Liquid-phase noncatalytic oxidation of monoterpenoids with nitrous oxide*

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A series of monoterpenoids differing in the number of double bonds and the pattern of their substitution were tested in the liquid-phase noncatalytic oxidation with nitrous oxide (N_2O). The structure of olefins has a significant effect on the oxidation route. In the case of terpenoids containing 1,1-disubstituted double bond, *nor*-carbonyl compounds are formed with high selectivity.

Key words: nitrous oxide, alkene oxidation, monoterpenes.

In recent years, nitrous oxide (nitrogen(I) oxide, N_2O) has provoked ever increasing interest of researchers as an effective oxygen donor in selective oxidation of many organic compounds both in the liquid and gas phases. Catalyzed direct oxidation of benzene to phenol,[1] epoxidation of alkenes,[2] and oxidation of alcohols[3] are examples of using N_2O as an oxidant. However, the ability of nitrous oxide to accomplish liquid-phase noncatalytic oxidation of alkenes, resulting in selective formation of carbonyl compounds, is probably most intriguing.[4] This method is obviously attractive for oxidative functionalization of olefins, components of basic hydrocarbon raw materials, in particular, isoprenoids.

Quite a few examples of successful nitrous oxide oxidation of acyclic, carbo- and heterocyclic alkenes,[4,5] and unsaturated polymers[6] are known to date. In order to extend the range of possible synthetic applications of this reaction, we studied the oxidation behavior of terpene type olefins, which give diverse practically valuable products of oxidation.

Results and Discussion

This study deals with the behavior of unsaturated monoterpene hydrocarbons, differing in the number and positions of double bonds, *viz.*, β-pinene (**1**), limonene (**2**), carvone (**3**), 3-carene (**4**), 2-carene (**5**), and dehydrolinalool (**6**), in the liquid-phase oxidation with nitrous oxide.

The oxidation was carried out for 12 h at 250 °C in a substrate—benzene—N_2O system (50—70 atm). The major reaction products were identified using GC/MS analysis by comparing their full mass spectra and retention indexes with the same data for reference compounds. In some cases, the products were isolated using column liquid and preparative gas liquid chromatography, and the molecular structures of the products were subsequently determined using NMR and IR spectroscopy and mass spectrometry data. The results of nitrous oxide oxidation experiments of olefins **1—6** are summarized in Table 1.

β-Pinene (**1**) containing one exocyclic double bond in the molecule undergoes destructive oxidation with a 83% selectivity to give a *nor*-carbonyl compound, nopinone (**7**) (Scheme 1). The second oxidation product, *cis*-dihydromyrtenal (**8**), is present in the mixture only in minor amounts (6% of the total reaction products).

The limonene molecule (**2**) contains two double bonds, each being able to react with N_2O. However, the different degrees of substitution at the double bonds suggest that their abilities to react with N_2O would also differ. Indeed, 4-acetyl-1-methylcyclohexene (**9**) resulting from destructive oxidation of the isopropenyl double bond is the pre-

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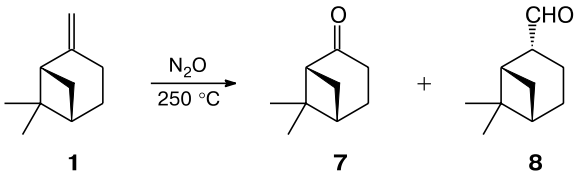
Table 1. Results of oxidation experiments of monoterpenoids **1—6** with nitrous oxide

Substrate	Conversion (%)	Product distribution according to GLC (%)
1	19.1	82.7 (**7**), 5.8 (**8**)
2	72.8	52.3 (**9**), 6.7 (**10**), 1.8 (**11´**), 2.5 (**11″**), 13.0*
3	57.6	64.9 (**12**), 35.1 (**13**)
4	22.1	10.4 (**14´**), 17.6 (**14″**), 31.0 (**15**), 8.1 (**17a**), 21.7 (**17b**), 2.7 (**18**)
5 → **19**	72.8	24.0 (**20**), 18.5 (**21**), 8.7 (**22**) 14.4**
6 → **23**	54.8	16.1 (**26**), 31.2 (**27**), 35.2 (**28**)

