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Aminium Salts Catalyzed Rearrangement of α-Pinene and β-Ionone Oxides

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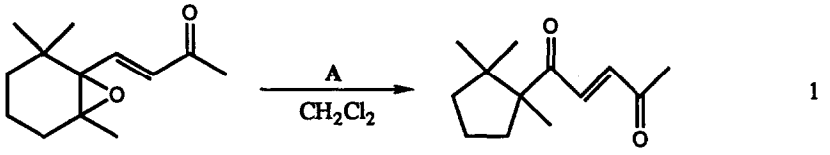
Abstract: β-ionone and α-pinene oxides **1, 3** isomerize rapidly and selectively to 1-(1,2,2-trimethylcyclopent-1-yl)-pent-2-en-1,4-dione **2** and the industrially important 2,2,3-trimethyl-3-cyclopentene acetaldehyde **4**. under the influence of catalytic amounts of aminium salts **A,B**. In order to find insights into the mechanism of our procedure, protic and Lewis acids-catalyzed rearrangements have also been reconsidered.

Introduction

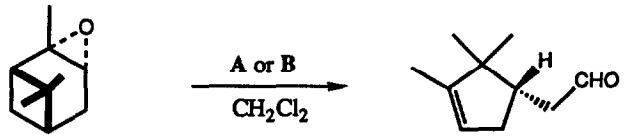
Recently, we reported that aminium salt initiation represents a powerful protocol for the isomerization of oxiranes into their corresponding carbonyl compounds. Undoubtedly, the fast conversion of β-ionone oxide **1** into 1-(1,2,2-trimethylcyclopent-1-yl)-pent-2-en-1,4-dione **2**, induced by catalytic amounts of *tris*-(*p*-bromophenyl) aminium hexachloroantimonate $(p\text{-}BrC_6H_4)_3N^{\dagger}\ SbCl_6^-$ [E^{red} = 1.16 V. *vs* SCE] **A**, was the most intriguing result, [1] (equation 1):



1 **2** 1

The exceedingly high efficiency and selectivity of this new catalytic procedure were totally unexpected, if compared with those observed in the several protic-and Lewis acids induced processes.[2] In the first instance, this behaviour was ascribed to a plausible chain radical cation mechanism induced by the aminium salt, a well known one-electron oxidizing agent.[3]

We now report the results of a more systematic study, showing that aminium salts can be fruitfully employed to induce the isomerization of another suitable oxirane, *i.e* α-pinene oxide **3**, into 2,2,3-trimethyl-3-cyclopenteneacetaldehyde **4**, an important intermediate for the synthesis of santalol, a component of several fragrances,[4] as well as of necrodane-type monoterpenes, with a remarkable insect-repellant activities[5] (equation 2). However, further experimental results have also been collected for the substrate **1**.



3 4 2

Protic acids, zinc chloride and some other typical Lewis-acid catalysts are included for comparison.

Results and Discussion

By following a general protocol, methylene chloride solutions of **1** or **3** were treated with catalytic amounts of **A** under stirring at room temperature. Analyses of the strongly acidic reaction mixtures, performed by gc/ms chromatography revealed the rapid disappearance of the starting materials and the formation of major reaction products (90-80%), whose fragmentation patterns were consistent with those of **2** or **4**, respectively. Trace amounts of the isomer 2,2,4-trimethyl-3-cyclopentenacetaldehyde **5**, were also formed from **3**. The products, isolated by column chromatography, were fully characterized by physical, spectral data and by comparison with authentic samples, synthesized through a modified Arbusow's procedure.[6] Solvent effects influenced the activity and selectivity of the catalyst. In fact, the rate of reaction of **3** was apparently reduced in acetonitrile (15 h), whereas the selectivity was lower in diethyl ether solution. In this latter solvent an increasing amount of the isomer **5** (20 %) was observed. Other aminium salts, such as *tris*-(*o*,*p*-dibromophenyl)aminium hexachloroantimonate **B** can be successfully employed.

