

Some Transformations of (–)-(1*S*,4*R*)-1-Vinyl-7,7-dimethyl-bicyclo[2.2.1]heptan-2-one

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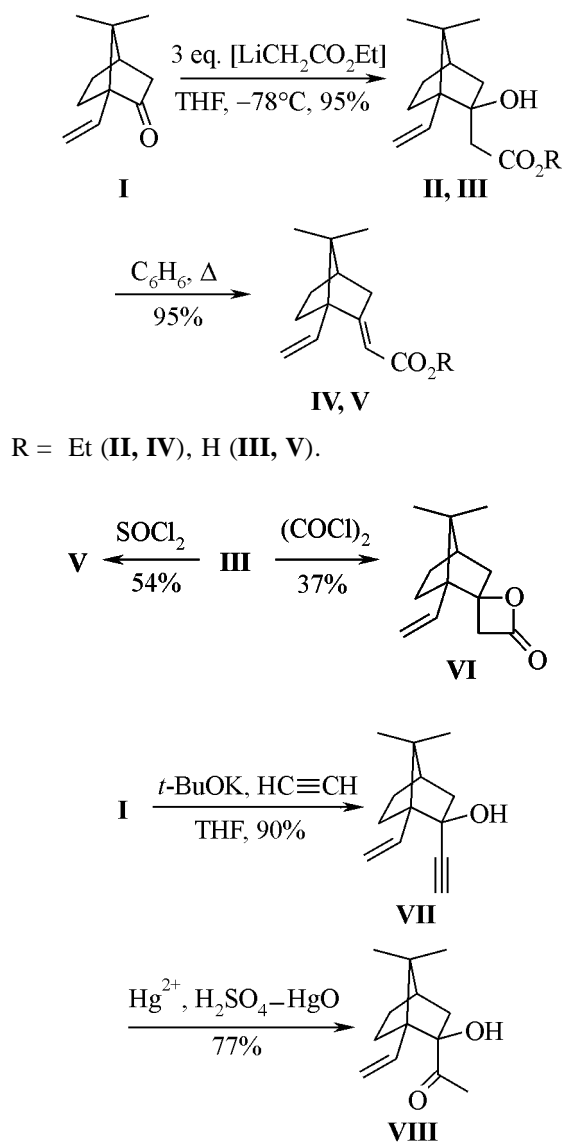
Abstract—Reactions were studied of (–)-(1*S*,4*R*)-1-vinyl-7,7-dimethylbicyclo[2.2.1]heptan-2-one with ethyl acetate lithium derivative, potassium acetylide, ozone, with a system OsO₄–N-methylmorpholine N-oxide, and some subsequent transformations of the products obtained.

Unsaturated ketone of bornane series (**I**) [1] is an attractive chiral initial compound for the synthesis of *gem*-dimethyl-containing natural terpenoids, in particular, taxoids [2–5], and building blocks thereto [6, 7]. Looking for synthons suitable for subsequent intramolecular transformations (cyclization) we investigated some reactions of compound **I** involving its keto and vinyl groups.

Reactions involving keto group. Note that ketone **I** is prone to enolisation and therefore its reactions with basic C-nucleophiles (organometallic compounds) are virtually impossible. We overcame this difficulty by applying less basic but strongly nucleophilic organocerium intermediates [8, 9]. We showed that lithium derivative of ethyl acetate cleanly reacted with ketone **I** by 1,2-addition to the carbonyl group at –78°C in THF yielding adduct **II**. We formerly [10] obtained this compound by carrying out Reformatsky reaction with compound **I** under special conditions (ICH₂CO₂Et, Zn, traces of I₂, PhH, Δ) in no more than 50% yield. We failed to optimize the process due to the reversibility of Reformatsky reaction.

