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OXIDATION OF CEDRANE AND CEDROL WITH IODINE TRIS-(TRIFLUOROACETATE)

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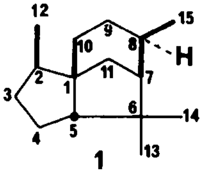
Iodine tris-(trifluoroacetate) (ITT) is reported to oxidize alkanes containing tertiary C-H bonds in minutes, and methylene groups in days, to form trifluoroacetates by "insertion" into C-H bonds. In the case of cyclohexane, along with cyclohexyl trifluoroacetate (16%), a mixture of esters of *cis*- and *trans*- 1,2 diols (30%) was obtained.[1]

We have now studied the action of ITT on the sesquiterpenes (8αH)-cedrane 1 and cedrol 7. The first one could have given the trifluoroacetate of the second one, or attack at C-2 could have taken place by analogy with ozone.[2] In fact, we have observed two novel reaction pathways, not yet obtained with this reagent.[3]

(8αH)-Cedrane 1 reacts rapidly at room temperature with ITT in dry CH_2Cl_2. After six hrs., the reaction mixture was worked up with alkaline hydrolysis of the esters formed. It gave, besides unreacted starting material (17%) and untractable minor products, essentially one product (78%, without optimisation, based on unrecovered starting material). This was shown by the usual spectral data to be a methyl-ketone, and structure 2 was tentatively



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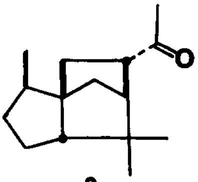

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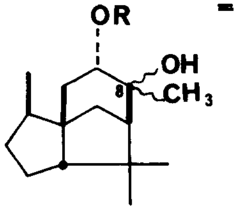


3: R=H, 8β-OH
4: R=Ts, 8β-OH
5: R=H, 8α-OH
6: R=Ts, 8α-OH

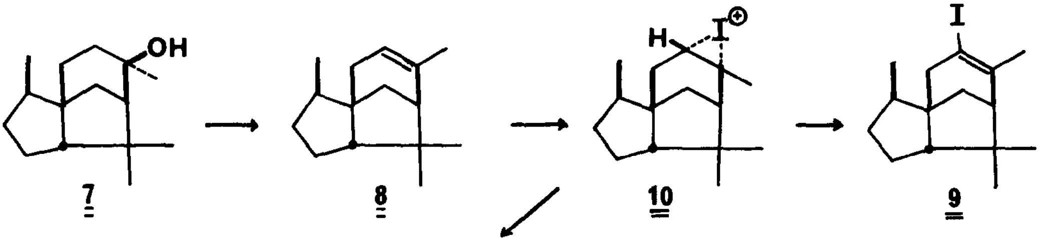
<u>Methyl-ketone (2)</u>: liq. $(\alpha)_D$+3.2°(c, 0.5% $CHCl_3$). 2,4 DNP: m.p. 182-185°. IR: 1715 Cm^{-1}. NMR(δ): 0.89(3H,d,J=7Hz), 0.96 & 1.09(3H,s,each), 2.14(3H,s), 2.95(1H,m). Mass: m/e 220 $C_{15}H_{24}O(M^{+\cdot}$,10%).

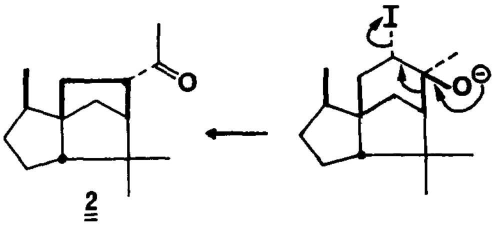
<u>Cis-glycol (5)</u>: m.p. 165°. $(\alpha)_D$-20°(c, 0.7% $CHCl_3$) IR: 3560, 3250, 1048 Cm^{-1}. NMR(δ): 0.9(3H,d,J=7 Hz), 1.05 & 1.17(3H,s,each), 1.4(3H,s), 3.75(1H,m). Mass: m/e 238 $C_{15}H_{26}O_2(M^{+\cdot}$, 9.4%).

<u>Mono-tosylate (6)</u>: m.p. 80-83. $(\alpha)_D$-8°(c, 0.35% $CHCl_3$). IR:[5] 3520, 1350, 1188, 1172 Cm^{-1}. NMR(δ): 0.75(3H,d,J=7Hz), 1.0 & 1.1(3H,s,each), 1.25(3H,s), 2.43(3H,s), 7.30-7.40(2H,m), 7.80-7.95 (2H,m).

assigned to it. This structure has been previously assigned to a substance obtained by base hydrolysis of the monotosylate 4 of the glycol 3.[4] The ir and nmr data of our sample fit perfectly with those published. We have confirmed the structure 2 (still tentative in ref.[4]) by treating with refluxing pyridine the monotosylate 6 derived from the *cis*-glycol 5, itself obtained from α-cedrene by osmium tetroxide hydroxylation, and therefore α,α.

Cedrol 7 reacts instantaneously with ITT. The crude product was treated with KOH in aqueous methanol and gave mainly three products: α-cedrene 8 (5%), the ketone 2 (11%), and 9-iodo-cedr-8-ene 9 (70%), converted to α-cedrene 8 by metal-halogen exchange (n-BuLi/THF, -78°C, 3 hrs.) and aqueous work-up.





9-Iodo-α-cedrene (9): liq. $(\alpha)_D$ -73°(c, 0.26% $CHCl_3$). IR: no OH or C=O absorption. PMR(δ): 0.84(3H,d,J=7Hz), 0.95 & 1.0(3H,s,each), 1.86 (3H,m), 2.45-2.70(2H,m), no olefinic protons. Mass: m/e 330 $C_{15}H_{23}I(M^{+\cdot}$, 40%), 203($M^{+\cdot}$-I, 29.6%).

Formally, products 2 and 9 could be derived from a similar intermediate 10, itself coming from α-cedrene 8, derived from 1 by dehydrogenation, from 7 by dehydration. However, it appears that the two pathways are in fact segregated, at least in part, but too little information is yet available to indulge in a mechanistic discussion.

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