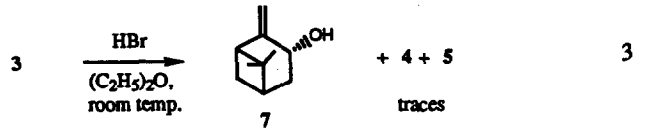
Given that our methylene chloride solutions were strongly acidic, this new catalytic version for the rearrangement of **3**, as well as of **1**, could be easily rationalized as a further example of acid-catalyzed process, mediated by aminium salts, according to Gasmann's proposal.[7]

However, the idea that the choice of reagents, solvents, structure effects and reaction conditions could totally alter not only the course of the rearrangement, but also the mechanism, induced us to investigate this process. The acid that would catalyze the process, and the step in which it is formed are not presently known.[7,8] In any case, there are not merely traces of contaminating acid in the aminium salts, responsible of the observed rearrangement. In fact the aminium salts, freshly prepared,[9] were repeatedly washed with dry diethyl ether until neutral solutions were obtained.

An obvious criterion for establishing a protic acid catalyzed mechanism is to subject the reagents to protic acid conditions. In this context, treatment of methylene chloride solutions of **3** with dry hydrogen bromide, at room temperature, yielded, within 15 min., **4** as the major product, together with *p*-cymene, 2,2,4-trimethyl-3-cyclopentenacetaldehyde **5**, 6-*endo*-bromo-1,5,5-trimethyl-bicyclo[2,2,1]-heptan-2-*exo*-ol **6**, *trans*-pinocarveol **7** and *trans* -pinocamphone in smaller amounts. Complex reaction mixtures were also observed on the substrate **1**.[2]

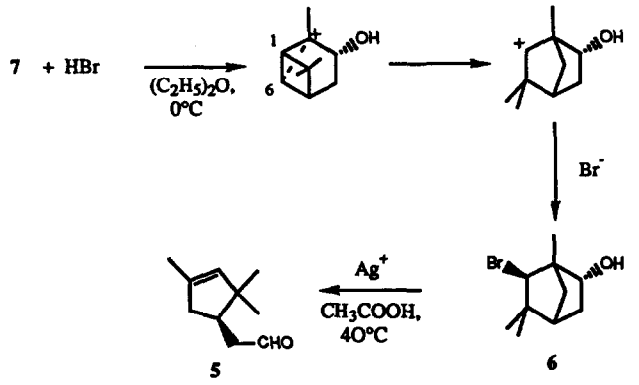
However, the reactions carried out by bubbling dry hydrogen bromide into diethyl ether solutions of **3**, revealed some interesting aspects, not previously recorded. In fact, we observed, within 3 h, the complete disappearance of the starting material and the formation (>85%) of *trans* -pinocarveol **7**, together with minor

amounts of **4** and **5**, instead of the reported bromohydrin **6**.[10] (equation 3). *Trans*-pinocarveol **7** was also obtained by treatment, at 150 °C, of **3** with zeolite 3A (NaKA) powder.[11]



Thus, the hydrogen bromide induced reactions of **3** showed different selectivities in the two solvents. In diethyl ether, the protonation of the oxygen and the subsequent epoxy ring opening was followed by a favoured deprotonation of the unrearranged carbenium ion intermediate, leading to **7**. This latter, by prolonging the bubbling of hydrogen bromide into the reaction medium, was converted into the bromohydrin **6**, intermediate in the synthesis of **5** (scheme 1).

Scheme 1



As a consequence, the Gassman's hypothesis,[7,8] did not appear plausible in our case.

On the other hand, the oxidation potentials of our non aromatic oxiranes **1,3** (greater than 2V vs SCE)[13] would preclude the suggestion that aminium salts may promote efficient, preliminary electron-transfer processes to radical cations **1,3**$^{+\cdot}$.