The hydrolysis of β-hydroxyester **II** with NaOH water solution provided oxyacid **III**. Compounds **II** and **III** readily undergo dehydration when heated in benzene solution with catalytic amounts of *p*-toluenesulfonic acid to afford α,β-unsaturated ester **IV** and acid **V**. Acid **V** can also be obtained at hydrolysis of ester **IV**. Acid **V** remains intact under conditions of iodolactonization (KI₃, THF–H₂O). This fact unambiguously proves the *E*-configuration of the tri-substituted double bond in compounds **IV** and **V**. The attempts to obtain acyl chloride from acid **V** under treatment with (COCl)₂ or SO₂Cl₂ even under stringent compounds were unsuccessful. The boiling of oxyacid **III** with SOCl₂ in the present of DMF traces resulted in acid **V**, however, in lower yield

Scheme 1.



than by the route (IV→V). In reaction with oxalyl chloride oxacyd **III** formed β-lactone **VI**.

We successfully carried out condensation of ketone **I** with an *sp*-hybridized nucleophile $KC\equiv C$. Whereas lithium acetylide in THF [11] from -78 to 20°C did not react with ketone **I**, the potassium acetylide ($HC\equiv CH$, THF, *t*-BuOK, 20°C) [12] formed with ketone **I** tertiary alcohol **VII**. The latter was cleanly converted into α-hydroxymethyl ketone **VIII** under conditions used in hydrolysis of terminal acetylenes catalyzed by Hg^{2+} [13] (Scheme 1).

Reactions involving terminal double bond. The oxidation of unsaturated ketone **I** by *N*-methylmorpholine *N*-oxide catalyzed by OsO_4 [14] proceeded cleanly and resulted in a quantitative yield of a mixture of diastereomeric diols **IX** in 3:1 ratio (Scheme 2). We failed to separate diols **IX** by chromatography on SiO_2 , but we obtained and isolated as individual compound acetonide **X** of the prevailing diol isomer. The configuration of the chiral center at the C' in acetonide **X** was not established. The ethynylation of diols **IX** readily occurred under synthesis conditions of alcohol **VII**. As a result was obtained in high yield a diastereomeric mixture of triols **XI**.

We performed selective ozonolysis of the terminal double bond in compound **IV** and isolated aldehyde **XII** and relatively stable isomeric trioxolanes **XIII** (Scheme 2).

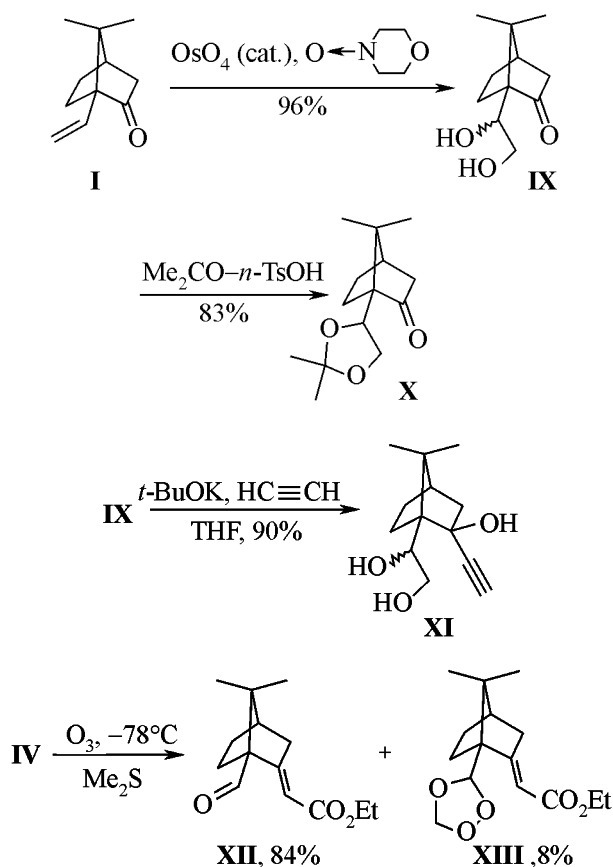
Summing up the results of the research reported above we conclude that were obtained several synthons promising for further application. The transformations described provide useful insight into the reactivity of compound **I**.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from samples prepared as thin films or mulls in mineral oil. 1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 at 300 and 75.47 MHz respectively in $CDCl_3$, internal reference TMS. The column chromatography was performed on silica gel L 100/160 (Lachema). TLC was carried out on Silufol plates. The optical rotation was measured on Perkin-Elmer instrument. Mass spectra were registered on MKh-1320 device at 70 eV, ionization chamber temperature 30–50°C.

