(±)-Phoracantholid I *via* the Caesium Carbonate-promoted Ring Closure of the Methanesulphonate of 9-Hydroxydecanoic Acid

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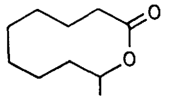
(±)-Phoracantholid I, a product from the secretion of the longicorn *Phoracantha synonyma*, has been synthesised *via* the caesium carbonate treatment of the methanesulphonate of 9-hydroxydecanoic acid, prepared from the easily accessible 9-oxo-derivative.

Phoracantholid I (decan-9-olide) (**1**) is a substance previously isolated from the metasternal secretion of the eucalyptus longicorn *Phoracantha synonyma*.[1] A one-step synthesis of 9-oxodecanoic acid (**2**) has been recently reported,[2] and we hoped that the caesium carbonate-promoted cyclization of the methanesulphonate of the corresponding hydroxy-acid (**3**), would provide a convenient short synthesis of this lactone (**1**). The hydroxy-acid (**3**) can also be prepared by reduction ($NaBH_4$,H_2–Pt) of (*E*)-9-oxodec-2-enoic acid (**4**), the queen substance of the honeybee queen *Apis mellifica*.[3]

The methanesulphonate of (**3**) was prepared from (**2**) ($NaBH_4$, $MeSO_2Cl$) and treated with Cs_2CO_3–*N*,*N*-dimethyl-



(1)

(**2**) $MeCO[CH_2]_7CO_2H$
(**3**) $MeCH(OH)[CH_2]_7CO_2H$
(**4**) $MeCO[CH_2]_5CH{=}CHCO_2H$
(**5**) $HO[CH_2]_7CH{=}CHCO_2H$
(**6**) $HO[CH_2]_9CO_2H$

formamide (DMF) for 4 days at 40 °C,[1] leading to a total yield of cyclized products of *ca.* 75%. T.l.c. on silica (Schleicher–Schüll, fluorescent, developing with hexane–ethyl acetate, 9 : 1), then 50% H_2SO_4 spray on lateral spots, 100 °C, or u.v. absorption for the conjugated compounds, allowed the separation of (**1**) R_f 0.60 (45%), also the dilactide, R_f 0.55 (m.s.; yield 25%), and the trilactide (5%). The lactone (**1**) is a colourless oil, m.s. 170 (M^{+}), n.m.r. (400 MHz, $CDCl_3$) δ 1.38 (3H, d, CH_3–CH–O–) and 5.00 (1H, m, J 6 Hz, CH_3–CH–O–). Using K_2CO_3 instead of Cs_2CO_3 gives a final yield of cyclization products of 70% but this included only 24% of the expected lactone (**1**).

We previously reported the PPh_3–ethylazodicarboxylate cyclization of royal jelly acid, (*E*)-10-hydroxydec-2-enoic acid (**5**), in which the corresponding dilactide is the main product and the lactone is formed in trace amounts (determined by mass spectroscopy).[5] We tried to apply the Cs_2CO_3–DMF treatment to the methanesulphonate of (**5**) but were unable to get more than 7% of the lactone, together with the dilactide (53%) and the other oligomers. It seems that the α,β unsaturated carboxy-function opposes the lactonization in such compounds. This conclusion was emphasised by the fact that the α,β-unsaturated hydroxy-acid obtained through $NaBH_4$ reduction of queen substance (**4**), gave similar results using this method (only 6% of the lactone, as determined from m.s.).

The Cs_2CO_3–DMF treatment of the methanesulphonate of (**6**) (10-hydroxydecanoic acid) obtained from (**5**) (H_2–Pt) gave (t.l.c., m.s.) a mixture of the lactone (R_f 0.70) and the dilactide (R_f 0.65) in the ratio 7 : 3.

As C_9 and C_{10} caesium ω-halogenoalkanoates do not give lactones under such conditions[1,6] our observations above may be related to the particular reactivity of the methanesulphonate group.

Thanks are due to Mrs. C. Fontaine for the n.m.r. determination on a Bruker WM 400 spectrometer and to Drs. B. C. Das and C. Girard for mass spectrometry on an AEI MS 50.

Received, 25th February 1982; Com. 205

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