In this context, a rather strongly endothermic initiation step is not atypical for chain radical cation processes on electron-rich substrates (see, the aminium salt-initiated cation radical Diels-Alder cyclodimerization of 1,3-cyclohexadiene). In fact, as reported by Bauld, the need of a steady low concentration of the reactive radical cation intermediate is more important than endothermicity of the initiation step.[8]

Aminium-salt initiated reactions were then performed in the presence of a sterically hindered, non nucleophilic base, as 2,6-di-*tert*-butylpyridine **DBP**.[7,8]

The hindered base criterion, that is generally suited for distinguishing between the two mechanistic pathways, differently influenced the reactivity of our substrates. In fact, if similar reactions of **3** were carried out with the aminium salt (10 mol %) and **DBP** (10 mol %), the base did not inhibit the rearrangement of the starting material, affording, slower, the same aldehyde **4** with high selectivity.[8] *Viceversa*, similar base-modified reactions of **1** appeared totally inhibited.

Thus, if a chain radical cation mechanism was still a conceivable hypothesis for the rearrangement of **3**, in the case of **1** the suppression of the rearrangement in the base modified reactions, together with the low selectivity observed in the protic acid reactions should exclude a chain radical cation rearrangement mechanism, as well as a protic acid induced process.

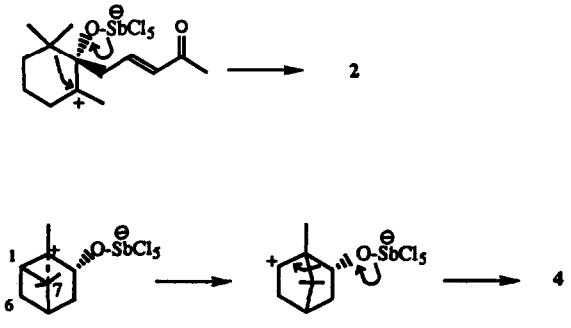
These experimental suggestions prompted us to compare the results of the aminium-salt induced reactions with those obtained by using the classical Lewis acids, *i.e.*, zinc halides ($ZnCl_2$, $ZnBr_2$).[11]

Zinc halides showed a better selectivity for the formation of campholenic aldehyde **4** (>90%) than aminium salts, whereas, these latter had an higher efficiency to promote the selective rearrangement of **1** into **2**.

However, the same observed selectivities might support the proposal that the mechanism of the aminium-salt induced processes was similar to that suggested by Schwegler in the metal halides-induced reactions of **3**.[11]

In our context, we believe that antimony pentachloride ($SbCl_5$), in equilibrium with the hexachloroantimonate ($SbCl_6^-$) moiety, would stabilize the carbenium ion intermediates formed by coordination of the metal to the oxygens. The subsequent, favoured attack of C6 or C7 on C2, respectively, would produce new intermediates, by which the elimination of antimony pentachloride would afford **2** or **4**, (scheme 2).

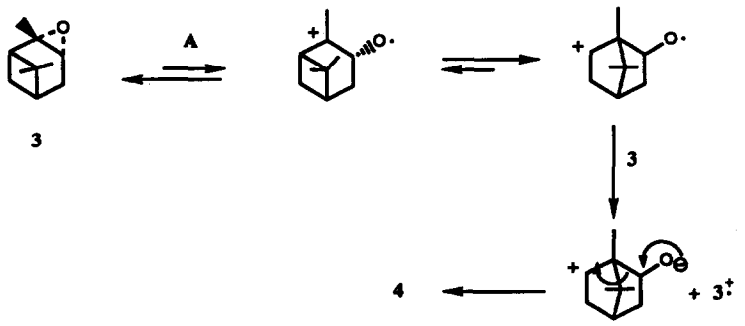
Scheme 2



Unfortunately, methylene chloride solutions of **1** and **3** reacted differently with catalytic amounts of antimony pentachloride ($SbCl_5$) in the same solvent. In fact, a very high efficiency and selectivity, similar to those observed in the aminium salt-induced reactions, were only recorded in the reaction of **1** to **2**, whereas, a reduced selectivity was observed in the same reactions of **3**, leading to complex reaction mixtures.

