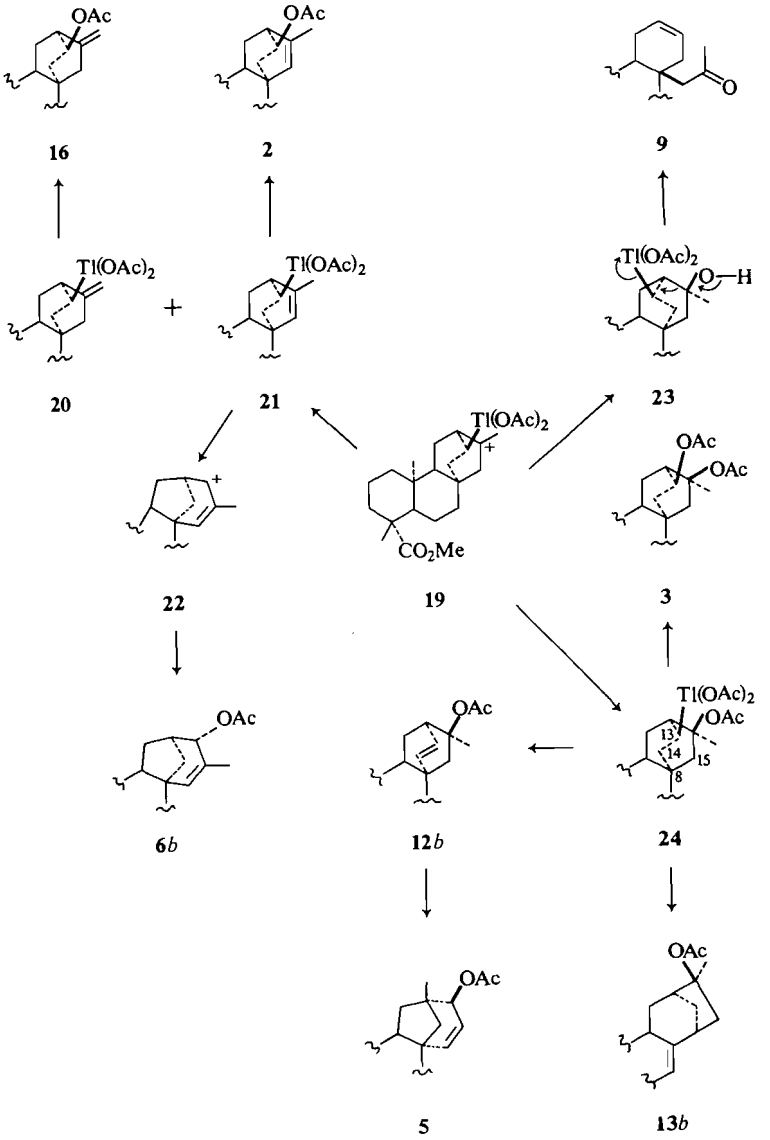
First, elimination of a proton can give **20** and **21**, from which the olefinic monoacetates **2** and **16** may derive. The stereochemistry of these products requires that the replacement of the —$Tl(OAc)_2$ group with —OAc proceed with retention (2). Migration of the C_{11}—C_{12} bond to C-13 upon heterolysis of the —$Tl(OAc)_2$ group in **21** would produce the allylic cation **22** and thence **6***b*. Diacetate **4** probably results from allylic oxidation of **2** and/or **16**.

Second, attack on the β-face (see below) of **19** by water generated in the formation of $Tl(OAc)_3$ from Tl_2O_3 may produce the tertiary alcohol **23**. This would be expected to fragment as shown (**23** arrows), furnishing the ketone **9**.

Third, attack by solvent (acetic acid) on **19** would give the tertiary acetate **24**, the stereochemistry of which is that expected (12) on the basis of *trans* opening of the cyclopropane ring. It has been suggested (12) that this cleavage involves 'a closely timed sequence in which the addition of metal salt and solvent occur in such a fashion as to preclude loss of stereochemistry.' In the present instance, even if addition of solvent were not concerted with

[4]Since our results do not allow us to draw any conclusions as to the nature of the electrophilic species involved, we have used $Tl(OAc)_3$ in **18** for convenience (*cf.* ref. 13).