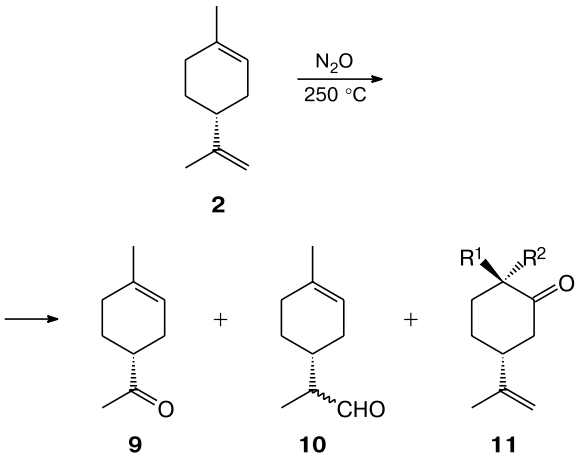
* Total cyclopropanation products.
** Cyclopropanation product.

Scheme 1



dominant component of the product mixture formed from limonene (52% of the total reaction products). As in the case of β-pinene, the product of oxidation of 1,1-disubstituted double bond with retention of the carbon skeleton, aldehyde **10** (a mixture of two diastereomers), is formed in a considerably lower amount (7% of the total reaction products) than the *nor*-carbonyl compound. The products resulting from oxidation of the endocyclic double bond, namely, *cis*- and *trans*-dihydrocarvones (**11´** and **11″**, respectively), are found in the mixture but their total amount does not exceed 5% (Scheme 2).

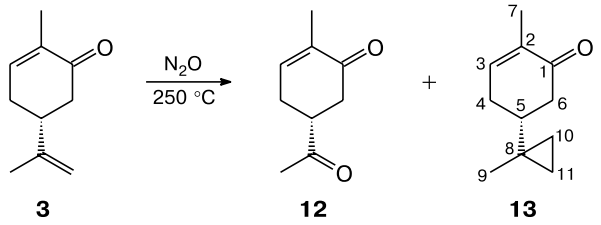
Scheme 2



R^1 = H, R^2 = Me (**11´**); R^1 = Me, R^2 = H (**11″**)

In the case of carvone (**3**), the selectivity of the oxidative process was even higher, the endocyclic double bond remaining totally intact, the reaction involving exclusively the isopropenyl double bond to give diketone **12** (Scheme 3). This is consistent with the results on the oxidation of model dienes, indicating a substantial deactivating effect of the carbonyl group on the reactivity of the double carbon—carbon bond conjugated with this group.[5]

Scheme 3



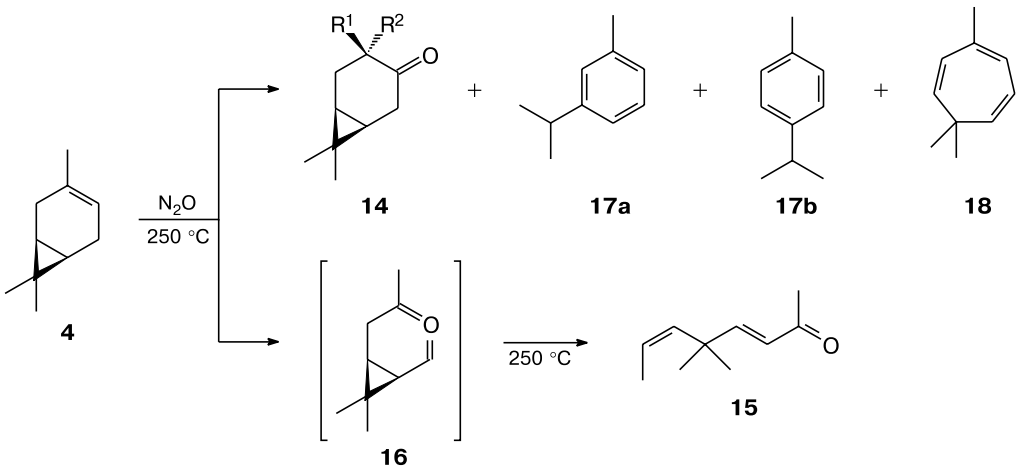
Apart from oxidation product **12**, the oxidation of carvone (**3**) affords *homo*-derivative **13** (yield 35%), resulting from cyclopropanation of the double carbon—carbon bond in the isopropenyl group. Cyclopropane *homo*-derivatives are formed through the addition of the methylene (carbene), liberated upon destructive oxidation of the terminal double bond, to the double bond of the initial substrate.[5] The products of methylene addition to the double bond were also found for other substrates, but in most cases, benzene used as the solvent was the main carbene acceptor, being converted into cycloheptatriene. In particular, oxidation of olefins **2** and **5** gives compounds identified, on the basis of their mass spectra, as *homo*-derivatives formed upon cyclopropanation.