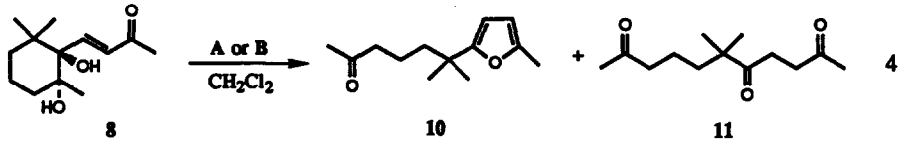
Thus, if a ($SbCl_5$) Lewis-acid catalyzed rearrangement is a consistent mechanistic pathway for β-ionone oxide **1**, the kinetic impetus for a chain radical cation rearrangement of **3** would be given by the fast exothermic isomerization of the pinane radical cation into the bornyl one, whose subsequent electron transfer with **3** would produce the intermediate leading to **4** and the radical cation **3**†, (scheme 3).

Scheme 3

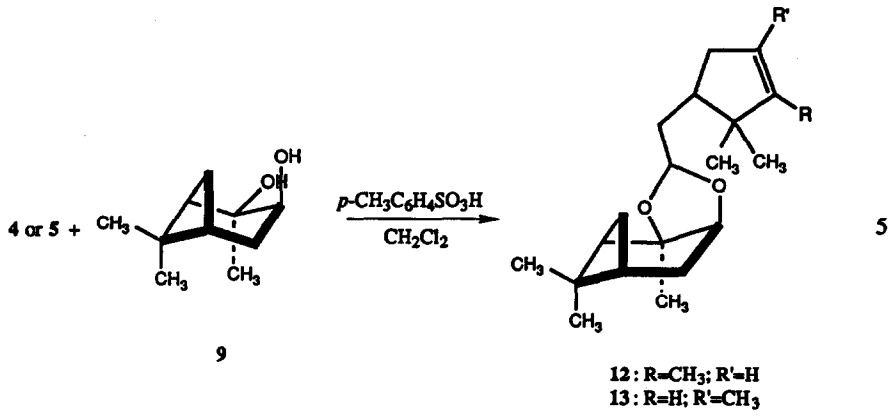


In this context, a further convincing proof came from the aminium salt-induced reactions of the corresponding 1,2-diols, *i.e.* 1,2-dihydroxy-β-ionone **8** and (1R, 2R, 3S, 5R)-pinan-1,2-diol **9**, electron-rich substrates with the same structure of our oxides.

The aminium salt or protic acid-induced reactions of **8**, leading to a mixture of 6-methyl-6-(5-methylfur-2-yl)-heptan-2-one **10** and 6,6-dimethylundecan-2,5,10-trione **11**, eq.4, appeared totally inhibited when performed in the presence of **DBP**.[14,15]



Methylene chloride solutions of **9** were apparently inert towards protic acids, whereas, at the same time, both unmodified and base modified aminium salt-induced rearrangements of **9** led to the same mixture of reaction products, which was fully characterized as a 1/1 mixture of the acetals **12**,**13**. Both acetals were prepared independently by acid-catalyzed reaction of pure aldehydes **4** or **5** with **9**, respectively, equation 5.



Though, further detailed investigations in the area are warranted, however, we believe that structure effects influence the mechanism of the aminium salt induced rearrangement processes. In other words, a chain radical cation mechanism appears the only reliable hypothesis, accounting for the aminium-salt induced processes on **3** and **9**.

Independently from the mechanistic discussions, these results provide one more attractive procedure for the rearrangement of particular oxides, which can afford useful synthons for more complex organic syntheses.