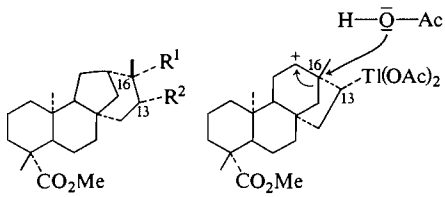
[5]The relatively large amounts of beyeranes found in one of these studies (10) are probably obtained by rearrangement of an initially formed atisane carbonium ion (1, 11).



SCHEME 1

ring opening, attack at C-16 would still be expected to take place preferentially on the β-face since α-attack would be severely hindered by the bulky —$Tl(OAc)_2$ substituent at C-13. Several pathways can be invoked to account for the subsequent fate of **24**. Thus, internal nucleophilic substitution gives the diacetate **3**. Alternatively, heterolysis of the —$Tl(OAc)_2$ group with (*a*) loss of a proton from the neighboring carbon (C-14) or (*b*) hydride shift from C-14 to C-13, migration of the C_8—C_{15} bond to C-14, and elimination of a proton from C-7, leads to the olefinic tertiary acetates **12***b* and **13***b*, respectively. The isolation of alcohol **12***a* lends credence to our previous suggestion (2) that **5** might be formed by rearrangement of acetate **12***b*. Ionization of the tertiary acetate function in **12***b* may be assisted by homoallylic participation (14).

Finally, one minor product, the diacetate of intermediate polarity (2) appears to have structure **25***b*. The n.m.r. spectrum shows singlets at τ 9.18 (3 H-20), 8.86 (3 H-18), 8.52 (3 H-17), and 8.12 (6H, 2 —OCOCH_3) and a multiplet



25 **26**

a $R^1 = R^2 = OH$
b $R^1 = R^2 = OAc$
c $R^1 = OAc$; $R^2 = Tl(OAc)_2$

at τ 5.10 (dd, J_{obs} = 3 and 6 Hz). The multiplicity of the last rules out the possibility that the diacetate is a 12α- or β-substituted kaurane or a 13α- or β-substituted atisane since its coupling pattern is very different from theirs (15). This, and the indication from its n.m.r. spectrum that the moiety $H_3C—C—OAc$ (τ 8.52) is present, leads to structures such as **25***b*. Support for structure **25***b* comes from the i.r. absorption of the derived diol, **25***a*, m.p. 195–197°, and a consideration of reaction pathways emanating from **1** which are satisfying on mechanistic grounds. Thus, the diol shows strong hydrogen bonding, $\Delta\nu_{OH} = 95\ cm^{-1}$, a value considerably larger than those recorded for simple cyclohexane vicinal diols but similar to those for certain related bridged systems (16). In addition, the following mechanistic pathway would account for the formation of **25***b*. Attack of the metal salt on the $C_{12}—C_{13}$ bond of **1** and attachment of the thallium substituent to C-13 would give the ion **26**. Wagner–Meerwein rearrangement with transfer of carbonium ion character to C-16 (see **26** arrows) and then capture of solvent at C-16 would give **25***c*. Steric and mechanistic arguments predict capture on the α-face. The diacetate **25***b* would then be generated from **25***c* with retention of stereochemistry (2) at C-13.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. For normal analytical and preparative t.l.c., chromatoplates were spread with Kieselgel G (Merck), while silver nitrate – silica gel chromatoplates in addition contained 12% of the former. Gas–liquid chromatography was carried out at 200° with a Varian Aerograph 1200 gas chromatograph using a stainless steel column (1/8 in. × 10 ft packed with 5% SE-30) and nitrogen as carrier gas with a flow rate of 25 ml/min. Light petroleum was of b.p. 60–80°. Proton magnetic resonance spectra were run on a Varian Associates A-60A or HA100 spectrometer in carbon tetrachloride unless otherwise stated using approximately 0.3 *M* solutions and tetramethylsilane as internal standard. Infrared spectra were recorded in carbon tetrachloride on a Beckman I.R.12 spectrophotometer. Microanalyses were by Mr. S. McKinnon, Guelph. Routine mass spectra were run on a Varian Associates CH7 instrument and high resolution mass spectra on an AEI MS 902 instrument equipped with a PDP8 computer at the N.T.H., Trondheim, Norway.