(-)-(1S,2S,4R)-1-Vinyl-2-hydroxy-7,7-dimethyl-2-ethoxycarbonylmethylbicyclo[2.2.1]heptane (II). A solution of lithium diisopropylamide prepared by

Scheme 2.



deprotonation of 0.96 g (9.44 mmol) of *i*-Pr₂NH with lithium butyl (6.8 ml of 1.38 N solution in hexane) in 30 ml of THF (0°C, Ar, 15 min) was cooled to -78°C, and within 5 min thereto was added a solution of 0.89 ml (9.13 mmol) of EtOAc in 10 ml of THF. The reaction mixture was stirred for 30 min, and then dropwise was added within 15 min a solution of 0.5 g (3.04 mmol) of ketoolefin **I** in 10 ml of THF maintaining the temperature at -78°C. Then the reaction mixture was warmed to room temperature and treated with NH_4Cl water solution. THF was distilled off in a vacuum, and from the residual water layer the products were extracted with ethyl acetate (3 × 50 ml). The combined extracts were washed with saturated water solution of NaCl, dried with Na_2SO_4 , filtered, evaporated, and the residue was subjected to chromatography on a column packed with SiO_2 (eluent hexane–ethyl acetate, 10:1) to afford 0.73 g (95%) of oily substance **II**. R_f 0.82 (hexane–ethyl acetate, 7:3). $[\alpha]_D^{20} -42^\circ$ (©10, $CHCl_3$). IR spectrum (ν , cm^{-1}): 1220, 1390, 1640, 1730, 3530. 1H NMR spectrum (δ , ppm): 0.78 s (3H, CH_3), 1.20 s (3H, CH_3), 1.25 t (3H, CH_3 , J 7.2 Hz), 1.45 m (4H,

1.70 m (1H), 2.20 m (2H), 2.43 d (1H, CH₂CO₂, *J* -14.1 Hz), 2.50 d (1H, CH₂CO₂, *J* -14.1 Hz), 3.85 s (OH), 4.10 q (2H, CH₂, *J* 7.1 Hz), 4.97 d.d (1H, H₂C=, *J* 17.7 and 2.1 Hz), 5.20 d.d (1H, H²C=, *J* 11.0 and 2.1 Hz), 6.15 d.d (1H, HC=, *J* 17.7 and 11.0 Hz). ¹³C NMR spectrum (δ, ppm): 14.08 (CH₃), 20.94 (CH₃), 21.63 (CH₃), 25.40 (C⁵), 26.50 (C⁶), 43.45 (CH₂CO₂), 45.59 (C⁴), 47.05 (C³), 50.70 (C⁷), 58.76 (C¹), 60.58 (CH₂O), 80.39 (C²), 116.59 and 136.28 (CH₂=CH), 173.31 (CO₂). Found, %: C 71.27; H 9.51. C₁₅H₂₄O₃. Calculated, %: C 71.39; H 9.59.