The degree of conversion of 3-carene (**4**) under these reaction conditions was only ~20%, which is in line with the low reactivity of the trisubstituted double bond already observed for limonene. In addition to the diastereomeric caran-4-ones (**14´** and **14″**), resulting from double bond oxidation with retention of the core of initial olefin **4**, the reaction gave acyclic ketone **15** (Scheme 4).

The most probable pathway to compound **15** is double bond cleavage in the substrate to give a monocyclic unsaturated ketone **16**, which undergoes thermal 1,5-homodienyl hydrogen atom shift, typical of vinylcyclopropanes.[7] The double bond configuration in product **15** is determined by the positions of substituents in the cyclopropane ring in the transition state of the sigmatropic rearrangement.

Apart from carbonyl compounds **14** and **15**, the mixture contains *m*- and *p*-cymols (**17a,b**) and 3,7,7-tri-

Scheme 4



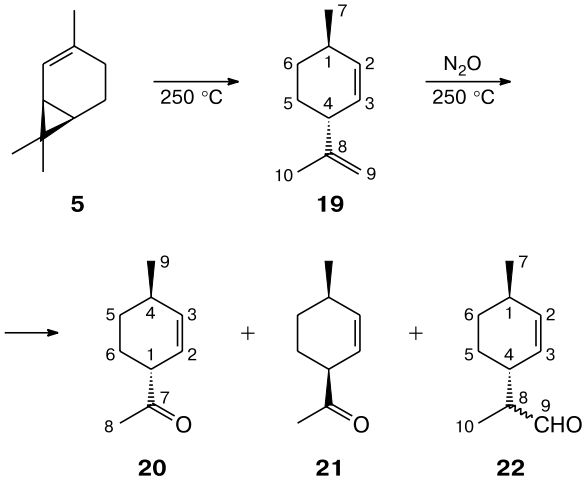
R^1 = H, R^2 = Me (**14′**); R^1 = Me, R^2 = H (**14″**)

methyl-1,3,5-cycloheptatriene (**18**) resulting from oxidative dehydrogenation of 3-carene.

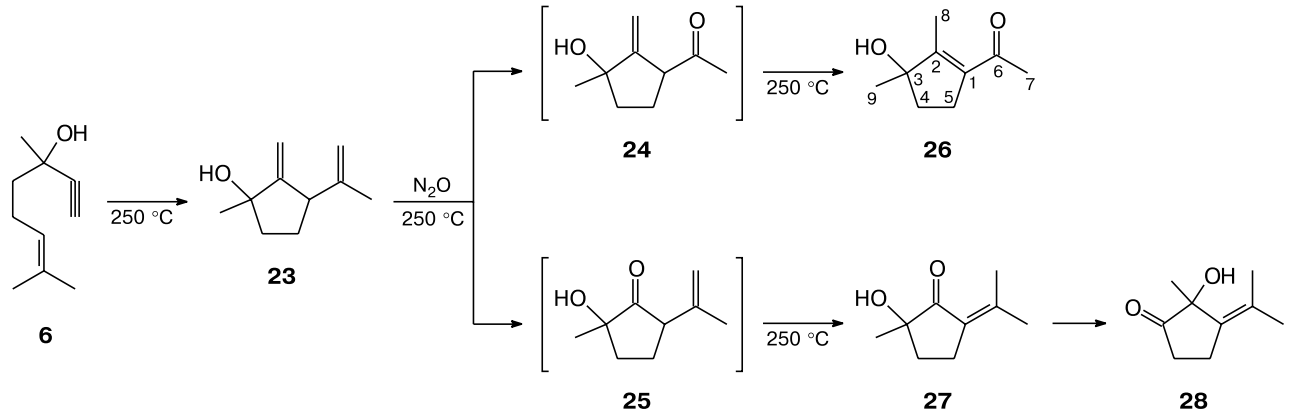
2-Carene (**5**) is isomerized at the reaction temperature to *trans*-isolimonene (**19**).[8] Although the accessibility of the endocyclic double bond in diene **19** is somewhat higher than in limonene (**2**), the products of oxidation of the isopropenyl double bond, carbonyl compounds **20**—**22**, are still the major reaction products (Scheme 5).