Separation of Further Products from the Oxidative Cleavage

The products (3.60 g) from the oxidative cleavage of **1** (3.40 g) were chromatographed over alumina (2). Seven fractions (1.227 g total) were collected using light petroleum – ethyl acetate (24:1) as eluant. The last three of these were combined (556 mg) and a minor component (**16**, 42 mg) separated by preparative t.l.c. over silver nitrate – silica gel (ethyl acetate – light petroleum) before isolation (2) of the alcohols corresponding to **2** and **5** from the rest of this material. This new acetate (**16**) crystallized from light petroleum and had m.p. 128–131°; τ 5.20 (br s, 3H, 2 H-17 + H-13), 7.98 (s, 3H, —OCOCH_3), 8.82 (s, 3 H-18), and 9.23 (s, 3 H-20).

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.55; H, 9.04.

The other four fractions (of the seven) from the alumina column were also combined (671 mg) and subjected to preparative t.l.c. (ethyl acetate – light petroleum, 3:97, run four times). The fractions obtained by this procedure were then subjected to further preparative t.l.c. this time on silica gel – silver nitrate (ethyl acetate, 3:97, run four times). This yielded a pure sample of **9** (82 mg) and a second component (**6***b*) in almost pure form. The remaining fractions were recombined and hydrolyzed with excess sodium hydroxide (0.5 g) in refluxing aqueous methanol (20 ml, 1:1) for 1 h. The hydrolysis mixture was separated by preparative t.l.c. first on silica gel (ethyl acetate – light petroleum, 1:10, run thrice) and then on silver nitrate – silica gel (ethyl acetate – light petroleum, 1:10, run thrice). This sequence afforded **11***a* (20 mg), **12***a* (74 mg), and **13***a* (41 mg).

Ketone **9** crystallized from light petroleum and had m.p. 101–104°; τ 4.92 (br s, 2H, H-12 + H-13), 7.67 (s, 2 H-15), 7.97 (s, 3 H-17), 8.85 (s, 3 H-18), and 9.34 (s, 3 H-20); *m/e* 332 (M).

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.88; H, 9.76.

Acetate **6***b*, which had τ 4.58 (br s, 1 H-15), 5.31 (d, 1 H-12, J = 3 Hz), 8.03 (s, 3H, —OCOCH_3), 8.43 (br s, 3 H-17), 8.83 (s, 3 H-18), and 9.36 (s, 3 H-20), failed to crystallize and was hydrolyzed with excess sodium hydroxide (0.1 g) in refluxing aqueous methanol (10 ml, 1:1) for 1 h. The alcohol (**6***a*, 44 mg) was recovered from the reaction mixture by preparative t.l.c. (ethyl acetate – light petroleum, 1:10, run thrice). After crystallization from light petroleum it had m.p. 148–150°; τ 4.60 (br s, 1 H-15), 6.43 (d, 1 H-12, J = 3 Hz), 8.31 (br s, 3 H-17), 8.82 (s, 3 H-18), and 9.31 (s, 3 H-20).

Mol. Wt. Calcd. for $C_{21}H_{32}O_3$: 332.2352. Found (high resolution mass spectrometry): 332.2356.

The known (4) alcohol **11***a* had m.p. 142–145° (lit. (4) m.p. 148°) on crystallization from light petroleum;

τ 8.71 (s, 3 H-17), 8.83 (s, 3 H-18), and 9.22 (s, 3 H-20). Alcohol **12***a* was obtained as an oil; τ 3.82 (m, 1 H-14), 4.00 (m, 1 H-13), 8.83 (s, 3 H-18), 8.91 (s, 3 H-17), and 9.62 (s, 3 H-20); in the presence of 0.4 *M* ratio of Eu(DPM)$_3$ to **12***a* τ 2.90 (m, 1 H-14), 3.22 (m, 1 H-13), 6.25 (s, 3 H-17), 8.50 (s, 3 H-18), 8.85 (s, 3 H-20); ν_{max} 3620 and 1740 cm^{-1}.

Mol. Wt. Calcd. for $C_{21}H_{32}O_3$: 332.2352. Found (high resolution mass spectrometry): 332.2353.

Alcohol **13***a* after crystallization from light petroleum had m.p. 120–121°; τ 4.82 (m, 1 H-7), 8.70 (s, 3 H-17), 8.83 (s, 3 H-18), and 9.36 (s, 3 H-20); *m/e* 146 (M − 18 − 168).

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.88; H, 9.76.