(-)-(1*S*,2*S*,4*R*)-1-Vinyl-2-hydroxy-7,7-dimethyl-2-carboxymethylbicyclo[2.2.1]heptane (III). To a solution of 0.5 g (1.98 mmol) of acetate **II** in 20 ml of MeOH was added 20 ml of 0.25 N water solution of NaOH. The reaction mixture was stirred at 20°C (reaction monitoring by TLC). On completion of the reaction (~10 h) the reaction mixture was diluted with water (10 ml), methanol was distilled off, and the neutral impurities were extracted from the water layer with hexane. Then the water solution was acidified with 10% H₂SO₄ till pH 3, and acid **III** was extracted into ethyl acetate. The combined extracts were dried with sodium sulfate, filtered, and evaporated to obtain 0.42 g (95%) of acid **III**. *R*_f 0.38 (hexane-ethyl acetate, 7:3). mp 85–86°C, [α]_D²⁰ -37° (© 10, CHCl₃). IR spectrum (ν, cm⁻¹): 1640, 1720, 3430. ¹H NMR spectrum (δ, ppm): 6.14 d.d (1H, HC=, *J* 17.8 and 11.0 Hz), 5.19 d.d (1H, H₂C=, *J* 11.0 and 2.4 Hz), 5.02 d.d (1H, H₂C=, *J* 17.8 and 2.4 Hz), 3.35 br.s (CO₂H), 2.43 d (1H, CH₂CO₂, *J* -14.1 Hz), 2.50 d (1H, CH₂CO₂, *J* -14.1 Hz), 2.20 m (1H), 2.16 d (1H, H^{3e}, *J* 13.2 Hz), 2.05 br.s (OH), 1.70–1.82 m (3H), 1.58 d (1H, H^{3e}, *J* 13.2 Hz), 1.40 m (1H), 1.23 s (3H, CH₃), 1.10 m (1H), 0.88 s (3H, CH₃). ¹³C NMR spectrum (δ_C, ppm): 20.32 (CH₃), 21.14 (CH₃), 24.78 (C⁵), 25.85 (C⁶), 42.07 (CH₂CO₂), 45.43 (C⁴), 46.14 (C³), 50.03 (C⁷), 58.42 (C¹), 79.28 (C²), 115.61 and 136.36 (CH₂=CH), 174.17 (CO₂). Found, %: C 69.53; H 8.86. C₁₃H₂₀O₃. Calculated, %: C 69.61; H 8.99.

(-)-[1*S*,4*R*,2(2')*E*]-1-Vinyl-7,7-dimethyl-2-ethoxycarbonylmethylbicyclo[2.2.1]heptane (IV). A solution of 0.2 g (0.79 mmol) of hydroxyester **II** and 15 mg (0.08 mmol) of toluenesulfonic acid in 20 ml of benzene was boiled for 1 h eliminating water into a Dean–Stark trap. After a usual workup of the reaction mixture and purification of the product on SiO₂ was isolated 0.18 g (95%) of oily α,β-unsaturated ester **IV**. *R*_f 0.73 (hexane-ethyl acetate, 7:3). [α]_D²⁰ -36° (© 1, CHCl₃). IR spectrum (ν,

cm⁻¹): 1210, 1665, 1720. ¹H NMR spectrum (δ, ppm): 0.80 s (3H, CH₃), 0.83 s (3H, CH₃), 0.90–1.00 m (1H), 1.20–1.35 m (2H), 1.25 t (3H, CH₃, *J* 7.0 Hz), 1.75–2.10 m (3H), 2.42 d.d (1H, H^{3e}, *J* 19.0 and 2.0 Hz), 2.87 br.d.d (1H³, *J* 19.0 and 3.0 Hz), 4.10 q (2H, OCH₂, *J* 7.2 Hz), 5.10 d.d (1H, *J* 17.4 and 1.4 Hz), 5.32 d.d (1H, *J* 10.9 and 1.4 Hz), 5.75 d.d (1H, *J* 17.4 and 10.9 Hz) (CH=CH₂), 5.55 br.s (1H, CH). ¹³C NMR spectrum (δ_C, ppm): 14.40 (CH₃), 19.92 (CH₃), 19.95 (CH₃), 27.05 (C⁵), 29.07 (C⁶), 38.49 (C³), 44.93 (C⁴), 49.44 (C⁷), 59.38 (CH₂O), 60.57 (C¹), 110.13 (CHCO₂), 118.03 and 135.70 (CH₂=CH), 167.07 (CO₂), 173.48 (C¹). Found, %: C 76.70; H 9.41. C₁₅H₂₂O₂. Calculated, %: C 76.88; H 9.46.