Like 2-carene, dehydrolinalool (**6**) cannot withstand the drastic reaction conditions: at 250 °C, the starting monoterpenoid undergoes carbocyclization to give cyclic dienol **23** as a mixture of two diastereomers.[9] Presumably, oxidation of dienol **23** affords carbonyl compounds **24** and **25**. However, these compounds are missing from the product mixture, the reaction giving unsaturated keto alcohols **26** and **27** (yields 16 and 31%), resulting from the sigmatropic rearrangement of the enol form of **24** and **25** (Scheme 6). Comparison of the heats of formation

Scheme 5



Scheme 6



of compounds **24—27** estimated by AM1 and PM3 calculations attests to higher thermodynamic stability of ketones **26** and **27** with respect to their isomers. Unsaturated keto alcohol **28**, formed probably upon migration of the methyl group in isomer **27**, is formed in 35% yield.

Experimental

Commercial (−)-β-pinene (>99%, Fluka), (*R*)-(+)-limonene (97%, Aldrich), (L)-(−)-carvone (99%, Acros), and (+)-2-carene (97%, Aldrich) were used. (+)-3-Carene with $[\alpha]_D^{20}$ +16.0 (d_4^{20} 0.863) was obtained by distillation of common pine (*Pinus silvestris*) needle oil, racemic dehydrolinalool was prepared by condensation of acetylene with 6-methyl-5-hepten-2-one. Medical nitrous oxide (99.8%) produced by the Cherepovets plant Azot was used as the oxidant. All solvents were freshly distilled prior to use.

GC/MS analysis of reaction mixtures was performed on a Hewlett-Packard G1081A instrument consisting of an HP 5890 gas chromatograph, series II, and an HP MSD 5971 mass selective detector; ionizing electron energy 70 eV; an HP5 column (5% diphenyl, 95% dimethylsiloxane), 30 m × 0.25 mm × 0.25 μm; helium as the carrier gas, 1 mL min^{-1}; column temperature programming mode: 2 min at 50 °C, heating at 10 °C min^{-1}, and 5 min at 280 °C; temperature of the ion source 173 °C; data collection rate 1.2 scan s^{-1} in the mass range of 30—650 amu. The components of mixtures were identified by comparing their full mass spectra and retention indexes with the corresponding data for reference compounds.[10] The contents of the components in the mixture were calculated from the peak areas without correction factors.

NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.132 (^{1}H) and 125.758 MHz (^{13}C)) at room temperature (+25 °C) for solutions in $CDCl_3$ with a concentration of 25—50 mg mL^{-1}. The solvent signals δ_H 7.24 ($CHCl_3$) and δ_C 76.90 ($CDCl_3$) were used as internal standards. IR spectra were recorded on a Bruker Vector-22 instrument for 2% solutions in $CHCl_3$. High-resolution mass spectra were measured on a Finnigan MAT 8200 spectrometer (50—100 °C, EI, 70 eV). The optical rotation was determined on a Polamat A polarimeter at λ = 578 nm.

Oxidation of olefins with nitrous oxide (general procedure). The oxidation experiments were carried out in a 25-cm^3 stainless-steel autoclave type reactor (Parr) equipped with a manometer and a magnetic stirrer. A solution of olefin (0.5 g) in benzene (10 cm^3) was placed into the reactor and the reactor was tightly covered with a lid. Air was removed from the reactor by vacuum pump for 30 s, the reactor was purged with nitrous oxide, and then N_2O was introduced to an equilibrium pressure of 25 atm. After addition of the reactants, the reactor was heated at a rate of 6 °C min^{-1} to 250 °C (during heating, the pressure in the reaction system increased to 50—70 atm) and the system was kept for 12 h at this temperature. After completion of the experiment, the reactor was cooled to room temperature, pressure was slowly reduced, and the composition of the reaction mixture was analyzed by GC/MS. The resulting benzene solution was concentrated in vacuum of a water-jet pump. The mixture components were separated using a combination of column chromatography (KSK silica gel with particle size of 0.140—0.315 mm activated for 6 h at 130 °C; a hexane—ethyl acetate mixture with AcOEt concentration gradient from 0 to 50% or a hexane—CH_2Cl_2 mixture with CH_2Cl_2 concentration gradient from 0 to 100%) and preparative gas chromatography (a 4.5 m × 6 mm column, 15% OV-101/N-AW-DMCS; nitrogen as a carrier gas, 60 mL min^{-1}; column temperature 150 °C).