Experimental Section

Melting points were taken on an electrothermal apparatus and are uncorrected. ^{1}H-and ^{13}C-NMR spectra were recorded on a Varian XL-200 MHz or Bruker AM500 MHz instruments. IR, MS spectra were performed, respectively, on a Perkin-Elmer FT-1710 (KBr pellets), and on a Hewlett and Packard GC/Mass MSD 5970 instruments. GC analyses were carried out on a Hewlett and Packard gas chromatograph, model 5750 B, on columns (1/4"x15 feet) packed with SP 2100 (5% on Supelcoport 100/120). TLC were performed on silica gel sheets with fluorescent indicator (Stratocrom SIF-Carlo Erba). Dichloromethane was purified by washing with sulphuric acid solution, distillation over calcium hydride and then stored in the dark under nitrogen atmosphere and over molecular sieves. The starting materials **1** and **8** have been synthesized by m-CPBA oxidation of β-ionone and subsequent hydrolisis of the oxide,[1,15] whereas **3** and **9** are pure commercial samples (Aldrich Co). Aminium salts have been synthesized following the procedure reported in literature.[9]

General procedure for the isomerization of β-ionone oxide by using aminium salts

Catalytic amounts of tris(p-bromophenyl) aminium hexachloroantimonate **A** (83 mg, 0.1 mmol) were added to a solution of epoxide **1** (208 mg, 1 mmol) in distilled methylene chloride (10 ml) with stirring. The intensely blue colour of the solution faded within 1h. The solvent was removed in vacuum and the residue adsorbed on silica gel. The column chromatography (silica gel, eluant petroleum ether/diethyl ether 10/1 v/v)

afforded, after the amine, 1-(1,2,2-trimethylcyclopent-1-yl)-pent-2-ene-1,4-dione 2 (190 mg, 90%), fully characterized through the following spectral data: ir(KBr): υ = 2942, 1680, 1613, 1459, 1358, 1291, 1241, 1036, 1019, 979 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 200 MHz): δ = 6.76 (d, J = 15.6 Hz, 1H), 6.28 (d, J = 15.6 Hz, 1H), 2.27 (s, 3H), 2.23-1.21 (m, 6H), 1.13 (s, 6H), 0.92 (s, 3H) ppm; ^{13}C-nmr ($CDCl_3$, 200 MHz): δ= 204.1, 197.9, 136.1, 134.9, 59.37, 44.29, 40.37, 34.32, 28.99, 25.34, 24.44, 20.21, 19.63 ppm; ms m/e (%) = 208 (M^+, 1), 140 (7), 125 (13), 111 (64), 109 (16), 98 (78), 97 (37), 95 (11), 70 (16), 69 (100), 67 (13), 55 (67), 53 (12), 43 (93), 41 (53). These data are consistent with those reported in literature.[2]

A similar product was isolated, in high yields, by reacting methylene chloride solutions of 1 with different catalysts, as $SbCl_5$, tris (o,p-dibromophenyl) aminium hexachloroantimonate $(Br_2C_6H_3)_3 N^+ SbCl_6^-$ **B**, zinc chloride or bromide ($ZnCl_2$, $ZnBr_2$).

As already reported in the literature,[2] the reactions with dry hydrogen bromide in methylene chloride or diethyl ether, afforded complex mixtures of products and were only studied by gc/ms spectrometry.

General procedure for the isomerization of α-pinene oxide using aminium salts

Catalytic amounts of tris(p-bromophenyl) aminium hexachloroantimonate A (165 mg, 0.2 mmol) were added to a solution of epoxide 3 (304 mg, 2 mmol) in distilled methylene chloride (10 ml) with stirring.The intensely blue colour of the solution faded within 2h. The solvent was removed in vacuum and the residue adsorbed on silica gel. The column chromatography (silica gel, eluant petroleum ether/diethyl ether 10/1) afforded 2,2,3-trimethyl-3-cyclopentene acetaldehyde 4 (250 mg, 82 %), fully characterized through the following spectral data and comparison with an authentic sample.[5]