Fractions from the original alumina column eluted with light petroleum – ethyl acetate (23:2) were combined (966 mg total) and subjected to preparative t.l.c. (ethyl acetate – light petroleum, 1:9, run thrice). This yielded (2) **3** and **4** and a compound (**25***b*, 109 mg) of intermediate polarity. The last even after repeated preparative t.l.c. contained traces of **4**. This material (84 mg) which had τ 5.10 (dd, 1 H-13, J_{obs} = 3 and 6 Hz) 8.52 (s, 3 H-17), 8.86 (s, 3 H-18), and 9.18 (s, 3 H-20) was hydrolyzed with sodium hydroxide (0.4 g) in refluxing aqueous methanol (20 ml, 1:1) for 3 h. The product mixture (72 mg) was subjected to preparative t.l.c. (ethyl acetate – light petroleum, 1:4) and afforded substrate (15 mg) and diol **25***a* (26 mg). The latter on crystallization from benzene – light petroleum had m.p. 195–197°; τ ($CDCl_3$) 6.18 (dd, 1 H-13, J_{obs} = 3.5 and 5 Hz), 8.75 (s, 3 H-17), 8.83 (s, 3 H-18), and 9.22 (s, 3 H-20); ν_{OH} (2 mg/ml) 3610, 3515, 3348 cm^{-1}; ν_{OH} (0.5 mg/ml) 3610 and 3515 cm^{-1}.

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 71.89; H, 9.69.

Solvolysis of the Tosylate 7

The alcohol (35 mg) derived (2) from **2** was treated with excess *p*-toluenesulfonyl chloride (30 mg) in pyridine (2 ml) overnight. The reaction mixture (one spot on t.l.c., less polar than substrate) was diluted with ether and washed twice with chilled hydrochloric acid (1 *M*) and then water. The product (31 mg, 89%) was purified by preparative t.l.c. (ethyl acetate – light petroleum, 1:9 run twice) and shown to be identical with **6***a* by m.p., mixture m.p., t.l.c., and n.m.r.

*Reduction of the Ketone **9** with Sodium Borohydride*

The ketone **9** (22 mg) was treated with excess sodium borohydride (25 mg) in ethanol (5 ml) at 20° for 3 h. The alcohol **10** formed, was purified by preparative t.l.c. (ethyl acetate – light petroleum, 1:5) and then crystallization from light petroleum. It (16 mg) had m.p. 79°; τ 4.47 (br s, 2H, H-12 + H-13), 7.5–8.15 (m, 4H, 2H-11 + 2H-14), 8.85 (s, 3 H-18), 8.87 (d, 3 H-17, J = 6 Hz), and 9.33 (s, 3 H-20).

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25. Found: C, 75.53; H, 10.13.

*Hydrogenation of Acetate **16***

Hydrogenation of **16** (25 mg) in ethyl acetate (10 ml) over palladized charcoal (5%, 15 mg) for 30 min afforded a single product which was purified by t.l.c. on silver nitrate – silica gel (ethyl acetate – light petroleum, 1:10, run thrice). This oil (18 mg) was shown by n.m.r., t.l.c., and g.l.c. to be identical with the major product, **17***b*, obtained by hydrogenation of **2**. Hydrolysis of the oil with sodium hydroxide (0.1 g) in refluxing aqueous methanol (10 ml, 1:1) for 3 h yielded **17***a* (14 mg, 88%), which crystallized from ethyl acetate – light petroleum. This alcohol had m.p. 132–134° and was identical (m.p., mixture m.p., t.l.c., and n.m.r.) with an authentic sample (2) of **17***a*.

*Treatment of Methyl ent-Trachyloban-19-oate (**1**) with Acetic Acid*

The ester **1** (100 mg) was heated in 20 ml glacial acetic acid at 75° for 5 days. The solvent was evaporated and the residue separated by preparative t.l.c. (ethyl acetate – light petroleum, 1:5 run thrice). One major product (**11***b*, 23 mg, 19%) was recovered. It crystallized from light petroleum and had m.p. 143–144°; τ 8.05 (s, 3H, —OCO*CH*$_3$), 8.46 (s, 3 H-17), 8.84 (s, 3 H-18), and 9.22 (s, 3 H-20).

Anal. Calcd. for $C_{23}H_{36}O_4$: C, 73.37; H, 9.64. Found: C, 73.34; H, 9.77.

We thank Dr. T. Anthonsen, N. T. H., Trondheim, Norway, for the high resolution mass spectra. The financial support of the National Research Council of Canada and of the Province of Ontario through an operating grant (to R.McC.) and an Ontario Graduate Fellowship (to H.M.C.), respectively, is gratefully acknowledged.

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