5*R*-Acetyl-2-methyl-2-cyclohexen-1-one (12). R_f 0.22 (CH_2Cl_2), $[\alpha]^{19}_{578}$ −13 (*c* 6.67, $CHCl_3$). The NMR and mass spectra agree with published data.[11]

2-Methyl-5*R*-(1-methylcyclopropyl)cyclohex-2-en-1-one (13). R_f 0.44 (CH_2Cl_2), $[\alpha]^{19}_{578}$ +8.9 (*c* 4.27, $CHCl_3$). The ^{1}H NMR spectrum coincides with published data.[12] ^{13}C NMR ($CDCl_3$), δ: 199.2 (s, C(1)); 144.1 (d, C(3)); 135.7 (s, C(2)); 44.3 (d, C(5)); 42.1 (t, C(6)); 29.6 (t, C(4)); 19.2 (q, C(9)); 18.5 (s, C(8)); 15.9 (q, C(7)); 12.5, 12.6 (both t, C(10), C(11)). MS, *m*/*z* (I_{rel} (%)): 164 [M]$^+$ (6), 136 (38), 122 (25), 121 (15), 109 (51), 108 (61), 107 (38), 106 (15), 95 (35), 94 (16), 93 (65), 91 (19), 82 (100), 81 (78), 80 (12), 79 (42), 77 (16), 72 (17), 67 (20), 55 (14), 54 (35), 53 (24), 41 (25), 39 (27).

5,5-Dimethylocta-3*E*,6*Z*-dien-2-one (15). R_f 0.66 (hexane—AcOEt, 2 : 1 v/v). ^{1}H NMR ($CDCl_3$), δ: 1.21 (s, 6 H, CMe_2); 1.57 (dd, 3 H, C(8)H$_3$, $J_{8,7}$ = 7.0 Hz, $J_{8,6}$ = 1.1 Hz); 2.24 (s, 3 H, C(1)H$_3$); 5.33 (dq, 1 H, H(6), $J_{6,7}$ = 11.3 Hz, $J_{6,8}$ = 1.1 Hz); 5.43 (dq, 1 H, H(7), $J_{7,6}$ = 11.3 Hz, $J_{7,8}$ = 7.0 Hz); 6.04 (d, 1 H, H(3), $J_{3,4}$ = 16.2 Hz); 6.88 (d, 1 H, H(4), $J_{4,3}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 199.0 (s, C(2)); 156.3 (d, C(4)); 136.6 (d, C(6)); 126.9 (d, C(3)); 125.9 (d, C(7)); 38.4 (s, C(5)); 28.3 (2 q, CMe_2); 26.9 (q, C(1)); 14.3 (s, C(8)). MS, *m*/*z* (I_{rel} (%)): 152 [M]$^+$ (2), 138 (7), 137 (65), 123 (17), 110 (9), 109 (92), 107 (5), 95 (20), 94 (9), 93 (10), 91 (9), 82 (11), 81 (17), 79 (31), 77 (12), 69 (6), 67 (50), 65 (6), 55 (22), 53 (9), 43 (100), 41 (20), 39 (14).