ir(KBr): υ = 3039, 2957, 2931, 2869, 2839, 2716, 1728, 1488, 1463, 1445, 1385, 1362, 1313, 1286, 1272, 1116, 1073, 1034, 1015, 800 cm^{-1}; ^{1}H-nmr (CD_3COCD_3, 500 MHz): δ = 9.77 (dd, J = 1.8, J = 2.4 Hz, 1H), 5.13-5.12 (m, 1H), 2.57 (ddd, J = 1.8, J = 4.1, J = 15.9 Hz, 1H), 2.38 (ddd, J = 2.4, J = 10.3, J = 15.9 Hz, 1H), 2.37-2.33 (m, 1H), 2.27 (dddd, J = 10.3, J = 4.1, J = 8.9, J = 7.8 Hz, 1H), 1.86 (dddq, J_d = 1.9, J_d = 8.9, J_d = 15.5, J_q = 2.6 Hz, 1 H), 1.60 (dt-like, J_d = 2.6, J_t = 1.6 Hz, 3H), 1.08 (s, 3H), 0.80 (s, 3H) ppm; ^{13}C-nmr ($CDCl_3$): δ= 202.8, 148.0, 121.6, 47.0, 45.2, 44.3, 35.6, 25.7, 20.4, 12.5 ppm; ms m/e (%) = 152 (M^+, 2), 137 (1), 119 (4), 109 (21), 108 (100), 95 (31), 93 (76), 91 (23), 81 (16), 79 (13), 77 (16), 67 (29), 55 (12), 53 (12), 43 (10), 41 (28), 39 (20).

General procedure for the isomerization of α-pinene oxide using metal halides

To suspensions of anhydrous $ZnBr_2$ or $ZnCl_2$ (1 mmol) in toluene (20 ml) were added solutions of the corresponding epoxide 3 (1520 mg, 10 mmol). The mixtures were stirred at room temperature until no more starting material was detected by gc/ms chromatography (12-36h). Then a solution of AcOH (0.5 ml) in H_2O (5ml) was added. The mixtures were diluted with toluene(2 ml), washed with H_2O sat. aq. $NaHCO_3$ soln., dried (Na_2SO4), and by roto-evaporation adsorbed on silica gel. The subsequent column chromatographies (silica gel, eluent petroleum ether/diethyl ether 10/1) afforded pure 2,2,3-trimethyl-3-cyclopentene acetaldehyde 4, (1360 mg, 90 % yield) The product, b.p. 70°C/14 torr, has been fully characterized as reported above.

General Procedure for the isomerization of 3 using dry hydrogen bromide

Dry hydrogen bromide (HBr) was gently bubbled into a diethyl ether (10 ml) solution of **3** (1520 mg, 10 mmol) at room temperature. The progress of the reaction was monitored by gc/ms chromatography until completion (2-3h.). Then, it was quenched with H_2O (10 ml) and the organic substrates extracted with diethyl ether (2x15 ml). The organic phase, washed twice with H_2O (2x5 ml), dried (Na_2SO_4), evaporated, was then adsorbed on silica gel. The silica gel column chromatography, eluent petroleum ether/diethyl ether 10/1, afforded 1200 mg (80 %) of pure **7**, fully characterized through the following spectral data: ir (KBr): υ = 3408, 3074, 2977, 2950, 2937, 2922, 1647, 1370, 1026, 1005, 897 cm^{-1}; ^1H nmr (CD_3COCD_3, 500 MHz): δ = 4.94 (dd, J = 0.9, J = 1.8 Hz, 1H), 4.72-4.71(m, 1H), 4.35 (d-like, J =7.7 Hz, 1H), 2.90 (s, broad, 1H), 2.45 (t-like, J = 5.5 Hz, 1H), 2.31 (dddd, J = 2, J = 5.5, J = 6, J = 9.6 Hz, 1H), 2.20 (ddt-like, J_d = 7.7, J_d = 14.6, J_t = 2.0 Hz, 1H), 1.95-1.90 (m, 1H), 1.80 (ddd, J = 1, J 4.2, J = 14.4 Hz, 1H), 1.79 (d-like J = 9.5 Hz, 1H), 1.25 (s, 3H), 0.63 (s, 3H) ppm; ^{13}C nmr ($CDCl_3$): δ = 156.11, 111.4, 67.0, 50.6, 40.4, 39.9, 34.5, 27.9, 25.9, 21.9 ppm; ms m/e (%) = 152 (M^+, < 1), 134 (20), 119 (35), 109 (25), 105 (14), 95 (19), 93 (26), 92 (100), 91 (70), 83 (55), 81 (39), 79 (31), 77 (24), 70 (64), 69 (39), 67 (23), 55 (99), 53 (33), 43 (39), 41 (99) 39 (65). Minor amounts of **4** and **5** have been detected by gc/ms spectroscopy.

