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A Total Decyclisation of Jaeschkeanadiol

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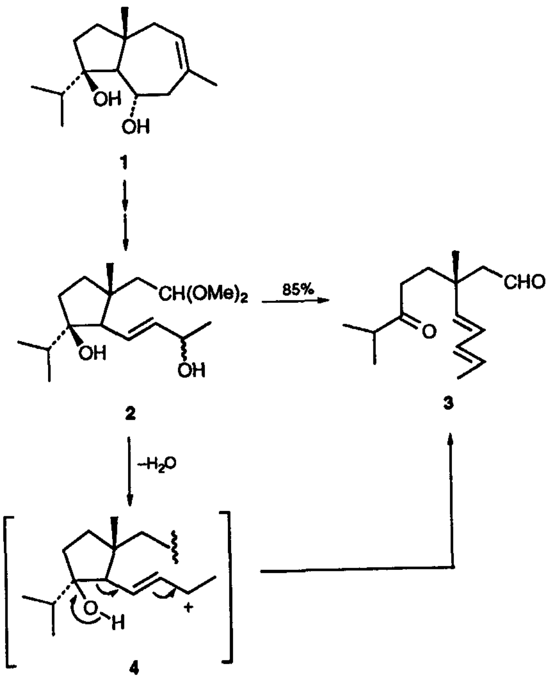
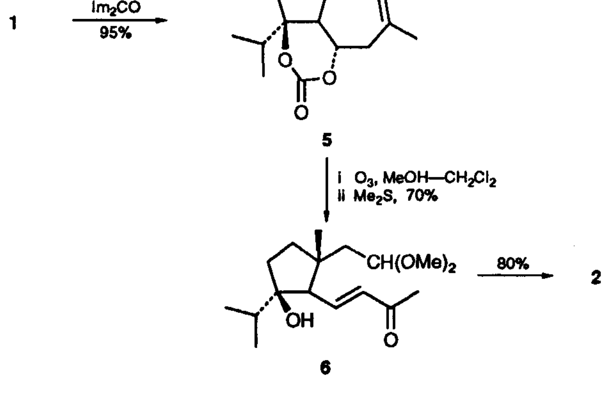
The reaction of epimerical diols **2** with $LiBF_4$ in MeCN gives the product of fragmentation **3**.



In the course of conducting a synthetic scheme to transform a natural sesquiterpenoid jaeschkeanadiol **1**[1,2] into monocyclopentanoids, in particular, into appropriately modified prostanoids, the occurrence of an unusual, smooth fragmentation leading to the acyclic system **3** was observed at the dimethylacetal **2** deblocking stage using $LiBF_4$ in MeCN.[3] It can be noted that the stereochemical uniformity of the reaction observed (the *E*,*E*-isomer **3** is formed) confirms that the decyclisation **2** proceeds *via* a carbonic intermediate **4**.



Allylic alcohol **2** obtained in the **1**→**3** transformation was formed by ozonolytic cleavage of the carbonate of jaeschkeanadiol **5** and subsequent boron hydride reduction of enone **6** (MeOH, −40 °C).† Commonly, a version of the 'two-stage fragmentation' of jaeschkeanadiol described above is of theoretical interest and also opens a way to the new homochiral units of type **3**, which may be widely applied in total synthesis.

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† Characterization data for jaeschkeanadiol (4β,6α-dihydroxydaux-8-ene) **1**. M.p. 83–85 °C (EtOAc), $[\alpha]_D^{25}$ +38.0 ° (*c* 1.0, $CHCl_3$).

(1*R*, 2*R*, 3*R*)-3-Methyl-1-isopropyl-2(3α,β-hydroxy-*E*-but-1-enyl)-3-(2-dimethoxyethyl)cyclopentan-1-ol **2**, mixture of 3α- and 3β-epimers in the ratio 4:6, oily liquid. ^{1}H NMR (δ, $CDCl_3$): 0.86 (d, 3H, *J* 4.2 Hz) and 0.93 (d, 3H, *J* 4.0 Hz, $-CMe_2$), 1.06 (s, 3H, Me), 1.27 (d, 3H, *J* 6.3 Hz, Me), 1.49–1.79 (m, 6H, CH_2), 2.07 (d, 1H, *J* 5.6 Hz, C^2H), 2.46 (br s, 1H, OH), 3.28 (s) and 3.29 (s, 6H, OMe), 4.09–4.46 [m, 2H, $CH(OMe)_2$ and =CH–C–)], 5.52–5.72 (m, 1H, CH=). ^{13}C NMR (δ, $CDCl_3$): 17.36 and 18.08 ($CHMe_2$), 22.52 (22.29- β-epimer) (Me), 23.56 (Me), 34.01 (33.81- β-epimer)(C^4), 36.73 (36.42- β-epimer)(C^5), 37.73 ($CHMe_2$), 43.47 (CH_2), 44.71 (C^3), 52.35 (OMe), 58.03 (C^2), 68.88 (68.41- β-epimer) (CHOH), 85.77 (C^1), 102.94 (OCHO), 127.87 (126.70- β-epimer) (=CH–C–O), 138.45 (138.25- β-epimer) (CH=).

(6*R*)-2,6-Dimethyl-6-(2-oxoethyl)-3-oxoundeca-7*E*,9*E*-diene **3**, oily liquid, $[\alpha]_D^{25}$ −59.7 ° (*c* 2.54, $CHCl_3$). UV (λ_{max}/nm): 228.45 (EtOH). ^{1}H NMR (δ, $CDCl_3$): 1.07 (d, 6H, *J* 7.0 Hz, CMe_2), 1.15 (s, 3H, Me), 1.74 (d, 3H, *J* 6.0 Hz, MeC=), 1.60–1.80 (m, 2H, C^5H_2), 2.25–2.45 (m, 4H, C^4H_2, CH_2), 2.57 (quin., 1H, *J* 7.0 Hz, C^2H), 5.49 (d, 1H, *J* 15.7 Hz, -C^7H=), 5.66 (dq, 1H, *J* 6.0 and 15.2 Hz, $C^{10}H$), 5.90–6.10 (m, 2H, C^8H, C^9H), 9.7 (t, 1H, *J* 2.8 Hz, CHO). ^{13}C NMR (δ, $CDCl_3$): 17.98 (Me), 18.17 and 18.23 ($CHMe_2$), 23.43 (CH_3), 34.97 (C^5 and C^4), 37.85 (C^6), 40.91 (C^2), 53.76 (CH_2CHO), 128.95, 129.38, 131.05 and 136.0 (C^7, C^8, C^9, C^{10}), 202.79 (CHO), 214.15 (C=O); MS *m*/*z* 236 $[M]^+$, 221 $[M-Me]^+$, 218 $[M-H_2O]^+$, 207 $[M-CHO]^+$, 193 $[M-CH_2CHO]^+$, 177, 123, 109, 107, 95, 93, 91, 83, 71, 43 $[CH_2CHO]^+$ (max).

Carbonate of jaeschkeanadiol **5**. M.p. 102–103 °C (lit.,[2] 102–103 °C), $[\alpha]_D^{25}$ −41.44 ° (*c* 0.98, MeOH).

^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AM–300 spectrometer of operating frequencies 300 and 75.47 MHz, respectively, internal standard TMS, solvent $CDCl_3$. Mass spectra were determined on a mass spectrometer MX–1303, ionising voltage energy 70 eV. Optical rotations were measured at 25 °C on a Perkin-Elmer Polarimeter M-141.

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