

yielded the title compound as its hydrochloride in amorphous form (28 mg). ^1H NMR (D_2O , 85°C) showed, *inter alia*, δ 3.60 (3 H, s, OMe group), δ 2.86 (3 H, s, *N*-methyl group) and δ 4.73 (1 H, d, $J_{1,2}$ 8.5 Hz, anomeric proton).

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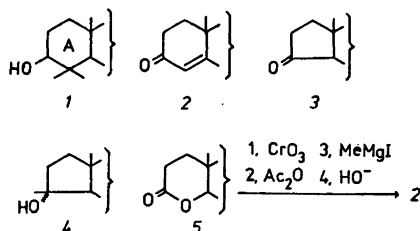
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The Exhaustive Baeyer-Villiger Oxidation of Cyclic α,α -Dimethyl-substituted Ketones: δ -Lactones from 1,1-Dimethyl-2-decalones and Triterpene-3-ones

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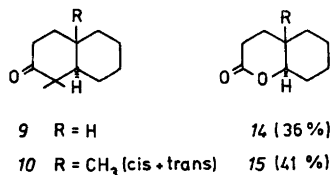
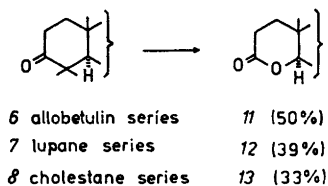
The reconstruction of a triterpenoid ring A (*1*) into a steroid-type 4-en-3-one system (*2*) is a problem of long standing.¹ The Voser procedure^{2,3} and later modifications⁴⁻¹⁰ involve the dehydration and oxidation of *1* to a ring A cyclopentan-3-one (*3*) followed by methylation (to give *4*), ring cleavage and cyclisation to furnish *2* in 5-7 steps and 2-11% overall yield. The ketone *3* may also be oxidised to the ring A 4-oxa-3-one (*5*) which will then give *2* as shown in 39% yield^{11,12} (9.4% overall from *1*).



Another route¹³ is based on the photochemical cleavage of the 4-derived nitrite, giving *2* in 6% yield from *3*. The most efficient among the published 4,4-bisdemethylation procedures utilised¹⁴ the second-order Beckmann oxime cleavage (from 5 α H-lanostan-3-one), giving the corresponding 4-en-3-one (*2*) in 8 steps in 25% overall yield. A related route has been used¹⁵ to effect 4,4-bisdemethylation without 4,5-dehydrogenation in unspecified yield in 8 steps.

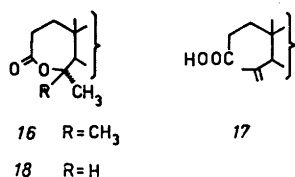
One of us has reported¹⁶ a case of exhaustive Bayer-Villiger oxidation of the pentacyclic triterpene allobetulone (*6*), giving *11* in 50% yield on treatment with peracetic acid and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Provided this reaction is general, a short new route for the 4,5-dehydrogenative 4,4-bisdemethylation (*1* \rightarrow *2*) of triterpenes and related compounds would be at hand, as the lactones *5* can be transformed to the enones *2* in 4 steps in *ca.* 40% yield.^{11,12}

Further studies now reported show that the reaction is general for condensed cyclic α,α -dimethyl-substituted ketones. The ketones (*7-10*) are oxidised with peracetic acid/boron trifluoride etherate to give the lactones *12-15*



(isolated yields). Only the 5 α H lactones (except for 15) could be detected by TLC and ¹H NMR. Other protic or Lewis acids tested (H₂SO₄, FSO₃H, TsOH, AlCl₃, FeCl₃, ZnCl₂, BCl₃, BBr₃, BI₃) proved to be inferior to BF₃·Et₂O. *o*-Sulfoperbenzoic acid¹⁷ which is at the same time a peracid and a strong protic acid did not, however, react with the ketones 7–10.

Concerning the overall reaction pathway we found that the normal Baeyer-Villiger product 16 and its ring-opened form 17 are likely intermediates as they are oxidised under the peracetic acid/BF₃·Et₂O conditions to the same lactone 11 (cf. the related *m*-chloroperbenzoic acid/H₂SO₄ oxidation¹⁸ 8 → 18 involving an 8-step mechanism *via* 16 and 17). We are now studying further the mechanism of the peracetic acid/BF₃·Et₂O reaction.



Experimental. For general experimental information see Ref. 22.

Peracetic acid oxidations. The α,α -dimethyl-substituted ketone (1–2 mmol) was stirred in CH₂Cl₂ (12 ml) with a mixture of 2.4 ml (20 mmol) of BF₃·Et₂O and 9.6 ml (60 mmol) of commercial 40% AcOOH. After 16 h at 6°C the mixture was treated with aqueous NaHCO₃, dried and chromatographed on prep. TLC plates (Merck 60 PF₂₅₄₊₃₆₆, elution with CHCl₃:light petroleum 40–60°, 9:1) to give the lactone.

23,24-Dinor-4-oxa-3-lupanone (13), m.p. 220–222°C (EtOH), [α]_D +46.5° (c 0.07); 1750 cm⁻¹; δ 3.85 (1 H d d, $J_1 = 6$ Hz, $J_2 = 9.5$ Hz); *m/e* (%) 400 (8.6) M⁺, 385 (10.9) M–CH₃, 357 (18.5) M–CH(CH₃)₂.

4-Oxa-3-cholestanone (13), m.p. 116°C (lit.¹⁹ m.p. 115–117°C); IR, ¹H NMR and MS as reported.¹⁹ In particular, the 5 α H appears¹⁹ at δ 3.95 as a d-of-d system, $J_{5\alpha,5\alpha} = 5$ Hz, $J_{5\alpha,5\beta} = 11$ Hz. The epimeric 5 β H would appear²¹ at δ 4.13, $W_{\frac{1}{2}}$ 3 Hz.

trans-2-Oxabicyclo[4.4.0]-3-decanone (14), oil; IR and ¹H NMR as reported,²⁰ *m/e* (%) 154 (5.5) M⁺.

6-Methyl-2-oxabicyclo[4.4.0]-3-decanones (15), oil; 1740 cm⁻¹; 4.08 (1 H m, 1-H), 1.07 (3/2 H s, 6-Me in *cis*-15²²), 0.97 (3/2 H s, 6-Me in *trans*-15²³); *m/e* (%) 168 (2.6) M⁺.

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