However, if a continous stream of HBr was bubbled, after the total conversion of **3**, we observe a slow conversion of **7** into a new major reaction product, showing a fragmentation pattern consinstent with that of 6-*endo*-bromo-1,5,5-trimethyl-bicyclo[2,2,1]-heptan-2-*exo*-ol **6**. The reaction mixture, quenched as usual, after work up, led to 1720 mg (70 %) of pure **6**. A similar result was obtained by bubbling, at 0°C, hydrogen bromide into a diethyl ether solution of pure *trans*-pinocarveol **7**. The reaction product was fully characterized through physical and spectral data: m.p. 118-119 °C from petroleum ether; 40-70°C; ir (KBr): υ =3274, 2978, 2958, 2941, 1453, 1251, 1059, 998, 863, 793 cm^{-1}; ^1H nmr ($CDCl_3$, 500 MHz): δ = 3.98-3.93 (m, 1H), 3.82 (s, 1H), 2.26 (ddd, J=2.9, J=7.2, J=13.6 Hz, 1H), 1.75-1.74 (m, 1H), 1.58 (dd, J=1.5, J=10.7, 1H), 1.49-1.46 (m, 1H), 1.30 (broad s, 1H), 1.18 (dt, J_t=3.9, J_d=13.6 Hz, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C nmr ($CDCl_3$): δ = 73.4, 71.2, 54.3, 46.1, 39.7, 38.1, 38.0, 30.1, 26.0, 15.3 ppm; ms m/e (%) = 234 (M^+ + 2, < 1), 232 (M^+, < 1), 219 (8), 217 (8), 175 (2), 173 (2), 153 (13), 152 (19), 137 (89), 119 (12), 109 (100), 108 (89), 107 (13), 95 (56), 93 (51), 91 (20), 81 (17), 79 (19), 77 (17), 69, 15, 67 (34), 55 (22), 53 (15), 43 (27), 41 (40), 39 (22).

Conversion of 6 into 2,2,4-trimethyl-3-cyclopenteneacetaldehyde 5

The bromo-alcohol **6** (0.5 g) was mixed with acetic acid (3 ml) and silver nitrate (0.2 g.) and the whole kept at 40 °C for 1h. The reaction mixture was quenched with H_2O (5 ml) and then extracted with diethyl ether (15x 2 ml), washed with H_2O (10x 2 ml), and dried (Na_2SO_4). After work up 0.3 g (>90 % yield) of **5** were isolated. The structure has been confirmed through the following spectral data: ir (KBr): υ = 3025, 2956, 2927, 2864, 2718, 1728, 1624, 1463,1448, 1384, 1282, 1241, 1123, 1040, 823 cm^{-1}; ms m/e (%) = 152(M^+, 26), 137(26), 119(16), 109(41), 108(100), 107(13), 95(80), 93(93), 91(39), 81(26), 79(21),77(28), 67(49), 55(17), 53(17), 43(17), 41(40), 39(32); ^1H nmr (CD_3COCD_3, 500 MHz): δ= 9.76 (t-like due to dd, J = 2 Hz, 1H), 5.15-5.13 (m, 1H), 2.56 (ddd, J = 1.8, J = 3.9, J = 15.8 Hz, 1H), 2.36 (ddd, J = 2.3, J = 10.1, J = 15.8 Hz, 1H), 2.40-2.26 (m, 2H), 2.0 (dddq, J_d = 3.2, J_d = 8.5, J_d = 15.3, Jq = 1.3 Hz, 1H), 1.63 (ddd, J = 0.9, J = 1.3,

J = 1.4 Hz, 3H), 1.02 (s, 3H), 0.80 (s, 3H) ppm; ^{13}C-nmr ($CDCl_3$): δ= 202.8, 136.6, 135.7, 46.3, 45.1, 43.7, 42.1, 28.0, 22.4, 16.5 ppm.