(-)-[1*S*,4*R*,2(2')*E*]-1-Vinyl-7,7-dimethyl-2-carboxymethylbicyclo[2.2.1]heptane (V) was obtained by dehydration of acid **III** by procedure described above for compound **IV**. Yield of oily acid **V** 95%. *R*_f 0.40 (hexane-ethyl acetate, 7:3). [α]_D²⁰ -38° (© 10, CHCl₃). IR spectrum (ν, cm⁻¹): 820, 990, 1655, 1700. ¹H NMR spectrum (δ, ppm): 0.74 s (3H, CH₃), 0.95 m (1H), 1.20 m (2H), 1.54 d.d (1H, H³, *J* 19.2 and 2.0 Hz), 1.75–2.10 m (2H), 2.40 d.d (1H, H^{3e}, *J* 19.2 and 2.0 Hz), 2.87 m (1H), 5.07 d.d (1H, *J* 17.6 and 1.7 Hz), 5.30 d.d (1H, *J* 10.9 and 1.7 Hz), 5.72 d.d (1H, *J* 17.6 and 10.9 Hz) (CH=CH₂), 5.53 br.s (1H, CH). ¹³C NMR spectrum (δ_C, ppm): 19.01 (CH₃), 19.96 (CH₃), 27.04 (C⁶), 28.97 (C⁵), 38.97 (C³), 44.86 (C⁴), 49.57 (C⁷), 61.07 (C¹), 109.94 (CH), 118.37 and 135.44 (CH=CH₂), 173.03 (C²), 176.83 (COO).

(-)-(1*S*,2*S*,4*R*)-1-Vinyl-7,7-dimethylbicyclo[2.2.1]heptane-2-spiro-2'-(4'-oxoxetane) (VI). A solution of 0.2 g (0.89 mmol) of acid **III**, 0.39 ml (4.45 mmol) of oxalyl chloride, and 0.01 ml of DMF in 10 ml of benzene was boiled for 1 h. After evaporating the solvent the residue was subjected to chromatography on SiO₂ to isolate 0.07 g (37%) of compound **VI**. *R*_f 0.57 (hexane-ethyl acetate, 7:3). mp 50–51°C. [α]_D²⁰ -44° (© 5, CHCl₃). IR spectrum (ν, cm⁻¹): 990, 1640, 1775. ¹H NMR spectrum (δ, ppm): 0.95 s (3H, CH₃), 1.03 s (CH₃), 1.20–1.35 m (1H), 1.50–1.95 m (6H), 2.32 d (1H, *J* 17.0 Hz) and 2.40 d (1H, *J* 17.0 Hz) (CH₂COO), 5.18 d.d (1H, *J* 11.0 and 1.3 Hz), 5.27 d.d (1H, *J* 17.0 and 1.3 Hz), 5.90 d.d (1H, *J* 17.0 and 11.0 Hz) (CH=CH₂). ¹³C NMR spectrum (δ_C, ppm): 23.05 (CH₃), 24.07 (C⁶), 24.50 (CH₃), 24.82 (C⁵), 33.94 (CH₂), 40.39 (C³), 46.57 (C⁷), 48.51 (C⁴), 57.20 (C¹), 93.31 (C²), 115.86 and 135.07 (CH=CH₂), 176.77 (COO). Mass spectrum, *m/z*: 206 [M]⁺, 191

$[M-CH_3]^+$, 178 $[M-CO]$, 164, 163, 151, 150, 147, 136, 135, 123 $[M-C_4H_3O_2]^+$ (I_{max}), 98, 91, 83, 69, 55, 41. Found, %: C 75.48; H 8.69. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.79.

(-)-(1S,2S,4R)-1-Vinyl-2-hydroxy-7,7-dimethyl-2-ethynylbicyclo[2.2.1]heptane (VII). Purified gaseous acetylene was bubbled at room temperature through a solution of 0.41 g (3.65 mmol) of *t*-BuOK in 30 ml of THF. After 10 min to the turbid solution within 20 min was added dropwise a solution of 0.2 g (1.22 mmol) of ketoolefin **I** in 5 ml of THF (the solution became brown). The reaction mixture was treated with a saturated aqueous NH_4Cl solution, the organic layer was separated, and the water layer was extracted with ethyl acetate (4–50 ml). The combined extracts were dried on Na_2SO_4 , filtered, evaporated, and the residue was purified by chromatography on SiO_2 (eluent hexane–ethyl acetate, 10:1). We obtained 0.21 g (90%) of oily compound **VII**. R_f 0.57 (hexane–ethyl acetate, 10:1). $[\alpha]_D^{20} -50^\circ$ (c 10, $CDCl_3$).

