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Mendeleev Commun., 1991, **1**(1), 36–37
Mendeleev Communications

Synthesis of Four Racemic Rosane Diterpenes

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All four possible racemic *cis*- and *trans-B/C-*$\Delta^{5(10),15}$-rosadienes **1–4** have been prepared starting from the common 4,5,9,10-bis-seco precursor **5**.

Cyclic isoprenoids possessing the rosane skeleton and biogenetically related to the representative series of tri- and tetra-cyclic diterpenes[1] have been attractive targets for synthetic chemists for many years. This has been demonstrated by various reports of the total[2] or partial[3–7] synthesis of rosanes/rimuenes. The partial syntheses were achieved mainly using cationic transformations of the related pimaranes which became available recently *via* the biogenetic type cyclization of linear geranylgeranyl-[8] or bicyclic labdane[3,5,9] precursors. Here we describe an alternative approach to racemic *trans*- and *cis-B/C*-rosadienes **1–4** based on cationic cyclization of the regular monocyclic diterpenol **5**[10] prepared for this purpose (Scheme 1).

Under the conditions recommended[11] previously for similar conversions of structurally related oligoalkenes, the triene **5** was easily transformed [FSO_3H (10 mol equiv.), 2-nitropropane, − 80 °C] into a mixture of unknown tricyclic alcohols **6**:**7**:**8**:**9** ≃ 3:1:4:3† in 88% yield. Kinetically controlled protonation of **5** is thought to produce the intermediate pimarenol **11** *via* the cation **10**. Subsequent protonation of **11** followed by a *syn*-1,2-shift of the angular methyl group of the resultant ion **12** then affords the *cis-B/C*-rosenols **8** and **9** as the major products.[5,6,12] The formation of the minor epimers at C-13, *trans-B/C*-rosenols **6** and **7**, may be explained on the basis of the key carbocation **10** (Scheme 1).

It should be noted that the observed preferential generation

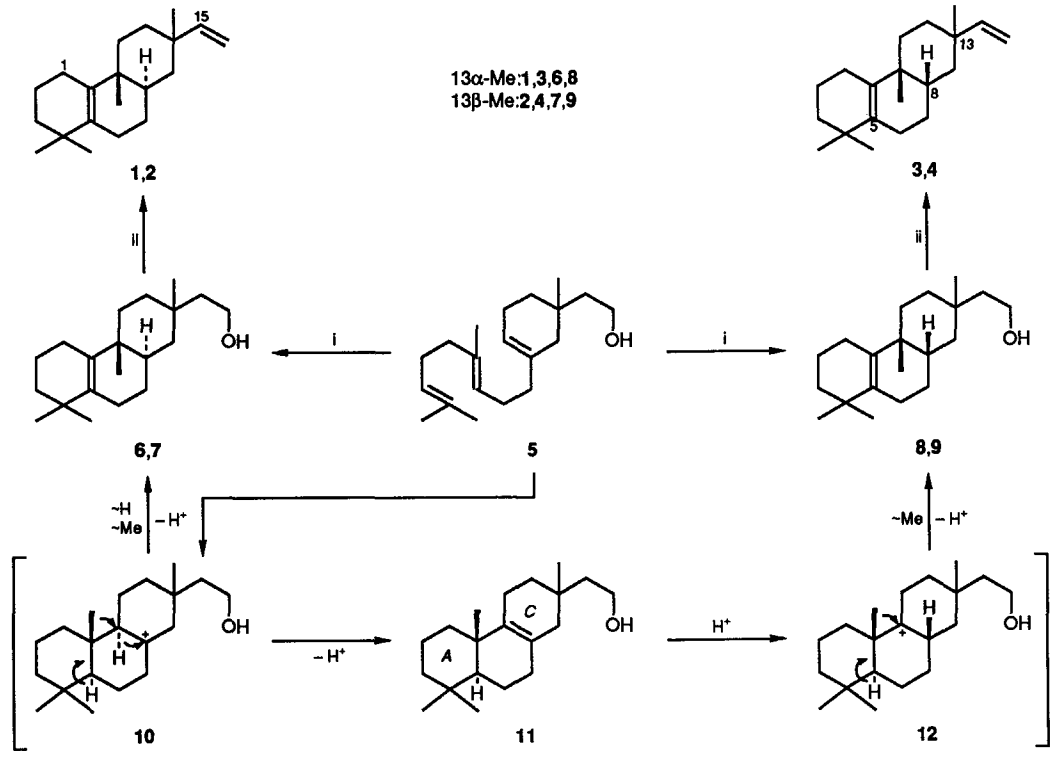
† HPLC analysis data obtained on a Separon SGX column (Czechoslovakia, 5 μm, 300 × 3.3 mm) and ethyl acetate–heptane (3:17, 0.6 ml min^{-1}) as eluent.