Synthesis of acetals 12 and 13

Equimolecular amounts of (1R, 2R, 3S, 5R)-2,3-pinane diol **9** (85 mg, 0.5 mmol) were added to solutions of aldehydes **4** and **5** (76 mg, 0.5 mmol) in distilled methylene chloride (5 ml), containing catalytic amounts of *p*-toluensulphonic acid, as catalyst. The reactions were monitored by gc/ms chromatography until the total disappearance of the starting materials (2 h). The solvent was removed in vacuum and the residues adsorbed on silica gel. The column chromatographies (silica gel, eluant petroleum ether/diethyl ether 9.5/0.5) afforded the corresponding acetals **12,13**, whose structures were fully characterized through the following spectral data, respectively:

12: ir (KBr): υ = 3035, 2952, 2868, 1464, 1449, 1416, 1385, 1375, 1361, 1281, 1250, 1144, 1127, 1084, 1047, 1034, 1016, 999, 945, 892, 797 cm^{-1}; ms (m/e %): 304 (M^+, 10), 234 (6), 136 (19), 135 (47), 109 (45), 108 (80), 107 (19), 93 (100), 92 (23), 91 (16), 83 (9), 81 (13), 79 (16), 77 (10), 69 (15), 67 (19), 55 (19), 43 (51), 41 (34); ^{1}H nmr ($CDCl_3$, 500 MHz): δ =5.20-5.19 (m, 1H), 4.89 (dd, J = 3.8, J = 6.3 Hz, 1H), 3.88 (d, J = 7.7 Hz, 1H), 2.36-2.30 (m, 1H), 2.14 (ddt-like, J_d = 7.8, J_d = 14.3, J_t = 2.1 Hz, 1H), 2.07 (dddd, J = 2, J = 5.5, J = 6, J = 10.2 Hz, 1H), 2.00-1.84 (m, 5H), 1.78 (ddd, J = 3.5, J = 6.2, J = 13.3 Hz, 1H), 1.69 (ddd, J = 3.8, J =11.2, J = 13.3 Hz, 1H), 1.63 (d, J = 10.3 Hz, 1H), 1.58 (dt-like, J_d = 3.1, J_t =1.6 Hz, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 0.97 (s, 3H), 0.81 (s, 3H), 0.74 (s, 3H) ppm; ^{13}C-nmr ($CDCl_3$, 500 MHz): δ=148.26, 121.82, 100.62, 83.24, 77.07, 50. 85, 46.99, 45.96, 40.11, 37.82, 35. 84, 34.09, 32.81, 27. 25, 25.60, 25. 56, 25.09, 23.98, 19. 70, 12.57 ppm.

13: ir (KBr) υ = 3027, 2961, 2946, 2876, 1451, 1417, 1378, 1365, 1282, 1252, 1140, 1090, 1050, 1038, 1016, 996, 943, 897 cm^{-1}; ms (m/e %): 304 (M^+, 5), 136 (18), 135 (48), 109 (33), 108 (47), 107 (18), 93 (100), 92 (24), 91 (18), 83 (11), 79 (17), 77 (12), 69 (15), 67 (22), 55 (21), 43 (59), 41 (41); ^{1}H nmr ($CDCl_3$, 200 MHz): δ = 5.10 (s, br, 1H), 4.88 (dd, J = 4.0, J = 6.1 Hz, 1H), 3.88 (d, J = 7.6 Hz, 1H), 2.32-1.69 (m, 11H), 1.63 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 1.01 (s, 3H), 0.81 (s, 3H), 0.76 (s, 3H) ppm. ^{13}C-nmr ($CDCl_3$, 200 MHz): δ=136.79, 135.96, 104.42, 107.02, 76.92, 50.64, 46.22, 45.38, 42.19, 39.96, 37.75, 33.83, 32.71, 27.91, 27.20, 25.54, 25.03, 23.98, 22.12, 16.74 ppm.

The two acetals show, by gc, different retention times.

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