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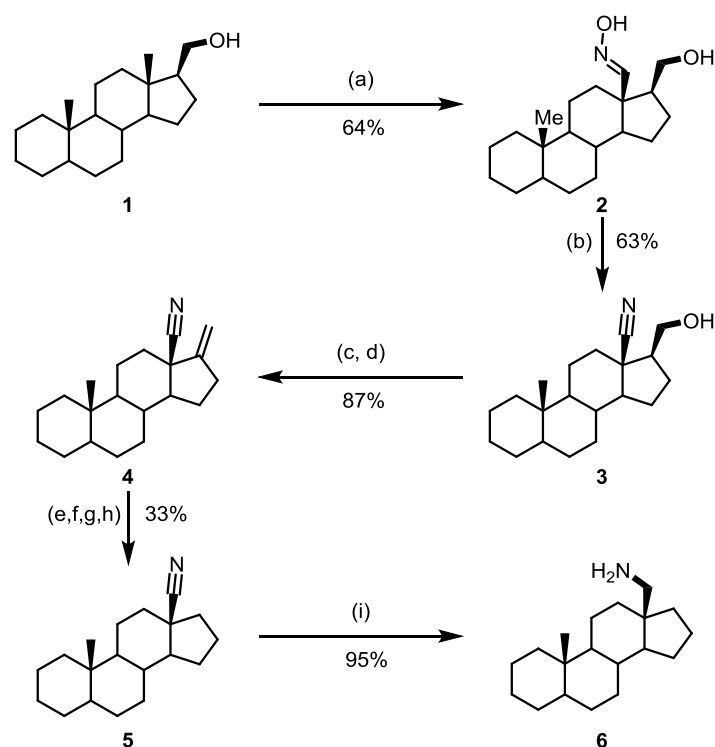
Deamination reaction of 18-aminoandrostane gave after hydrogenation 14 β -androstane and 18-*nor*-D-*homo*-androstane. By GCMS comparison with geological samples from Oman containing three unknown fossil C₁₉H₃₂ biomarkers two of the unknown could be clearly identified to be the obtained 14 β -androstane and 18-*nor*-D-*homo*-androstane.

Molecular Fossils – an Important Tool in Modern Geochemistry

The structure and distribution pattern of steranes allow a deep look insight into geological history. Knowing the structure of those biomarkers, organic geologists are able to trace them back to potential biogenic ancestors in precursor organisms. Mass spectral investigations of 550-million-year-old crude oils samples from the Oman Salt Basin indicate the appearance of three unknown C₁₉ steranes (C₁₉H₃₂, *m/z* = 260; 19A, 19B, and 19C) of interest.^[1]

Synthesis of 18-Aminoandrostane 6

18-Aminoandrostane **6** was synthesized in nine steps from alcohol **1**. In a key step transformation the C18 methyl group was functionalized by Barton reaction. The oxime **2** was dehydrated to nitrile **4** with the Mukaiyama reagent. The alcohol **3** was removed by oxidation of selenyl ether to give alkene **4**. The C17 site chain was then successively removed by dihydroxylation, periodate cleavage and removing the carbonyl group by thio acetalization and Raney nickel reduction. Further reduction of nitrile **5** with LiAlH₄ gave amine **6** in 11% overall yield.^[2]



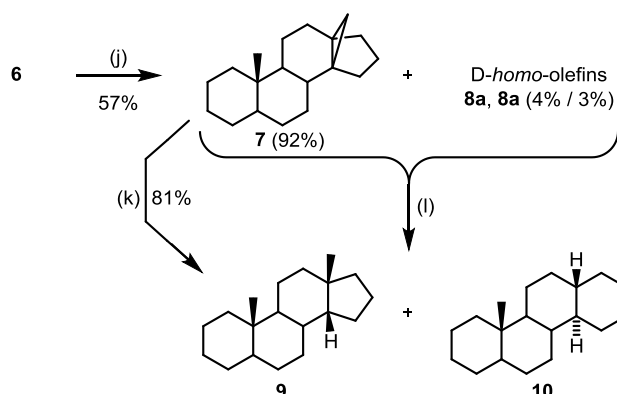
Scheme 1: Reagents and conditions (a) 1. *t*BuONO, CHCl₃, rt, 0.5 h; 2. acetone, UV-light, 20 min; 3. *i*-PrOH, 82°C, 2 h, rt; (b) 2-chloro-1-methylpyridiniumiodide, NEt₃, DCM, 40°C, 24 h; (c) 2-(NO₂)C₆H₄SeCN, *n*Bu₃P, THF, 3 h, 66°C; (d) H₂O₂, H₂O, THF, 66°C, 4 h; (e) K₂O₈, NMO, THF, acetone, H₂O, rt, 40 h; NaIO₄, THF, H₂O, reflux, 4 h; (f) (CH₂SH)₂, *p*TosOH · H₂O, C₆H₆, 80°C, 16 h; (g) Raney-Ni, EtOH, 3.5 h, 78°C; (i) LiAlH₄, THF, 20 h, 66°C.

Deamination Reaction of Amine 6 and Hydrogenation

Diazotation of primary amine **6** furnished a mixture of cyclopropane compound **7** and D-*homo*-olefins **8a** and **8b** in a ratio of 92:4:3 (**7/8a/8b**, by GCMS). Prior to palladium catalyzed hydrogenation acidic treatment was required to obtain the androstane derivatives **9** and **10**. However, ionic hydrogenation of cyclopropane derivative **7** by TFA and Et₃SiH gave pure 14 β -androstane **9** (Scheme 2). Whereas compound **10** was already elucidated by previous studies,^[1] it was possible to obtain a crystal structure of compound **9** to be 14 β -androstane (Figure 1).^[2]

14 β -Androstane Turned out to be the Molecular Fossil

Coelution experiments of 14 β -androstane **9** with the natural 500-Million-year-old sample from the south oman salt basin show a perfect match with the constituent "19B" (Figure 2).^[2]



Scheme 2: Reagents and conditions (j) NaNO₂, H₂O, AcOH, DCM, rt, 2 h; (k) TFA, Et₃SiH, DCM, -20°C, 2 h; (l) 1. TFA, CHCl₃, -20°C, 2 h; 2. H₂ (4 bar), Pd/C, 50°C, 2 d.

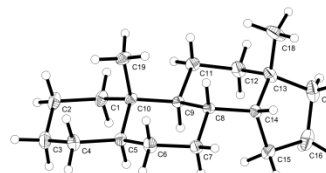


Figure 1: ORTEP representation of the molecular structure of **9**.

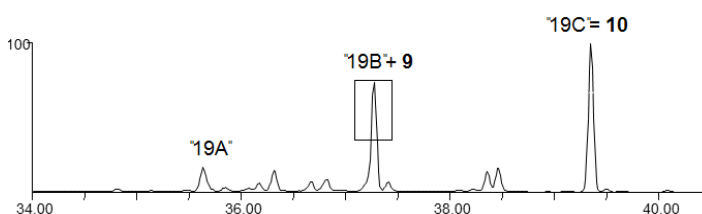


Figure 2: GC of coelution experiment with androstane **9** and the crude oil hydrocarbons. The box at the top of the GC peak shows a perfect match on a DB-5MS column.