***trans-p*-Mentha-2(3),8(9)-diene (19)** was obtained by thermolysis of 2-carene for 3 h at 220 °C. The ^{1}H NMR spectrum of compound **19** coincides with published data.[13] ^{13}C NMR ($CDCl_3$), δ: 149.4 (s, C(8)); 134.0 (d, C(3) or C(2)); 129.2 (d, C(2) or C(3)); 109.6 (t, C(9)); 43.5 (d, C(4)); 31.0 (t, C(6)); 30.3 (d, C(1)); 28.0 (t, C(5)); 21.7 (q, C(10)); 20.4 (q, C(7)). MS, *m*/*z* (I_{rel} (%)): 136 [M]$^+$ (55), 122 (5), 121 (52), 108 (13), 107 (68), 105 (13), 95 (8), 94 (21), 93 (84), 92 (10), 91 (36), 81 (12), 80 (13), 79 (100), 78 (7), 77 (31), 68 (33), 67 (31), 65 (9), 55 (18), 53 (16), 51 (8), 43 (8), 41 (24), 39 (22).

1*R*-Acetyl-4*R*-methyl-2-cyclohexene (20). R_f 0.61 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 0.96 (d, 3 H, C(9)H$_3$, $J_{9,4}$ = 7.1 Hz); 2.15 (s, 3 H, C(8)H$_3$); 3.07 (m, 1 H, H(1)); 5.68 (m, 2 H, H(2), H(3)). MS, *m*/*z* (I_{rel} (%)): 138 [M]$^+$ (30), 123 (12), 96 (8), 95 (100), 94 (15), 93 (14), 91 (6), 80 (9), 79 (19), 77 (11), 67 (41), 65 (5), 55 (18), 53 (7), 43 (61), 41 (9), 39 (8).

1*S*-Acetyl-4*R*-methyl-2-cyclohexene (21). R_f 0.61 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 0.95 (d, 3 H, C(9)H$_3$, $J_{9,4}$ = 7.1 Hz); 2.16 (s, 3 H, C(8)H$_3$); 3.01 (m, 1 H, H(1)); 5.73 (br.s, 2 H, H(2), H(3)). MS, *m*/*z* (I_{rel} (%)): 138 [M]$^+$ (17), 123 (7), 96 (9), 95 (100), 94 (16), 93 (11), 91 (4), 80 (9), 79 (13), 77 (9), 67 (37), 65 (4), 55 (16), 53 (6), 43 (60), 41 (9), 39 (7).

1*R*,4*R*-*p*-Menth-2-en-9-al (22) (1 : 1 diastereomer mixture). R_f 0.55 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 0.95 (3 H, C(10)H$_3^{(2)}$, $J_{10,8}$ = 2.8 Hz); 0.97 (3 H, C(10)H$_3^{(1)}$, $J_{10,8}$ = 2.8 Hz); 1.03 (3 H, C(7)H$_3^{(1)}$, $J_{7,1}$ = 7.0 Hz); 1.04 (3 H, C(7)H$_3^{(2)}$, $J_{7,1}$ = 7.0 Hz); 5.44 (d, 2 H, H(2)$^{(1)}$ + H(2)$^{(2)}$, $J_{2,3}$ = 10.0 Hz); 5.59 (d, 2 H, H(3)$^{(1)}$ + H(3)$^{(2)}$, $J_{3,2}$ = 10.0 Hz); 9.67 (d, 1 H, H(9)$^{(1)}$, $J_{9,8}$ = 1.8 Hz); 9.69 (d, 1 H, H(9)$^{(2)}$, $J_{9,8}$ = 1.5 Hz). MS, *m*/*z* (I_{rel} (%)): 152 [M]$^+$ (7), 123 (14), 121 (7), 109 (9), 95 (56),

94 (100), 93 (16), 91 (10), 81 (27), 79 (51), 77 (14), 68 (13), 67 (34), 55 (20), 53 (9), 43 (7), 41 (17), 39 (12).

3-Isopropenyl-1-methyl-2-methylidenecyclopentanol (23) (a 7 : 3 diastereomer mixture) was obtained by thermolysis of dehydrolinalool for 1 h at 240 °C. The diastereomers were separated by column chromatography on SiO_2 (a hexane—AcOEt mixture with AcOEt concentration gradient from 0 to 30% was used as the eluent); R_f 0.56 and 0.49 (hexane—AcOEt, 1 : 1 v/v). The NMR spectra of the isolated isomers were identical to those described previously.[14] MS for the major diastereomer, m/z (I_{rel} (%)): 152 $[M]^+$ (1), 137 (50), 134 (16), 123 (11), 121 (20), 119 (43), 109 (47), 105 (11), 97 (14), 95 (85), 94 (89), 93 (27), 91 (32), 84 (14), 81 (35), 80 (10), 79 (100), 77 (26), 71 (12), 69 (22), 67 (41), 65 (10), 55 (18), 53 (16), 43 (88), 41 (25), 39 (22). MS for the minor diastereomer, m/z (I_{rel} (%)): 152 $[M]^+$ (1), 137 (100), 134 (71), 123 (13), 119 (48), 109 (58), 105 (10), 95 (23), 94 (13), 93 (23), 91 (32), 84 (22), 81 (31), 79 (78), 77 (25), 71 (12), 69 (26), 67 (40), 55 (18), 53 (15), 43 (85), 41 (26), 39 (23).