IR spectrum (ν , cm^{-1}): 1190, 1390, 1640, 2130, 3320, 3500. 1H NMR spectrum (δ , ppm): 0.85 s (3H, CH_3), 0.9 m (1H), 1.20–1.40 m (2H), 1.20 s (3H, CH_3), 1.70–2.45 m (4H), 2.50 s (1H, $C\equiv CH$), 5.30 d.d (1H, J 17.5 and 1.5 Hz), 5.40 d.d (1H, J 11.0 and 1.5), 6.05 d.d (1H, J 17.5 and 11.0 Hz). ^{13}C NMR spectrum (δ_C , ppm): 23.24 (CH_3), 23.40 (CH_3), 28.70 (C^6), 30.67 (C^5), 47.86 (C^3), 50.25 (C^4), 51.18 (C^7), 61.27 (C^1), 73.99 ($C\equiv CH$), 80.42 (C^2), 89.81 ($C\equiv C$), 120.59 and 136.81 ($CH=CH_2$).

(-)-(1S,2S,4R)-2-Acetyl-1-vinyl-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptane (VIII). A mixture of solutions of 0.1 g (0.53 mmol) of alcohol **VII** in 5 ml of acetone and 0.01 g (0.05 mmol) of HgO in 20 ml of 5% sulfuric acid was boiled for 0.5 h. The solution was cooled to room temperature, neutralized with a solution of $NaHCO_3$ till pH 7, the reaction products were extracted into ethyl acetate (3×50 ml). The combined extracts were dried on Na_2SO_4 , filtered, evaporated in a vacuum. The residue was subjected to chromatography on SiO_2 (hexane–ethyl acetate, 7:3). We obtained 0.08 g (77%) of compound **VIII**. R_f 0.46 (hexane–ethyl acetate, 7:3). mp 80–82°C, $[\alpha]_D^{20} -53^\circ$ (c 1, $CHCl_3$). IR spectrum (ν , cm^{-1}): 1632, 1696, 3424. 1H NMR spectrum (δ , ppm): 0.77 s (3H, CH_3), 0.90 m (1H), 1.18–1.25 m (1H), 1.20 s (3H, CH_3), 1.70–1.90 m (4H), 2.18 s (3H, CH_3), 2.50 s (1H, OH), 5.07 d.d (1H, J 11.0 and 1.7 Hz), 6.20 d.d (1H, J 11.0 and 17.8 Hz) ($CH=CH_2$). ^{13}C NMR spectrum (δ_C , ppm): 20.37 (CH_3), 21.15 (CH_3), 25.11 (C^6), 25.62 (C^5), 26.93 (CH_3), 40.62 (C^3), 45.76 (C^4), 52.00 (C^7), 57.50 (C^1), 89.50

(C^2), 117.73 and 135.09 ($CH=CH_2$), 209.5 [$O(CO)$]. Found, %: C 75.24; H 9.79. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.68.

