Approaches to Triterpene Synthesis.[1] Methyl Group Migration during Catalytic Hydrogenation of Some Precursors

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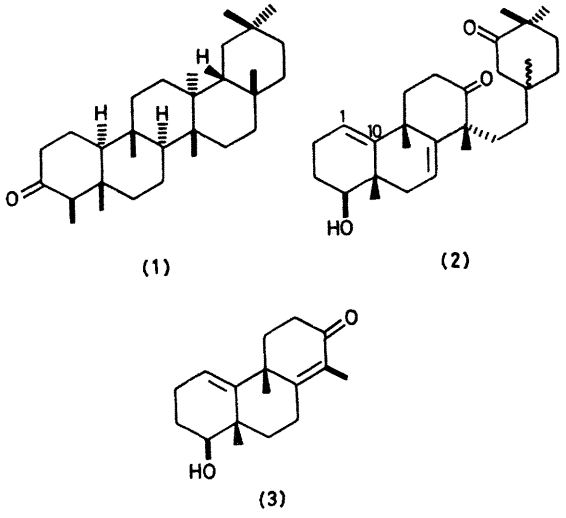
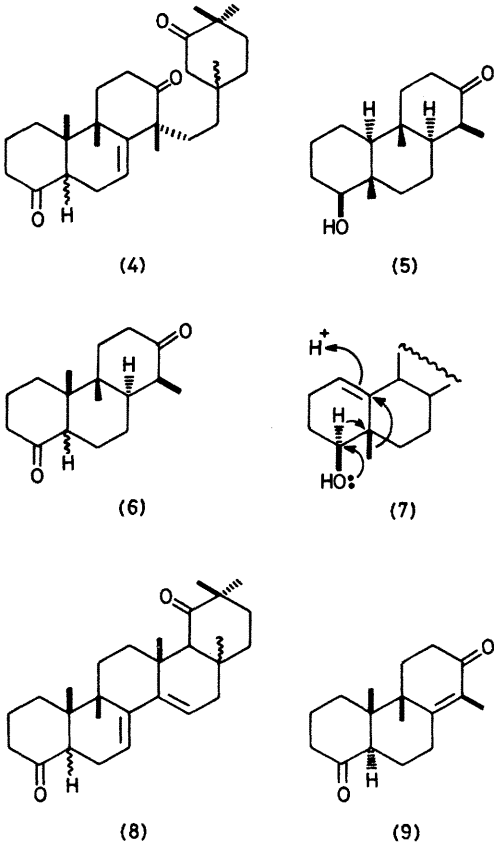
Summary An unusual methyl migration during catalytic hydrogenation of some synthetic triterpene precursors is described.

DURING our studies aimed at the total synthesis of pentacyclic triterpenes such as friedelin (**1**)[2] we have prepared the precursor (**2**) from (**3**).† Our synthetic method from (**2**) called for a catalytic hydrogenation of both double bonds, expecting addition of hydrogen from the less hindered α-face of the molecule. Previously we have shown[3] that similar reductions are in fact highly stereoselective when using palladium–charcoal as the catalyst and toluene under reflux as a solvent.



In the event, reduction of (**2**) for 4 days gave 70% of compound (**4**), m.p. 159—161 °C (^{13}C n.m.r. 214·59, 215·52, and 216·03 p.p.m., 3 × C=O) as well as unchanged starting material. Similarly, (**3**) was slowly reduced in boiling xylene during 2 days to yield the expected product (**5**) (40%), m.p. 177—187 °C, together with the rearranged species (**6**) (47%), m.p. 145—146 °C (^{13}C n.m.r. 212·38 and 214·69 p.p.m., 2 × C=O). The corresponding benzyl ethers of (**2**) and (**3**) showed the same behaviour while reduction of the acetates or the oxidised species (ketone at C-4) gave no evidence of substantial reduction or rearrangement after 5 days.

Presumably the prolonged hydrogenation conditions necessary for reaction in these cases lead to slow protonation of the 1,10 double bond (steroid numbering) in (**2**) and (**3**) followed by methyl migration and hydride shift as shown in (**7**), the hydroxy group driving this transposition. In fact this migration was also observed on treatment of (**2**) or (**3**) with toluene-*p*-sulphonic acid in boiling xylene when the major products (>80%) were tentatively identified as (**8**) and (**9**).



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† All synthetic materials are racemic; for convenience, only that enantiomer bearing a direct relationship to the natural material is shown. All compounds reported exhibit correct combustion analysis values and expected spectroscopic data (i.r., m.s., ^{1}H and ^{13}C n.m.r.).

[1] For previous paper in this series see J. W. ApSimon, S. Badripersaud, M. L. Post, and E. J. Gabe, *Canad. J. Chem.*, 1978, **56**, 2150.
[2] For the only reported total synthesis of friedelin see R. E. Ireland and D. M. Walba, *Tetrahedron Letters*, 1976, 1071.
[3] J. W. ApSimon, P. Baker, J. Buccini, J. W. Hooper, and S. Macaulay, *Canad. J. Chem.*, 1972, **50**, 1944; J. W. ApSimon, S. Badripersaud, J. W. Hooper, R. Pike, S. I. Birnbaum, C. Huber, and M. L. Post, *ibid.*, 1978, **56**, 2139.