1-Acetyl-3-hydroxy-2,3-dimethylcyclopent-1-ene (26). R_f 0.27 (hexane—AcOEt, 1 : 1 v/v). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 3 H, C(9)H_3); 1.85 (ddd, 1 H, H(4), $J_{4,4'}$ = 13.4 Hz, $J_{4,5}$ = 7.2 Hz, $J_{4,5'}$ = 9.2 Hz); 1.91 (br.s, OH); 1.99 (t, 3 H, C(8)H_3, $J_{8,5'}$ = 2.0 Hz); 2.01 (ddd, 1 H, H(4′), $J_{4',4}$ = 13.4 Hz, $J_{4',5}$ = 8.1 Hz, $J_{4',5'}$ = 2.0 Hz); 2.22 (s, 3 H, C(7)H_3); 2.42 (ddd, 1 H, H(5), $J_{5,5'}$ = 15.8 Hz, $J_{5,4'}$ = 8.1 Hz, $J_{5,4}$ = 7.2 Hz); 2.60 (dddq, 1 H, H(5′), $J_{5',5}$ = 15.8 Hz, $J_{5',4}$ = 9.2 Hz, $J_{5',4'}$ = 2.0 Hz, $J_{5',8}$ = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 199.2 (s, C(6)); 154.9 (s, C(2)); 135.3 (s, C(1)); 84.7 (s, C(3)); 38.8 (t, C(4)); 30.0 (q, C(7)); 29.7 (t, C(5)); 24.7 (q, C(9)); 11.5 (q, C(8)). IR ($CHCl_3$), ν/cm^{-1}: 3598, 1678, 1653. MS, m/z (I_{rel} (%)): 154.09916 (154.09937 for $C_9H_{14}O_2$) $[M]^+$ (5), 139 (29), 136 (15), 127 (6), 121 (7), 111 (13), 99 (5), 97 (8), 93 (5), 85 (10), 77 (5), 69 (6), 67 (6), 57 (5), 55 (8), 53 (5), 43 (100), 41 (9), 39 (8), 29 (5), 28 (10), 27 (6).

2-Hydroxy-5-isopropylidene-2-methylcyclopentanone (27). R_f 0.42 (hexane—AcOEt, 1 : 1 v/v). The ^{1}H NMR spectrum of compound **27** coincides with published data.[15] ^{13}C NMR ($CDCl_3$), δ: 208.0, 151.7, 127.7, 78.1 (all s); 33.9, 24.2 (both t); 24.1, 23.8, 20.9 (all q).

2-Hydroxy-3-isopropylidene-2-methylcyclopentanone (28). R_f 0.42 (hexane—AcOEt, 1 : 1 v/v). ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 3 H); 1.79 (ddq, 3 H, J = 2.3 Hz, J = 1.5 Hz, J = 0.8 Hz); 1.91 (q, 3 H, J = 0.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 202.1, 154.8, 127.8, 72.0 (all s); 35.0, 30.8 (both t); 24.3, 21.2, 11.2 (all q).

Retention indexes of the compounds: 1136 (**7**), 1182 (**8**), 1130 (**9**), 1215 and 1217 (**10**), 1197 (**11′**), 1205 (**11″**), 1332 (**12**), 1348 (**13**), 1194 (**14′**), 1187 (**14″**), 1142 (**15**), 1022 (**17a**), 1024 (**17b**), 970 (**18**), 973 (**19**), 1097 (**20**), 1087 (**21**), 1175 and 1176 (**22**), 1071 and 1092 (**23**), 1272 (**26**), 1209 (**27**), 1220 (**28**).

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