(1R,4R)-1-[(1R,S)-1,2-Dihydroxyethyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-one (IX). To a solution of 0.2 g (1.22 mmol) of ketoolefin **I** and 0.18 g (1.34 mmol) of *N*-methylmorpholine *N*-oxide in 30 ml of aqueous acetone (1:1) was added 0.5 ml of 0.1% OsO_4 solution in *t*-BuOH, and the reaction mixture was stirred for 0.5 h. Then acetone was distilled off, the reaction products were extracted with ethyl acetate (3×50 ml). The combined extracts were dried on Na_2SO_4 , filtered, and evaporated. The residue was subjected to chromatography on SiO_2 (hexane–ethyl acetate, 7:3) to isolate 0.23 g (96%) of compound **IX** as diastereoisomers mixture in the ratio 3:1 (1H NMR). mp 103–105°C. IR spectrum (ν , cm^{-1}): 1180, 1385, 1740, 3400. **Main diastereomer.** R_f 0.31 (hexane–ethyl acetate, 1:1). 1H NMR spectrum (δ , ppm): 1.00 s (3H, CH_3), 1.10 s (3H, CH_3), 3.18 br.s (OH), 3.50–3.95 m (3H, CH_2O , CHO). ^{13}C NMR spectrum (δ_C , ppm): 21.20 (CH_3), 21.27 (CH_3), 25.24 (C^5), 26.56 (C^6), 43.65 (C^3), 44.61 (C^4), 47.81 (C^7), 63.44 (C^1), 64.04 (CH_2O), 71.66 (CHO), 217.76 (CO). **Minor diastereomer.** R_f 0.34 (hexane–ethyl acetate, 1:1). 1H NMR spectrum (δ , ppm): 1.09 s (3H, CH_3), 1.40 s (3H, CH_3), 3.18 br.s (OH), 3.50–3.95 m (3H, CH_2O , CHO). ^{13}C NMR spectrum (δ_C , ppm): 19.97 (CH_3), 21.95 (CH_3), 25.72 (C^5), 26.56 (C^6), 43.65 (C^3), 44.30 (C^4), 48.09 (C^7), 62.94 (CH_2O), 64.04 (C^1), 70.51 (CHO), 220.98 (CO). Found, %: C 67.12; H 9.02. $C_{11}H_{18}O_3$. Calculated, %: C 66.64; H 9.15.

(1R,4R)-7,7-Dimethyl-1-[(1R or S)-1,2-O-isopropylideneethyl]bicyclo[2.2.1]heptan-2-one (X). A solution of 0.20 g (1.01 mmol) of diol **IX** and 0.01 g of *p*-toluenesulfonic acid in 20 ml of acetone was stirred at room temperature for 24 h. Then into the reaction mixture was added 0.05 g of solid $NaHCO_3$, the solvent was evaporated, and the residue subjected to chromatography on SiO_2 to isolate 0.15 g (83% with respect to the main isomer) of individual compound **X**. R_f 0.50 (hexane–ethyl acetate, 7:3). $[\alpha]_D^{20} -34^\circ$ (c 1, $CHCl_3$). IR spectrum (ν , cm^{-1}): 1100, 1180, 1390, 2130, 3310, 3450. 1H NMR spectrum (δ , ppm): 0.83 m (1H), 0.94 s (3H, CH_3), 1.06 s (3H, CH_3), 1.20–1.40 m (2H), 1.28 s (3H, CH_3), 1.35 s (3H, CH_3), 1.76 d (1H, H^3 , J 18.3 Hz), 2.00 m (1H), 2.10–2.20 m (1H), 2.32 d.t (1H, H^{3e} , J 18.3 and 3.9 Hz). ^{13}C NMR spectrum (δ_C , ppm): 20.11 (CH_3), 21.09 (CH_3), 21.09 (C^5), 25.25 (CH_3), 26.28 (CH_3), 26.90 (C^6), 43.36 (C^3), 43.85 (C^4),

47.95 (C⁷), 62.94 (C¹), 66.78 (CH₂O), 72.41 (CHO), 107.57 (OCMe₂O), 217.50 (CO). Found, %: C 70.44; H 9.23. C₁₄H₂₂O₃. Calculated, %: C 70.56; H 9.30.