‡ ^{13}C *NMR data* (75 MHz, $CDCl_3$) for **6**: δ 25.27 (C-1), 19.97 (C-2), 41.15 (C-3), 34.04 (C-4), 133.32 (C-5), 26.08 (C-6), 25.40 (C-7), 37.83 (C-8), 37.70 (C-9), 136.60 (C-10), 34.04 (C-11), 31.88 (C-12), 32.72 (C-13), 39.99 (C-14), 49.15 (C-15), 59.50 (C-16), 23.56 (C-17), 29.06 (C-18), 27.90 (C-19), 17.09 (C-20).

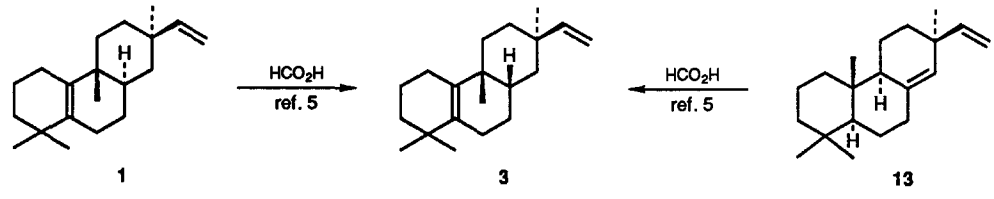
For **7**: 25.25 (C-1), 19.94 (C-2), 40.89 (C-3), 34.02 (C-4), 135.26 (C-5), 25.94 (C-6), 25.39 (C-7), 37.76 (C-8), 37.20 (C-9), 130.66 (C-10), 34.23 (C-11), 31.89 (C-12), 32.53 (C-13), 39.93 (C-14), 39.47 (C-15), 59.94 (C-16), 30.16 (C-17), 29.11 (C-18), 27.88 (C-19), 17.42 (C-20).

For **8**: 23.77 (C-1), 19.94 (C-2), 40.05 (C-3), 34.26 (C-4), 134.69 (C-5), 25.62 (C-6), 20.43 (C-7), 36.43 (C-8), 37.36 (C-9), 130.66 (C-10), 31.50 (C-11), 34.64 (C-12), 32.21 (C-13), 38.83 (C-14), 49.00 (C-15), 59.08 (C-16), 22.24 (C-17), 29.35 (C-18), 27.76 (C-19), 30.09 (C-20).

For **9**: 23.89 (C-1), 20.00 (C-2), 40.06 (C-3), 34.30 (C-4), 134.68 (C-5), 25.68 (C-6), 20.52 (C-7), 36.53 (C-8), 37.14 (C-9), 130.84 (C-10), 31.52 (C-11), 34.97 (C-12), 31.97 (C-13), 38.79 (C-14), 39.25 (C-15), 59.80 (C-16), 30.25 (C-17), 29.29 (C-18), 27.80 (C-19), 29.80 (C-20).



Scheme 1 *Reagents and conditions*: i, FSO_3H–Pr^iNO_2, – 80 °C, 10 min; ii, (*a*) NaH–tetrahydrofuran, (*b*) CS_2, (*c*) MeI, (*d*) toluene, 215 °C, 7 h



Scheme 2

of *cis-B/C*-rosenols **8** and **9** from the 4,5,9,10-bis-seco precursor **5** is in accordance with the earlier observation[5] of the thermodynamically controlled acid catalysed isomerisation of *trans-B/C*-rosadiene **1** or pimaradiene **13**, mainly to the *cis-B/C*-diene **3** possessing the same relative configuration at C-13 as the above rosenol **8**, (Scheme 2).

Careful column chromatography of the above mixture over silica gel afforded the individual components **6–9** (on the 0.3–0.5 g scale and with *ca.* 95% purity) which were identified comprehensively by elemental and spectral‡ (including ^1H and ^{13}C NMR as well as two-dimensional homo- and heteronuclear techniques) analyses. In addition, Chugaev dehydration of the individual primary alcohols **6–9** smoothly furnished the respective rosadienes **1**,[13] **2**,[6] **3**[5] and **4**[6] whose spectral data conformed with those reported. Hence, cationic cyclization of the trienol **5** may be regarded as a simple route to these tricyclic dienes.

Received in USSR, 26th November 1990
Received in UK, 17th December 1990; Com. 0/05385F

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