(1R,4R)-2-Hydroxy-1-[(1R,S)-1,2-dihydroxyethyl]-7,7-dimethyl-2-ethynylbicyclo[2.2.1]heptane (XI) was obtained in 90% yield from diol **IX** and potassium acetylide by the same procedure as compound **VII**. A mixture of diastereomers, 2:1. IR spectrum (ν, cm⁻¹): 1185, 1390, 2130, 3310, 3400. mp 106–108°C. **Main diastereomer.** R_f 0.12 (chloroform–methanol, 10:1). ¹H NMR spectrum (δ, ppm): 1.05 s (3H, CH₃), 1.30 s (3H, CH₃), 2.58 s (1H, C≡CH). ¹³C NMR spectrum (δ_C, ppm): 22.22 (CH₃), 23.55 (CH₃), 26.41 (C⁵), 27.07 (C⁶), 46.97 (C⁴), 49.74 (C³), 50.84 (C⁷), 57.94 (C¹), 64.01 (CH₂O), 72.94 (CHO), 77.68 (C²), 75.85 and 88.59 (C≡CH). **Minor diastereomer.** R_f 0.14 (chloroform–methanol, 10:1). ¹H NMR spectrum (δ, ppm): 1.0 s (3H, CH₃), 1.40 s (3H, CH₃), 2.63 s (1H, C≡CH). ¹³C NMR spectrum (δ_C, ppm): 21.29 (CH₃), 23.20 (CH₃), 26.55 (C⁵), 29.06 (C⁶), 46.05 (C⁴), 49.19 (C³), 49.74 (C⁷), 56.00 (C¹), 64.64 (CH₂O), 71.85 (CHO), 78.50 (C²), 75.85 and 88.81 (C≡CH).

(-)-[1S,4R,2(2')E]-(7,7-Dimethyl-1-formyl-2-ethoxycarbonylmethylenebicyclo[2.2.1]heptane (XII) and **[1S,4R,2(2')E]-7,7-dimethyl-1-[(3R,S)-1,2,4-trioxolan-3-yl]-2-ethoxycarbonylmethylenebicyclo[2.2.1]heptane (XIII)**. Through a solution of 0.27 g (1.15 mmol) of acetate **IV** in 50 ml of CH₂Cl₂ at -78°C was bubbled O₃ at a rate 45 mmol h⁻¹ for 2 min. Then the reaction mixture was flushed with argon, 0.25 ml (3.36 mmol) of Me₂S was added, the temperature was raised to ambient, and the reaction mixture was left overnight. On the next day the solvent was evaporated, and the raw residue was purified by column chromatography on SiO₂. We obtained 0.23 g (84%) of compound **XII** and 0.03 g (8%) of diastereomers mixture of compound **XIII**. **Compound XII.** ¹H NMR spectrum (δ, ppm): 1.02 s (3H, CH₃), 1.09 s (3H, CH₃), 1.25 t (3H, CH₃, J 6.2 Hz), 5.15 t (1H, =CH, J 2.2 Hz), 9.82 s (1H, OCHO). ¹³C NMR spectrum (δ_C, ppm): 14.30 (CH₃), 19.36 (CH₃), 20.48 (CH₃), 38.63 (C³), 46.19 (C⁴), 52.20 (C⁷), 59.82 (OCH₂), 67.24 (C¹), 111.73 (=CH), 166.35 (CO₂), 166.81 (C²). **Compound XIII.** Diastereomers mixture in ~1:1 ratio. ¹H NMR spectrum (δ, ppm): 0.92 s (2CH₃), 1.05 s (CH₃), 1.08 s (CH₃), 1.25 t (3H, CH₃, J 6.2 Hz), 1.20–1.50 m (2H), 1.70–2.15 m (3H), 2.30–2.50 m

(1H), 2.85– 3.10 m (1H), 4.10–4.20 m (2H, CH₂O), 4.97 s, 4.98 s, 5.28 s, 5.30 s (2H, OCH₂O), 5.14 s and 5.18 s (1H, OCHO), 5.90 t (1H, =CH, J 2.2 Hz). ¹³C NMR spectrum (δ_C, ppm): 14.30 (CH₃), 20.31 (CH₃), 20.57 (CH₃), 26.52, 26.73, 26.78 and 26.95 (C⁵, C⁶), 38.13 and 38.33 (C³), 45.70 and 45.90 (C⁴), 49.22 and 49.83 (C⁷), 57.72 and 57.80 (C¹), 59.59 (OCH₂), 93.97 (OCH₂O), 103.25 (OCHO), 111.29 and 111.38 (=CH), 167.33 (CO₂), 167.91 and 168.54 (C²).

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